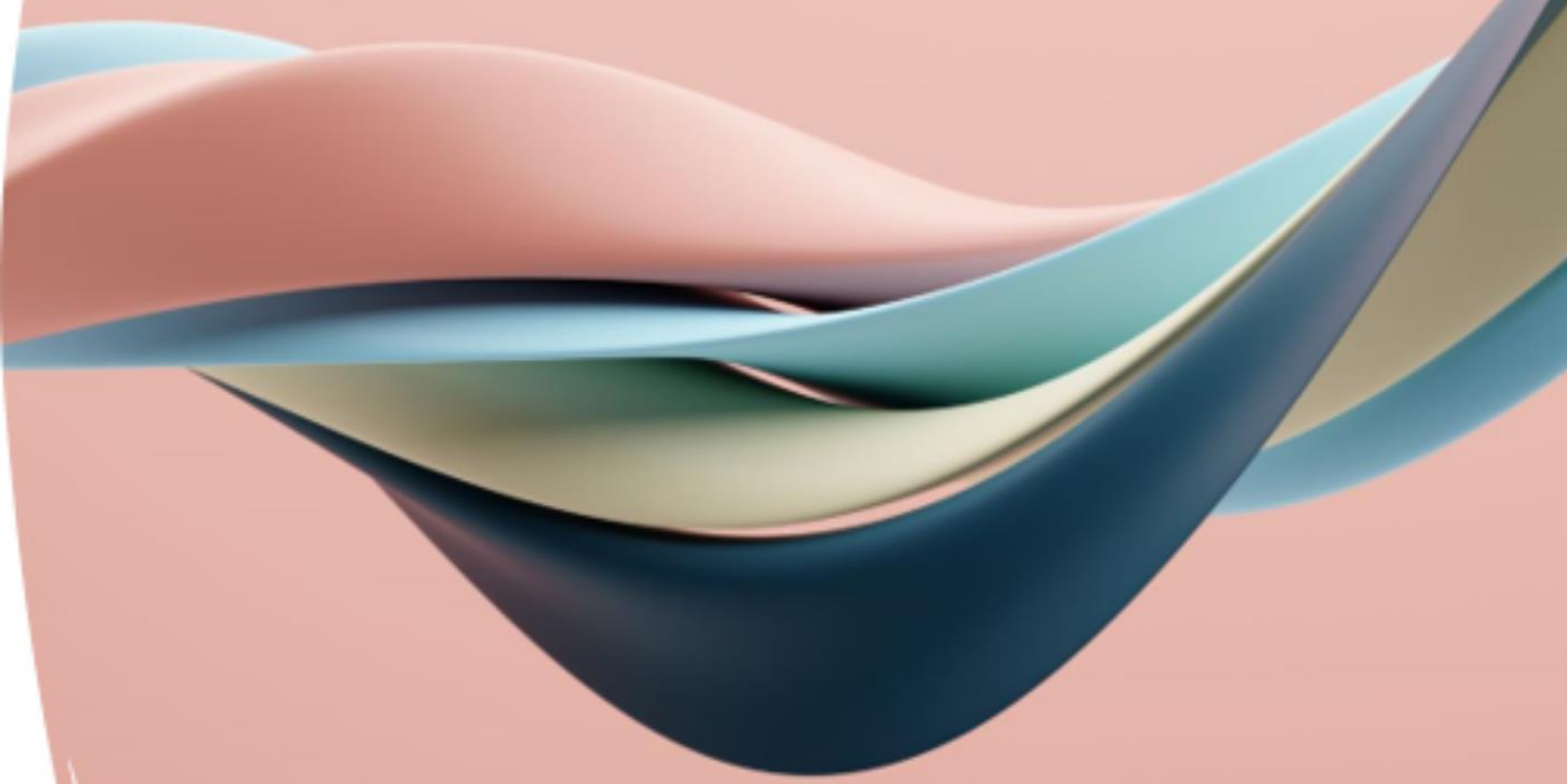
8th International Solvothermal and Hydrothermal Association Conference

SPAIN

VALLADOLID

2023, September 10-13

BOOK OF ABSTRACTS



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8TH INTERNATIONAL SOLVOTHERMAL AND HYDROTHERMAL ASSOCIATION CONFERENCE

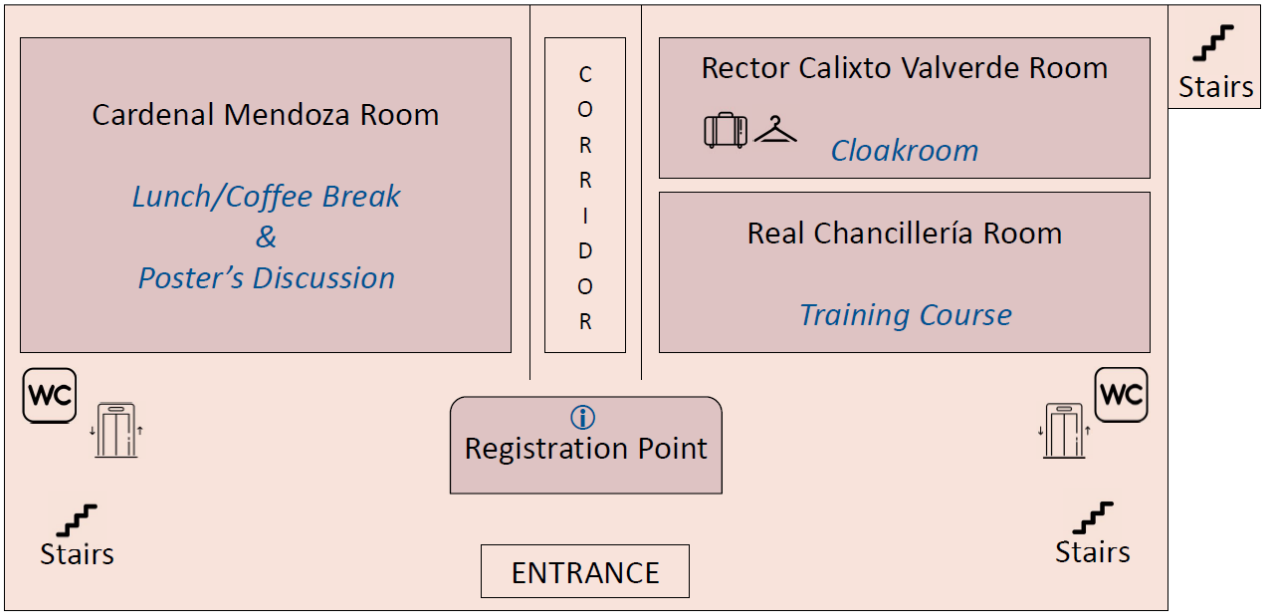
CONDE ANSÚREZ CONGRESS PALACE

CONGRESS LAYOUT

SECOND FLOOR	Paraninfo Room		
	Paraninfo Hall		
FIRST FLOOR	Claudio Moyano Room	Corridor	José Zorrilla Room
	Rey Felipe Room		Dr. Luis de Mercado Room
GROUND FLOOR	Cardenal Mendoza Room	Corridor	R. Calixto Valverde Room
			Real Chancillería Room
	Registration Point		
Access - Entrance			
Parking		Garden	

CONDE ANSÚREZ CONGRESS PALACE

GROUND FLOOR



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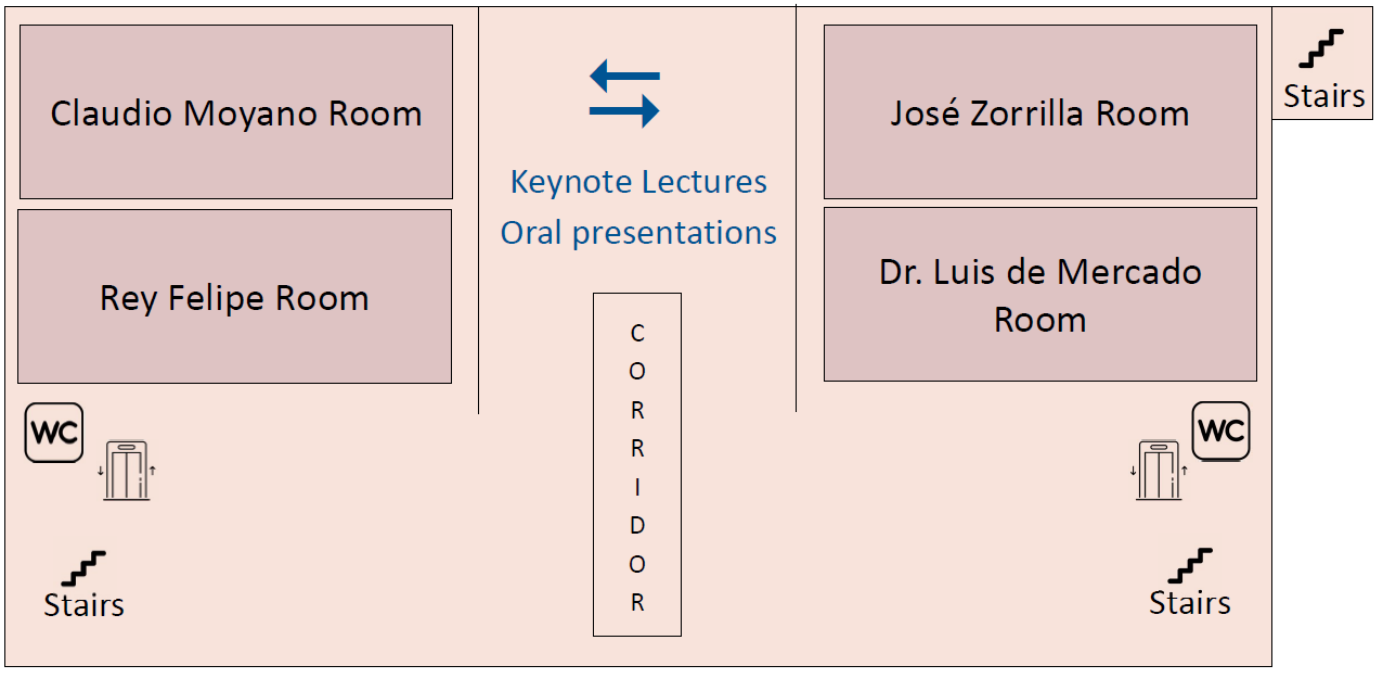
1st FLOOR



CONDE ANSÚREZ CONGRESS PALACE

2nd FLOOR

SOCIAL PROGRAM

Registration & Welcome Cocktail

DATE: September 10th, Sunday 6.30 p.m. – 9:00 p.m.

VENUE: "Pera Limonera" Restaurant

PROGRAM AND SERVICE: Welcome and networking, finger food style reception.

Guided sightseeing tour

DATE: Sept 11, Monday, 6:30 p.m.

MEETING POINT: Plaza San Pablo

DURATION: 90-120 min.

Places to see: Plaza San Pablo: San Pablo Church, Pimentel Palace, San Gregorio School-The National Sculpture Museum., Cathedral, University, Gutierrez Passage, Plaza Mayor square and surroundings.

Gala dinner

DATE: Sep 12, Tuesday, 8:30–11:30 p.m.

VENUE: 'Casa del Sol'. Science Museum

Training course: From the Lab to the Industry

DATE AND VENUE: Sept 11 - 12, Monday and Tuesday, 5:30 p.m – 7:30 p.m.

Room Real Chancillería - Palacio de Congresos Conde Ansúrez, Valladolid

PROGRAM AND SERVICE: 4 lectures given by experts of the highest international level in the world of solvothermal and hydrothermal processes.

ISHA 2023 Award Ceremony

DATE AND VENUE: Sep 12, Tuesday, after the “round table”.

Palacio de Congresos Conde Ansúrez, Valladolid

PROGRAM AND SERVICE: ISHA 2023 participants can submit their proposal to the ISHA committee at their convenience. The announcement of the award winners will take place during the conference.

CONFERENCE PROGRAM

Monday - September 11th, 2023

8.50 - 19:30

Plenary Lecture. Round Table

Keynote Lectures

Oral Presentations

Awards Ceremony

Training Course I

Council ISHA Meeting

Tuesday - September 12th, 2023

9:00 - 19:30

Plenary Lecture. Round Table

Keynote Lectures

Oral Presentations

Training Course II

Wednesday - September 13th, 2023

9:00 - 14:30

Plenary Lecture. Round Table

Keynote Lectures

Oral Presentations

Closing ceremony

8th International Solvothermal and Hydrothermal Association Conference

ISHA 2023

Valladolid, Spain
September 10th–13th, 2023

8th INTERNATIONAL SOLVOTHERMAL AND HYDROTHERMAL ASSOCIATION CONFERENCE

ISHA 2023

MONDAY – SEPTEMBER 11th, 2023

8:50 - 9:00	**CONFERENCE OPENNING REMARKS** *(Room Paraninfo)*			
9:00 - 10:00	**PLENARY LECTURE:** HYDROTHERMAL-ENABLED SUSTAINABLE MANUFACTURING - THE EXPERIENCE AND VISIONS. **Prof. Richard Riman** - Rutgers, The State University of New Jersey, USA *(Room Paraninfo)*			
10:00 - 11:00	**Round table:** CLIMATE ACTIONS AND INNOVATION OPPORTUNITIES. Chairman: Juan García Serna *(Room Paraninfo)* SPEAKERS: Richard Riman, Miriam Unterlass and Richard Tilley			
11:00 - 11:30	Coffee break & Poster's discussion *(Room Cardenal Mendoza)*			
	KEYNOTE LECTURES			
11:30 - 12:00	**Room Rey Felipe II - Nanomaterials and Nanofluids** *Chair: Tad Adschiri* 81563. DEVELOPMENT OF ULTRA SMALL METAL NANOPARTICLES USING CONTINUOUS FLOW REACTOR Akira Yoko, Tohoku University (Japan)	**Room Dr. Luis de Mercado - Nanomaterials and Nanofluids** *Chair: Richard Tilley* 81168. NANOSTRUCTURED MAGNETIC MATERIALS Lise-Marie Lacroix, INSA- Toulouse (France)	**Room José Zorilla- Hydrothermal Liquefaction** *Chair: Danilo Cantero* 80828. THERMOCHEMICAL CONVERSION OF LOW DENSITY POLYETHYLENE (LDPE) TO VALUE-ADDED OIL IN SUPERCRITICAL WATER Bushra Al-Duri, University of Birmingham (UK)	**Room Claudio Moyano - Reaction Engineering & Catalysis** *Chair: María José Cocero* 81549. LOW TEMPERATURE CATALYTIC SUPERCRITICAL WATER GASIFICATION FOR CONTINUOUS HYDROGEN GENERATION FROM BIOMASS WASTEWATER Edward Lester, University of Nottingham (UK)
	ORAL PRESENTATIONS			
12:00 - 12:15	79539. DEVELOPMENT OF A CONTINUOUS FLOW HYDROTHERMAL SYNTHESIS PROCESS FOR NANO HYDROXYAPATITE: TOWARDS A NEW GENERATION OF FERTILIZERS Regina Burve, Technical University of Denmark (Denmark)	79941. SUSTAINABILITY AND QUALITY: HYDROTHERMAL INJECTION SYNTHESIS OF MAGNETIC NANOMATERIALS Annie Regan, Trinity College Dublin (Ireland)	81715. HYDROTHERMAL LIQUEFACTION OF RESIDUAL BIOMASS FOR SUSTAINABLE AVIATION FUEL PRODUCTION Ana Fernández, PressTech-BioEcoUVa - University of Valladolid (Spain)	80876. MICROWAVE-INTENSIFIED SOLVOTHERMAL APPROACH TO GLYCEROL VALORIZATION CATALYZED BY GRAPHENE OXIDE Armando Quitain, Kumamoto University (Japan)
12:15 - 12:30	81706. SIMULTANEOUS MACRO- AND NANO- DESIGN OF HYDROXYAPATITE PARTICLES BY HYDROTHERMAL PROCESSES Andrea Ruffini, CNR-ISSMC (Italy)	79478. SOLVOTHERMAL SYNTHESIS OF METALOXIDE SPHERICAL ASSEMBLIES AND THEIR APPLICATIONS Kazuya Kobiro, Kochi University of Technology (Japan)	80881. DEAMINATION OF BIO-OIL USING HYDROTHERMAL LIQUEFACTION INTENSIFIED WITH SUPERCRITICAL CARBON DIOXIDE Taisei Nagamine, Kumamoto University (Japan)	80746. MEDIA MATTERS: THE IMPACT OF THE ALGAL GROWTH WATER ON SUPERCRITICAL WATER GASIFICATION Kieran Heeley, University of Birmingham (UK)
12:30 - 12:45	79891. HYDROTHERMAL SYNTHESIS OF SURFACE-MODIFIED ZrO_2 NANOPARTICLES FOR DEVELOPING SCINTILLATION DETECTORS Akito Watanabe, Tohoku University (Japan)	79946. SOLVOTHERMAL SYNTHESIS OF SOLUBLE, SURFACE MODIFIED METAL OXIDE NANOCRYSTALS Peter Dunne, Trinity College Dublin (Ireland)	80808. SUPERCRITICAL WATER VALORIZATION OF CHITIN IN A CONTINUOUS REACTION SYSTEM Andrea Casas González, PressTech-BioEcoUVa - University of Valladolid (Spain)	80773. HYDROTHERMAL DECHLORINATION OF POLYVINYL CHLORIDE FOR CHEMICAL RECYCLING Douglas Hungwe, Hosei University (Japan)
12:45 - 13:00	81612. TOWARDS FUNCTIONAL NANOMATERIAL INKS FOR 3D-PRINTED ELECTRONICS VIA CONTINUOUS FLOW HYDROTHERMAL SYNTHESIS Robyn Worsley, University of Nottingham (UK)	81732. MULTI-STEP SYNTHETIC APPROACH FOR BUILDING HIERARCHICAL NANOSTRUCTURES Lucy Gloag, University of Technology Sydney (Australia)	80477. HYDROTHERMAL REACTIONS OF ALKYLAMINES IN SUB- AND SUPERCRITICAL WATER STUDIED BY NMR SPECTROSCOPY Ken Yoshida, Tokushima University (Japan)	81737. MICROWAVE HYDROTHERMAL PREPARATION OF REDUCED GRAPHENE OXIDE INDUCED P-AGO/N-MOO3 HETEROSTRUCTURES FOR ENHANCED PHOTOCATALYTIC ACTIVITY THROUGH S-SCHEME MECHANISM AND ITS ELECTROCHEMICAL PERFORMANCE Shivanna Srikantaswamy, University of Mysore (India)
13:15 - 14:15	Lunch *(Room Cardenal Mendoza)*			
14:15 - 15:15	**AWARDS CEREMONY & PROF. BYRAPPA TRIBUTE** *(Room Paraninfo)*			
	KEYNOTE LECTURES			
15:15 - 15:45	**Room Rey Felipe II - Inorganics and Surface** *Chair: Masahiro Yoshimura* 80177. FORMATION OF DISPERSIVE ANATASE TiO_2 SUB-MICRO SPHERES FROM Mg/Al-BEARING TIOSO4 SOLUTION VIA HYDROTHERMAL HYDROLYSIS-CALCINATION ROUTE Fan Yang, Tsinghua University (China)	**Room Dr. Luis de Mercado - Inorganics and Surface** *Chair: Miriam Unterlass* 81676. SCALABLE SELF-ASSEMBLY OF ALL-DIELECTRIC NANOPARTICLE MONOLAYER METAMATERIALS Raul Barbosa, The University of Texas (USA)		**Room José Zorilla- CO_2 C&S** *Chair: Angel Martín Martínez* 81585. STUDY OF THE SCALING UP OF PROCESSES FOR CO2 TRANSFORMATION IN HYDROTHERMAL MEDIA María Dolores Bermejo Roda, PressTech-BioEcoUVa - University of Valladolid (Spain)
15:45 - 16:15	Coffee break & Poster's discussion *(Room Cardenal Mendoza)*			
	KEYNOTE LECTURE	**ORAL PRESENTATIONS**		
16:15 - 16:30	81764. SOLUTION SYNTHESIS CHEMISTRY OF MULTIFUNCTIONAL STRUCTURAL SYSTEMS Dan Wang, Chinese Academy of Sciences (China)	80154. INFLUENCE OF TEMPERATURE ON WET FORMATION OF ε-$Zn(OH)_2$ PRECUSORS AND ZnO WHISKERS Shuyu Lin, Tsinghua University (China)		81467. SUSTAINABLE MAGNETIC FRAMEWORK COMPOSITES FOR EFFICIENT CO_2 CAPTURE John Luke Woodliffe, University of Nottingham (UK)
16:30 - 16:45		80174. SEPARATION AND UTILIZATION OF P-BEARING RESOURCES BY HYDROCYCLONE AND HYDROTHERMAL METHODS Xiang Lan, Tsinghua University (China)		81768. THE ROLE OF METAL OXIDE PREPARATION METHODS ON CHEMICAL LOOPING COMBUSTION OF BIOCHARS Fatih Gulec, University of Nottingham (UK)
16:45 - 17:00	**ORAL PRESENTATIONS** 80723. CONTINUOUS FLOW HYDRO- AND SOLVOTHERMAL SYNTHESES OF PIEZOELECTRIC AND MAGNETIC NANOMATERIALS Robyn Worsley, University of Nottingham (UK)	79928. AUTOMATION AT THE LAB-SCALE: METAL NANOPARTICLES ANCHORED ON FLEXIBLE POLYURETHANE SPONGES SYNTHESIZED HYDROTHERMALLY AS CATALYSTS FOR FULLY AUTOMATED REACTIONS Olivier Gazil, University of Konstanz (Germany)		81523. HYDROTHERMAL REDUCTION OF CO_2 BY USING CATALYSTS AND BIOMASS RESIDUES Maira Ivette Chinchilla Dueñas, PressTech-BioEcoUVa - University of Valladolid (Spain)
17:00 - 17:15	80175. ENHANCED CH4 SENSING BY ZnO/CeO_2/Pd COMPOSITE Renjie Chen, Tsinghua University (China)			80740. CO_2-LOADED AMINES CONVERSION TO FORMIC ACID: NEW PERSPECTIVES FOR GREEN H_2 AND CO_2 UTILIZATION Luana Cristina dos Santos, BioEcoUVa - University of Valladolid (Spain)
17:30 - 19:30	TRAINING COURSE I: *Everything your PhD isn't teaching you* *(Room Real Chancillería)*			
18:00 - 19:30	Council ISHA Meeting			
18:30 - 20:00	**Guided sightseeing tour** *(Meeting point: Plaza San Pablo)*			

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ISHA 2023

TUESDAY – SEPTEMBER 12th, 2023

9:00 - 10:00	**PLENARY LECTURE:** WATER, SOLVENTS AND CATALYSIS: PAVING THE WAY FOR SUSTAINABLE LIGNOCELLULOSIC BIOREFINERIES. **Pablo Domínguez de María** - Sustainable Momentum, Spain *(Room Paraninfo)*
10:00 - 11:00	**Round table:** SUCCESSFUL INDUSTRIAL APPLICATIONS. Chairman: Danilo Cantero *(Room Paraninfo)* SPEAKERS: Derek Carlson, Pablo Dominguez and Cyril Aymonier.
11:00 - 11:30	Coffee break & Poster's discussion *(Room Cardenal Mendoza)*

KEYNOTE LECTURES

11:30 - 12:00	Room Rey Felipe II - Properties	Room Dr. Luis de Mercado - Sustainability	Room José Zorilla - Material Synthesis	Room Claudio Moyano - Material Synthesis
	Chair: Jalel Labidi	*Chair: Juan García Serna*	*Chair: Edward Lester*	*Chair: Akira Yoko*
	80888. NANOSIZED EFFECT ON ELECTRONIC/LOCAL STRUCTURES IN ULTRAFINE CeO_2 NANOMARTICLES BY X-RAY ABSORPTION/EMISSION SPECTROSCOPY Kakeru Ninomiya. Tohoku University (Japan)	82062. SOLVO-/HYDROTHERMAL PROCESSES FOR MATERIALS RECYCLING: TOWARDS A CIRCULAR ECONOMY Cyril Aymonier. Université de Bordeaux & ICMCB-CNRS (France)	81762. SYNTHESIS OF SUBSTITUTED PETROLEUM BY HYDROTHERMAL REACTION OF BIOMASS -COMBINING PULP & PAPER INDUSTRY AND CHEMICAL INDUSTRY TOWARD CARBON NEUTRAL SOCIETY- Tadafumi Adschiri. Tohoku University (Japan)	80824. ACTIVATED ELEMENTAL Se - A VIABLE SYNTHETIC PRECURSOR FOR ROOM-TEMPERATURE SYNTHESIS OF HIGH PERFORMANCE MATERIALS Kirill Kovnir. Iowa State Universit & US DOE Ames National Laboratory (USA)

ORAL PRESENTATIONS

12:00 - 12:15	80834. MODELLING AND EXPERIMENTAL MEASUREMENTS OF CO_2 SOLUBILITY IN AQUEOUS AMINES Juan Diego Arroyave Roa. TermoCal-BioEcoUVa - University of Valladolid (Spain)	79791. DIRECT FABRICATION OF DESIGNED PIEZOELECTRIC MATERIALS BY HYDROTHERMAL ROUTE Thi Nghi Nhan Nguyen. National Cheng Kung University (Taiwan)	78295. HYDROTHERMAL ASSISTED SYNTHESIS OF MXENES AND THEIR COMPOSITES WITH EXCELLENT GAS SENSING PERFORMANCE Shu Yin. Tohoku University (Japan)	81688. FLOW VISUALISATION TECHNIQUE FOR OPTIMISATION OF CONTINUOUS-FLOW HYDROTHERMAL REACTOR DESIGN Thomas Huddle. University of Nottingham (UK)
12:15 - 12:30	79947. MAPPING THE CONTROLLED HYDROTHERMAL SYNTHESIS OF MATERIALS WITH PRINCIPAL COMPONENT ANALYSIS Peter Dunne. Trinity College Dublin (Ireland)	81498. THREE-DIMENSIONAL CARBON AEROGEL DERIVED FROM ELECTRONIC WASTE FOR THE ADSORPTION OF PHENOL FROM WASTEWATER Marut Jain. Univ. of Queensland (Australia) & Indian Institute of Technology Delhi (India)	79724. A DESIGN CONCEPT FOR HYDROTHERMAL AND SUBHYDROTHERMAL SYNTHESIS OF HIGH-PERFORMANCE POLYIMIDES Daniel Alonso Cerrón-Infantes. University of Konstanz (Germany) & CeMM (Austria)	81630. DEVELOPING CFD MODELS FOR CONTINUOUS HYDROTHERMAL SYNTHESIS REACTOR AND PERFORMANCE EVALUATION OF CFD MODELS VIA IMAGE PROCESSING Ahmet Erdogan. University of Nottingham (UK) & Inonu University (Turkey)
12:30 - 12:45	80742. DENSITIES OF AQUEOUS 3-AMINO-1-PROPANOL, 2-AMINO-2-METHYL-1-PROPANOL AND THEIR BLENDS AT HIGH PRESSURES Luana Cristina dos Santos. BioEcoUVa - University of Valladolid (Spain)	79931. IN-SITU CATALYTIC HYDROPROCESSING SOLVOTHERMAL CO-LIQUEFACTION OF WASTE BIOMASS WITH A PETROLEUM FEEDSTOCK Abhisek Sahoo. Indian Institute of Technology (India)	80726. HYDROTHERMAL SYNTHESIS OF $BaCr_2(P_2O_7)_2$ PARTICLES AND NEAR-INFRARED REFLECTANCE CHARACTERISATION: INFLUENCE OF REACTION PARAMETERS Diego Carrillo. CINVESTAV of the National Polytechnic Institute (Mexico)	81674. CAN MACHINE LEARNING ACCELERATE MATERIALS DEVELOPMENT USING HYDROTHERMAL SYNTHESIS? Thomas Huddle. University of Nottingham (UK)
12:45 - 13:00	80509. SOLUBILITY OF NO FROM COMBUSTION GASES IN AMINE SOLUTIONS Nataly Alejandra Castro Ferro. PressTech-BioEcoUVa - University of Valladolid (Spain)		79817. STIRRING HYDROTHERMAL SYNTHESIS OF COMPOSITION-CONTROLLED (K,Na)NbO$_3$ PARTICLES Pradeep Ellawala Kankanamge. Technical University of Denmark (Denmark)	81716. TELESCOPED FLOW SYNTHESIS AND CRYSTALLISATION OF PARACETAMOL Karen Robertson. University of Nottingham (UK)
13:00 - 14:15	Lunch *(Room Cardenal Mendoza)*			
14:15 - 15:15	**PLENARY LECTURE:** THE POWER OF WATER: A VERSATILE SOLVENT FOR MATERIALS SYNTHESIS. **Miriam Unterlass** - University of Konstanz, Germany *(Room Paraninfo)*			

KEYNOTE LECTURES

15:15 - 15:45	Room Rey Felipe II - Applications	Room Dr. Luis de Mercado - Sustainability	Room José Zorilla - Material Synthesis	Room Claudio Moyano - Polymers, Composites and Hybrids
	Chair: María José Cocero	*Chair: Danilo Cantero*	*Chair: Ken Yoshida*	*Chair: Richard Riman*
	THE ROLE OF HYDROTHERMAL AND SOLVOTHERMAL SOLVENT IN BIOMASS CONVERSION Jaehoon Kim. Sungkyunkwan University (South Korea)	80813. HYDROTHERMAL AQUEOUS CONDENSATE - A NEW PLAYER IN FOOD WASTE VALORISATION FOR SUSTAINABLE USE IN AGRICULTURE Roy Posmanik. Volcani Institute (Israel)	80769. SILICATE-BASED COOL PIGMENTS DEVELOPMENT UNDER SUBCRITICAL AND SUPERCRITICAL HYDROTHERMAL CONDITIONS Juan Carlos Rendón Angeles. CINVESTAV of the National Polytechnic Institute (Mexico)	81648. ENVIRONMENTALLY FRIENDLY, HIGH STABILITY METAL-ORGANIC FRAMEWORK SYNTHESIS IN SECONDS Hashim. A Alhashimi. University of Nottingham (UK)
15:45 - 16:15	Coffee break & Poster's discussion *(Room Cardenal Mendoza)*			

ORAL PRESENTATIONS

16:15 - 16:30	79949. DIVERSITY-ORIENTED SOLVOTHERMAL SYNTHESIS OF DIHYDROPYRIDINE DIKETONES Lukas Lelmhofer. CeMM Research Center for Molecular Medicine (Austria)	81552. THE MANUFACTURE AND USE OF METAL ORGANIC FRAMEWORKS AS A MEANS TO SEPARATE CO2 FROM FLUE GAS STREAMS - FROM BENCH TO PILOT TO FULL SCALE Edward Lester. University of Nottingham (UK)	79919. ADDITIVE-ASSISTED HYDRO- AND SOLVOTHERMAL SYNTHESIS OF CRYSTALLINE AROMATIC ORGANIC HIGH-PERFORMANCE POLYMERS Florian Vollstaedt. University of Konstanz (Germany)	79912. COVALENTLY LINKED PIGMENT@METAL OXIDE HYBRID MATERIALS BY ONE-POT SOLVOTHERMAL SYNTHESIS Frank Saller. University of Konstanz (Germany)
16:30 - 16:45	80889. MICROWAVE HYDROTHERMAL TREATMENT FOR THE EXTRACTION OF BIOACTIVE COMPOUNDS AND BIOPOLYMERS FROM THE LICHEN EVERNIA PRUNASTRI Julie Queffelec. CINBIO - University of Vigo (Spain)	HYDROTHERMAL DECOMPOSITION OF PLASTIC - VALORIZATION OF NON-RECYCLABLE MIXED PLASTIC WASTE Ran Darzi. Israel Institute of Technology (Israel)	79944. HYDROTHERMAL INJECTION: SYNTHETIC CONTROL BY REACTION ENGINEERING Peter Dunne. Trinity College Dublin (Ireland)	81731. IN-DEPTH STUDY OF ORGANIC SALT INTERMEDIATES OF THE HYDROTHERMAL SYNTHESIS OF IMIDES Celine Kuchler. University of Konstanz (Germany)
16:45 - 17:00	81536. EXTRACTION AND DEGRADATION KINETICS OF PECTIC OLIGOSACCHARIDES (POS) FROM ONION SKIN WASTES USING SUBCRITICAL WATER Oscar Benito-Román. University of Burgos (Spain)	80856. RECENT ADVANCE IN HYDROTHERMAL SYNTHESES OF LAYERED TRANSITION METAL COMPOUNDS FOR ENERGY AND ENVIRONMENT APPLICATIONS Guangshe Li. Jilin University (China)	81521. HYDROTHERMAL INJECTION FOR PHASE-CONTROLLED $CaCO_3$ SYNTHESIS Adrian Sanz Arjona. University of Copenhagen (Denmark)	79915. SYNTHESIS OF QUINOXALINE-BASED DIAMINES AND THEIR HYDROTHERMAL POLYMERIZATION TO POLYIMIDES Tobias Klenk. University of Konstanz (Germany)
17:00 - 17:15	81705. DIRECT RECYCLING OF LITHIUM-ION BATTERIES POSITIVE ELECTRODES PRODUCTION SCRAPS, AN INNOVATIVE PROCESS ASSISTED BY SUPERCRITICAL CO_2 Philippot Gilles. Université de Bordeaux & ICMCB-CNRS (France)		81632. CAN MACHINE LEARNING HELP TO DEVELOP NOVEL METAL OXIDE NANOCOMPOSITES IN A CONTINUOUS HYDROTHERMAL PROCESS? Thomas Huddle. University of Nottingham (UK)	
17:30 - 19:30	TRAINING COURSE II: *Everything your PhD isn't teaching you (Room Real Chancillería)*			
20:30 - 22:30	**ISHA 2023 Conference Gala dinner: Casa del Sol (Science Museum)**			

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ISHA 2023

WEDNESDAY – SEPTEMBER 13th, 2023

9:00 - 10:00	**PLENARY LECTURE:** ATOMICALLY PRECISE SYNTHESIS OF METAL NANOPARTICLES FOR CATALYSIS. **Prof. Richard Tilley** - University of New South Wales, Sydney, Australia *(Room Paraninfo)*
10:00 - 11:00	**Round table:** ISHA 2030. Chairwoman: María José Cocero *(Room Paraninfo)* SPEAKERS: Masahiro Yoshimura, Tadafumi Adschiri and Ed Lester.
11:00 - 11:30	Coffee break & Poster's discussion *(Room Cardenal Mendoza)*

KEYNOTE LECTURES

11:30 - 12:00	Room Rey Felipe II - Process Design	Room Dr. Luis de Mercado - Sustainability	Room Claudio Moyano - Biorefinery and Separations
	Chair: Akira Yoko	*Chair: Edward Lester*	*Chair: Danilo Cantero*
	79859. WHY OUR SUBJECTS HAVE SHIFTED FROM HYDROTHERMAL PROCESSES TO SOFT, SOLUTION PROCESSES? Masahiro Yoshimura. National Cheng Kung University (Taiwan)	81631. CONTINOUS HYDROTHERMAL SYNTHESIS OF METAL OXIDE NANOPARTICLES/NANOCOMPOSITES Hossein Anbari. University of Nottingham (UK)	81273. NEW VINEGAR PRODUCTION FROM VINEGAR PROCESSING RESIDUE BY THE SUBCRITICAL WATER HYDROLYSIS AND ACETIC ACID FERMENTATION Mitsuru Sasaki. Kumamoto University (Japan)

ORAL PRESENTATIONS

12:00 - 12:15	79986. HEAT TRANSFER IN SUPERCRITICAL WATER REACTOR Mihail-Călin Licu. Institute of Physical Chemistry "Ilie Murgulescu" (Romania)	79998. HIGH-TEMPERATURE WATER AS VERSATILE REACTION MEDIUM TOWARDS LOPHINE ANALOGUES Fabian Amaya García. University of Konstanz (Germany)	80895. POLYURETHANE ADHESIVES FROM PINUS RADIATA LIGNIN BIOPOLYOLS Fabio Hernández. UPV/EHU - University of the Basque Country (Spain)
12:15 - 12:30	79923. EXPLORING THE HYDROTHERMAL LANDSCAPE THROUGH AUTOMATION IN FLOW: CHALLENGES AND OPPORTUNITIES Robert Pazdzior. University of Konstanz (Germany)	80424. FABRICATION OF POROUS MATERIALS USING FLUORESCENT WASTE LAMPS BY HYDROTHERMAL HOT PRESSING (HHP) Zully Matamoros-Veloza. TECNM-Instituto Tecnológico de Saltillo (Mexico)	81576. HYDROLYSIS OF THE TRIGLYCERIDES OF SUNFLOWER SEED OIL USING SUBCRITICAL AND SUPERCRITICAL WATER Enkeledo Menalla. PressTech-BioEcoUVa - University of Valladolid (Spain)
12:30 - 12:45	79843. A PERSPECTIVE ON IMPROVING ENERGY EFFICIENCY IN ELECTROCHEMICAL CO_2 REDUCTION: THE POTENTIAL OF HYDROTHERMAL SYSTEMS Takaaki Tomai. Tohoku University (Japan)	80116. DEVELOPING A SOLVOTHERMAL REACTION CELL FOR IN SITU NEUTRON SCATTERING OF CRYSTALLISATION Mark Crossman. University of Warwick (UK)	81551. SYNTHESIS OF LAYERED DOUBLE HYDROXIDES FOR SORBING PHARMACEUTICALS FROM WASTEWATER Edward Lester. University of Nottingham (UK)
12:45 - 13:00	82815. SUBCRITICAL WATER PRETREATMENT OF BREWER'S SPENT GRAINS FOR VALUE-ADDED PRODUCTS AND BIOENERGY RECOVERY IN A BIOREFINERY CONCEPT William G. Sganzerla. VORN Bioenergy GmbH (Germany)	79913. SUPERCRITICAL WATER IMPREGNATION OF ZINC OXIDE NANOPARTICLES ON CARBON SUPPORT Florentina Maxim. "Ilie Murgulescu" Institute of Physical Chemistry (Romania)	80877. CO_2-INTENSIFIED HYDROTHERMAL CLEAVAGE OF GLYCOSIDIC BONDS IN CITRUS BIOFLAVONOIDS Armando Quitain. Kumamoto University (Japan)
13:00 - 13:15	**Closing ceremony *(Room Paraninfo)***		
13:15 - 14:30	Lunch *(Room Cardenal Mendoza)*		

PLENARY LECTURES

MONDAY – SEPTEMBER 11th, 2023

9:00 - 10:00 ROOM PARANINFO

HYDROTHERMAL-ENABLED SUSTAINABLE MANUFACTURING - THE EXPERIENCE AND VISIONS.

Prof. Richard Riman - Rutgers, The State University of New Jersey, USA
Distinguished Professor, Founder, Chief Scientist

Richard Riman joined Rutgers University's Department of Materials Science and Engineering in 1986 as an assistant professor after earning his Ph.D. at MIT.
His research explores engineering principles for synthesizing and processing ceramics and aims to make sustainable processes that match or improve incumbent commercial high-temperature processes for materials manufacturing. Aside from his current focus on structural materials, his past expertise encompasses commercial innovation in electronic-, optical-, and bio-materials manufacturing. In recognition of his work, he has received many national and international awards, including the ISHA Lifetime Achievement Award, and mentions in TV and radio media. He is the author or co-author of nearly 200 patents and over 200 peer-reviewed journal articles.
Around the world, Richard Riman has established cooperative agreements with private companies, government laboratories, and government agencies. He has founded 5-cleantech companies to manufacture innovative materials, including Solidia Technologies, RRTC, and Queens Carbon. These companies focus on green manufacturing methods for construction materials useful for consumer, building, and infrastructure applications.

TUESDAY – SEPTEMBER 12th, 2023

9:00 - 10:00 ROOM PARANINFO

WATER, SOLVENTS AND CATALYSIS: PAVING THE WAY FOR SUSTAINABLE LIGNOCELLULOSIC BIOREFINERIES.

Pablo Domínguez de María - Sustainable Momentum, S.L., The Canarias Islands, Spain
PhD in Biocatalysis, Founder | CEO | CSO at Sustainable Momentum, SL

Dr. habil. Pablo Domínguez de María is the Founder, CSO and CEO of Sustainable Momentum, S.L, a consultancy firm providing technical expertise in biorefineries, biocatalysis and sustainable chemistry, as well as strategic support for innovation and training in European Projects.
He holds BSc´s in Pharmacy and Chemistry, and a PhD in Biocatalysis (2002). He worked in industry during 6.5 years (2003-2009, two years at Evonik AG, in Germany, and 4.5 years at AkzoNobel BV in the Netherlands) being involved in different projects regarding sustainable chemistry, organocatalysis, neoteric solvents and white biotechnology. In 2009 he joined RWTH Aachen University (Technical Chemistry Department, ITMC) as Group Leader. In 2015 he successfully defended his Habilitation (Thesis: Bio-based catalysis for petroleum-free biorefineries and fine chemicals).
He has co-authored > 120 scientific publications and book chapters (h-index 39, > 5200 citations), and several patents and books.

TUESDAY – SEPTEMBER 12th, 2023

14:15 - 15:15 ROOM PARANINFO

THE POWER OF WATER: A VERSATILE SOLVENT FOR MATERIALS SYNTHESIS.

Miriam Unterlass - University of Konstanz, Germany
Professor of Solid State Chemistry

Miriam Unterlass studied chemistry, materials science, and chemical engineering in Würzburg, Southampton, and Lyon. Between 2009 and 2011, she worked on her PhD thesis at the Max Planck Institute of Colloids and Interfaces, followed by a postdoc at ESPCI in Paris. In December 2012, she established her research group “Advanced Organic Materials” at the Institute of Materials Chemistry at Technische Universität Wien (TU Wien).
In September 2018, Miriam obtained her habilitation venia docendi in materials chemistry and in June 2019, she became assistant professor at TU Wien. She joined CeMM as an adjunct principal investigator in 2018 and in June 2021, she became full professor of solid-state chemistry at the University of Konstanz (Germany).
The research interests of Miriam Unterlass are centered on compounds that are rich in aromatic and heterocyclic moieties. These materials show interesting optoelectronic properties and can be used as dyes, for example. A major focus lies on the discovery of new compounds and the development of novel, environmentally friendly, non-toxic, and highly efficient synthetic techniques, especially via hydrothermal synthesis. Miriam is committed to research transfer: She founded her first company, UGP materials, in 2017 and develops graphic design materials and courses on scientific topics.

WEDNESDAY – SEPTEMBER 13th, 2023

9:00 - 10:00 ROOM PARANINFO

ATOMICALLY PRECISE SYNTHESIS OF METAL NANOPARTICLES FOR CATALYSIS.

Prof. Richard Tilley - University of New South Wales, Sydney, Australia
Professor in Chemistry

Professor Richard Tilley is the Director of Electron Microscope Unit and a Professor in the School of Chemistry at the University of New South Wales. He graduated with a Master of Chemistry from Oxford University and then completed his PhD at the University of Cambridge, after which he was a Postdoctoral Fellow at the Toshiba basic R&D Center, Tokyo. He leads a research team focused on the solution synthesis of nanocrystals for catalysis and biomedical imaging.

ROUND TABLE

MONDAY – SEPTEMBER 11th, 2023

10:00 - 11:00 **ROOM PARANINFO**

Round table: CLIMATE ACTIONS AND INNOVATION OPPORTUNITIES. Chairman: Juan García Serna

SPEAKERS: Richard Riman, Miriam Unterlass and Richard Tilley

TUESDAY – SEPTEMBER 12th, 2023

10:00 - 11:00 **ROOM PARANINFO**

Round table: SUCCESSFUL INDUSTRIAL APPLICATIONS. Chairman: Danilo Cantero

SPEAKERS: Derek Carlson, Pablo Dominguez and Cyril Aymonier.

WEDNESDAY – SEPTEMBER 13th, 2023

10:00 - 11:00 **ROOM PARANINFO**

Round table: ISHA 2030. Chairwoman: María José Cocero

SPEAKERS: Masahiro Yoshimura, Tadafumi Adschiri and Ed Lester.

MONDAY

11:30-13:00

A. Applications & Products

Nanomaterials and nanofluids

KEYNOTE LECTURE

ORAL PRESENTATIONS

8th International Solvothermal and Hydrothermal Association Conference
ISHA 2023
Valladolid, Spain
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MONDAY – SEPTEMBER 11th, 2023

Room Rey Felipe II – Nanomaterials and Nanofluids

11:30 - 12:00 KEYNOTE LECTURE 81563

DEVELOPMENT OF ULTRA SMALL METAL OXIDE NANOPARTICLES USING CONTINUOUS FLOW REACTOR

Akira Yoko[1], Yuki Omura[2], Nobutaka Chiba[2], Kakeru Ninomiya[3], Maiko Nishibori[3], Tadafumi Adschiri[1,4]

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To exploit the unique properties depending on nano-size effects of metal oxides, a new synthesis method was explored. Utilizing the rapid hydrolysis reaction under hydrothermal conditions, metal oxide nanoparticles were synthesized from metal organic complex with small size and narrow size distribution.
High conversion was achieved within several tens of millisecond, and particles formed just after the nucleation were obtained. As shown in Figure 1, particles grow with two stages; initially particles grow rapidly by collision and coalescence and then grow slowly by dissolution and reprecipitation.
For the materials, CeO2, ZrO2, and the solid solution of them were successfully synthesized with small particle size as less than 2 nm with organic modifiers. Precise control of particles size was achieved only by changing reaction time based on the intensive reaction kinetics and precursor chemistry.
The key phenomena to control particle size in ultrasmall size region (< 5 nm), was the initial coalescence of small particles formed after the nucleation (Figure 1). Coalescence was controlled by organic modifications, reaction temperature, and reaction time. The rate of coalescence was different between different materials. The developed synthesis method must broaden new properties of metal oxides, which has been unexplored.

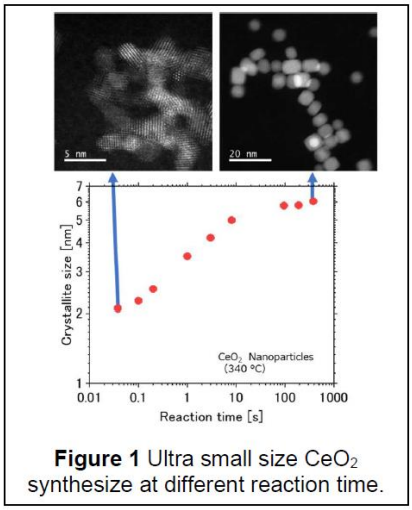

Figure 1 Ultra small size CeO_2 synthesize at different reaction time.

Keywords: Continuous flow synthesis, Nucleation, Ultra-small nanoparticles, Metal oxide, Coalescence.

MONDAY – SEPTEMBER 11th, 2023

Room Dr. Luis de Mercado - Nanomaterials and Nanofluids

11:30 - 12:00 KEYNOTE LECTURE 81168

NANOSTRUCTURED MAGNETIC MATERIALS

Lacroix, L.M.[1,2], Lecerf I.,[1] Maties G. D.,[1] Blon, T.,[1] Leïchlé T.,[3,4] Viau, G.[1]

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The fabrication of micrometric magnets and their integration into portable devices reveal great interests for telecommunications, automotive, biomedical and space applications, but still remain highly challenging. The bottom-up approach for nanostructured magnets is an interesting alternative route to the classical rare earth metallurgy or thin film deposition. Indeed, the recent progresses in the magnetic nanoparticle synthesis allow a good control of the particle size, shape and chemical composition. For instance, single-crystalline Co nanorods (NRs) can be quantitatively prepared by the polyol process and combine a high magnetization and a large magnetic anisotropy.[1]
These anisotropic particles constitute building blocks of primary choice for permanent magnet, providing that high volume fraction and good alignment degree are obtained.[2] We recently reported a versatile assembly process benefiting from magnetophoresis force:[3] the NRs dispersed in solution can be attracted towards high magnetic field gradient regions, driving controlled assemblies at desired location of the substrate. Capillary forces encountered during the solvent evaporation then yield dense assemblies of controlled size and shape.[3]
Integrated submillimeter magnets as well as millimetric self-standing magnets were obtained. A first proof of concept of our nanostructured magnets as actuating force into a micro-electro-mechanical-system (MEMS) gravimetric sensor will finally be presented.[4]

Keywords: Co nanorods, Directed self-assembly, MEMS sensor, permanent magnet.

*(1) Anagnostopoulou, E.et al. Nanoscale **2016**, 8 (7), 4020–4029.*
*(2) Ener, S.et al. Acta Mater. **2018**, 145, 290–297.*
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Room Rey Felipe II – Nanomaterials and Nanofluids

12:00 - 12:15 ORAL PRESENTATION 79539

DEVELOPMENT OF A CONTINUOUS FLOW HYDROTHERMAL SYNTHESIS PROCESS FOR NANO HYDROXYAPATITE: TOWARDS A NEW GENERATION OF FERTILIZERS

Burve, R., Kiebach, W.-R., Grivel, J.-C.

Department of Energy Conversion and Storage, Technical University of Denmark, Anker Engelunds Vej, building 301, 2800 Kgs.Lyngby, Denmark
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The synthesis of biocompatible hydroxyapatite nanoparticles (HAp NPs) has gained significant attention due to their potential applications in various fields, including biomedicine, environmental remediation, and agriculture. It was proposed that HAp NPs could become one of the alternatives to conventional fertilizers as a source of phosphorus. Nanofertilizers offer several advantages such as a slow release of nutrients and improved nutrient uptake efficiency. Foliar application of these nanofertilizers could help reducing environmental impact even more [1, 2]. However, to evolve this technology, firstly, a fast, environmentally friendly, and scalable synthesis of HAp NPs should be developed.
It was shown earlier that the use of supercritical water in a one-stage continuous hydrothermal process can be implemented for the synthesis of HAp NPs rods with length 65 or 140 nm depending on the selected temperature regime [3]. In this study a similar reactor design but with the addition of a second mixing stage is used [4]. The primary goal of the research is to develop a synthesis method that enables control over the size of the nanoparticles. In addition to that, smaller particle sizes should be achieved as we believe this might improve NPs penetration through the leaf cuticle. Phase formation of the produced NPs was confirmed by X-ray diffraction. Particle size and shape were investigated by transmission electron microscopy. It was shown that the use of a second mixing stage allows to decrease the particle size up to 30 nm without compromising crystallinity. In addition to using different mixing stages, adjusting pH and controlling the flow speed allow to tune the size of the produced HAp NPs from 30 to 80 nm. The experimental setup allows for continuous synthesis of phase pure and highly crystalline HAp NPs, ensuring reproducibility and scalability of the process.

Keywords: Hydroxyapatite, nanofertilizers, supercritical water, hydrothermal reactor.

[1] F. Zulfiqar, M. Navarro, M. Ashraf, N.A. Akram, S. Munne-Bosch, Plant Sci., 2019, 289, 110270.
[2] A.A.A. Elsayed, A. EL-Gohary, Z.K. Taka, H.M. Farag, M.S. Hussein, K. AbouAitah, Sci. Hortic., 2022, 295, 110851.
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Acknowledgements: The present work was supported by the project "Biocompatible nanofertilizers for targeted delivery and programmed release of essential mineral ions in crops" Nr. NNF21OC0066114, funded by Novo Nordisk Foundation Challenge Programme 2021 – Smart Nanomaterials for Application in Life-Science.

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12:15 - 12:30 ORAL PRESENTATION 81706.

SIMULTANEOUS MACRO- AND NANO- DESIGN OF HYDROXYAPATITE PARTICLES BY HYDROTHERMAL PROCESSES

A. Ruffini[1], F. Pupilli[1], S. Sprio[1], A. Tampieri[1]

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Hydroxyapatite is the main inorganic phase of the natural bone, and it can be used as essential raw material in tissue engineering and regenerative medicine, in the production of bone substitutes owning biomimetic, osteoconductive and osteoinductive properties.
The control of the micro- and nano-structure of hydroxyapatite particles, during its synthesis, is fundamental for the success in several applications, like the realization of scaffold by sintering, drug delivery system, bone and tooth fillers, adsorptive materials, prosthetics, in vitro implants, etc.
This work aims to provide an overview for the realization of micro- and nano-metric hydroxyapatite particles, with the desired morphology of the crystals, through hydrothermal processes (synthesis in aqueous solution, at high pressure and temperature, in a closed system), starting from commercial calcium carbonate. Compared to other techniques, in this conditions hydroxyapatite precipitates from an overheated solution, with better control over the regulating of the speed and uniformity of nucleation, growth and maturation, which affect the particle size, the morphology and aggregation of crystals, the thermal stability and stoichiometry.
It is discussed how some hydrothermal synthesis parameters (e.g. pH, temperature, process time) are fundamental to control these characteristics. For example, based on the pH condition, crystalline growth along the hydroxyapatite c-axis leads to preferential growth up and different morphologies, from plate to nanorod crystals, obtained under neutral, acid or basic conditions. Furthermore, the control of growth direction of hydroxyapatite is necessary for simulate the crystallization of bone minerals within the collagen fibrils in bone tissue, according to a preferential orientation.
SEM microscopy, XRD, ICP-OES and FTIR spectroscopy techniques have been used to characterize the particle size distribution, the growth direction, the chemical composition and the crystalline phases. In addition, the saturation index of reaction systems under different conditions is considered in order to explore the mechanism of formation of hydroxyapatite.

Keywords: crystals nanodesign, morphology control, hydroxyapatite, regenerative medicine
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[2] Ali Rafique M.M. et al., 2018, Hydrothermal Processing of Phase Pure and Doped Hydroxyapatite and its Characterization, Journal of Encapsulation and Adsorption Sciences, 8(1). DOI: 10.4236/jeas.2018.81002
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12:30 - 12:45 ORAL PRESENTATION 79891.

Hydrothermal synthesis of surface-modified ZrO2 nanoparticles for developing scintillation detectors

A. Watanabe[1], M. Koshimizu[2], A. Yoko[3], G. Seong[4], T. Tomai[5], T. Adschiri[3], Y. Hayashi[1], Y. Fujimoto[1], K. Asai[1]

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3 WPI-AIMR, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
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Metal-loaded liquid scintillators have been used in many neutrino and high-energy physics experiments. We developed ZrO2 nanoparticle-loaded liquid scintillators as novel metal-loaded systems using a super/subcritical hydrothermal process to achieve high performance. However, the loading amount of Zr was limited to 0.33 wt%1 because of the low affinity between the modifier and solvent. A key strategy for increasing the concentration limit of ZrO2 nanoparticles is to improve their dispersibility through surface modification. In this study, we attempted dual-molecule modification2 to develop ZrO2 nanoparticles that disperse well in the solvents of liquid scintillators. We selected 6-phenylhexanoic acid and 8-phenyloctanoic acid as modifiers. The two modifiers were mixed with 0.1 M ZrOCl2, the ZrO2 precursor, at a stoichiometric ratio of 1:1:8. The dual organically modified ZrO2 nanoparticles were synthesized through a batch-type subcritical hydrothermal method at 300 ºC for 10 min under 30 MPa. The synthesized nanoparticles were analyzed by XRD, TEM, TGA, and ICP-AES.
TEM observations confirmed the formation of nanoscale particles, with the average particle size being 6.8 ±1.6 nm. XRD analyses indicated the presence of tetragonal and monoclinic crystal phases, and the crystallite size was determined to be 6.8 ±2.4 nm. The matching of the particle and crystallite sizes indicates the formation of ZrO2 single nanocrystals. According to TGA, the weight percentage of the modifiers was 14.1%. From the results of TEM and TGA, the surface modification density was calculated to be 2.7 molecules/nm2. The atomic concentration of Zr in the nanoparticle-loaded liquid scintillation mixture was measured to be 1.0 wt% by ICP-AES; this is of the same order as other types of liquid scintillators used in neutrino experiments3. Thus, we succeeded in loading ZrO2 nanoparticles into liquid scintillators at a high concentration.

Keywords: Scintillator, ZrO2 nanoparticles, Surface modification, Radiation detection,
[1] A. Watanabe, et al., Nanomaterials, 2021, 11(5), 1124.
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12:45 - 13:00 ORAL PRESENTATION 81512.

TOWARDS FUNCTIONAL NANOMATERIAL INKS FOR 3D-PRINTED ELECTRONICS VIA CONTINUOUS FLOW HYDROTHERMAL SYNTHESIS

Worsley, R.[1,2], Bastola, A.[2], Hague, R.[2], Tuck, C.[2], Lester, E.[1]

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Material jetting techniques, such as inkjet printing, are showing great promise for the scalable, digital fabrication of electronic devices with arbitrary complexity.1 Conductive inks are already commercially available, whilst complex functionalities such as magnetism are difficult to obtain in printed features; materials synthesised via traditional routes are often unsuitable for jetting, and factors including particle size and shape may all affect electromagnetic performance.
Continuous hydrothermal production methods are capable of generating a wide variety of functional nanomaterials;2 the products are suspended in solution and delivered at scale, with a high degree of control over the particle characteristics, rendering this synthesis approach highly complementary to functional ink formulation work. Furthermore, nanoparticles resulting from hydrothermal syntheses typically possess an increased coverage of surface hydroxyl groups, rendering them amenable to capping agent functionalisation - an often-crucial step in obtaining stable, uniform dispersions of electro-active particulate fillers within printable inks.
In this work, a counter-current nozzle reactor3 within a bench-scale continuous-flow system is used to synthesise cobalt ferrite nanoparticles (CoFe2O4), with a view to formulating magnetic inks for 3D-printed devices. Generally, 0.01-0.10 M aqueous cobalt-iron precursor solutions are fed, at room temperature, upwards into the reactor with a flow of between 5-25 mL min-1, meeting 5-25 mL min-1 of sub/supercritical water, between 200-450 °C, leading to product formation. Pressure is maintained at 240 bar. A capping agent flow may also be fed into the system part-way through product cooling to enable in-line particle functionalisation.
Magnetometry data indicate that the synthesised CoFe2O4 products are magnetically semi-soft. Batch functionalisation of these nanoparticles with silane coupling agents vastly improves their stability within common UV-curable polymeric inks. In-flow functionalisation tests have begun, improving the commercial viability of the ink production, and jetting investigations are also underway; the initial printed structures demonstrate good response to external magnets.

Keywords: Continuous Flow, Magnetic, Multimaterial Jetting, 3D-Printing, Functionalisation
[1] G. L. Goh, H. Zhang, T. H. Chong and W. Y. Yeong, Adv. Electron. Mater., 2021, 7, 2100445.
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[3] International Patent, WO/2005/077505, 2005.

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12:00 - 12:15 ORAL PRESENTATION 79941.

SUSTAINABILITY AND QUALITY: HYDROTHERMAL INJECTION SYNTHESIS OF MAGNETIC NANOMATERIALS

Regan, A.[1,2], Thanh, N.T.K.[3], Dunne, P.W.[1]

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[2]CDT ACM, AMBER, Trinity College Dublin, College Green, D02 PN40 Dublin 2, Ireland
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Magnetic nanomaterials such as the spinel-type oxides, MFe_2O_4 (M = Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}) have emerged as key materials in nanomedicine, with highly tuneable properties, accessed by varying composition or surface modification with functional ligands.[1] Their biomedical applications such as magnetic hyperthermia, an adjuvant to cancer therapies, require the nanoparticles to be water-dispersible, biocompatible, and possess sufficiently high magnetic saturation.[2] As such, control of these properties is essential in the synthesis of these materials. While there are many examples in the literature of ways to obtain iron oxide nanoparticles, there is a happy medium between synthetic control and sustainability that has not yet been realised by any one technique in particular. The present work aims to provide a comparison of some of the most commonly employed synthetic techniques for producing nanoparticles for this application; assessing each method in terms of both synthetic control of material properties as well as compliance with green chemistry principles. In doing so, this talk will introduce the promising capabilities of a new technique — a novel, custom-built hydrothermal injection reactor — designed to combine the green sensibilities of traditional hydrothermal synthesis with the synthetic control of the popular hot injection and thermolysis methods. A variety of spinel ferrites have been targeted by each of these synthetic techniques, each characterised by powder X-ray diffraction, electron microscopy, and magnetometry, before narrowing in on cobalt ferrite ($CoFe_2O_4$) – a hard ferromagnet which offers high chemical stability and good saturation magnetisation. It has been found that hydrothermal injection synthesis allows the formation of $CoFe_2O_4$ nanoparticles with size, monodispersity, surface capping, and magnetic properties comparable to those obtained by conventional thermolysis, but with the added green credentials of hydrothermal processing. Thus, this work will showcase a new sustainable route to magnetic nanoparticles with suitable properties for use in nanomedicine – bringing green chemistry to this rapidly expanding field.

Keywords: sustainability, magnetism, nanomaterials, biomedical, reactor design

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*[2] V. Mameli, Nanoscale, 2016, **8**, 10124-10137.*

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MONDAY – SEPTEMBER 11th, 2023

Room Dr. Luis de Mercado – Nanomaterials and Nanofluids

12:15 - 12:30 ORAL PRESENTATION 79478.

SOLVOTHERMAL SYNTHESIS OF METALOXIDE SPHERICAL ASSEMBLIES AND THEIR APPLICATIONS

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Solvothermal synthesis is one of the powerful tools preparing inorganic nanomaterials. Much effort has been paid to optimize reaction conditions obtaining desired nanomaterial properties. We have prepared porous spherical nanoparticle assemblies consisted of (metal) oxide named MARIMOs under various reaction conditions including solvents, temperatures, heating rates, heating times, additives, *etc*.[1] In this paper, we summarize the preparation of MARIMO assembles made of TiO_2,[1] ZrO_2,[2] Nb_2O_5,[3,4] SnO_2,[5] CeO_2,[6] and their composites.
Metal alkoxides such as 2-propoxide and 1-butoxide were well soluble to polar organic solvents. In the cases of TiO_2, Ni_2O_5, and ZrO_2 MARIMO synthesis, these alkoxides were used with formic acid (TiO_2 and Ni_2O_5) and acetylacetone (ZrO_2) as additives, and methanol (TiO_2 and Ni_2O_5) and ethanol (ZrO_2) as solvents. On the other hand, metal nitrates are also well soluble to many polar solvents. CeO_2 MARIMO was synthesized using $Ce(NO_3)_3$, triethylene glycol as an additive, and acetonitrile as a solvent. In case SnO_2 MARIMO, a combination of $SnCl_4$, triethylene glycol, and methanol was applied.

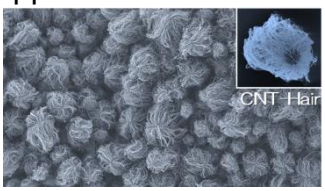

Fig. 1. SEM image of CNT-Hair conjugates

These MARIMO assemblies were applied to an anode material for lithium-ion batteries (Ni_2O_5),[3,4] a cathode catalyst for fuel cells (SnO_2),[5] and a filler for polymer composite resins.[7] One of the interesting applications is micrometer-sized spherical core catalysts for carbon nanotube (CNT).[8] A FeO_x-ZrO_2 composite MARIMO assembly was solvothermally prepared from a precursor solution containing $Zr(O^nBu)_4$, $Fe(NO_3)_3$, acetylacetone, and ethanol. The obtained core catalyst was subjected to chemical CVD using ethyne gas as a carbon source, which produced a new class of metamaterial “CNT-hair” conjugate rather than “CNT sea urchin” structure in expectation of isotropic absorption of polarized light and electromagnetic waves (Fig. 1).

Keywords: Solvothermal, Spherical, (Metal)oxide, Carbon nanotube, Metamaterial.
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Room Dr. Luis de Mercado – Nanomaterials and Nanofluids

12:30 - 12:45 ORAL PRESENTATION 79945.

Solvothermal synthesis of soluble, surface modified metal oxide nanocrystals

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Metal oxides, such as titanium and tin oxide, exhibit an array of properties which have made them integral to many applications, from the mundane, to the exotic. Both titanium oxide and tin oxide have long been exploited as pigments, for example, later becoming known as the prototypical photocatalytic and gas-sensing materials, respectively.[1] An increasingly popular alternative to conventional synthesis/deposition methods is the generation of solution processable hybrid metal oxide nanoparticles. This approach offers exceptional flexibility, both chemically and physically, as dispersions of preformed colloidal nanocrystals may be used to coat flat substrates, irregularly shaped objects or to generate supported catalysts, composites, or gels.[2]
Here we report the production of highly dispersible (doped) titanium and tin oxide nanocrystals by postsynthetic modification of hydrous oxide precursors by solvothermal treatment with trifluoroacetic acid. The amorphous hydrous titania precursor is found to crystallise to the anatase phase under these conditions by an initial internal rearrangement, concurrent with surface modification. The obtained hybrid nanoparticles highly dispersible in polar aprotic solvents such as acetone. Interestingly, while applying this approach to tin oxide also yields dispersible nanocrystals, it has been found that extended solvothermal treatment of hydrous rutile tin oxide in trifluoroacetic acid leads to the emergence of an apparently new tin oxide phase, exhibiting a diffraction pattern consistent with the braking of the 4_2 screw axis symmetry of the rutile structure. This new modification of the rutile structure is tentatively attributed to fluorination of the tin oxide nanocrystals under solvothermal conditions.

Keywords: Solvothermal, Hybrid Nanoparticles, Anatase, Tin Oxide

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Room Dr. Luis de Mercado – Nanomaterials and Nanofluids

12:45 - 13:00 ORAL PRESENTATION 81732.

MULTI-STEP SYNTHETIC APPROACH FOR BUILDING HIERARCHICAL NANOSTRUCTURES

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Abstract
Hierarchical network structures, ranging from MOFS and DNA origami on the molecular scale to 3D foams on the micron scale, are a class of materials that generate unique optical, magnetic and conductivity properties. Here, a strategy for producing a 3D interconnected framework with nanoscale dimensions will be presented.[1] These nanoscale frameworks are synthesised by growing core and branch blocks to build up the structure in iterative steps (Figure). The results presented will include high resolution and scanning transmission electron microscopy of each of these blocks, to show how cubic and hexagonal crystal phases can be combined to form these nanoscale framework structures.[2] The nanoscale frameworks presented here illustrate a new concept for catalytic support materials.[3] Electrochemical analysis will be presented that shows that the nanoscale frameworks have an ultra-high surface area and are highly conductive. By coating the nanoscale frameworks with catalytically active Ni/Fe-oxyhydroxide, the effectiveness of an interconnected, 3D nanostructure as electrocatalytic supports will be shown.

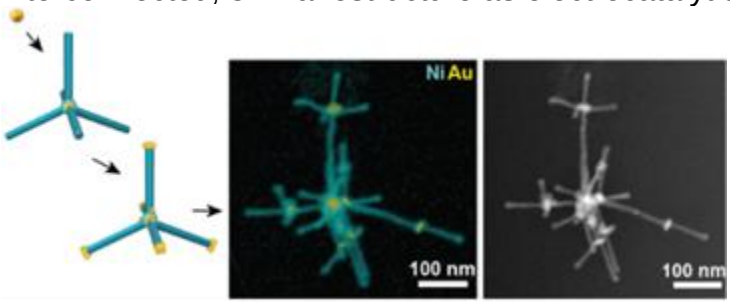

Figure: Illustration of the step-wise synthesis of nanoscale frameworks.

Keywords: Nanomaterials, electrocatalysis, nanoparticle synthesis, electrode materials

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B. Processes

Hydrothermal Liquefaction

KEYNOTE LECTURE

ORAL PRESENTATIONS

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Room José Zorilla– Hydrothermal Liquefaction

11:30 - 12:00 KEYNOTE LECTURE 80828.

Thermochemical conversion of Low Density Polyethylene (LDPE) to Value-Added Oil in Supercritical Water

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Addressing this global challenge requires reconsideration of the way plastics are produced, consumed, and discarded. The growth of global plastics production from the current value of 300 mMt to a predicted 500 mMt by 2050, has already outgrown the world's capacity to control plastics pollution.1
Chemical recycling technologies use heat and/or solvents to decompose waste plastics. For instance, solvolysis de-polymerizes single component plastics streams into monomers, whereas pyrolysis decomposes mixed plastic wastes into diverse mixtures of pyrolysis oils, gases and chars. Pyrolysis product streams require extensive and costly downstream processing. SCWH offers several advantages over other existing technologies comprising higher naphtha yield2,3, lower gas and char yields, fewer processing steps, no catalysts requirement, and improved energy-positivity.
This work introduces CircuPlast as a supercritical water-based process of hydrocracking (SCWH) plastic wastes into commodity chemicals. CircuPlast aims at continuous processing of mixed waste plastics to produce naphtha-range compounds of C5 - C14 carbon chain length, a prime feedstock to manufacture high-quality plastics.
Following a successful techno-economic feasibility assessment, and in preparation for the continuous prototype construction, preliminary experiments were conducted to gain insight into the various products' release with reaction temperature and time. Decomposing low-density polyethylene (LDPE) in a 25mL bomb reactor using 20/80 w/w LDPE/water ratio with no catalyst, resulted in a 100% conversion, no char formation, and 90% w/w yield of C5 - C20 oils in 30 minutes, at 465 ºC. This is certainly an encouraging outcome for the path ahead.

Keywords - Supercritical water, LDPE, conversion, packaging plastics.

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Room José Zorilla– Hydrothermal Liquefaction

12:00 - 12:15 ORAL PRESENTATION 81715.

HYDROTHERMAL LIQUEFACTION OF RESIDUAL BIOMASS FOR SUSTAINABLE AVIATION FUEL PRODUCTION

Fernández, A.[1], Magdaleno, I.[1], García-Serna, J.[1], Cantero, D.[1]

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Decarbonizing aviation is arguably the greatest challenge facing the air transport industry due to long lifespan of the airplanes and cost of solutions1. While aviation is responsible for approximately 1.9% of global greenhouse gas emissions from fossil fuels2, aviation emissions are rising quickly. From a life-cycle perspective, using sustainable aviation fuel (SAF) to replace Traditional Aviation Fuel (TAF) leads to a reduction in carbon emission from air flights. Since aircraft are not able to switch to alternative energy sources (like hydrogen or electricity) in the foreseeable future, aircraft will remain to rely on liquid fuels. Therefore, SAF made from renewable feedstock is one of the most important short-term options to significantly reduce the industry's carbon footprint and at the same time also reduce the dependency on the petroleum industry. In addition, SAF can be blended with fossil jet fuel and that the blended fuel requires no special infrastructure or equipment changes, and has the same characteristics and meets the same specifications as fossil jet fuel[3].
The objective is to convert biomass wastes (pine, eucalyptus, coffee residues) into a biocrude oil through a hydrothermal liquefaction. Hydrothermal oils are typically proposed as an alternative fuel after catalytic upgrading4. The hydroprocesing was carried out in a benchscale batch high-pressure reactor (autoclave). The process parameters such as particle size, feed volume, pressure and agitation speed were held constant, whilst the temperature (150- 350ºC), batch time (0-60 min) and pH (3, 5, 10) were varied and optimized. The effect of the different conditions on the quality of the hydroprocessed oil was evaluated in terms of elemental composition, chemical compound distribution, and fuel properties. The quality of the bio-oils produced depends on the process but also on the resource. The results are being scale up to continuous operation in plug flow reactors, increasing the process productivity.

Keywords: non-edible feedstocks, hydrothermal liquefaction, bio-oil, sustainable aviation fuel.

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Room José Zorilla– Hydrothermal Liquefaction

12:15 - 12:30 ORAL PRESENTATION 80881.

DEAMINATION OF BIO-OIL USING HYDROTHERMAL LIQUEFACTION INTENSIFIED WITH SUPERCRITICAL CARBON DIOXIDE

Nagamine T.[1], A. T. Quitain.[2], Y. Inomata[3], T. Kida[4]

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Fossil fuels are used in many aspects of everyday life and are necessary for people's lives. However, fossil fuels are finite substances and will eventually be depleted. In addition, the use of fossil fuels emits large amounts of carbon dioxide, which is a greenhouse gas. Recently, biomass-based fuels have attracted attention as an alternative to fossil fuels. One of the advantages of biomass-derived fuels is that they are more sustainable than other renewable energies in terms of supply. Another advantage is that they are not affected by weather conditions, as is the case with solar and wind power. In addition, the combustion of biomass-based fuels does not significantly increase carbon dioxide emissions by virtue of the carbon cycle, thus making them an environment-friendly energy source. However, the existing refining processes for this type of fuels are costly. In this study, we propose the use of hydrothermal liquefaction (HTL) in the deamination of bio-oil as an alternative to the conventional expensive process of hydrogenation. Deamination is an essential step in the refining process because it reduces the amount of the pollutant NOx released after the combustion of fuels. As an intensification strategy to HTL, supercritical carbon dioxide was introduced into the system to generate an acidic environment necessary to remove the amino-groups in the various compounds that are present in bio-oil. The main products in the bio-oil produced by HTL treatment with aspartic acid were found to be long-chain alkenes and nitrogen-containing heterocyclic compounds, and GC-MS results showed that the use of supercritical CO_2 suppressed the formation of nitrogen-containing heterocyclic compounds.

Keywords: Deamination, Bio-oil, Hydrothermal liquefaction, Carbon dioxide

Acknowledgements: The authors gratefully acknowledge the financial support from JSPS Grant-in-Aid for Scientific Research (Grant Numbers 17KK0118 and 18K05202), the Japan Science and Technology Agency via the e-ASIA joint research program in the field of Bioenergy (SICORP Grant Number JPMJSC18E2) and JSPS Bilateral Joint Research Program with Valladolid University (Spain).

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Room José Zorilla– Hydrothermal Liquefaction

12:30 - 12:45 ORAL PRESENTATION 80808.

Supercritical water valorization of chitin in a continuous reaction system

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Chitin is an abundant biopolymer of [β-1,4-poly(n-acetyl-D-glucosamine)] units, produced by crustaceans, mollusks, insects, and fungi. Nowadays, chitin is discarded in massive amounts (6–8 million tons/year) as waste from the seafood industry, being underexploited as biomass resource1. Chitin has high interest as a biocompatible and biodegradable material, but also as a source of biologically active oligosaccharides and monomers, N-acetylglucosamine (depolymerization) and glucosamine (deacetylation). These monomers constitute nitrogen-containing building blocks and open the way to biorefineries of alternative biomasses, such as sea-wastes, to obtain molecules of interest, such as furan- or amine-based monomers1. Several studies have shown that chitin, like cellulose, can be dissolved and hydrolyzed in supercritical water (SCW) due to the change in its properties (water density and ionic product, among others); however, due to the high chitin crystallinity, this process occurs less easily2.
The present work aims to investigate the mechanisms of chitin transformation in SCW medium (400°C and 25MPa), using ultrafast sudden expansion microreactors (SEMR) in a continuous system (residence time 0.1s - 2s). Special attention was paid to the effect of residence time and reaction temperature, using the Overend and Chornet3 severity factor (SF) (7.9 to 9.0), on the solubilization and depolymerization processes. Commercial chitin was used as raw material and characterized by elemental analysis (EA), FT-IR, Particle Size Distribution (PSD) and XRD. Total Organic Carbon, Total Nitrogen, pH and HPLC were used to characterize the liquid product; and solid fraction was characterized by EA, FT-IR, PSD and XRD for comparison with raw material. The results show that, within the studied conditions, chitin could not be fully depolymerized in SCW, at highest SF tested, the solid fraction was still 40%. Higher SF caused partial solubilization and particle size reduction of the solid fraction, and presumably promoted gasification. The presence of water-soluble by-products in every experiment gave us a hint of side reactions competing with depolymerization. Molecular weight analysis of solid products by intrinsic viscosity is being developed to evaluate the depolymerization tendency as a function of SF.

Keywords: Chitin, SCW hydrolysis, N-acetylglucosamine, glucosamine, ultrafast reactor.
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Acknowledgements: This work was supported by Spanish Ministry of Science and Innovation (project PID2020-119481RA-I00), the Regional Government of Castilla y León and FEDER-EU, program CLU-2019-04.

MONDAY – SEPTEMBER 11th, 2023

Room José Zorilla– Hydrothermal Liquefaction

12:45 - 13:00 ORAL PRESENTATION 80477.

Hydrothermal Reactions of Alkylamines in Sub- and Supercritical Water Studied by NMR Spectroscopy

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Hydrothermal reactions of aliphatic amines have recently gained importance in relation to the application of amines as film-forming corrosion inhibitors for steam–water cycles. Film-forming amines (FFAs) can form a hydrophobic protective film on the inner surface of the metal tubes of steam generators,1 providing effective corrosion protection during frequent shutdowns due to variable renewable energy such as solar power. In our recent study,2 the kinetics and mechanism of the hydrothermal reactions of ethylammomiun cation ($EtAH^+$) and *n*octylammonium cation (OctAH+) were examined for comparison with the corresponding neutral amines to elucidate their reaction products and pathways at sub- and supercritical temperatures of 300–400 °C as model reactions of aliphatic ammonium cations. We analyzed the reaction of ^{13}C-^{15}N-labeled EtAH+ using NMR spectroscopy and revealed that the initial hydrolysis to ethanol, known as the main path,3 is followed by the elimination reaction producing ethene and the disproportionation reaction giving diethylammonium cation. The $OctAH^+$ yields octene and octanol, each of which isomerizes to thermodynamically more stable species as the major products. Comparisons were made between the reactions of the neutral amines and ammonium cations to highlight their different reactivity. The hydrolysis, alkene formation, and dehydration of alcohols to alkenes were all found to be accelerated at low pH. These results indicate that the corrosion protection effect of film-forming amines will be maintained under practical conditions with pH values as high as around 9 to 10, and hence side reactions involving byproducts will be suppressed.

Keywords: Film Forming Amines, Supercritical Water, Nuclear Magnetic Resonance Spectroscopy

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Acknowledgements:
This study is supported by Grants-in-Aid for Scientific Research (nos. 19K05585, 20K05433, and 23K04680) from the Japan Society for the Promotion of Science (JSPS). K.Y. is also grateful for the research fund from the Japan Association for the Properties of Water and Steam (JPAPWS).

B. Processes

Reaction Engineering & Catalysis

KEYNOTE LECTURE

ORAL PRESENTATIONS

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MONDAY – SEPTEMBER 11th, 2023

Room Claudio Moyano – Reaction Engineering & Catalysis

11:30 - 12:00 KEYNOTE LECTURE 81549.

LOW TEMPERATURE CATALYTIC SUPERCRITICAL WATER GASIFICATION FOR CONTINUOUS HYDROGEN GENERATION FROM BIOMASS WASTEWATER

Chai Siah Lee, Alex V. Conradie, Edward Lester
Lee, C.S.[1,2], Lester, E.[1], Conradie, A.V.[2]

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A continuous hydrothermal process is demonstrated, for the first time, that can operate at low gasification temperature (430 °C) and residence time (20 s) by combining supercritical water gasification (SCWG) and partial oxidation with *in situ* synthesis of virgin metal oxide nano-catalyst. This process addresses the challenges associated with catalyst deactivation of a fixed bed, tedious homogenous catalyst separation after the process and/or the need for high operating temperatures. Industrial biomass wastewater was used as the feedstock for generating hydrogen and methane-rich syngas, with a metal oxide nano-catalyst as a valuable co-product and cleaner water, lower in chemical oxygen demand (COD) and total organic carbon (TOC), as a liquid product.
Using olive wastewater as the feedstock, this gasification study experimentally investigated the impact of multiple variables: (1) COD feed concentration, (2) the *in situ* synthesis of different metal oxide nano-catalysts, (3) the partial oxidation coefficient (ɳ) and (4) the nano-catalyst precursor solution concentration. The optimum conditions for the generation of hydrogen and methane from olive wastewater were a feed COD of 38.6 g/L, ɳ = 0.8, and 60 mM precursor concentration for the *in situ* synthesis of Fe_2O_3 nano-catalyst. These optimised conditions were further investigated using spent lees and stillage. The efficiency of hydrogen and methane yields and COD reduction were in the order of stillage > spent lees > olive wastewater. The highest hydrogen molar selectivity, hydrogen and methane yields at 18.8 %, 17 and 11.4 mol/(kg biomass) respectively were obtained with stillage feedstock. Gasification, COD and TOC reduction efficiencies were 68.8–71.7 %, 72.6–76.5 % and 53.9–55.7 % respectively, with this process.
Importantly, this process was further validated by showing stable, steady-state gasification performance in terms of gas yields with olive wastewater, stillage and spent lees as the feedstocks during continuous operation for 40 min without any significant drop in performance. This study exemplifies that the co-generation of catalyst during SCWG is a promising and economically feasible direction for large-scale continuous generation of hydrogen and methane from different types of biomass wastewater at < 450 ◦C, whilst lowering its COD and TOC.

Keywords: Supercritical water gasification, Biomass wastewater, Metal oxide nano-catalyst, Continuous hydrothermal synthesis, Hydrogen.
Acknowledgements: The authors gratefully acknowledge all the support received from the University of Nottingham Research Beacon of Excellence: Green Chemicals, technical support from the Advanced Biofuel Solutions Ltd, the wastewater source from the Warner's Distillery Ltd and Sedamyl UK. Finally, the authors would like to express their deep gratitude to the Supergen Bioenergy Hub for providing the Supergen Rapid Response Flexible Funding (grant number: RR 2021_7) and the EPSRC (Grant number EP/R032807/1) in support of this study.

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12:00 - 12:15 ORAL PRESENTATION 80876.

MICROWAVE-INTENSIFIED SOLVOTHERMAL APPROACH TO GLYCEROL VALORIZATION CATALYZED BY GRAPHENE OXIDE

Quitain, A. T.*[1], Y. Ogasawara,[2] S. Uchikado,[2] J.K.N. Agutaya,[3] M. Sasaki,[4] Y. Inomata,[5] S. Assabumrungrat[6], T. Kida[5]

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The increase in atmospheric carbon dioxide associated with increased consumption of fossil fuels has led to serious global warming and other abnormal weather conditions. Thus, renewable energy sources with low environmental impact are attracting attention. Biodiesel is a substance used as an alternative fuel to gasoline, and biodiesel production is expected to increase rapidly in the future. This will result to problems of disposal of glycerol (Gly), which accounts for about 10 wt% of the byproducts of synthesized biodiesel. Glycerol can be converted to glycerol *tert*-butyl ether (GTBE), a compound that can be added to biodiesel to increase its cetane number. A novel solvothermal synthesis process was developed by employing the synergy of microwave irradiation and graphene oxide (GO) catalysts. The effects of microwave heating, reaction time, temperature, TBA-to-glycerin molar ratio, catalyst amount on the etherification reaction were investigated. Microwave heating due to its inherent characteristics of being internal, high speed and selective favors conversion of glycerin and selectivity to glycerol *di-* and *tri*-tert-butyl ethers compared to conventional method. Highest conversion of glycerol to GTBE of 51.1 % (selectivity to MTBG : 32 %, selectivity to DTBG + TTBG : 19.1 %) was obtained at reaction time of 240 min, at 130 ^{o}C, at TBA/glycerol molar ratio of 6, at 13.5 wt% catalyst amount, 3.49 mmol/g acidic site concentration using microwave power of 600 W. It was also observed that the amount of DTBG increased with increasing reaction time, while MTBG decreased due likely to further conversion to DTBG. The high catalytic performance of GO at high temperature is attributed to the incorporation of hydrophilic functional groups on the hydrophobic carbon surface. Addition of carbon dioxide into the system was also found to have positive effect on the yield.

Keywords: Glycerol, Microwave, Solvothermal, Glycerol tert-Butyl Ether, Graphene Oxide
Acknowledgements: The authors gratefully acknowledge the financial support from JSPS Grant-in-Aid for Scientific Research (Grant Numbers 17KK0118 and 18K05202), the Japan Science and Technology Agency via the e-ASIA joint research program in the field of Bioenergy (SICORP Grant Number JPMJSC18E2) and JSPS Bilateral Joint Research Program with Chulalongkorn University (Thailand) and Valladolid University (Spain).

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Room Claudio Moyano – Reaction Engineering & Catalysis

12:15 - 12:30 ORAL PRESENTATION 80746.

Media Matters: The impact of the algal growth water on supercritical water gasification

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According to the Paris agreement, greenhouse gas (GHG) emissions need to be reduced by 45% by 2030 and net zero by 2050.This work presents supercritical water gasification (SCWG) of microalgae as a process to supply hydrogen with zero or potentially negative GHG emissions, with a less detrimental environmental impact than other biomass sources1. Previous studies of SCWG of microalgae have covered a range of strains, catalysts, and operating conditions. In most of these studies, de-ionised water was added to dry concentrates of algae to form the gasification medium. On a commercial scale, the additional energy requirements would seriously limit the economic feasibility of the process. In addition, the supernatant water contains many ions (e.g. K+, Na+, OH, Fe3+, Cl-) that are present in the growth media, which are shown to catalyse SCWG2. Thus, the use of de-ionised water may not be representative of a real system. This study investigates the effect of using the algal growth water as the reaction media in the SCWG of glucose and microalgae, under a range of system conditions. Reactions were conducted in a 25m tubular reactor of 3.86mm internal diameter. Two catalysts, namely KOH and ruthenium-on-carbon (Ru/C), were employed. Chlorella vulgaris was the chosen microalgal strain. The results show that the growth water in the SCWG of glucose (450-550°C, 23-25 MPa, 1- 3%wt, 32s), impacted a significant increase in CO2, and decrease in CO contents of the gas stream. This effect was also observed in the presence of Ru/C catalyst and in the SCWG of Chlorella vulgaris, along with a significant increase in hydrogen yield. However, there was no significant change observed in the presence of KOH. Additionally, an increase in residue left in the reactor (tar and char) was observed in glucose SCWG without a catalyst, while an increase in total gas yield was observed when Ru/C was present. Therefore, the growth water has a catalytic effect on SCWG so should be considered in laboratory experiments.

Keywords: Microalgae, Supercritical water gasification, Renewable Energy, Hydrogen

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Room Claudio Moyano – Reaction Engineering & Catalysis

12:30 - 13:45 ORAL PRESENTATION 80773.

HYDROTHERMAL DECHLORINATION OF POLYVINYL CHLORIDE FOR CHEMICAL RECYCLING

Douglas Hungwe[1], Satomi Hosokawa[1], Yuki Yamasaki[1]

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Hydrothermal dechlorination of PVC into benign-chlorine-free precursors for chemical recycling is key to achieving a circular economy for one of the most commonly used plastics worldwide.[1] Hydrothermal transformation at high temperatures predominantly occurs via elimination reaction often attended by marked carbonization reactions intensified by acidic conditions.[2] The products thus furnished are highly thermally stable and recalcitrant materials not amenable to liquefaction or low-temperature thermochemical conversion. We propose that the reaction conditions be tuned to favor dechlorination via nucleophilic substitution to yield a predominantly PVOH-rich structure which addresses the challenges mentioned above. An intensive literature review[3] reveals that there are a number of basic knowledge gaps that require addressing prior mechanism optimization; chief among them is that 90% of reactors used in such studies are steel reactors prone to chlorine-induced corrosion which releases metal ions into the reaction media and possibly introduces perturbations. While it is known from a qualitative viewpoint that hydrothermal dechlorination occurs via competitive elimination and nucleophilic substitution mechanism, there is a lack of quantitative data to corroborate this data. Furthermore, the phenomena which govern the maximum reaction rate in alkaline conditions are not fully understood. Positive interaction between the cations was confirmed when the simultaneous use of 1 mmol/L Fe^{2+} and 0.25 mmol/L Ni^{2+} achieved the same catalytic performance as 5 mmol/L Fe^{2+} or 10 mmol/L Ni^{2+}. The experimental design revealed that dechlorination and its improvement were temperature-dependent ($p < 0.0001$). Ni^{2+} and Fe^{2+} exerted quadratic and linear effects, respectively, on dechlorination. Quantitative analysis of the mechanism showed that nucleophilic substitution contribution in amine-assisted hydrothermal dechlorination achieved at least 40%. The maximum dechlorination rate was achieved when particle agglomeration was prevented during hydrothermal dechlorination. There is need for validation of kinetic data for results obtained using steel reactors.

Keywords: Hydrothermal dechlorination, Catalysis, mechanism,

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MONDAY – SEPTEMBER 11th, 2023

Room Claudio Moyano – Reaction Engineering & Catalysis

12:45 - 13:00 ORAL PRESENTATION 81737.

Microwave hydrothermal preparation of reduced graphene oxide induced p-AgO/n-MoO_3heterostructures for enhanced photocatalytic activity through *S*-scheme mechanism and its electrochemical performance

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Through a powerful and modest closed system Microwave hydrothermal process, a methodological analysis is made in the rational synthesis of the reduced graphene oxide induced p-AgO/n-MoO_3 (RGAM) heterostructures. These have strong p-n junction heterostructures with considerable electron-hole recombination functioning as solar catalysts. The enhanced photocatalytic activity through the plasmonic step scheme (*S*-scheme mechanism) describes the effective charge recombination process. The energy band positions, band gap, and work function are determined to understand the Fermi level shifts. This describes the *S*-scheme mechanism by UPS analysis which assessed an electron transfer between AgO and MoO_3 and yielding work function values of 6.34 eV and 6.62eV, respectively. This photocatalytic activity aids in dye removal by 94.22 % and heavy metal such as Chromium (Cr) are eliminated by the surface action of sunlight on the produced material during solar irradiation. Electrochemical studies such as photocurrent calculations, cyclic voltagram, and electrochemical impedance spectroscopy for RGAM heterostructures were also carried out. The study helps to broaden the search and extensive development of new hybrid carbon composites. This study also gives further findings of new perspective on how to synthesize nanomaterials by investigating their photocatalytic and electrocatalytic characteristics for a variety of applications in environmental domains.

Keywords: *Chromium, Photocatalytic degradation, S-Scheme mechanism.*

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MONDAY

15:15-17:15

A. Applications & Products

Inorganics and Surface

KEYNOTE LECTURE

ORAL PRESENTATIONS

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Room Rey Felipe II – Inorganics and Surface

15:15 - 15:45 KEYNOTE LECTURE 80177.

Formation of dispersive anatase TiO_2 sub-micro spheres from Mg/Al-bearing $TiOSO_4$ solution via hydrothermal hydrolysis-calcination route

Fan Yang[1], Shuyu Lin[1], Lan Xiang[1]
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Corresponding author: xianglan@mail.tsinghua.edu.cn

Titanium-bearing blast furnace slag (TBFS) is an important Ti-bearing resource, which can be converted to Mg/Al-bearing $TiOSO_4$ solution ($TiOSO_4$: 0.81 mol·L^{-1}, $MgSO_4$: 0.46 mol·L^{-1}, $Al_2(SO_4)_3$: 0.39 mol·L^{-1}, H_2SO_4: 1.03 mol·L^{-1}) by dissociation with concentrated H_2SO_4 followed by water leaching[1].

In this work, dispersive anatase TiO_2 spheres with uniform particle sizes were produced from the Mg/Al-bearing $TiOSO_4$ solution via hydrothermal hydrolysis-calcination route. $TiOSO_4$ was hydrothermally converted to H_2TiO_3 ($TiOSO_4 + H_2O = H_2TiO_3 + H_2SO_4$) at 150°C, H_2TiO_3 was then converted to TiO_2 by calcination ($H2TiO3 = TiO2 + H2O$) at 800°C.

The experimental results indicated that the increase of H_2SO_4 concentration in the Mg/Al-bearing $TiOSO_4$ solution from 1.50 mol·L^{-1} to 3.50 mol·L^{-1} inhibited the hydrothermal hydrolysis of $TiOSO_4$ (150°C, 4.0h) and promoted the formation of dispersive H_2TiO_3 particles with large primary particle sizes (agglomerate sizes: 2.36 μm□ 280 nm, primary particle sizes: 40 nm □ 250 nm). Uniform dispersive anatase TiO_2 sub-micro spheres (230 ± 47nm) formed by calcination of H_2TiO_3 (originated from the Mg/Al-bearing $TiOSO_4$ solution with 3.50 mol·L^{-1} H_2SO_4) at 800 °C for 1.0 h, while un-uniform anatase TiO_2 mixtures composed of small sphere (diameter: 50-100nm) and rods (length: 200-350nm, diameter: 100-200nm) formed by calcination of H_2TiO_3 (originated from the Mg/Al-bearing $TiOSO_4$ solution with 1.50 mol·L^{-1} H_2SO_4) at the same condition.

Keywords: TiO_2 spheres, Mg/Al-bearing $TiOSO_4$ solution, hydrothermal hydrolysis, calcination.

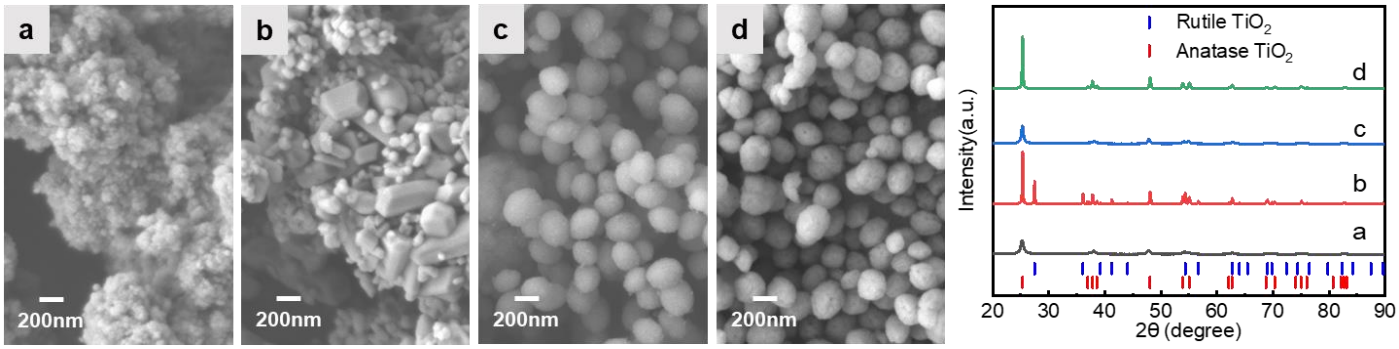

Figure 1. Influence of H_2SO_4 conc. on morphology of H_2TiO_3 (a, c) and anatase TiO_2 (b, d) H_2SO_4 conc. (mol·L^{-1}): a, b-1.5, c, d-3.5.

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Acknowledgements: This work was financially supported by the National Science Foundation of China (No. 21978153, 51774191).

MONDAY – SEPTEMBER 11th, 2023

Room Dr. Luis de Mercado – Inorganics and Surface

15:15 - 15:45 KEYNOTE LECTURE 81676.

SCALABLE SELF-ASSEMBLY OF ALL-DIELECTRIC NANOPARTICLE MONOLAYER METAMATERIALS

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We have developed an aerosolized jet spray method to form monolayers of dense hexagonal close-packed sub-micrometer particles (300 – 700 nm) on liquid interfaces. Uniform titanium dioxide (TiO2) and amorphous silicon (a-Si) particles were made via sol-gel and solvothermal methods, respectively. TiO2 particles were generated by hydrolysis and condensation of titanium tetraisopropoxide and a-Si particles were synthesized by decomposition of trisilane in supercritical *n*-hexane at 410 °C. The particles are spherical and readily dispersed in a variety of organic solvents. The particles are deposited onto a liquid interface using an ultrasonic spray coater to achieve relatively large area (200 cm2) close-packed monolayers in less than a minute. The monolayers can be transferred from the liquid interface to various solid substrate materials including metals, polymers, and glass, in addition to non-planar surfaces. The range of order of the particles in the layer depends on the nanoparticle surfaces, such as hydrophobicity and ionic/steric surface stabilizing compounds. This low-cost, high-throughput deposition technique could be readily integrated into commercial spray coat manufacturing processes and monolayers of these high dielectric constant particles have the potential for application as antireflection coatings, optical metasurfaces, transparent electrodes, or as substrates for biomedical sensing.

Keywords: Dielectric, Monolayers, self-assembly, Spherical Particles

Acknowledgements:
This research was partially supported by the U.S. National Science Foundation through Award #1828974 (NRT-INFEWS: Graduate Student Education: Reducing Energy Barriers For Novel Water Supply Use in Sustainable Agriculture) granted to The University of Texas at Austin.

MONDAY – SEPTEMBER 11th, 2023

Room Rey Felipe II – Inorganics and Surface

16:15 - 16:45 KEYNOTE LECTURE 81764.

Solution Synthesis Chemistry of Multifunctional Structural Systems

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As a typical multifunctional structural systems, great progress has been made in the preparation and application of hollow multi-shelled structure (HoMS) during the past decade. In this presentation we will describe new synthetic method in solution system for HoMS as well as their compositional and geometric manipulation and then review their applications in energy conversion and storage, sensor, catalysis, drug delivery and so on. The correlations between the geometric properties of HoMS and their specific performance are highlighted in wide applications of energy conversion and storage, environmental treatment and biological medicine, including dye-sensitized solar cells, lithium ion batteries, supercapacitors, sensors, photocatalysis, photo-thermal conversion and drug delivery. These results demonstrate that the geometry has a direct impact on the properties and potential applications of such materials. Finally, the emergent challenges and future developments of HoMS are further discussed..

Keywords: hollow multi-shelled structure, Solution Synthesis, Energy Conversion.

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MONDAY – SEPTEMBER 11th, 2023

Room Rey Felipe II – Inorganics and Surface

16:45 - 17:00 ORAL PRESENTATION 80723.

CONTINUOUS FLOW HYDRO- AND SOLVOTHERMAL SYNTHESES OF PIEZOELECTRIC AND MAGNETIC NANOMATERIALS

Worsley, R.[1,2], Bastola, A.[2], Hague, R.[2], Tuck, C.[2], Lester, E.[1]

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Piezoelectric and magnetostrictive materials are capable of converting mechanical energy into electrical and magnetic energies, and vice versa, through the direct and inverse piezoelectric and magnetostrictive effects, respectively. As such, these materials find use within a diverse range of applications, including in sensors, actuators, and energy harvesters.1 Barium titanate is a common ceramic material exhibiting piezoelectric characteristics; its continuous production in supercritical water has been demonstrated,2 however, the nanoscale particles produced exist mostly in the dielectric cubic phase, with the tetragonal phase required for piezoelectricity. The tetragonal-cubic transition depends upon many factors, including particle size, shape, and surface chemistry.3 The same factors similarly influence magnetic material performance.
Continuous flow hydro- and solvothermal synthesis methods are capable of generating a wide variety of nanomaterials, with a high degree of control over the particle characteristics, allowing electromagnetic properties to be tailored.4 In this work, a counter-current nozzle reactor5 within a bench-scale flow system is used to synthesise various piezoelectric and magnetic metal oxides. Typically, a ‘cold’ stream of water-soluble metal precursors is fed, at a concentration between 0.01-0.10 M, upwards into the reactor to meet a downward flow of sub/supercritical fluid, leading to rapid product nucleation. The downflow temperature is held between 200-450 °C, and the pressure is maintained at 240 bar, with flow rates between 5-25 mL min-1 utilised.
Barium titanate (BaTiO3), barium ferrite (BaFe12O19), cobalt ferrite (CoFe2O4) and nickel cobalt oxide (NiCo2O4) syntheses are demonstrated. Synthesis parameter variation yields BaTiO3 nanoparticles of differing size and shape, yet all samples still exist predominantly in the dielectric phase. Magnetic characterisations indicate that the BaFe12O19 demonstrates hard magnetic behaviour, whilst the CoFe2O4 and NiCo2O4 are magnetically semi-soft.

Keywords: Continuous Flow, Magnetic, Piezoelectric, Nanomaterials

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MONDAY – SEPTEMBER 11th, 2023

Room Rey Felipe II – Inorganics and Surface

17:00 - 17:15 ORAL PRESENTATION 80175.

Enhanced CH_4 sensing by ZnO/CeO_2/Pd composite

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Enhanced CH_4 sensing based on metal oxide semiconductor (MOS) is attracting much attention owing to its wide application in safety guarantee situations such as natural gas and coal mine, etc.[1] The present work reported a facile way for enhanced CH_4 sensing based on the urchin-shaped hierarchical ZnO/CeO_2/Pd sensitive material. ZnO nanorods with an average length of 1 μm and an average diameter of 15 nm were fabricated using ε-$Zn(OH)_2$ as the precursor,[2] then the ZnO nanorods were sequentially loaded with CeO_2 (average particle size: 8 nm) and Pd (average particle size: 3 nm) via impregnation route at 80 °C (Figure 1a and 1b). Compared with ZnO/Pd composite, ZnO/CeO_2/Pd composite exhibited a decrease of the optimum sensing temperature from 180 °C to 160 °C and an increase of the response from 90% to 106% for CH_4 sensing (500 ppm) (Figure 1c). The enhanced CH_4 sensing performance of ZnO/CeO_2/Pd composite may be attributed to the co-catalytic effect of CeO_2 in the catalytic oxidation of CH_4 by Pd nanoparticles.
Keywords: CH_4, enhanced sensing, ZnO/CeO_2/Pd composite

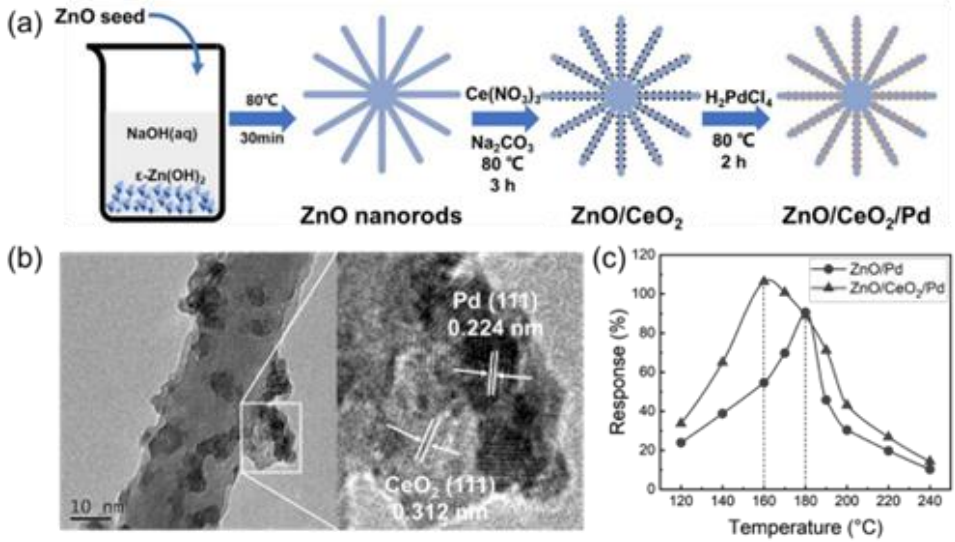

Figure 1. Fabrication(a) and TEM image(b) of ZnO/CeO_2/Pd composite, as well as variations of responses of ZnO/Pd and ZnO/CeO_2/Pd with temperature(c)

[1] *Jiao, M., Chen, X., Hu, K., et al. Rare Met. 2021, 40 (6), 1515–1527.*
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Acknowledgements: This work was supported by the National Natural Science Foundation of China (No. 21978153) and the National Key Research and Development Program (No.2019YFC1905803).

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Room Dr. Luis de Mercado – Inorganics and Surface

16:15 - 16:30 ORAL PRESENTATION 80154.

Influence of temperature on wet formation of ε-$Zn(OH)_2$ precusors and ZnO whiskers

Shuyu Lin[1], Lan Xiang[1]

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A facile wet way was developed to synthesis ZnO whiskers from ε-$Zn(OH)_2$ precursors, using $ZnSO_4$ and NaOH as the raw materials. ε-$Zn(OH)_2$ precursors formed by mixing 2.0 mol·L^{-1} $ZnSO_4$ and 4.0 mol·L^{-1} NaOH at 5-25°C, keeping the molar ratio of Zn^{2+} to OH^- as 2:5. ε-$Zn(OH)_2$ precursors were then aged at 25°C for 24.0 h followed by reaction at 80-120ºC for 2.0 h. The experimental results indicated that the formation of ZnO whiskers from ε-$Zn(OH)_2$ in NaOH solution was carried out mainly via two steps: the formation of ZnO seeds from ε-$Zn(OH)_2$ via mainly the solid conversion of ε-$Zn(OH)_2$ to ZnO at room temperature, and the heterogeneous growth of ZnO whiskers on the surface of ε-$Zn(OH)_2$ via mainly dissolution-precipitation route. The decrease of temperature from 25ºC to 5ºC promoted the formation of ε-$Zn(OH)_2$ precursors with smaller particle sizes (15 μm□3 μm) which favoured the subsequent dissolution of ε-$Zn(OH)_2$ in NaOH solution; on the other hand, the decrease of temperature from 25 ºC to 5ºC fabricated the formation of ε-$Zn(OH)_2$ precursors with higher stabilities which inhibited the solid conversion of ε-$Zn(OH)_2$ to ZnO, and reduced the number of ZnO seeds formed at room temperature, leading to the formation of ZnO whiskers with bigger sizes. For example, ZnO whiskers with average length of about 6 μm and average diameter of about 350 nm were produced at 80ºC from ε-$Zn(OH)_2$ formed at 5ºC, while ZnO whiskers with average length of about 3 μm and average diameter of about 150 nm were produced at 80ºC from ε-$Zn(OH)_2$ formed at 25ºC. Figure 1g shows the variations of soluble zinc with reaction time in conversion of ε-$Zn(OH)_2$ formed at 5-25ºC to ZnO whiskers in 1.0 mol.L^{-1} NaOH at 80ºC. The decrease of the soluble zinc after 40 min should be connected with the slower dissolution of ε-$Zn(OH)_2$ compared with the deposition of soluble Zn. The increase of temperature from 5ºC to 25ºC for ε-$Zn(OH)_2$ formation led to the quicker decrease of the soluble zinc, indicating that ε-$Zn(OH)_2$ formed at lower temperature was easier to be dissolved in NaOH solution.

Keywords: ZnO whiskers, one-dimensional growth, ε-$Zn(OH)_2$.

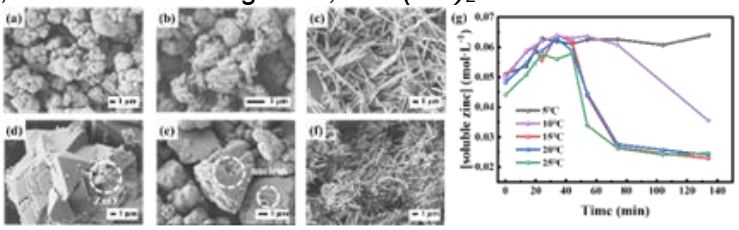

Figure 1. Morphology of ε-$Zn(OH)_2$ formed at 5°C (a) and 25ºC(d), aging products originated from a (b) and d (e), ZnO whiskers prepared from a (c) and d (f), (g) variations of soluble zinc with reaction time in conversion of ε-$Zn(OH)_2$ to ZnO whiskers.

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Acknowledgements: This work was supported by the National Natural Science Foundation of China (No.21978153 and No.52274410).

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MONDAY – SEPTEMBER 11th, 2023

Room Dr. Luis de Mercado – Inorganics and Surface

16:30 - 16:45 ORAL PRESENTATION 80174.

Separation and utilization of P-bearing resources by hydrocyclone and hydrothermal methods

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With the decrease of high-quality phosphate ores (P_2O_5≥30wt%), the use of low-grade phosphate ores (P_2O_5≥20wt%) is becoming more and more emergent. Another problem is the use of the huge amount of phosphogypsum (PG, 80 million tons/year), which is the by-product in the wet production of phosphoric acid.

Firstly, a novel semi-through hydraulicbarrier hydrocyclone (S-Hb) was developed for the separation of low-grade phosphate ores. The fluid dynamics simulation showed that the adaptation of the semi-through hydraulicbarrier hydrocyclone led to the decrease of the short-circuit flow rate from 13.3% to 7.17% and the increase of the separation efficiency from 92.3% to 97.5%. The experimental results confirmed that the quaternary S-Hb process was effective for the separation impurities from the low-grade phosphate ores, leading to the increase of P-content in phosphate ores from 17.5% to 23.6%[1], compared with the P-content of 21.4% in the case of hydrocyclone without S-Hb structure.

Secondly, a phase conversion way was developed to remove eutectic phosphorus from PG. The contents of eutectic phosphorus in PG reduced from 0.58% to 0.01% after sintering PG in air at 165℃ for 4.0h followed by acidic treatment in 1.0% H_2SO_4 for 4.0h at room temperature[2].

Finally, $CaSO_4$•0.5H_2O whiskers with a diameter of 1-5 μm and a length of 100-400 μm were prepared from the purified gypsum by hydrothermal method.

Keywords: low-grade phosphate ore, phosphogypsum, hydrocyclone, $CaSO_4$•0.5H_2O whisker

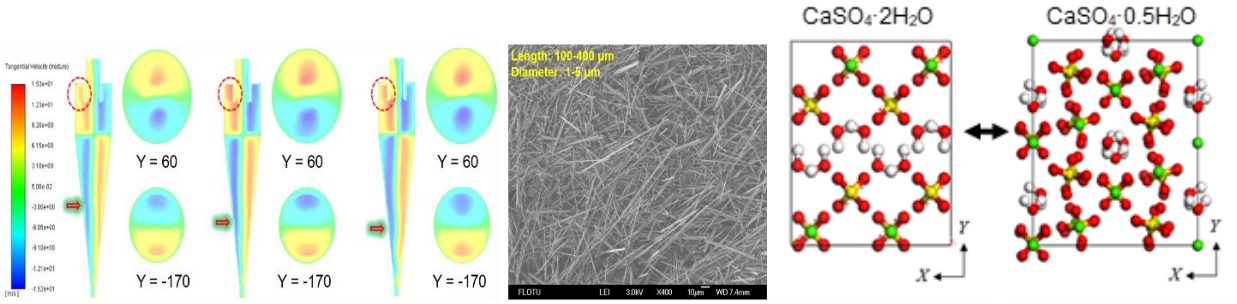

Figure 1. Performance intensification of hydrocyclone and morphology of $CaSO_4$•0.5H_2O whiskers

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Acknowledgements: This work was financially supported by National Science Foundation of China (No. 21978153) and National Key Research and Development Program of China (2019YFC1905803).

MONDAY – SEPTEMBER 11th, 2023

Room Dr. Luis de Mercado – Inorganics and Surface

16:45 - 17:00 ORAL PRESENTATION 79928.

AUTOMATION AT THE LAB-SCALE: METAL NANOPARTICLES ANCHORED ON FLEXIBLE POLYURETHANE SPONGES SYNTHESIZED HYDROTHERMALLY AS CATALYSTS FOR FULLY AUTOMATED REACTIONS

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Within the field of catalytic nanoparticles (NPs), gold nanoparticles (AuNPs) have generated great interest from both fundamental and applications perspectives.1,2 AuNPs are extremely attractive as catalysts for mild reaction conditions they impart, i.e., they are often active at low temperatures and in aqueous systems.2 Classically, AuNPs of well-controlled sizes are generated by reduction of gold salts employing reducing agents (e.g., citrates or sodium borohydride), solvents (e.g., toluene or *n*-heptane), and surfactants to stabilize the NPs (e.g., dodecanethiol or dodecylamine).1 Other noble metal NPs are synthesized similarly.3 In the majority of metal NP syntheses, the employed solvents, reductants, and stabilizers pose significant risks to human health and the environment.
Here, we demonstrate that all these chemicals but the metal precursors, can be avoided by using solely “hot water” for generating AuNPs, AgNPs, and PdNPs, supported on a monolithic polyurethane foam (PUF). We employ a commercial PUF acting as both support and reducing agent during synthesis.4 The PUF facilitates the repeated use of the NPs as catalyst, as it can be soaked and squished repeatedly without loss of the well-anchored NPs. To evaluate the catalytic properties of the NPs@PUF, the reduction of 4-nitrophenol to 4-aminophenol was employed as model reaction. NPs@PUF were used first by manual soaking and subsequent squishing of reactant solutions. Second, their semi-automated use with a robotic arm was employed. Third, we have developed their use in a fully automated platform. This framework can easily be incorporated as a step to automate parts of more complex organic syntheses.
We have developed a new, facile, and environmentally friendly procedure to synthesize immobilized noble metal (Au, Ag, Pd) NPs on porous PUFs. Furthermore, we tested the NPs@PUF materials in depth, demonstrating their high catalytic activities for the reduction of 4-nitrophenol to 4-aminophenol and their high reusability. As we illustrate, reactions can easily be automated thanks to the use of a programmed mechanical arm compressing and decompressing the flexible foam.

Keywords: Metallic Nanoparticles, Heterogenous Catalysis, Hydrothermal Synthesis.
1. M. C. Daniel and D. Astruc, Chem Rev, 2004, 104, 293-346.
2. M. Stratakis and H. Garcia, Chem Rev, 2012, 112, 4469-4506.
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Acknowledgements: Austrian Science Fund (FWF) for the financial support under grant No. START Y1037-N38 and NSERC for the financial support via the Discovery Grant program and CGS D.

B. Processes

CO_2 capture and sequestration

KEYNOTE LECTURE

ORAL PRESENTATIONS

8th International Solvothermal and Hydrothermal Association Conference
ISHA 2023
Valladolid, Spain
September 10th–13th, 2023

MONDAY – SEPTEMBER 11th, 2023

Room José Zorilla- CO_2 C&S

15:15 - 15:45 KEYNOTE LECTURE 81385.

Study of the scaling up of procesesses for CO_2 transformation in hydrothermal media

Bermejo, M.D.[1,*], Chinchillla, M.I.[1], Dos Santos, L.C.[1], Quintana-Gómez, L.[1], Goicoechea, A.[1], Ciordia-Asenio, V.[1], Almarza, M.[1], Pérez-Franco I.[1], Martín,[1] A.,

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Increasing efforts are made in the last times in order to reduce the CO_2 concentration in atmosphere, and among them are capture and CO_2 storage, even capturing CO_2 from dilute sources. Nevertheless, the cost of this process is high. It could be reduced if the CO_2 could be used as a raw material to produce chemicals or fuels.
In the Universidad de Valladolid, we have been working in the development of processes for transforming the CO_2 captured in aqueous basic media to formic acid, a promising substance as platform chemical and liquid organic hydrogen carrier. The processes carried out in hydrothermal media present the advantages of increasing the reactivity of CO_2 and selectivity towards formic acid. In addition, the effluent of capturing CO_2 in basic media, with amines of NaOH can be directly introduced in the reactor without purification or compressing the stream of CO_2.
Results obtained so far have been very promising. Nevertheless, for developing the process and reach the industrial level, a previous study of the scaling up of the process and construction of a pilot plant is necessary. To do so, we are studying the reduction of CO_2 captured as bicarbonate using biomass waste in a semincontinous plant, using a bed of biomass through which a flow of aqueous bicarbonate is circulated. Main products as acetic, formic and lactic acid can be obtained at different temperatures and residence times, between 150 and 300ºC.
The reduction of CO2 captured with 3-Amino-1-propanol and 2-Amino-2-methyl-1-propanol is possible using gaseous H2 at temperatures between 70 and 125 ºC and pressures between 25 and 75 bar obtaining yields of formic acid as high as 68% in batch. Currently we are working in the design of a continuous facility that integrates the capture of CO_2, the production of hydrogen in an electrolytic cell and the reaction.

Keywords: Pilot plant, Amines, CCU, Formic acid, Green H_2, Biomass

Acknowledgements: This work/project was supported by the Regional Government of Castilla y León and the EU-FEDER program (CLU-2019-04 and CL-EI-2021-06).

MONDAY – SEPTEMBER 11th, 2023

Room José Zorilla- CO_2 C&S

16:15 - 16:30 ORAL PRESENTATION 81467.

SUSTAINABLE MAGNETIC FRAMEWORK COMPOSITES FOR EFFICIENT CO_2 CAPTURE

John Luke Woodliffe[1], Amy-Louise Johnston[2], Michael Fay[3], Rebecca Ferrari[2], Rachel L Gomes[2], Ed Lester[1], Ifty Ahmed[1], Andrea Laybourn[1]

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Metal-organic frameworks (MOFs) have shown excellent potential for carbon dioxide capture applications due to their high sorption capacities and selectivities.[1] However, MOFs are typically insulating, so thermal CO_2 regeneration is challenging at scale.[2] This can be overcome by inclusion of magnetic nanoparticles within the MOF structure, enabling rapid and energy efficient regeneration using induction heating.[3] In this presentation we discuss the development of novel magnetic framework composites (MFCs) comprised of MOF UTSA 16(Zn) and Fe_3O_4 nanoparticles using a two-step procedure. Firstly, a scalable single-step continuous hydrothermal synthesis method is used to produce highly pure, stable, and crystalline citrate-coated Fe_3O_4 nanoparticles with high magnetisation (78 emu/g). Next, these nanoparticles were incorporated into UTSA-16(Zn) via a rapid microwave-assisted direct-growth strategy to form the MFCs (81-83% yield), which demonstrate high CO_2 adsorption capacities (2.8-3.3 mmol/g) and recyclability, and heat rapidly in an applied magnetic field for CO_2 release (e.g. 60 °C in 8 seconds). Methods used herein are also applicable to other MOFs, opening routes to a variety of sustainable MFCs for impact across a range of applications. Our work also addresses the sustainability and scalability challenges faced by MFCs required for industrial application, using inexpensive and widely available materials.

Keywords: MOF, magnetic nanoparticles, induction heating, carbon capture, continuous-flow hydrothermal.

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MONDAY – SEPTEMBER 11th, 2023

Room José Zorilla- CO_2 C&S

16:30 - 16:45 ORAL PRESENTATION 81758.

THE ROLE OF METAL OXIDE PREPARATION METHODS ON CHEMICAL LOOPING COMBUSTION OF BIOCHARS

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This study aims to investigate the feasibility of using a wide range of metal oxides (Cu, Co-, and Mn-based) prepared through continuous hydrothermal conversion and co-precipitation methods for the conversion of biomass/biochars into bioenergy via chemical looping combustion (CLC). Chemical looping technologies have emerged as attractive processes for clean energy applications through a wide range of process configurations i.e. combustion, gasification, and reforming. The unique oxygen separation system of chemical looping technologies makes them a preferred pathway to NetZero emissions with a smaller carbon footprint compared to the conventional gasification and combustion process. In combination with bioenergy, chemical looping potentially creates a net negative option. Among various Bioenergy with Carbon Capture and Storage (BECCS) technologies, CLC offers the lowest CO_2 avoided cost (£62 ± 33 per tonne CO_2) but also presents the largest relative uncertainty. A major challenge in chemical looping applications is screening and selection of suitable metal oxides (as oxygen carriers) with high chemical conversion rates, complete reaction reversibility, fast reaction kinetics, high oxygen carrier capacity, and the capability of maintaining high mechanical performances in several cycles. This challenge can be addressed by developing advanced novel metal oxide nanocomposites via continuous hydrothermal conversion and co-precipitation methods. Following the preparation of Cu, Co-, and Mn-based metal oxide nanocomposites using near and supercritical conditions, the combustion of biochars were conducted using a thermogravimetric analyser (TGA) to evaluate the performance of these metal oxides under varying operating conditions (temperatures: 700-900 °C). The results revealed a high combustion efficiency (>90 wt.%) for biochars when employing stoichiometrically required amounts of Cu-, Co-, and Mn-based oxygen carriers prepared through continuous hydrothermal conversion. In-depth characterizations using techniques such as XRD and SEM were employed to propose potential combustion mechanisms for biochars with oxygen carriers, facilitating kinetic analysis of the technology. The findings from this study contribute to the advancement of chemical looping combustion technology and offer valuable insights into the feasibility of CLC for the conversion of biomass/biochar into bioenergy.

***Keywords**: Hydrothermal, Co-precipitation, Metal oxide nanocomposites, Chemical Looping Combustion, CO_2 Capture, BECCS.*
***Acknowledgement:** This research was funded by EPSRC [EP/S036113/1], Connected Everything II. The authors also gratefully acknowledge the financial support provided by the University of Nottingham's "FPVC Research Acceleration Fund" in 2022.*

MONDAY – SEPTEMBER 11th, 2023

Room José Zorilla- CO_2 C&S

16:45 - 17:00 ORAL PRESENTATION 81523.

HYDROTHERMAL REDUCTION OF CO_2 BY USING CATALYSTS AND BIOMASS RESIDUES

Chinchilla, M.I.[1], Chain, F.A.[1], Martín A.[1], McGregor J.[2], Bermejo, M. D.[1]

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The present work aims to determine the best conditions for the hydrothermal reduction of CO_2 captured in basic solutions such as $NaHCO_3$, in the presence of metal catalysts (Pd/C 5%, Pd/C 10%, granular activated carbon, powdered activated carbon, Ru/C 5%), some already evaluated in a previous work[1], and various biomass residues (beet, pine needles, vermicompost, cork, softwood and cellulose) acting as reducing agents. The experiments were performed in order to evaluate the possibility to obtain high value-added products such as formic acid (hydrogen vector).
The reactions were carried out in horizontal batch reactors. The highest yields of formic acid were obtained at 300 ºC and 2 hours of reaction, by using Pd/C 5% as catalysts and the residue of softwood or cellulose as reducing agents. The reaction provided yields of formic acid of about 12% (soft wood) and 18% (cellulose).
In the reduction of captured CO_2 with biomass, the formic acid produced can come from the oxidation of biomass or from the reduction of $NaHCO_3$. The origin of formic acid was investigated using NMR analysis with $NaH^{13}CO_3$ as carbon source. It was found that when using softwood residues, palladium on carbon 5% catalyst generates the highest amount of formic acid from $NaH^{13}CO_3$ (73% of the total yield of formic acid came from the captured CO_2 and 27% remaining came from the biomass).

Key words: CO_2, Biomass, Hydrothermal conditions, Formic acid

References
Chinchilla, M.I.; Mato, F.A.; Martín, Á.; Bermejo, M.D. Molecules 2022, 27, 1652.

Acknowledgements:
This project has been funded by the Ministry of Science and Universities through project RTI2018-097456-B-I00 and by the Junta de Castilla y León through project by FEDER FUNDS under the BioEcoUVa Strategic Program (CLU-2019-04)

MONDAY – SEPTEMBER 11th, 2023

Room José Zorilla- CO_2 C&S

17:00 - 17:15 ORAL PRESENTATION 80740.

CO_2-loaded amines conversion to formic acid: new perspectives for green H2 and CO2 utilization

Dos Santos, L.C.[1,2], Quintana-Gómez, L.[1], Goicoechea, A.[1], Ciordia-Asenio, V.[1], Almarza, M.[1], Segovia, J. J.[2], Martín,[1] A., Bermejo, M.D.[1,*]

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CO2 capture and utilization (CCU) has gained important attention in recent years since less than 200 Mt/y is used for compound production (almost 60 % is dedicated to urea production), while the global CO2 emissions is estimated to be 67 % higher than that value1. The production of chemicals that can be further used as fuels or raw materials in food, pharmaceutical, and chemical industries can improve such CO2 demand offsetting CO2 storage high costs2. In this context, CO2 captured by amines (resulting in carbamates and bicarbonate formation) followed by its reduction to generate formic acid (FA) is a potential alternative, since large-scale facilities using such capturing technology are currently operative. The aim of this work was to reduce the CO2 captured in aqueous amine [3-Amino-1-propanol (AP, 3.7 %, wt.) or 2-Amino-2-methyl-1-propanol (AMP, 5.0 %, wt.)], to produce FA using H2(g) as reductant and Pd/C as the catalyst. For the reaction, a stainless steel, 25 mL reactor (Parr 4791 Micro Stirred reactor, Parr Instruments) was set to the following conditions: fixed 0.05 g Pd/C and 10 mL CO2-loaded aqueous amine solution, and H2(g) pressure range of 25-75 bar, temperatures of 70-125 ºC and reaction time of 60 or 120 min. Total inorganic carbon (TOC-V CHS, Shimadzu) confirmed the CO2 concentration prior to each reaction and formic acid was quantified using HPLC (module e2695, Waters), coupled with refractive index detector, thus allowing calculation of conversion yield (%, mol FA/mol CO2). The highest conversion yield (67.8 ± 3.8 %) was achieved for AP under 125 ºC, 75 bar, and 120 min. Such higher yields suggest that CO2-loaded amines reduction using H2 is a promising technology for CCU goals that could be integrated into the current process already functioning in gas treatment plants.

Keywords: Amines, CO2 reduction, Formic acid, Green H2.
1 H. Yamada, Polymer J., 2021, 53, 93-102.
2 A. Yusuf et al., J. Clean. Prod., 2019, 237, 117760.

Acknowledgements: This work/project was supported by the Regional Government of Castilla y León and the EU-FEDER program (CLU-2019-04 and CL-EI-2021-06).

TUESDAY

11:30-13:00

D. Fundamentals, Metrology and Modeling

Properties

KEYNOTE LECTURE

ORAL PRESENTATIONS

TUESDAY – SEPTEMBER 12th, 2023

Room Rey Felipe II – Properties

11:30 - 12:00 KEYNOTE LECTURE 80888.

Nanosized effect on electronic/local structures in ultrafine CeO_2 nanomarticles by X-ray absorption/emission spectroscopy

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CeO_2 has a high oxygen storage capacity (OSC) and oxygen mobility derived from Ce^{4+}/Ce^{3+}. CeO_2 nanoparticles (NPs) with {100} surface exposure synthesized by supercritical hydrothermal conditions show high OSC capacity in the temperature range as low as 150 °C. Moreover, it has been reported that the Ce atomic positions of these particles are significantly displaced, and the lattice expands when the particle size is smaller than about 6 nm [1]. In this study, we investigated the electronic structure of CeO_2 NPs prepared by the supercritical hydrothermal synthesis method [2], using synchrotron x-ray absorption (XAS) and emission (XES) spectroscopy.

Ce L_3-edge XAS spectra of CeO_2 NPs were the same as that of bulk CeO_2 regardless of particle size, indicating that the coordination number is unchanged, and the crystal structure of CeO_2 is maintained down to the nanoscale. On the other hand, Ce $M_{4,5}$-edge XAS spectra showed a significant increase in the intensity of the absorption peak at ~889 eV as the particle size decreased. This feature suggests that the 4f1 electron configuration, which is the oxidation state of Ce^{3+}, occurs instead of the 4f0 electron configuration, which represents the oxidation state of Ce^{4+}. Since this feature indicating a Ce^{3+} state was also observed in the absence of oxygen vacancies, this may be attributed to lattice distortion effects in the sub-nanometer region. Furthermore, in the O K-edge XAS spectra, the peak intensity arising from the O 2p hybridized with the Ce 4f (~531 eV), 5d e_g (~535 eV), and t_{2g} (~537 eV) orbitals decreased as the size of CeO_2 NPs was reduced. Our results suggest that lattice distortion of CeO_8 in the sub-nanometer-sized NPs causes a loss of cubic symmetry, resulting in a Ce^{3+}-like state in which the 4f and 5d conduction band orbitals are partially filled.

Keywords: X-ray absorption spectroscopy, X-ray emission spectroscopy, cerium oxide

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Acknowledgments:
This study was supported by grants from the Japan Society for the Promotion of Science (JSPS), KAKENHI (Grant Number 21H05010).

TUESDAY – SEPTEMBER 12th, 2023

Room Rey Felipe II – Properties

12:00 - 12:15 ORAL PRESENTATION 80834.

MODELLING AND EXPERIMENTAL MEASUREMENTS OF CO_2 SOLUBILITY IN AQUEOUS AMINES

Arroyave, J.D., Pérez Milian, Y., Vega Maza, D., Moreau, A., Paredes, X., Segovia J.J., Martín, M.C.

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This work is focused on the thermodynamic study of vapor-liquid equilibrium (VLE) of carbon dioxide in separate aqueous blends of Monoethanolamine (MEA) and *N*-Methyldiethanolamine (MDEA) with a modified mathematical model based on Kent-Eisenberg1 approach (M-KE). The model was correlated for the MEA+H2O+CO2 system with 485 literature data points corresponding to a wide range of amine molar concentrations (1.6 – 7) M, temperature (313.15 - 443.15) K and CO2 partial pressures (0.001 – 19812) kPa. In the same way, for the MDEA+H2O+CO2 system, the model was adjusted with 431 data points corresponding to molar concentrations between (1.69 - 4.28) M, temperature between (298.15 - 473.15) K and partial pressures between (0.001 – 6117) kPa. Also, Krichevsky-Kasarnovsky (KK) correlation was coupled with M-KE model to predict the experimental data at CO2 loadings higher than 1 mol-CO2/mol-Amine typically presented in the high pressure and low temperature region. Furthermore, a Van Ness-type apparatus has been constructed as a static-isochoric method to measure VLE of CO2 in aqueous amines suitable for a total pressure up to 10 MPa. The home-built equipment is employed to achieve thermodynamic equilibrium under isochoric conditions in a cell of stainless steel (AISI-316L) to prevent the corrosion effect of solvents and this setup was validated against literature data for 30 wt.% of MEA. The correlated results obtained with the model are compared with the experimental values reported in literature and found to be in good agreement with an average absolute relative deviation lower than 10%. The model can predict the speciation of unreacted amine, protonated amine, carbamates, carbonates and CO2 solubilized without chemical reaction. The Quasi-Newton optimization method used for the M-KE model shows better performance compared with other methods commonly used for this kind of semi-empirical approaches. Finally, the technique proposed in this work shows an accurate, simple, and versatile experimental technique to measure VLE data.

Keywords: CO2 solubility, Vapor-Liquid equilibria, MEA, MDEA, Static-isochoric apparatus.

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Acknowledgements: This work is funded by Spanish Ministry of Science and Innovation project PID2021-125749OB-I00 and EURAMET, EMPIR project number: 21GRD06. JDA is funded by Predoctoral contract Uva 2021, cofounded by Banco Santander. D.V.M. thanks his fellowship "Beatriz Galindo Senior", BEAGAL18/00259. X.P. acknowledges his "María Zambrano" fellowship.

TUESDAY – SEPTEMBER 12th, 2023

Room Rey Felipe II – Properties

12:15 - 12:30 ORAL PRESENTATION 79947.

Mapping the Controlled Hydrothermal Synthesis of Materials with Principal Component Analysis

Bathe, A.S.,[1] Sanz Arjona, A.,[1] Regan, A.,[1,2] Flandrin, C.,[1] Dunne, P.W.[1]

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Despite their growing importance hydrothermal and solvothermal techniques remain largely "black box" processes, as they require sealed pressurised vessels, such that *in-situ* monitoring is restricted to synchrotron-based experiments.[1] As a result, gaining insights into hydrothermal reaction mechanisms, and thus design of reaction systems to achieve desired product characteristics commonly requires exhaustive empirical testing with the concomitant demands on characterising obtained products *ex-situ*. This can represent a significant time sink and obstacle to screening of reaction conditions for materials discovery or optimisation.
We show here that the statistical method of Principal Component Analysis (PCA) may be readily applied to the large library of laboratory powder X-ray diffraction data acquired from the extensive screening of reaction conditions under both conventional batch and injection hydrothermal methods.[2] This is demonstrated in the case of cerium dioxide, CeO_2, which is known to exhibit size- and shape-dependent catalytic properties, as well as polymorphic cadmium sulfide, CdS, and calcium carbonate, $CaCO_3$. Combined analysis of simulated and real data easily reveals trends emerging from the variation of reaction conditions such as precursor choice, temperature, and time, which may be correlated to key material properties such as phase, size and unit cell parameters.
This approach may allow for the faster and easier mapping of the hydrothermal synthesis landscape, enhancing material discovery and process optimisation.

Keywords: Hydrothermal, XRD, Polymorphism, Principal Component Analysis

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TUESDAY – SEPTEMBER 12th, 2023

Room Rey Felipe II – Properties

12:30 - 12:45 ORAL PRESENTATION 80742.

Densities of aqueous 3-Amino-1-propanol, 2-Amino-2-methyl-1-propanol and their blends at high pressures

Dos Santos, L.C.[1,2], Moreau, A.2, Pérez-Milian, Y.[2], Vega-Maza, D.[2], Bermejo, M.D.[1], Segovia, J. J.[2,*]

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Aqueous amines solutions are currently considered the systems with a highly promising effectiveness in CO2 capture, and in the past decade, there has been a persistent search for applications of methods to allow CO2 capture and utilization (CCU)1. Some of the CCU methods imply the application of temperatures and pressures higher than the atmospheric2. Monoethanolamine (MEA) is the most studied amine, with thermodynamic properties under a wide range of pressures and temperatures well described in literature3 despite the current evidence of possible uses of other alkanolamines, including those with steric hindrance. However, a few works in the literature report the thermodynamic properties of such amines and their blends under high pressure. This work presents density values of 3-Amino-1-propanol (AP), 2-Amino-2-methyl-1-propanol (AMP) (with steric hindrance effect), and their blends (reagents purity ≥ 95%). The measurements were performed in a vibrating tube densimeter (Anton Paar DMAHPM) calibrated with water and vacuum, with an uncertainty ($k = 2$) less than ± 0.7 kg/m3, which determines the period of oscillation which is further related to the fluid density4. The densimeter was previously automatized and validated by Segovia et al.5 The measured compositions of amines + water systems varied from 5-40 % wt., under temperatures and pressures ranging from 20-120 ºC and 1-1000 bar, respectively. The densities were fitted using the modified Tammann-Tait equation, and fitted parameters presented an AAD < 0.02 %. For the aqueous amine systems at the same composition, temperature, and pressure, densities presented the following results: ρAP > ρAP+AMP > ρAMP. For instance, knowledge of such data can further allow the dimension of reactor and other equipment used in new methods to improve CO2 conversion rates.

Keywords: Alkanolamines, Vibrating tube densimeter, CCU.
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Acknowledgements: This work/project was supported by the Regional Government of Castilla y León and the EU-FEDER program (CLU-2019-04 and CL-EI-2021-06).

TUESDAY – SEPTEMBER 12th, 2023

Room Rey Felipe II – Properties

12:45 - 13:00 ORAL PRESENTATION 80509.

SOLUBILITY OF NO FROM COMBUSTION GASES IN AMINE SOLUTION

Castro-Ferro, N.[1], Vaquerizo L.[1]

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This work studies the absorption of nitric oxide (NO) in primary amine (AMP) and tertiary amine solutions (TEA, MDEA), which can be used as an alternative treatment to the two main technologies used nowadays to control NOx emissions in flue gas streams: selective catalytic reduction (SCR) and selective non-catalytic reduction (SCNR)[1]. To analyze NO solubility, each amine solution, at 40% w/w concentration, was placed inside a reactor that has a temperature controller and a manometer for pressure measurement. Before the experiment, the amine solution was degassed using liquid nitrogen and vacuum. After two repetitions, it was assumed that the amine was fully degassed. The reactor was preheated at 35°C and once the temperature was stable, the solubility at different absorption pressures was evaluated (1, 3, 5, and 7 bar) by measuring the pressure decay inside the reactor. Using the ideal gas law and the difference between the initial and the final pressure the amount of NO solubilized in the absorbent liquid was determined. The results for the amines evaluated are AMP: 3.61x10^{-3} $\frac{mol}{atm\ L}$, TEA: 3.31x10^{-3} $\frac{mol}{atm\ L}$ and MDEA: 2.28 x10^{-3} $\frac{mol}{atm\ L}$. The results obtained are higher than the NO absorption in water[2] 1.90x10^{-3} $\frac{mol}{atm\ L}$ but lower compared to the CO_2 absorption in MDEA[3] 6.54 $\frac{mol}{atm\ L}$. According to Fine, N. et al, for tertiary amines (TEA and MDEA) the absorption of NO is in form of nitrate and nitrite and for primary amines (AMP) the reaction will form unstable nitrosamines which will ready deaminate into a carbonization and nitrogen gas. Because of the facility to create nitrosamines rather than nitrate and nitrite[4], the highest absorption was found by AMP. Further analysis will be performed to verify that the adsorption in AMP is giving unstable nitrosamines or whether there is some absorption as nitrate and nitrites. Other types of absorbent liquids such as alcohols and sulfites will be tested to determine which could be the better option for NO solubility.

Keywords: Absorption, Nitric Oxide, Solubility.

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Acknowledgements: This work/project was supported by the Regional Government of Castilla y León and the EU-Feder program (CLU-2019-04)

C. Sustainability and Environment

Sustainability

KEYNOTE LECTURE

ORAL PRESENTATION

TUESDAY – SEPTEMBER 12th, 2023

Room Dr. Luis de Mercado – Sustainability

11:30 - 12:00 KEYNOTE LECTURE 82062.

SOLVO-/HYDROTHERMAL PROCESSES FOR MATERIALS RECYCLING: TOWARDS A CIRCULAR ECONOMY

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Solvo-/hydrothermal processes have played a central role in the development of green chemistry in the last decades. In the continuity, they can now offer the opportunity to bring Materials Science into the Circular Economy. Most of the resources/raw materials are not in Europe. The solution is in urban mines if we can discover and develop recycling technologies to transform an end of life material into a raw material of recycling. The main objective of this presentation will be to highlight this novel axis of development of solvo-/hydrothermal processes in the field of materials recycling with the following cases: recycling fibers (carbon, glass and natural fibers) from fiber reinforced polymers (FRP), recycling critical metals from the new technologies of energy (rare-earth-based magnets, Li-ion batteries,…), recycling food packagings and shoes. One version of the solvo-/hydrothermal process can bring a solution to the regeneration of FFP2 facemasks.
The first part of the presentation will concern an introduction to circular economy and the associated challenges. Will follow an overview of the solvo-/hydrothermal processes which are developed for materials recycling, namely solvo-/hydrolysis reactions-based technologies (mainly with water and alcohols as solvents) and delamination-based technologies for complex materials (mainly carbon dioxide as solvent with a possible addition of co-solvents). Beyond the scientific and technical aspects, the environmental impact of these technologies will be addressed using Life Cycle Assessment (LCA). For instance, a comparative analysis will be proposed to position the solvo-/hydrolysis technology among others for the recycling of carbon fibers from composite materials but also for the recycling of bonded magnets.
The last part of this presentation will be dedicated to technology transfer of this family of processes with the example of IDELAM. Since its foundation in 2019, IDELAM has been developing the scCO2-based technology for an extensive number of applications. Since the first year dedicated to the proof of concept on a large number of products, the start-up has gained a growing interest from industrial manufacturers, recycling centres or eco-organisms and has been labelled by the Solar Impulse Foundation. IDELAM is now transitioning from its capital risk founding toward its capital risk development, and intends to strengthen its collaboration with ICMCB with the development of new projects regarding the use of solvo-/hydrothermal-based technologies for recycling.

Keywords: Circular economy, Recycling, Materials, Solvo-/Hydrothermal, LCA

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TUESDAY – SEPTEMBER 12th, 2023

Room Dr. Luis de Mercado – Sustainability

12:00 - 12:15 ORAL PRESENTATION 79791.

Direct fabrication of designed piezoelectric materials by hydrothermal route

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Piezoelectric materials have been widely used in pressure sensors, acoustic transducers, and high-voltage generators. Recently, piezoelectric charges induced by mechanical vibrations are used to drive catalytic redox reactions in photocatalyst applications and nanogenerators [1-2]. In the present study, we have developed various nano/microstructure designed piezoelectric materials such as ZnO, BiFeO3, BaTiO3, ZnSnO3, and their composites were fabricated through the hydrothermal method, focusing on piezo-composite thin film formations and their piezo-related applications. The formation of a p–n junction based on piezoelectric materials with narrow band gap semiconductors has shown encouraging results on photo-applications in visible region. The piezo-photocatalytic applications such as piezo-photodegradation and piezo-photoelectrochemical water splitting of piezoelectric materials were studied under light irradiation and external stress. BiFeO3/ZnO, BaTiO3/Ag2O and ZnSnO3/SnO composites exhibited high performance photodegradation for organic pollutants. By combining the piezoelectric potentials and built-in electric field in the interface of the p-n junction, the photocatalyst efficiency of composites was greatly enhanced. Moreover, piezoelectric films have been extended to advanced piezo-nanogenerators (PENGs) applications. The energy harvesting performance of the BiFeO3/ZnO-based PENG device was measured under different compressive pressure amplitudes. The measured output voltage and current are varied proportionally to the applied stress, which sufficiently demonstrates the fast response as well as the high sensitivity of the BiFeO3/ZnO-based PENG. In addition, the piezotronic effect on the performance of the BiOBr-Ag2O/ Carbon fiber-based glucose sensor was systematically studied by varying both the glucose concentration and compressive strain. Ag2O nanoparticles are decorated on BiOBr nanosheets, forming a p-n junction with a larger active surface, preventing photocorrosion effect. The piezo-electrochemical results indicated that the piezotronic effect significantly increased the sensitivity and stability of the BiOBr- Ag2O/Carbon fiber-based glucose sensors. This study presents a comprehensive review of fabrication by hydrothermal method for various designed piezoelectric materials, and multiapplications of piezo-thin films, including photodegradation, photoelectrochemical water splitting, glucose sensing and piezo-nanogenerators.

Keywords: hydrothermal, direct fabrication, piezoelectric materials, piezo-photocatalyst, nanogenerator.

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Acknowledgements: This work was partially supported by the Taiwan Ministry of Science and Technology under grant numbers MOST 106-2221-E-006-053-MY3 and MOST 109-2221-E-006-129.

TUESDAY – SEPTEMBER 12th, 2023

Room Dr. Luis de Mercado – Sustainability

12:15 - 12:30 ORAL PRESENTATION 81498.

THREE-DIMENSIONAL CARBON AEROGEL DERIVED FROM ELECTRONIC WASTE FOR THE ADSORPTION OF PHENOL FROM WASTEWATER

Marut Jain[1, 2, 3], Abhisek Sahoo[2], Prashant Ram Jadhao[2], Sadaf Aiman Khan[1, 2, 3], K. K. Pant[2], Zyta M. Ziora[3], Mark A. T. Blaskovich[3]

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Our environment is constantly contaminated by industrial activity and waste production. Finding cost-effective and practical strategies to reduce pollution produced by petrochemical industries and refineries is of primary concern. Additionally, we should look for a way to recycle electronic trash as its production is going up to 5% per year, according to a report from 2019 [2], totalling over 53.6 million metric tons. Therefore, our concept presented here aims to use electronic waste to eliminate the significant contaminants present in wastewater from petrochemical refineries, which are phenol and its derivatives [1]. The carbon material from the electronic waste was recovered utilizing the pyrolysis and ultrasonication procedure. The resulting hybrid aerogel can filter phenol from industrial wastewater with up to 95% removal efficiency. The central composite design-response surface methodology (CCD-RSM)-based ANOVA study demonstrated a strong agreement between quadratic model predictions. In a pilot plant, the raw material of electronic waste was directly pyrolyzed. The solid substance was then ultrasonically treated to remove metal impurities from the char. The final product was combined with carboxy methyl cellulose, heated hydrothermally, and then freeze-dried at –50 °C to create a gel-like substance. The resulting aerogel was then heated to 700 °C and activated with KOH. By employing varying mass ratios of carbon and carboxymethyl cellulose (1:05, 1:1, and 1:2), three distinct types of aerogels were created, and each was comprehensively characterized using scanning electron microscopy, HRTEM, FT-infrared spectroscopy, X-ray diffraction, and Raman spectroscopy. The aerogel with a 1:0.5 mass ratio was determined to be superior to the others and was employed for the adsorption of phenol in batch and column studies. The outcomes from our preliminary study show that synthetic aerogel is a powerful tool for efficiently removing phenol from industrial effluent.

Keywords: electronic waste, wastewater, adsorption, sustainability, column study.

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TUESDAY – SEPTEMBER 12th, 2023

Room Dr. Luis de Mercado - Sustainability

12:30 - 12:45 ORAL PRESENTATION 79931.

IN-SITU CATALYTIC HYDROPROCESSING SOLVOTHERMAL CO-LIQUEFACTION OF WASTE BIOMASS WITH A PETROLEUM FEEDSTOCK

Abhisek Sahoo[1], Thallada Bhaskar[2], Kamal K. Pant[1]

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Biomass has gained significant recognition as a potential alternative for producing liquid fuel. However, the high oxygen content, poor stability, and low heating value of bio-oil render it unsuitable for widespread application and make it an inadequate fuel choice on a large scale1. The co-liquefaction of biomass-derived biocrude in petroleum refineries is thought to be a realistic and cost-effective method for creating low-carbon fuels2. In this study, the agricultural residue, like rice straw with petroleum feedstock such as vacuum gas oil at different ratios, was subjected to solvothermal liquefaction, using ethanol as an H2 donor solvent and a NiCo/Al co-precipitation catalyst under varying temperatures and constant pressure. The catalytic performance of bimetallic NiCo/Al catalysts was superior to that of the monometallic Ni/Al and Co/Al catalysts in the context of the hydroprocessing reaction3. The results demonstrated a synergistic outcome, as the process increased the yield of liquid products and enhanced their quality, such as lower oxygen content, higher thermal stability, and improved selectivity also. The GC-MS analysis indicated that the bio-liquid fuel possessed a relatively low level of phenol, suggesting that it had a less toxic and hazardous nature. The bio-liquid fuel obtained through this method exhibited enhanced physical properties and demonstrated good fuel potential when compared to bio-liquid obtained through the pyrolysis process.

Keywords: Biomass; Bimetallic catalyst; Hydroprocessing; Liquefaction; Upgradation

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B. Processes

Material Synthesis

KEYNOTE LECTURE

ORAL PRESENTATIONS

TUESDAY – SEPTEMBER 12th, 2023

Room José Zorilla– Material Synthesis

11:30 - 12:00 KEYNOTE LECTURE 81762.

Synthesis of substituted petroleum by hydrothermal reaction of biomass -Combining pulp & paper industry and chemical industry toward carbon neutral society-

Wahyudiono, Akira Yoko, and Tadafumi Adschiri

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Significant efforts have been made to establish a carbon neutral society (zero total CO_2 emission by 2050) all over the world, including introduction of renewable energies (PV, wind, biomass, geothermal energy etc.), reducing energy consumption etc. Regarding the production of chemical products, the raw material, petroleum, should be replaced with the use of waste polymers, CCU (CO_2 usage with H_2) or biomass as renewable hydrocarbons. In Japan, 26 M carbon t/year of naphtha is imported, while Japanese forest has a potential to supply the same amounts of hydrocarbons (carbon basis). One of the methods to convert biomass to oil is the hydrothermal reaction process. This paper describes the potential of this technologies, with showing our previous basic research results of cellulose conversion, lignin conversion in SCW, and with demonstrating the newly obtained results of oil recovery from saw dust. Thermal energy requirement analysis was also conducted to verify the high possibility of this process. Finally, the process features were compared with those of the other possible processes, such as rapid thermal pyrolysis process, catalytic thermal conversion, and gasification process.

Keywords: Substituted petroleum, Hydrothermal reaction, Biomass, Carbon neutral society

TUESDAY – SEPTEMBER 12th, 2023

Room Claudio Moyano – Material Synthesis

11:30 - 12:00 KEYNOTE LECTURE 80824.

Activated elemental Se - a viable synthetic precursor for room-temperature synthesis of high performance materials

Kirill Kovnir

Department of Chemistry, Iowa State University
US DOE Ames National Laboratory

Se-containing materials often synthesized by solution-assisted from toxic and expensive organo-Se precursors. We are reporting a facile alternative utilizing elemental Se which is cheap and non-toxic. Elemental Se reagent has a drawback of low solubility and reactivity resulting in sluggish kinetics at low temperatures. A process of elemental Se activation was developed resulting in stable solution of multiple Se species confirmed with ^{77}Se NMR studies, including R-Se-Se-R and never detected before “naked” Se_2^{2-}. Dynamic equilibrium between the produced Se species allow to perform reactions at wide temperature ranges including room temperature. We have demonstrated the applicability of such activated Se for synthesis of different all-inorganic and hybrid organic-inorganic metal selenide with outstanding magnetic, superconducting, and thermoelectric properties.

TUESDAY – SEPTEMBER 12th, 2023

Room José Zorilla- Material Synthesis

12:00 - 12:15 ORAL PRESENTATION 78295.

HYDROTHERMAL ASSISTED SYNTHESIS OF MXENES AND THEIR COMPOSITES WITH EXCELLENT GAS SENSING PERFORMANCE

Yin, S.[1,*], Yang, M.[1], Okawa, A.[1], Hasegawa, T. [1], Wang, Z.[2], Hermawan, A.[3]

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Recently, the new two-dimensional(2D) material MXenes, which are layered materials based on transition metal carbides, are considered to have high application potential in the field of gas sensing because of its rich functional groups, high electron mobility and large specific surface area. Generally, typical MXenes, Ti3C2Tx and Nb2CTx, are prepared by an etching process using concentrated HF aqueous solution with MAX phase precursors of Ti3AlC2 and Nb2AlC. In the present research, the MXenes (M=Ti/Nb/V) were successfully prepared by hydrothermal treatment using the mixed fluoride and hydrochloric acid solution as the etching solution. It was found that all MXenes have two-dimensional layered structures, and their gas sensing properties changed with their composition, surface functional groups, and surface/edge status. The Ti3C2Tx has obvious gas sensing response in N2 base gas. While the V2CTx has no obvious gas response because of its poor layered structure. On the other hand, the Nb2CTx possessed uniform layered structure and large layer spacing and showed excellent gas response for various VOC gases with high response value, low detection limit, fast response speed, high selectivity, and reliable cycle stability in air base gas. At the same time, some oxide/MXene composites, such as SnO-SnO2/MXene etc., were also successfully synthesized using MXene and related precursors under hydrothermal conditions. In a typical synthesis process, 100 mg Ti3C2Tx was introduced in 100 mL of deionized water, followed by magnetic stirring for 1 h. After that, 0.45 g of the precursor, such as SnCl2·2H2O and 0.36 g of urea were added into the above solution, then 30mL hydrochloric acid was added dropwise. The dispersion was magnetically stirred for 30 min, followed by hydrothermal treatment in a Teflon-lined autoclave at 120oC for 8 h, to obtain a SnO-SnO2/ Ti3C2Tx nanocomposites. It was also found that the gas sensing performance of MXene could be improved by surface modification with some nanosized semiconductor oxides. The VOC gas sensing performance of oxide/ Ti3C2Tx MXene, such as CuO/MXene, was superior to other oxide/2D materials such as CuO/MoS2 and CuO/rGO. Also, the formation of nanoscale SnO-SnO2 p-n heterojunction on the surface of MXene greatly enhanced the performance of MXene. The SnO-SnO2/Ti3C2Tx sensor exhibited improved acetone gas sensing response of 12.1 (Rg/Ra) at room temperature, which were nearly 11 and 4 times higher than those of pristine Ti3C2Tx and pristine SnO-SnO2, respectively. The MXene-based materials and their composites possessed excellent gas sensing performance, including the gas response, gas selectivity, and decrement of their working temperatures, indicating their potential for various VOCs detection.

Keywords: MXene, Hydrothermal, Composites. Gas sensing

TUESDAY – SEPTEMBER 12th, 2023

Room José Zorilla– Material Synthesis

12:15 - 12:30 ORAL PRESENTATION 79724.

A DESIGN CONCEPT FOR HYDROTHERMAL AND SUBHYDROTHERMAL SYNTHESIS OF HIGH-PERFORMANCE POLYIMIDES

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For their outstanding materials performances (exceptional high temperature stability, high chemical resistance, and high mechanical strength) high-performance polyimides (PIs) are intensively used in advanced technologies. As PIs are fully organic materials, they are additionally lightweight. PIs are used for a variety of high-end engineering applications in various shapes: As flexible films in microelectronics,1 as foams for, e.g., thermal insulation, as gas separation and filtration membranes, or as electrodes for battery applications.2 PI synthesis and production still rely exclusively on reactions performed at high temperatures (>300 °C), using harmful solvents (e.g., *N*-methyl-pyrrolidone, NMP) and carcinogenic catalysts (e.g., isoquinoline). These reactants and reaction conditions are harmful to the environment and human health. Moreover, NMP – such as most of the used harmful chemicals – are about to be restricted for commercial use according to the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulation. Therefore, alternative syntheses towards PIs are strongly needed. Among several reported strategies, we have recently provided examples of synthesizing PIs under hydrothermal conditions, without requiring additional promoters or co-solvents.3,4 With this contribution we present new general strategies for producing a wide range of PIs by either hydrothermal synthesis or using water as medium at lower temperatures (T<100 °C). Depending on the polymerization happening in the hydrothermal or subhydrothermal regimes, drastically different PI morphologies (e.g., particles vs. foams) are generated. Consequently, adjusting the reaction temperature in water allows for tuning a range of materials properties associated with morphology. This strategy is based on a molecular design concept allowing the starting compounds to react in water over a wide range of temperatures. Therefore, PIs can be obtained in various shapes relevant to application, e.g., microparticles, free-standing films, coatings, and foams.

Keywords: Hydrothermal synthesis, High-performance polyimides, Materials design
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Acknowledgements: We thank the Austrian Science Fund's (FWF) START programme under grant no. Y1037-N28.

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TUESDAY – SEPTEMBER 12th, 2023

Room José Zorilla– Material Synthesis

12:30 - 12:45 ORAL PRESENTATION 80726.

Hydrothermal synthesis of $BaCr_2(P_2O_7)_2$ particles and Near-Infrared reflectance characterisation: Influence of reaction parameters

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The present study investigates the reflectance properties and synthesis of $BaCr_2(P_2O_7)_2$ particles produced in a hydrothermal condition in an alkaline medium. The crystallisation of BaCr2(P2O7)2 was triggered under various hydrothermal conditions to determine the effect of temperature and reaction time on obtaining a single phase. Solutions of the reagents were mixed in a Teflon vessel, filling it to 50% of its capacity. Colloid formation occurred after adding an alkaline NaOH solution, which was stirred for 5 minutes at 500 rpm. The autoclave vessel was sealed and heated to the desired temperature range of 150 to 240 ºC for different reaction intervals ranging from 3 to 48 h. X-ray diffraction (XRD) results revealed that $BaCr_2(P_2O_7)_2$ crystallisation starts at a temperature as low as 150 ºC for 6 hours, regardless of the NaOH concentration used in the hydrothermal reaction. The diffraction patterns were indexed with the BaCr2(P2O7)2 phase [1] and with the secondary phase $BaCr_2PO_{13}$ (card COD96-901-6408) [2]. These cards were employed for Rietveld refinement calculations, which showed a high-reliability accuracy as indicated by the *Rwp* fitting refinement value.
Additionally, it was found that the reaction products contained a significant percentage of the secondary phase of $BaCr_2PO_{13}$. The crystallisation of pseudospherical particles ranging in size from 70 to 60 nm was observed at 150 ºC for 48 h. Furthermore, considering these particles' nanoscale morphology and size, the reaction products are estimated to exhibit high reflectance capability in the near-infrared radiation (NIR).

Keywords: BaCr2(P2O7)2, BaCr2PO13, Hydrothermal, Reflectance, Near Infrared Radiation.

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Acknowledgements: DECR is indebted to the support from CONACYT throughout a research scholarship for conducting this research.

TUESDAY – SEPTEMBER 12th, 2023

Room José Zorilla– Material Synthesis

12:45 - 13:00 ORAL PRESENTATION 79817.

STIRRING HYDROTHERMAL SYNTHESIS OF COMPOSITION-CONTROLLED $(K,Na)NbO_3$ PARTICLES

Chandima P. Ellawala Kankanamge, and Astri Haugen

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One of the most promising lead-free ferroelectric material systems is based on $(K,Na)NbO_3$. Hydrothermal synthesis is one widely used technique that offers composition and morphology controlled $(K,Na)NbO_3$ powders crucial for producing high-performance piezo-ceramics.
In this work, conventional and stirring hydrothermal treatments of solutions containing Nb_2O_5 and KOH/NaOH mixtures were carried out at 190 ˚C. Conventional hydrothermal treatment with KOH/NaOH ≤ 50% produced $NaNbO_3$ cubes. A mixture of $K_5Na_3Nb_6O_{19}{\cdot}9H_2O$ hexagonal plates and $NaNbO_3$ cubes was obtained with KOH/NaOH - 75%/25%, only with 100% KOH was $KNbO_3$ obtained.
Products obtained by stirring hydrothermal synthesis, showed better size uniformity than with the conventional synthesis. Furthermore, stirring hydrothermal treatment of KOH/NaOH-75%/25%, produced only $K_5Na_3Nb_6O_{19}{\cdot}9H_2O$ plates. The fact that the formation of $NaNbO_3$ in 75% KOH was completely avoided by stirring hydrothermal synthesis indicates that the ionic smaller size may not be the only reason Na^+ diffusion is favored. To explain the generally highly favorable inclusion of Na^+ relative to K^+ into the niobate lattice, we propose a reaction mechanism considering the kinetics.
By reducing the conventional hydrothermal treatment time to 1 – 6 hours we could isolate reaction intermediates. Previous *in-situ* studies reported that the hydrothermal reactions of Nb_2O_5 and NaOH proceed through $Na_7HNb_6O_{19}.15H_2O$, and $Na_2Nb_2O_6.H_2O$ intermediates.[1] Our experiments also indicate a similar reaction pathway for Nb_2O_5 and NaOH/KOH mixtures. In KOH/NaOH-75%/25%, $K_5Na_3NbO_6.9H_2O$ and $NaNbO_3$ co-existed, however $Na_2Nb_2O_6.H_2O$ was not detected at any reaction anytime. This indicates, the reaction was at steady state, and the formation and $Na_2Nb_2O_6.H_2O$ is the slowest step, which may occur at microenvironment spots. Stirring during hydrothermal synthesis homogenize the solution removing microenvironments. This further slow-down the formation of $Na_2Nb_2O_6.H_2O$ and avoids the propagation of the reaction. Stirring-hydrothermally synthesized $K_5Na_3Nb_6O_{19}{\cdot}9H_2O$ intermediates were calcined to obtain $K_{0.7}Na_{0.3}NbO_3$ plates. For scaling-up our synthesis, continuous flow hydrothermal synthesis of $(K,Na)NbO_3$ is also studied. $(K,Na)NbO_3$ particles (100g/day) were successfully obtained by continuous flow synthesis.

Keywords: Hydrothermal, Lead-free, Piezoelectric, Niobate
References:

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TUESDAY – SEPTEMBER 12th, 2023

Room Claudio Moyano – Material Synthesis

12:00 - 12:15 ORAL PRESENTATION 81588.

FLOW VISUALISATION TECHNIQUE FOR OPTIMISATION OF CONTINUOUS-FLOW HYDROTHERMAL REACTOR DESIGN

T. Huddle[1], A. Erdogan[2], S. Brown, A. Mehew, E. H. Lester[1], F. Güleç[1,2]*

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Flow systems are generally simple; they use high-pressure components and fittings that are readily available off-the-shelf and are relatively cheap. However, it's possible to design countless flow system that achieve the same process conditions (flow rate, temperature, residence time etc), but with entirely different arrangements of the components and fittings, which result in vastly different flow dynamics. Subtle differences such as the type or size of a fitting can result in changes in product yield, quality and even increase the chances of blockage. Branches from the main flow path (e.g. for pressure gauges, transducers, inserted thermocouples etc) present potential "stagnant (dead) zones", where material can become circulate and/or accumulate.

This study investigates the impact of fitting design vs the probability of product accumulation in stagnant zones created by the high-pressure fittings. These dead zones are common to many types of continuous-flow supercritical synthesis systems. Three separate approaches have been used for modelling fluid flow and mixing, in order to understand the impact of these dead zones.

Method **one** involves the use of pseudo fluid modelling, which is conducted at ambient temperature and pressure. The pseudo fluids, one containing a dye, are allowed to mix and flow through transparent (usually scaled up) Perspex blocks. Internal channels are bored through the Perspex blocks, designed to mimic typical component/fitting internals used for Supercritical flow systems. Method **two** uses the same Perspex blocks and adjusted flow conditions but instead of a dye polyamide (nylon 12) tracer particles are added to the flow. Video footage is captured, but particle tracking algorithms are applied during image analysis. This method has also been found to be efficient in identifying regions of flow recirculation and/or stagnant zones. Method **three** involves adding a chromophoric tracer to a flow through components or an entire flow system. As the tracer elutes from the components/system under investigation, it is detected by online UV-Vis analysis; the measured UV-Vis absorbance of the tracer against time correlates to the distribution of flow within the components under investigation.

All approaches will be considered and compared in this paper, as well as an appraisal of the use of fluid motion studies in stagnant zones, within various high-pressure fittings used in continuous flow systems.

Keywords: *Pseudo fluids, image analysis, fluid dynamics*
***Acknowledgement*:** This research was funded by EPSRC EP/R032807/1 Cognitive Chemical Manufacturing

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Room Claudio Moyano – Material Synthesis

12:15 - 12:30 ORAL PRESENTATION 81630.

DEVELOPING CFD MODELS FOR CONTINUOUS HYDROTHERMAL SYNTHESIS REACTOR AND PERFORMANCE EVALUATION OF CFD MODELS VIA IMAGE PROCESSING

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An understanding of a reactor's hydrodynamic behaviours could provide many useful insights related to reactors performance. The Residence Time Distribution (RTD) of a tracer in a reactor is one of the most important visualisation characteristics to understand the hydrodynamic. Computational Fluids Dynamic (CFD) is also used to determine RTD in the reactor by modelling fluid flow and provides many results and visualizations related to the fluid domain such as velocity, pressure, temperature, volume fraction, etc. However, in addition to the validation of CFD models, the discussion of CFD model outputs is often hindered by the difficulties arising from the similarity of the counters. These challenges frequently give rise to confusion and can result in the misinterpretation of results. Computational-based image processing offers a potential solution to this problem, as it can effectively address the challenges associated with the similarity of counters in CFD model outputs. The aim of this study is to conduct a numerical investigation into the hydrodynamics of a continuous hydrothermal process reactor, specifically a pipe-in-pipe reactor, utilised for the synthesis of metal-oxide nanoparticles. The study also aims to identify the most reliable and validated CFD models by incorporating image processing techniques. CFD models were developed to understand the RTD of a tracer, injected into the fluid domain of the reactor, for the different reactor configurations (in a grayscale channel) under unsteady state flow conditions. In order to analyse the optimum picture, each CFD output (contour images) was then processed using a novel pixel analysis method in MATLAB. In this method, a ranking is used by normalizing the error values obtained for each CFD output with the range “0-1”.

***Keywords**: Computational Fluid Dynamics, Continuous Hydrothermal Synthesis, Machine Learning, Image Processing.*

***Acknowledgement:** Authors acknowledge This research was funded by EPSRC [EP/S036113/1], Connected Everything II.*

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Room Claudio Moyano – Material Synthesis

12:30 - 12:45 ORAL PRESENTATION 81574.

CAN MACHINE LEARNING ACCELERATE MATERIALS DEVELOPMENT USING HYDROTHERMAL SYNTHESIS?

T. Huddle[1], E. H. Lester[1]

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Solvothermal and hydrothermal flow reactors offer numerous advantages to working with batch reactors; Scalability, safety, greater control of process variables, online analysis and the potential for autonomous process optimisation through the use of machine learning and/or artificial intelligence (AI) models. In a continuous flow system, altering flow rates affects “residence time” (i.e. the time the precursor(s) are exposed to the process conditions in the reactor), but it also affects the mixing dynamics. There are at least 10 variables (e.g. temperature, pressure, precursor material, precursor concentration(s), flow rate, flow ratio etc), and this potentially creates an infinite number of experiments (dependent on the selected resolution) with variable parameters that could be attempted when seeking to make a new specification of nanomaterial.

Considering a scenario where just two process parameters are to be optimised (e.g. temperature and pressure), with the goal of generating the maximum yield of product from the process, when one is fixed and the other is screened for an optimal value, this optimal value changes when the parameters of the second is modified. This is because the parameters are interdependent; if one parameter is changed, it affects the other. A grid scan is one approach to finding the optimal compromise between the two parameters, but testing just ten different incremental values for each of the two parameters requires 100 experiments. This approach becomes even more impractical where more than two variables need to be optimized. A grid scan of 10 incremental values of 10 interdependent variables would require ten billion experiments.

Alternatively, AI methods can be used to optimize interdependent process parameters, using smart algorithms. The algorithms are capable of finding the optimal compromise of process parameter values in a profoundly reduced number of experiments, compared to a grid scan approach. AI models are therefore perfectly suited to continuous hydrothermal flow system process parameter optimisation because they can monitor products with online analysis in flow. By employing the algorithms, they can directly modify process variables, in order to quickly establish the optimal parameters for generating the target the material.

The utilization of advanced hardware such as graphics processing unit (GPU) tensor cores, accelerates the training and inference processes of machine learning models. Tensor core harnessing enabled by specialized hardware components facilitates efficient matrix operations and boosts the performance of deep learning algorithms. This advancement empowers faster model training and inference, facilitating real-time control and decision-making in nanomaterial production processes.

Keywords: Machine Learning, *Artificial Intelligence (AI), Cognitive manufacturing, Continuous hydrothermal synthesis.*

***Acknowledgement*:** This research was funded by EPSRC grant number EP/R032807/1 Cognitive Chemical Manufacturing

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Room Claudio Moyano – Material Synthesis

12:45 - 13:00 ORAL PRESENTATION 81716.

TELESCOPED FLOW SYNTHESIS AND CRYSTALLISATION OF PARACETAMOL

Holland, B.,[1] **Mead, O.,**[1] **MacCormack, T.,**[1] **McMullen, R.,**[1] **Lester, E.,**[1] **Turyanska, L.,**[1] **Robertson, K.**[1]

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Flow chemistry offers high control of reaction conditions through excellent heat and mass transfer. These benefits are increasingly taken advantage of in research labs as skills are being taught through undergraduate courses and and kit becomes more accessible.[1] One of the most exciting areas with increasing publications is that of telescoped synthesis, where two synthesis steps are directly combined without an interrupting work-up step in between.[2] Exploiting the same advantages from flow synthesis, flow crystallisation in plug flow reactors has seen a surge of interest in research labs in the past 8 years, with a particular interest in using segmented flow to prevent fouling and improve mass transfer.[3] Telescoping flow synthesis with flow crystallisation improves sustainability, through the removal of unnecessary interruptive steps and can greatly improve both yield and particle attributes such as crystal size distribution (CSD). To date there have been very few combined flow synthesis and crystallisation examples published, largely due to the discrepancy in flow rates required for each step; flow synthesis will typically use 10 µl/min – 1 ml/min, whilst flow crystallisation will typically require >5 ml/min net flow rate to achieve efficient mixing in the larger tubing required to avoid blockages.

Here we present a telescoped synthesis and crystallisation of paracetamol, achieved through using tri-phasic segmented flow. By exploiting the additional flow rate of two immiscible phases, we can keep the solution flow rate low and accessible for traditional flow synthesis whilst increasing the net flow rate of crystallisation to that appropriate for the 3.2 mm internal diameter crystalliser tubing. Rapid prototyping of flow synthesis reactor was effected through 3D printing with a design focus on maximum mixing intensity whilst minimising residence time distribution – analysed using a novel image analysis procedure. Based on a previously published crystalliser,[4] using the spatiotemporal link of flow technologies, the nucleation and growth regions of paracetamol crystallisation is physically separated, thus providing excellent control over the growth of paracetamol crystallisation. An impinging jet mixer design coupled with an ultrasonic nucleation section and temperature cycling crystal growth was found to be the most effective overall design; conversion of paracetamol is shown to be >99% and crystal yield is >66% with a narrow CSD.

Keywords: flow technologies, telescoped synthesis and crystallisation, crystal growth
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TUESDAY

15:15-17:15

A. Applications & Products

Applications

KEYNOTE LECTURE

ORAL PRESENTATIONS

TUESDAY – SEPTEMBER 12th, 2023

Room Rey Felipe II – Applications

15:15 - 15:45 KEYNOTE LECTURE

THE ROLE OF HYDROTHERMAL AND SOLVOTHERMAL SOLVENT IN BIOMASS CONVERSION

Jaehoon Kim. Sungkyunkwan University (South Korea)

TUESDAY – SEPTEMBER 12th, 2023

Room Rey Felipe II - Applications

16:15 - 16:30 ORAL PRESENTATION 79949.

DIVERSITY-ORIENTED SOLVOTHERMAL SYNTHESIS OF DIHYDROPYRIDINE DIKETONES

Leimhofer, L.1, Unterlass, M.M.1,2

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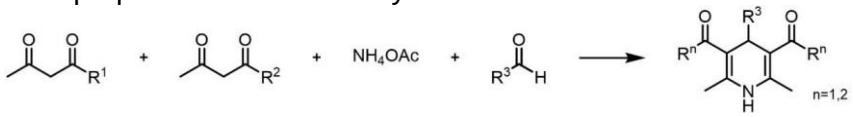
Dihydropyridines (DHPs, see Figure) are pharmaceutically active heterocyclic compounds, most importantly as blood pressure-lowering drugs. Moreover, DHPs are an isolable intermediate of the Hantzsch pyridine synthesis. There, a β-keto ester, an aldehyde, and a nitrogen source react with each other to the DHP in the first step, before the pyridine forms in the second reaction step.1 Alternatively, to β-keto esters, one can use β-keto ketones as CH- acidic starting compounds (see Figure) leading to DHPs bearing two ketone substituents (1,4- DHP diketones). While the literature contains numerous reports of 1,4-DHP diesters (aka 1,4- DHP dicarboxylates),2 there is only a comparatively small number of reports on 1,4-DHP diketone syntheses. These reports, feature only a limited breadth of scope, the use of excesses of some of the starting compounds, long reaction times, and the need for catalysts.3 Our research group has already shown that several different heterocyclic compounds, including quinoxalines4, rylene bisimides5, and perinones6 are accessible through hydrothermal synthesis.7
We here report an easy and efficient method for generating 1,4-DHP diketones that consists of reacting stoichiometric amounts of the starting compounds under solvothermal conditions. Our method allows for synthesizing a high number of 1,4-DHP derivatives within reaction times as short as 15 minutes. Hence, the method bears the potential to access this area of the biologically relevant chemical space efficiently. Our approach is diversity-oriented, i.e., leads on purpose to mixtures of 4 isomers. Consequently, all 4 isomers can be probed for desired properties simultaneously.



General reaction equation for the synthesis of 1,4-DHP diketones from two different 1,3 diketones ammonium acetate and an aldehyde in a multicomponent reaction.

Keywords: Solvothermal synthesis, 1,4-Dihydropyridine diketones, Diversity-oriented synthesis, Drug discovery.
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Acknowledgements: This work was funded by the Vienna Science and Technology Fund (WWTF) under grant number LS17-051 and the Austrian Science Fund (FWF) under grant no. START Y1037-N28.

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Room Rey Felipe II – Applications

16:30 - 16:45 ORAL PRESENTATION 80889.

Microwave hydrothermal treatment for the extraction of bioactive compounds and biopolymers from the lichen *Evernia prunastri*

Queffelec. J.[1], Torres. M.D[1], Domínguez. H.[1]

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In the current context of environmental crisis, efforts must be made to reduce energy consumption, contamination and to valorize bioactive compounds from renewable sources. Microwave pressurized hydrothermal extraction can be a sustainable alternative to conventional methods to recover compounds of interest as it is efficient, fast, safe and does not require the use of any organic solvent[1]. Lichen is an interesting source of bioactive compounds as each organism of this symbiosis synthesizes unique metabolites such as depsides, usnic acid, evernic acid, which can exhibit antitumoral, antioxidant or anti-inflammatory activity. Lichen cell-walls are also made of bioactive polymers like □ and □-glucans or galactomannans[2]. This work aims to extract and characterize bioactive compounds and biopolymers from the lichen *Evernia prunastri* and doing so using microwave hydrothermal extraction. The soluble extract characterization was done by spectrophotometry and high-pressure liquid chromatography and the rheological properties of the biopolymer were also measured. Anti-tyrosinase, anti-inflammatory and anti-tumoral properties of both soluble extracts and biopolymer were also assessed. Microwave extraction temperature has a great impact on the bioactive compounds and biopolymer recovery. The greatest antioxidant properties (60.2 ± 1.6 g Trolox eq/100 g extracts) and total phenolic compounds (12.5 ± 0.2 g gallic acid/100g of extract) are observed for the soluble extracts obtained at 140°C, the highest oligosaccharide content at 200°C and the highest yields for the polymer recovery at 160 and 180°C. Anti-tyrosinase activity was observed in all the tested samples whereas no inflammatory risk was found for the polymer. Polymer that also demonstrated the rheological properties of a gel after a simple thermal treatment, which could lead to applications in cosmetics, biomedicine, and food. Microwave hydrothermal treatment resulted to be therefore suitable for the recovery of compounds of interest with potential industrial applications.

Keywords: Microwave hydrothermal treatment, antioxidant, biopolymer.

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Acknowledgements:
Authors acknowledge Consellería de Cultura, Educación e Universidade da Xunta de Galicia (GRC-ED431C 2022/08). M.D.T. thanks the Ministry of Science, Innovation and Universities of Spain for her postdoctoral grants (RYC2018-024454-I) and Xunta de Galicia (ED431F 2020/01). J.Q. thanks the Early Stage Researcher (CINBIO22/001).

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Room Rey Felipe II – Applications

16:45 - 17:00 ORAL PRESENTATION 81536.

EXTRACTION AND DEGRADATION KINETICS OF PECTIC OLIGOSACCHARIDES (POS) FROM ONION SKIN WASTES USING SUBCRITICAL WATER

Benito-Román, Ó.[1], Melgosa, R. [1], Illera, A.E. [1], Sanz, M.T.1, Beltrán, S.[1]

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Pectic oligosaccharides (POS) have been proposed as a new class of prebiotics due to their ability to regulate microbiota in human intestine, their anti-oxidant properties compared to other commercial oligosaccharides or their anti-inflammatory and anti-obesity effects1. POS are commonly obtained by partial (acid and/or enzymatic) hydrolysis of pectin. However, the growing demand of POS as functional additives for the pharma and food industries requires new sources and greener extraction strategies. In this sense, onion skin wastes (OSW) can offer great potential, since every year more than 450,000 t of OSW are discarded2, whereas subcritical water (SubW) emerges as an interesting and environmentally friendly technique to recover different valuable compounds from natural solid matrices.
In this work the valorization of OSW as a source of POS using SubW was studied in a batch extractor at temperatures up to 165 ºC and extraction times up to 180 min. The extraction of POS was found to be time and temperature sensitive: the best extraction rates were found when the severity factor (log R0) was in the range 2.8-3.1. In this sense, the highest POS recovery (45% extraction yield of galacturonic acid) was achieved at 125 ºC and 150 min, yielding several families of POS based on the molecular weight (MW): the 78 kDa the most abundant, followed by 27, 17 and 7 kDa. The change in the MW with time and temperature was modelled according to a modified version of the Ekenstam equation, which allowed to predict the MW of the POS as a function of the extraction conditions and calculate the POS degradation energy of activation (116±2 kJ/mol). Besides POS molecular weight loss, the presence of free monosaccharides and degradation products (organic acids and furfural) was increased with the extraction conditions intensity. All in all, the hydrothermal extraction at temperatures between 125-145 ºC allowed to obtain POS with MW in the range 7-110 kDa with high degrees of branching, in contrast to the high MW (>300 kDa) and linear pectin obtained following the conventional acid water extraction processes. Other important structural differences in terms of degree of methylation (DM) and acetylation (DA) were also observed.

Keywords: Subcritical Water; Pectic Oligosaccharides, Kinetics, Extraction
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Acknowledgements: Agencia Estatal de Investigación [grant numbers PID2020-116716RJ-I00/ AEI / 10.13039/501100011033, PID2019-104950RB-I00 / AEI / 10.13039/501100011033 and TED2021-129311B-I00]

TUESDAY – SEPTEMBER 12th, 2023

Room Rey Felipe II – Applications

17:00 - 17:15 ORAL PRESENTATION 81705.

Direct recycling of lithium-ion batteries positive electrodes production scraps, an innovative process assisted by supercritical CO_2

N. Hayagan[1,4], F. Rabuel[2], L. Croguennec [1,4], C. Aymonier [1,4], M. Morcrette [2,3], R. Dedryvère [3,4], J. Olchowka [1,4], and G. Philippot [1,4]

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The ecological transition is at the center of our daily life and the issue of energy production and its storage are now the focus of many research projects. With the increasing electrification of our everyday life devices, in particular with the rise of electric vehicles, the question of the batteries' end-of-life, particularly the lithium-ion batteries (LIBs), becomes a real challenge. Indeed, the building elements of this type of batteries, such as copper, aluminum but especially cobalt or nickel are not only expensive, but also present in very localized areas and in limited quantities on earth. It is therefore essential to implement recycling processes for these batteries to reclaim these metals and meet the growing demand of the market. Recycling techniques such as pyro- and hydrometallurgy are already employed to recover elements of economic interest. However, these destructive processes have limitations: i) the purity of the recovered elements is not high enough to reuse them to make new batteries, and also, ii) they require either high-energy inputs or massive use of acids. On the other hand, the direct recycling strategy, which aims to separate the different parts of a battery and recycle them independently, therefore, becomes the most credible alternative to achieve this goal.
In this communication, we will focus on the use of supercritical carbon dioxide (scCO2) process for the direct recycling of LIBs positive electrodes production scraps. Indeed, production scraps can represent from 5 up to 30 wt.% of the electrode production. With the increased LIBs production rate, their recovery becomes a priority.1,2 The objective aims to separate all the electrode components while preserving their properties and integrity. For this, we use a technology based on supercritical CO2. We will first highlight the influence of several optimized parameters including the temperature, time, co-solvent ratio and dosages to successfully delaminate 100% of the active material. Multiple characterization techniques will then be combined to qualify the structure, chemical composition and physical properties of the recycled active material LiNi0.6Mn0.2Co0.2O2 (NMC622) and current collector (Al foil). Lastly, the performance of the recycled NMC622 electrode material in new batteries will be highlighted.

Keywords: Li-ion battery, direct recycling, supercritical CO2, production scraps

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C. Sustainability and Environment

Sustainability

KEYNOTE LECTURE

ORAL PRESENTATION

TUESDAY – SEPTEMBER 12th, 2023

Room Dr. Luis de Mercado - Sustainability

15:15 - 15:45 KEYNOTE LECTURE 80813.

HYDROTHERMAL AQUEOUS CONDENSATE – A NEW PLAYER IN FOOD WASTE VALORISATION FOR SUSTAINABLE USE IN AGRICULTURE

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The global challenge of achieving food-security requires smart recycling of energy, water and agrochemicals. Increased production of food waste in intensified agricultural systems is a major obstacle worldwide. The majority of these residues, rich in organic carbon and valuable nutrients, are currently wasted. Recycling the residue reduces use of resources and production of "exhaust-pipe" greenhouse gases and particulates. The hydrothermal technology, using subcritical water (170–350°C; 1–20 MPa) as the conversion media was intensively studied for a wide range of waste feedstocks including livestock manure, food waste and biosolids[1–4]. Most of the research in this area was motivated by energy recovery and therefore focused on the solid and oil phases. However, less attention has been given to the aqueous condensate – the process water remaining after the hydrothermal reaction. Pyrolysis aqueous condensate (PAC), a by-product of dry pyrolysis, was reported to be highly toxic, hindering its use. This talk will review two implementation opportunities of the hydrothermal aqueous condensate (HAC), focusing on the recovery of valuable agrochemicals. The first pathway is for an integrated weed management. We demonstrate the high potential of using HAC for pre-emergent herbicidal activity[5]. A different seed germination behavior of three tested species suggests a promising selectivity pattern. Heterocyclic aromatic organic compounds such as pyrazine and its derivatives were identified in high-temperature (250–300°C) HAC samples, which exhibited higher herbicidal activity relative to lower temperature reactions. The second utilization approach is by using diluted HAC as a bio-stimulant to improve plant growth and induce plant resistance against pathogens. The addition of low-temperature (175–200°C) HACs to plants indicated an advantage in physicochemical parameters and especially regarding plant antioxidant activity. In addition, plants that were treated with low-temperature HAC showed systemic resistance induction that was tested in three plant-pathogen systems. A greenhouse trial demonstrated the capacity of low-temperature HAC to improve growth and yield parameters of tomatoes. The described novel valorization pathways of HAC expand the circular economy of hydrothermal technology and can help to increase the recovery of energy and resources from organic waste.

Keywords: Hydrothermal extraction, Food waste valorisation, Herbicidal activity, Biostimulants, Circular economy

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8th International Solvothermal and Hydrothermal Association Conference
ISHA 2023
Valladolid, Spain
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TUESDAY – SEPTEMBER 12th, 2023

Room Dr. Luis de Mercado – Sustainability

16:15 - 16:30 ORAL PRESENTATION 81552.

THE MANUFACTURE AND USE OF METAL ORGANIC FRAMEWORKS AS A MEANS TO SEPARATE CO_2 FROM FLUE GAS STREAMS - FROM BENCH TO PILOT TO FULL SCALE

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CO_2 levels are a global concern and Net Zero is a global target (virtually). Europe has moved from 80% reduction targets in greenhouse gas emissions by 2050 to a Net Zero target. The USA has stated its intention to reach 100% carbon pollution-free electricity by 2035 and a net-zero emissions economy by 2050. Metal organic frameworks (MOFs) can act as a means to sequester CO_2 from flue gas, where CO_2 levels can be anything from 1% to 50%.

MOF based sequestration of CO2 requires selectivity (preferential removal of CO2) and a high rate of uptake with an high uptake capacity. These are all critical to the successful cycling of a MOF column using either pressure swing or temperature swing approaches.

The synthesis of MOFs can be achieved in many ways from mechanical, sonochemical to hydrothermal/solvothermal techniques. Many researchers around the world make MOFs in batch and flow, although batch is far more commonly used. At present, scale of production tends to be quite low i.e. grams to 10's or 100's of grams. Through the use of novel mixing reactors, we have been able to take grams per hour to kg's per hour to ton's per hour production rates.

Thermal and hydrothermal stability (does the MOF breakdown in hot, humid atmospheres?), energy penalties based on temperature and/or pressure swing cycling (how does energy penalty compare with amine scrubbers?), and life cycle assessment (does the MOF require energy intensive production pathways?).

This paper will present data on MOF synthesis in flow, and also give an overview of how they can be successfully used to remove CO2 from actual flue gas streams.

Keywords: Continuous Hydrothermal Synthesis, MOFs, CCS

TUESDAY – SEPTEMBER 12th, 2023

Room Dr. Luis de Mercado - Sustainability

16:30 - 16:45 ORAL PRESENTATION 80780

HYDROTHERMAL DECOMPOSITION OF PLASTIC – VALORIZATION OF NON-RECYCLABLE MIXED PLASTIC WASTE

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Plastic waste is a global environmental nuisance and a main source of pollution to water bodies, soil, and atmosphere. Currently, most plastic waste is landfilled or incinerated, but sometimes leaks untreated to the environment. Today, plastic recycling is based mainly on mechanical recycling that is designed to treat clean sorted mono-material streams (i.e., one type of thermoplastic polymer). Co-treatment and re-extrusion of two (or more) different polymers usually result in a nonhomogeneous low-quality recycled product. Multi-material multilayer plastics are ubiquitous in many sectors such as food packaging, agriculture, and laboratory chemical containers. They consist of several layers of different polymers and may also contain non-polymeric materials such as paper or foil. The low recycling potential of these inseparable polymers is due to mechanical recycling limitations and difficulties in identifying, sorting, and separating such products1. Advanced recycling solutions are focused on two alternatives: (1) to deconstruct the layers; or (2) to treat the mixed polymers as a whole2. The latter was tested by using hydrothermal processing)HTP(at subcritical conditions for plastic polymer conversion into other valuable products. Different polymers were shown to decompose by HTP into their original monomers at subcritical water conditions. For example, polyamide-6 (PA6) can be converted into ε-caprolactam3. Polyamide-66 (PA-66) decomposes into PA-66 oligomers, hexanediamine, and adipic acid4. Polyethylene terephthalate (PET) is converted to terephthalic acid and ethylene-glycol5. For polyolefins, such as polyethylene (PE) and polypropylene (PP), which are absent of heteroatomic bonds along the back-bone chain, depolymerization may occur at supercritical temperatures, typically >400°C6. Leveraging the existing knowledge of polymer reactivity and the resulting product characteristics, the current research focused on plastic mixture valorization in sub-critical water (300°C; 10 MPa). Here, we will present the degradation mechanisms of LDPE, PET, and PA polymers and the advantages of HTP for PET+PA mixture and LDPE+PA multilayered laminated film. Comprehensive chemical and physical analyses were made to detect products in all phases (solid, liquid, and gas). PET+PA6 mixture was converted mainly into monomeric compounds, with terephthalic acid crystalized as a solid product (>60% recovery), and ε-caprolactam concentrating in the liquid phase (>90% recovery). Due to the different chemical properties and phase distribution of the main products, a successful co-processing was achieved with high recovery7. Secondary products were also detected in all phases, attributed to both polymers. LDPE+PA mixture was examined using multilayered agricultural mulch film. The treatment resulted in efficient monomer recovery from the PA layer, while the remaining solids were characterized as LDPE, suitable for successive processing routes. These results indicate the potential of HTP to achieve closed-loop feedstock recycling of plastic waste. It can also promote complex waste processing and valorization, preventing landfilling of inseparable mixed or laminated polymers. Additional consequential study of decomposition mechanisms and process optimization is required to improve waste treatment alternatives and move towards a circular plastic economy.

Keywords: Subcritical water, Plastic waste, Monomer recovery, Circular economy

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TUESDAY – SEPTEMBER 12th, 2023

Room Dr. Luis de Mercado – Sustainability

16:45 - 17:00 ORAL PRESENTATION 80856.

Recent advance in hydrothermal syntheses of layered transition metal compounds for energy and environment applications

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Layered transition metal compounds are widely applied in energy storage and conversion, and biological medicine, owing to their special arrangement of atomic layers and polyhedral structural units with transition metal centres. Atomic-scale accurate synthesis of layered compounds with defined compositions and structures are still a highly challenging issue. Herein, we summarized the recent progress that we have achieved in hydrothermal syntheses of layered transition metal compounds at lower temperature, by taking good used of the unique features of thermodynamic conditions for lower-temperature hydrothermal systems. It is found that, when taking Mn/Ni/Co-based layered compounds as the main target materials, the phase structure, electronic structure, interlayer spacing and chemical bonding effect of several novel layered compounds were precisely regulated without apparently changing the structural ability. The transition metal ions in layers could be stabilized under hydrothermal condition to show several valence states that might be distributed in an ordered way for certain electronic directional movement. These layered transition compounds could be potentially used due to their optimized supercapacitors and CO preferential oxidation activities. From the relationships between structure and performance of layered transition metal compounds ever revealed, one discovered merits of layered transition metal compounds as represented by unique microstructural effect, electronic structure changes and catalytic conversion mechanism. Such a synthetic approach is also applicable to other materials like $Cu_xMn_{2-x}O_2$ and $CuCoO_2$-based composite for a broad range of applications.

Keywords: Hydrothermal syntheses, Transition metal oxides, Layered materials, Energy material.

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Acknowledgements: This work is financially supported by the National Natural Science Foundation of China (NSFC) (Grants 21671077, 21871106, 22101097, 22293040 and 22175070).

B. Processes

Material Synthesis

KEYNOTE LECTURE

ORAL PRESENTATIONS

TUESDAY – SEPTEMBER 12th, 2023

Room José Zorilla– Material Synthesis

15:15 - 15:45 KEYNOTE LECTURES 80769.

Silicate-based cool pigments development under subcritical and supercritical hydrothermal conditions

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Nanoparticle assembly of 3D hierarchical architectures has recently become a route for controlling the optical reflectance properties of various inorganic pigments. Cool inorganic pigments involve a group of several inorganic compounds with remarkably high reflection and low solar absorbance near the infrared spectrum (700–2500 nm). Therefore, these compounds attracted research interest in using them as reflecting media of the near-infrared radiation emitted in the light spectrum. The NI radiation corresponds to 52% of the solar radiation, and the phonon interaction with the surfaces exposed produces a localised heat increase caused by the phonon absorption. Therefore, highly reflective inorganic compounds might remarkably reduce heat generation and, consequently, the convective energy transfer inside the solid. Simultaneously, this might decrease the energy consumption of air conditioning systems. Hitherto, white pigments (TiO_2) have a high solar reflectance; however, the high commercial demand for these pigments does not satisfy the consumer's needs. Recently, a new strategy aiming at non-white cool pigment processing has been under study worldwide. It combines chromophore elements and complex metal oxide to synthesise a broader type of non-white inorganic pigments. Another factor under study is controlling the particle size and morphology for tuning the reflectance capability of various crystalline structural inorganic pigments.
We have focused on investigating the processing of various ancient silicate-based inorganic pigments via an intensified soft chemistry route. The research methodology involves the study of fundamental chemical features, such as single-step reaction equilibria, reaction kinetics, solvent pH, and alkalinity degree, parameters that are controlled under hydrothermal conditions for tunning the crystallisation of primary crystals and their subsequent 3D hierarchical self-assembly process. Three cases of study related to the production of cool pigments in the systems of BaO-CuO-SiO_2-H_2O and CaO-Cr_2O_3-SiO_2-$NaOH$-H_2O will be discussed in detail. The primary crystals 3D self-assembly process remarkably increased the optical properties, namely the pigment's colour and NIR reflectance. The hydrothermally synthesised nano-sized agglomerates exhibited high reflectance on the NIR (90 – 98%) compared to the TiO_2.

Keywords: *Hydrothermal processing, 3D Nanoparticle Hierarchical Growth, Cool Inorganic Pigments*

Acknowledgement: *JCRA is indebted and grateful for the support of the SNI. This study was supported by the federal research budget of the Centre for Research and Advanced Studies of the NPI (C-3000).*

TUESDAY – SEPTEMBER 12th, 2023

Room José Zorilla– Material Synthesis

16:15 - 16:30 ORAL PRESENTATION 79919.

ADDITIVE-ASSISTED HYDRO- AND SOLVOTHERMAL SYNTHESIS OF CRYSTALLINE AROMATIC ORGANIC HIGH-PERFORMANCE POLYMERS

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Organic high-performance polymers (HPPs) are defined through their excellent thermal stabilities, namely long-term durability (more than 10,000 h) at 177 °C and thermal decomposition temperatures above 450 °C.1 High thermal stability arises as a direct consequence of HPPs molecular built up: They contain a high amount of aromatic moieties in the polymer chain. The biggest and most diverse class of HPPs are so-called polyheterocyclics, consisting exclusively of aromatic and heterocyclic functions, where the heterocyclic functions are conventionally formed by cyclocondensation reactions.1 Prominent examples are polyimides (PIs) and polybenzimidazoles (PBIs). Classically, polyheterocyclics are synthesized by two-step procedures in harmful solvents and under harsh conditions. For instance, PIs are conventionally synthesized in toxic organic solvents such as *N*-methyl pyrrolidone (NMP) or dimethylformamide (DMF) with toxic catalysts (typically isoquinoline) to first generate a poly(amic acid), which can then be cyclized to the desired PIs at temperatures >400 ˚C, mainly yielding amorphous PIs. Yet, crystallinity is a desired feature as it enhances, e.g., thermal stability or directional properties such as electrical conductivity.
Recently we developed hydrothermal polymerization (HTP) as means to generate highly crystalline aromatic PIs2 and PBIs3 without the need for toxic solvents or catalysts. Furthermore, we were able to synthesize crystalline PIs not only in H2O as reaction medium, but also in H2O/alcohol mixtures, i.e., by solvothermal polymerization (STP).4
Here, we present our results of additionally employing soluble additives in the HTP and STP of HPPs. We comprehensively studied changes in reaction time, temperature, solvent, and the addition of various additives. Our results show that HPPs can be obtained at unhampered crystallinity in the presence of additives. Moreover, the presence of additives has strong morphological consequences. Through carefully adjusting the reaction parameters, these morphologies can be controlled.

Keywords: high-performance polymers, hydrothermal polymerization, solvothermal polymerization, crystalline polymers, morphology control
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Acknowledgements: The authors acknowledge the Austrian Science Fund (FWF) for the financial support under grant No. START Y1037-N38.

TUESDAY – SEPTEMBER 12th, 2023

Room José Zorilla- Material Synthesis

16:30 - 16:45 ORAL PRESENTATION 79944.

Hydrothermal Injection: Synthetic Control by Reaction Engineering

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As a simple, versatile, and green synthetic method hydrothermal (and solvothermal) techniques have seen a surge in interest in recent years, being applied to a wide variety of functional materials.[1] Conventional hydrothermal synthesis is typically performed by loading appropriate into a sealed vessel and subjecting the reaction mixture to prolonged heating. This approach generally offers great chemical flexibility and control, however the "heating-up" period which it involves has significant implications for other product properties such as phase and shape, particularly when dealing with polymorphic systems. Perhaps the most well-established synthetic method for achieving phase- and shape-control is that of hot-injection.[2] This relies on the use of high boiling point, petrochemically derived organic solvents and the temporal separation of nucleation and growth by initiating reactions by injection of reagent(s) only at precise temperatures.
Here we report on the development of a hydrothermal injection reactor which offers more precise control over reaction conditions within the hydrothermal space, by allowing the initiation of reactions at specific temperatures, akin to the hot-injection method. This hydrothermal injection technique has been applied to the synthesis of polymorphic cadmium sulfide and calcium carbonate, and is shown to offer a high degree of control over product phase, size, and shape, as revealed by powder X-ray diffraction and electron microscopy.

Keywords: Hydrothermal, Reactor Design, Polymorphism

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TUESDAY – SEPTEMBER 12th, 2023

Room José Zorilla– Material Synthesis

16:45 - 17:00 ORAL PRESENTATION 81521.

Hydrothermal Injection for Phase-Controlled $CaCO_3$ Synthesis

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Polymorph control has become essential in order to target the desired properties for a given applicability. For instance, **calcium carbonate (CaCO3)** is well known to be an essential component in nature and can be obtained in three different anhydrous phases: calcite, vaterite and aragonite. Natural biomineralization processes show great polymorph control,1 allowing different CaCO3 phases to serve various purposes in biological organisms.1–3 Increasingly researchers are trying to replicate this same degree of control to develop advanced functional materials by replicating the formation conditions present in nature.
Here we have applied a newly developed hydrothermal injection reactor to the synthesis of CaCO3. This system replicates the hot injection process using only water as a solvent. It allows a similar level of control over nucleation and growth, being considered as analogous to natural mineralisation processes occurring at hydrothermal vents.4 By varying reaction conditions, such as precursor choice, reagent ratios and injection temperature we have shown that this system can achieve a high degree of polymorph selectivity. The phase composition of the samples prepared have been confirmed by Rietveld analysis of the powder X-ray diffraction patterns, and typical morphologies are observed by electron microscopy (SEM). In order to fully represent the relationship of synthetic conditions to the phase of the obtained products we have applied principal component analysis (PCA) to the pair distribution function (PDF) of the powder X-ray diffraction patterns (PXRD). Therefore, a mapping of the optimal conditions needed to obtain each phase and the intrinsic connection of synthesis conditions *versus* polymorph selection was obtained.

Keywords: Hydrothermal, Hot-Injection, Calcium Carbonate, PDF, XRD

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TUESDAY – SEPTEMBER 12th, 2023

Room José Zorilla- Material Synthesis

17:00 - 17:15 ORAL PRESENTATION 81632.

CAN MACHINE LEARNING HELP TO DEVELOP NOVEL METAL OXIDE NANOCOMPOSITES IN A CONTINUOUS HYDROTHERMAL PROCESS?

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Developing interpretable machine-learning approaches for the digital manufacturing of metal oxide nanocomposites is crucial for novel and multifunctional composite synthesis. Metal oxides, metal oxide nanoparticles and metal oxide nanocomposites have a wide range of applications and it is significantly important to screen and select suitable types of metal oxides for specific type of processes. The research work aims to harness machine learning to correlate and validate an online analytical method with a traditional offline analytical method for metal oxide synthesis through a continuous hydrothermal conversion technology. Objectives of the research work include leveraging machine learning in order to optimise the production process parameters, enhance product quality, improve our understanding of nanocomposite material generation, and to improve overall efficiency in these domains. Fourier-transform infrared spectroscopy (FTIR), the online method employed for this research, presents the disadvantages of absorbance peak convolution and modest variation in results between samples; but it does offer the benefit of virtually instantaneous results. Conversely, X-ray diffraction (XRD) analysis is traditionally conducted offline and requires manual sample preparation which can be time-consuming; however, offline XRD analysis offers more precise and meaningful data than FTIR. The project will involve synthesising many products at known conditions and analysing using both methods. By comparing and validating the results it is hoped that the online method (FTIR) can be relied on as the sole analytical technique; given that the FTIR results are produced almost instantaneously, this would create an ideal scenario for rapid screening of process parameters for product optimisaion. Various machine learning models will be investigated for correlating the XRD and FTIR results. Supervised learning models trained with labelled data offer valuable insights into relationships between the analytical methods. The integration of deep learning architectures enables the extraction of complex patterns and nonlinear relationships, enhancing the accuracy of predictions and process optimisation. Unsupervised learning techniques, such as clustering and dimensionality reduction, aid in identifying hidden patterns and similarities between data. Both these methods help uncover intrinsic structures within the datasets. Finally, the incorporation of fuzzy logic gives the machine learning model the ability to handle uncertainties and imprecise information. Fuzzy logic allows for flexible reasoning, enabling the modelling of complex relationships and the development of adaptive control strategies.

Keywords: Machine Learning, *Metal oxide nanocomposites, Continuous hydrothermal synthesis, Artificial Intelligence, AI.*

***Acknowledgement*:** This research was funded by EPSRC [EP/S036113/1], Connected Everything II.

A. Applications & Products

Polymers, Composites and Hybrids

KEYNOTE LECTURE

ORAL PRESENTATIONS

TUESDAY – SEPTEMBER 12th, 2023

Room Claudio Moyano – Polymers, Composites and Hybrids

15:15 - 15:45 KEYNOTE LECTURE 81548.

ENVIRONMENTALLY FRIENDLY, HIGH STABILITY METAL-ORGANIC FRAMEWORK SYNTHESIS IN SECONDS

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Metal-organic frameworks (MOFs) are promising porous materials for several applications such as catalysis, sensors, supercapacitors, adsorption of organic molecules, and capturing various harmful gases such as H_2S and CO_2. Compared to conventional porous materials, MOFs possess tunable structures and chemical functionalities, making them advantageous in gas adsorption applications by influencing the selectivity of adsorption for specific gases, including H_2S and CO_2. By adjusting the pore dimensions, MOFs can be optimized to selectively capture and remove target molecules while excluding others [1].

This study focuses on the synthesis of Mg-CUK-1, a water-based, environmentally friendly MOF, which possesses high adsorption capacity and selectivity for H_2S and CO_2, with high recyclability. Moreover, it exhibits excellent thermal stability up to 500°C and structural stability even at up to 95% relative humidity[2]. The synthesis of Mg-CUK-1 using both microwave and conventional methods was explored to facilitate its future synthesis in continuous flow; a route which provides efficient mixing and heat transmission, straight-forward scale-up, and minimizes energy input. The microwave method successfully led to the synthesis of 30 mg of Mg-CUK-1 in just 6.8 seconds, which is the fastest reported procedure for the synthesis of Mg-CUK-1 on this scale to date.

When testing the microwave synthesized Mg-CUK-1, it was found that it has remarkable stability and a high adsorption capacity for pure CO_2, reaching 9.4% at 25 °C and 1 bar. The synthesis optimization of Mg-CUK-1 involved studying the effects of temperature, time, and molar ratio on the morphology and structure of the MOF. Increasing the molar ratio led to irregular and large particle sizes, while high temperature resulted in the formation of a new phase. Reducing the residence time improved the regularity and definition of the particles. These parameters play a critical role in achieving the desired characteristics and performance of Mg-CUK-1.

Keywords: Metal Organic Framework, Hydrothermal, Mg-CUK-1, Microwave, gas capture

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Acknowledgements: We sincerely acknowledge the Iraqi Ministry of Oil, Maisan Oil Company, and CNOOC for their generous financial support in this research. Additionally, we would like to express our gratitude to NMRC for their valuable technical assistance.

TUESDAY – SEPTEMBER 12th, 2023

Room Claudio Moyano – Polymers, Composites and Hybrids

16:15 - 16:30 ORAL PRESENTATION 79912.

COVALENTLY LINKED PIGMENT@METAL OXIDE HYBRID MATERIALS BY ONE-POT SOLVOTHERMAL SYNTHESIS

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Hybrid materials (HMs) consist of both organic and inorganic components, which are connected to each other by chemical bonds. HMs are very promising types of materials, as they often combine the high variety of functionalities of organic materials with properties typical for inorganic materials, such as high mechanical strength or high thermal and chemical stability. Ideally, synergistic properties arise, i.e., properties that go beyond the sum of properties of the individual constituents. Generally, HMs can be subdivided according to the strength of interaction between organic and inorganic constituents into class I and class II HMs.1 The former feature weak interactions such as H-bonding or van der Waals interactions, while the latter exhibit strong covalent interactions.1 In this contribution, we focus on class II HMs, with colorant molecules as the organic component and metal oxides (MxOy) as the inorganic component. Colorant@MxOy HMs are of interest for optoelectronic applications. Yet, their synthesis is intrinsically challenging, as the apolar organic colorant component and the inorganic polar MxOy component require different conditions for their respective formation.2 This issue can be addressed by employing solvothermal synthesis, which brings along finegrained temperature-tunability of the solvent properties and hence allows for finding the best possible compromise of the reaction medium for both components. Recently, we reported the one-pot hydrothermal synthesis of dye@SiO2 HMs. These materials were indeed class II HMs with nanoscopic dispersion of both components.3 Furthermore, these HMs showed synergistic properties.3 We have now set out to go beyond SiO2 as inorganic component, specifically towards MxOy that feature more interesting optoelectronic characteristics. With this contribution we show that pigment@MxOy class II HMs can be obtained solvothermally in one-pot. We discuss the choice of reaction parameters as a function of the employed precursors and for a range of different pigments. The produced HMs have been extensively characterized chemically and structurally. As we will show, the obtained class II HMs exhibit interesting structures and are, in contrast to our previous work, crystalline.

Keywords: Hybrid materials, Solvothermal Synthesis, Metal Oxides, Pigments
[1] P. Judeinstein, C. Sanchez, *J. Mater. Chem.*, 1996, **6**, 511-525
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Acknowledgements: We acknowledge the Austrian Science Fund (FWF) for financial support under grant No. START Y1037-N28 and thank Annette Foelske and Markus Sauer (TU Wien, Vienna, Austria) for XPS measurements and Alexandre Ponrouch (ICMA-CSIC, Barcelona, Spain) for electrochemical characterizations.

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TUESDAY – SEPTEMBER 12th, 2023

Room Claudio Moyano – Polymers, Composites and Hybrids

16:30 - 16:45 ORAL PRESENTATION 81731.

IN-DEPTH STUDY OF ORGANIC SALT INTERMEDIATES OF THE HYDROTHERMAL SYNTHESIS OF IMIDES

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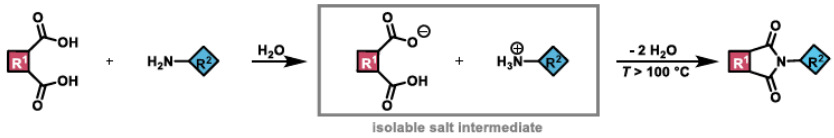
Cyclic imides, i.e., cyclic diacyl amides, can be generated by hydrothermal synthesis (HTS) from α, ω-dicarboxylic acids or 1,2-dicarboxylic acids and amines (**Scheme 1**).1 Isolable ammonium carboxylate salt intermediates (**Scheme 1**, centre) form in water at low *T*, i.e., at conditions that necessarily arise during heating up a non-stirred autoclave, for instance. Salt formation arises due to the difference in the p*K*A values of amine and carboxylic acid, which is sufficiently large for proton transfer.2 These salt intermediates play an important role for the subsequent HTS of imides. For instance, they can act as solid heterogenous nuclei for the growth of the imide products, and their solubilities in high-temperature water influence the subsequent HTS.



Scheme 1: Hydrothermal synthesis of imides via isolable salt intermediate.

With this contribution, we present an in-depth study of the formation, i.e., crystallization and growth, of these ammonium carboxylate salt intermediates. This endeavour is intrinsically challenging, as the here studied ammonium carboxylate salts are highly insoluble in protic polar solvents and hence form very rapidly at high supersaturation.
Therefore, we designed controlled precipitation set-ups employing one or more custom-designed and -built programmable syringe pumps. In these setups, we precipitate salts under a variety of different reaction conditions (concentrations, temperatures, solvents, additives, etc.) for studying the conditions' impact on the morphology of the salt crystallites. We here present the results of this study, which shows marked effects on morphology and potentially type of resulting crystalline state.

Keywords: Imides, Hydrothermal synthesis, Salt intermediates, Morphology control

[1] B. Baumgartner, M. Puchberger and M. M. Unterlass, *Polym. Chem.*, 2015, **6**, 5773-5781.
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Acknowledgements: We acknowledge the Austrian Science Fund (FWF) for financial support under grant No. START Y1037-N28 and thank D. A. Cerrón-Infantes for fruitful discussions.

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TUESDAY – SEPTEMBER 12th, 2023

Room Claudio Moyano – Polymers, Composites and Hybrids

16:45 - 17:00 ORAL PRESENTATION 79915.

SYNTHESIS OF QUINOXALINE–BASED DIAMINES AND THEIR HYDROTHERMAL POLYMERIZATION TO POLYIMIDES

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Polyimides (PIs) are essential in today's electronic industry, where they are used as films for insulating conducting parts in flexible circuits.1 The great interest in PIs is ascribed to their properties, e.g., outstanding chemical and thermal stability at low densities.2 These features hinder their processability by conventional routes – especially for fully aromatic PIs – as their rigid backbone often leads to the absence of melting and insolubility in virtually any solvent.3 Furthermore, the number of commercially available monomers for PIs, i.e., dianhydrides and diamines, is limited, which in turn limits the molecular diversity of accessible PIs and consequently the breadth of materials features. Consequently, the synthesis of custom-designed monomers is of great interest for generating novel PIs with altered materials properties.
Quinoxaline-based diamines present interesting monomer candidates, which we synthesized in the here presented project. First, they can be easily generated with a low number of reaction steps. Second, their electronic structure allows for intermolecular interactions, e.g., π-π-stacking. Employed as monomers, one can expect that the resulting polymer chains will also express these intermolecular interactions. Third, their bicyclic and rigid structure is expected to stabilize the polymer chains and their polarizable C-N-bonds are expected to endow quinoxaline-based PIs with solubility in polar solvents. In this contribution, we present the synthesis of two different quinoxaline-based diamine (QDA) monomers. Each of the two QDAs was generated in a four-step reaction. Subsequently, the custom-made QDAs were reacted with different commercially available aromatic dianhydrides under hydrothermal conditions, targeting quinoxaline-based polyimides (QPIs). The resulting QPIs were characterized with respect to their chemical nature, order, appearance, solubility, and thermal properties. The QPIs were obtained as amorphous materials and feature intriguing thermal stability and solubility, potentially enabling processing from solution.

Keywords: Polycondensation, Hydrothermal polymerization, Heteroaromatics
[1] A. Sezer Hicyilmaz, A. Celik Bedeloglu, *SN Appl. Sci.*, 2021, **3**, 1–22.
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Acknowledgements: This project was supported by the Austrian Science Fund's (FWF) START programme under grant no. Y-1037-N28 and the Vienna Science and Technology Fund (WWTF) under grant number LS17-051.

WEDNESDAY

11:30-13:00

B. Processes

Process Design

KEYNOTE LECTURE

ORAL PRESENTATIONS

WEDNESDAY – SEPTEMBER 13th, 2023

Room Rey Felipe II – Process Design

11:30 - 12:00 KEYNOTE LECTURE 79859

Why Our Subjects Have Shifted from Hydrothermal Processes to Soft, Solution Processes?

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Since I joined to Hydrothermal Laboratory in Tokyo Institute of Technology in 1978, I have devoted in Hydrothermal/Solvothermal studies and researches. [1] During those days, I have re-considered "What/How and Why Hydrothermal routes are important for materials in natural and human societies", then reached a conclusion that one must follow water cycle on the Earth to sustain human lives and Earth itself (Mother Nature). Our Human has seeked our development for comfortable and convenient lives, thus developed science and technology for those purposes. It has succeeded partially (places, times, occasion …etc) but not totally nor completely, thus the total sustainability has been destroying. This has been caused too much energies and resources have been used in modern Industries and Manufacturing including agriculture, fishery, forestery as of biological productions. Particularly, high technologies for advanced materials require (1) Sophisticated equipments, (2) Highly energetic processes and (3) Sophisticated resources, then exhaust huge amounts of heat (Entropy) and wastes. To prevent such exhausts heats and wastes, one must develop another direction of researches; that is, Soft Processing (Low-energetic production) for advanced materials using solution(s). [2,3] It is not easy because it requires (a) designed precursors, (b) designed reaction, (c) designed equips and (d) designed processings. We have succeeded (i) nano-structured particles and composites, (ii) functional films and coating, (iii) direct patterning of them, (iv) Integration of their 2D and 3D materials, then (v) continuous production of them by those Soft Solutions Processing. [4,5] We do hope ISHA peoples can develop further researches in those SSP.

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[3] Yoshimura, M., J. Mater. Sci.,41 [5], 1299-1306 (2006), 43[7], 2085-2103(2008).
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Room Rey Felipe II – Process Design

12:00 - 12:15 ORAL PRESENTATION 79986

HEAT TRANSFER IN SUPERCRITICAL WATER REACTOR

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Water in its supercritical state exhibits unique characteristics rendering it valuable for a variety of technological applications, such as the wastewater treatment, the thermochemical conversion of biomass for biofuels production, and the supercritical hydrothermal synthesis of nanoparticles.[1] For the successful implementation at large scale of the supercritical water (scH_2O) technologies, it is essential to optimize the working parameters of the scH_2O reactors in order to obtain the desired products and for energy savings. To set the optimal conditions, the issues related to the supercritical heat transfer should be addressed together with the fact that, at temperatures and pressures near the critical point, the water physical properties undergo significant changes, which correspond to the transition from the liquid-like (LL) to the gas-like (GL) regimes associated to the pseudo-boiling phenomenon[2]. In the present work, based on a large number of experimental data, we analyze the effect of pseudo-boiling on the supercritical heat transfer in the continuous flow scH_2O reactor of the NISA (*Neutron Imaging Supercritical-water Analysis*) equipment[3], used in our lab for the preparation of carbon supported metal oxides by scH_2O impregnation method.

All the experiments were conducted in transient regime, using ultrapure water flowing upwards through the reactor, at constant flow rate and heat flux, and isobaric conditions at 225, 250 and 270 bar. The heat transfer to the scH_2O was analyzed based on the correlation between the water temperature measured inside the reactor (T_R) during the pseudo-boiling transition with the temperature recorded at the reactor wall (T_{Wall}) and the temperature of the aluminum block heater (T_{Al}) used as the heating source. The plateau appearing in the T_R profile recorded over time, it indicates the point of the pseudo-boiling transition and reveals the existence of the two-phase like regime of scH_2O while the water changes its state from the LL to the GL regime. The deviation from the linearity of the T_{Wall} and the T_{Al} variation in time, which is observed at all working pressures, it suggests that the heat transfer to the scH_2O is enhanced while the system approaches the transitional region. Increasing the pressure, the persistence in time of the two-phase like regime is shorter, indicating higher rate of the pseudo-boiling transition as the pressure increases. The results presented and discussed here helps for a fundamental understanding of the correlation between the supercritical heat transfer and the pseudo-boiling phenomenon in water.

Keywords: Supercritical water, Supercritical heat transfer, Pseudo-boiling.
References:
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[2] F. Maxim, et al., Adv. Sci., 2021, 8, 2002312;
[3] F. Maxim, et al., Nat. Commun., 2019, 10, 4114.

Acknowledgements: This research is funded by Romanian CNCS/CCCDI—UEFISCDI, grant number PN-III-P4-ID-PCE-2020-1241. The work with NISA at the Romanian institution is possible due to the Research Collaboration Agreement with Paul Scherrer Institute, Switzerland, group of Prof. C. Ludwig.

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Room Rey Felipe II – Process Design

12:15 - 12:30 ORAL PRESENTATION 79923

EXPLORING THE HYDROTHERMAL LANDSCAPE THROUGH AUTOMATION IN FLOW: CHALLENGES AND OPPORTUNITIES

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Hydrothermal syntheses (HTS) are typically carried out by heating reactants in a closed container such as an autoclave or high-pressure vial in an oven or microwave continuously for hours or even days. While effective overall, throughput and scalability are limited when working in such a batchwise workflow. Low throughput and labour-intensive reaction outcome analysis can also stifle exploratory experimentation and reaction optimization, as time and cost become limiting factors. Continuous flow HTS is a promising answer to many of the limitations of batchwise synthesis. By increasing both heat and mass transfer, reaction duration can be significantly reduced while simultaneously improving reproducibility and scalability. This enables more rapid iteration and increases the potential for exploratory syntheses. Thus, to drive discovery of novel hydrothermal reactivity, validate and optimize candidate reactions, and to maintain the possibility to scale up production, we are developing an automated platform for HTS in flow. The heart of the discovery platform is a bespoke nozzle reactor, optimized for rapid and thorough mixing of heated and ambient flow paths. Process parameters such as flow rate, temperature, and pressure can be monitored and set programmatically. The reactor is fed by an in-house developed automated sampling system capable of combinatorial injection, mixing, and in-flow dilution of more than 100 reactants without interrupting flow to the reactor. Reactions are planned by the user or algorithmically for exploration or optimization. Outcome analysis can be carried out in-, off-, and online with various instrumentation. As we actively develop and expand the discovery platform, we hope to use it to explore novel chemistry, particularly in the underexplored organic hydrothermal domain.

Keywords: Hydrothermal synthesis, Flow, Automation, Discovery, High-throughput synthesis

References: [1] E. Lester, P. Blood, J. Denyer, D. Giddings, B. Azzopardi and M. Poliakoff, J. Supercrit. Fluids, 2006, 37, 209–214.

Acknowledgements: We acknowledge the Austrian Science Fund (FWF) for financial support under grant No. START Y1037- N28

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Room Rey Felipe II – Process Design

12:30 - 12:45 ORAL PRESENTATION 79843

A PERSPECTIVE ON IMPROVING ENERGY EFFICIENCY IN ELECTROCHEMICAL CO_2 REDUCTION: THE POTENTIAL OF HYDROTHERMAL SYSTEMS

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Carbon dioxide (CO_2) emissions have become a global concern of alarming proportions. To achieve a society with zero CO_2 emissions, we need society reform to move away from dependence on fossil resources. In this context, energy resources are transitioning from fossil fuels to renewable sources, such as solar cells and wind power, which generate electrical power directly. As a result, replacing thermochemistry with electrochemistry has become a recent hot topic in chemistry and chemical engineering. The development and utilization of waste chemical products, including plastics, biomass, and CO_2, are crucial for establishing a sustainable, circular society. These materials require a endothermic reduction process for their use, and electrochemical reduction is a promising approach. However, several challenges need to be addressed for the widespread implementation of this technology. These include low selectivity, slow reactions, high overpotential, sluggish reaction kinetics, and mass transport limitations, all of which lead to high energy consumption. In this work, we investigate the potential of a hydrothermal electrochemical reduction system to overcome the issue of low energy efficiency in CO_2 reduction. A high-temperature environment increases the ionic product of water and the diffusion coefficient in water, resulting in a more efficient electrochemical reaction. Moreover, CO_2 pressurization can compensate for the decrease in CO_2 solubility in water under high-temperature conditions. We demonstrated hydrothermal electrochemical CO_2 reduction and found that increasing the temperature enhances the current density and reduces the overpotential, resulting in improved energy efficiency with high CO selectivity. Furthermore, we conducted a technical assessment to evaluate the energy demand for heating and pressurization required to create hydrothermal conditions (10 MPa, 250 °C). Assuming the production of CO and H_2 through co-electrolysis of CO_2 with water and subsequent methanol synthesis, the energy required to prepare hydrothermal conditions is comparable to that required to compress and heat CO and H_2 in conventional methanol synthesis from syngas. Moreover, if the necessary heat is supplied by unused low-temperature waste heat from an industrial plant, energy consumption could be reduced, leading to further improvements in energy efficiency.

Keywords: CO_2, Hydrothermal electrochemical reduction, Technology assessment
Acknowledgements: This work was supported by JST FOREST Program, Grant Number JPMJFR206W

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Room Rey Felipe II – Process Design

12:45 - 13:00 ORAL PRESENTATION 82815

SUBCRITICAL WATER PRETREATMENT OF BREWER'S SPENT GRAINS FOR VALUEADDED PRODUCTS AND BIOENERGY RECOVERY IN A BIOREFINERY CONCEPT

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The aim objective of this work was to evaluate the application of subcritical water pretreatment of brewer's spent grains (BSG) as a sustainable technological process to produce biobased products and bioenergy in a biorefinery concept. The pretreatment of BSG was studied in a semi-continuous subcritical water hydrolysis process operated with a single and two sequential flow-through reactors to obtain a hydrolysate containing sugars, xylo-oligosaccharides, and amino acids. The subcritical water hydrolysis was carried out at 15 MPa, 5 mL water min^{-1}, and at different temperatures (80–180 °C). Experiments integrating subcritical water hydrolysis and anaerobic digestion were conducted to produce bioenergy (biomethane, electricity, and heat) and agricultural fertilizer. The results demonstrated that subcritical water hydrolysis attacked the BSG structure, releasing monosaccharides (47 mg g^{-1} carbohydrates), amino acids (42 mg g^{-1} proteins), and xylo-oligosaccharides (204 mg g^{-1} hemicellulose). The economic analysis of sugar production revealed that the separation of monosaccharides obtained by SWH is an advantage for the profitability of the industrial-plant process. In the case of xylo-oligosaccharides, the gross profit of the process with two sequential reactors was 30% higher when compared to the single subcritical reactor. In addition, the pretreatment was demonstrated to be profitable for recovering xylo-oligosaccharides. The hydrolysate obtained by subcritical water hydrolysis was applied in anaerobic digestion to elucidate the production of methane-rich biogas and bioenergy. The results demonstrated that the integration of subcritical water hydrolysis and anaerobic digestion increased the methane yield (747 L CH_4 kg^{-1} TVS) when compared to the anaerobic process without pretreatment (53 L CH_4 kg^{-1} TVS). For the process with pretreatment, the generation of electricity (134 kWh ton^{-1}) and heat (604 MJ ton^{-1}) were responsible for the mitigation of 44 kg $CO_{2\text{-eq}}$ ton^{-1}. Finally, the application of subcritical water hydrolysis of BSG is a sustainable pretreatment to produce value-added products and bioenergy, supporting the circular economy transition by reducing the carbon footprint of the beer industry.

Keywords: Lignocellulose, Biomass, Biogas, Sugars, Xylo-oligosaccharides.

Acknowledgements: This work was supported by the Brazilian Science and Research Foundation (CNPq, Brazil) (productivity grant 302451/2021-8) and São Paulo Research Foundation (FAPESP, Brazil) (grant numbers 2019/14938-4 for WGS and 2018/14582-5 for TFC).

C. Sustainability and Environment

Sustainability

KEYNOTE LECTURE

ORAL PRESENTATIONS

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WEDNESDAY – SEPTEMBER 13th, 2023

Room Dr. Luis de Mercado – Sustainability

11:30 - 12:00 KEYNOTE LECTURE 81631.

CONTINOUS HYDROTHERMAL SYNTHESIS OF METAL OXIDE NANOPARTICLES/NANOCOMPOSITES

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The synthesis of metal oxide nanoparticles and nanocomposites has gained significant attention due to their diverse applications in various fields, including catalysis, energy storage, environmental remediation, and biomedical engineering. Among the different synthesis methods available, continuous hydrothermal synthesis has emerged as a promising technique for producing metal oxide nanoparticles and nanocomposites with enhanced properties. Continuous hydrothermal synthesis offers several advantages over traditional batch syntheses methods, such as improved control over particle size, shape, and composition, as well as scalability and process efficiency. This synthesis approach involves the continuous flow of reactants (metal salts) through a hydrothermal reactor under controlled temperature and pressure conditions, leading to the nucleation and growth of metal oxide nanoparticles or the formation of nanocomposites in a continuous manner.

This research explores the continuous hydrothermal synthesis method as a means of preparing a wide range of metal oxide nanoparticles (specifically encompassing individual formulations of Fe, Cu, Co, and Mn-based metal oxides). Additionally, this research explores the synthesis of nanocomposites consisting of bimetallic or trimetallic combinations of Fe, Cu, Mn, and Co-based metal oxides under sub-, near, and supercritical conditions (300-400 °C). The primary objective of this investigation is to understand the synthesis of metal oxide nanocomposite and assess the suitability of these synthesised materials for the application of thermochemical energy storage. The physicochemical properties of synthesised metal oxide nanoparticles and nanocomposites are then characterised using online SEM, FTIR, and XRD. TGA testing at temperature ranges of 100-900°C enables redox and thermochemical energy storage capacities to be easily tested in cycling operations. The results demonstrate that continuous hydrothermal synthesis serves as a versatile and efficient method for the synthesis of metal oxide nanoparticles and nanocomposites. The synthesised materials exhibit promising properties for various applications, particularly in the realm of thermochemical energy storage and chemical looping combustion. These findings contribute to advancing the understanding and utilisation of continuous hydrothermal synthesis as a valuable approach for the tailored synthesis of metal oxide nanoparticles and nanocomposites.

Keywords: *Metal oxide nanocomposites, Continuous hydrothermal synthesis, Chemical looping, CO_2 Capture.*
***Acknowledgement*:** This research was funded by EPSRC [EP/S036113/1], Connected Everything II.

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Room Dr. Luis de Mercado – Sustainability

12:00 - 12:15 ORAL PRESENTATION 79998

HIGH-TEMPERATURE WATER AS VERSATILE REACTION MEDIUM TOWARDS LOPHINE ANALOGUES

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Liquid water is a non-toxic and abundant medium for chemical reactions. Moreover, water is extremely versatile as medium, since its physicochemical properties change as a function of the temperature. Compared with room temperature water, high-temperature water (HTW) features a lower average number of hydrogen bonds, a lower static dielectric constant, lower density, lower viscosity, and a higher ionic product. Consequently, HTW is a wellestablished reaction medium to perform a variety of transformations, including the synthesis and crystallization of inorganic minerals, waste degradation, and biomass valorization. The range of transformations achievable in HTW also includes organic synthesis. Nevertheless, the majority of studies deal with the aquathermolysis of small molecules at analytical scale, whereas synthetic means at preparative scale are by far less exploited. Across the different regimes of HTW, water between 150 °C and 250 °C exhibits an interplay between polarity and acido-basic properties that is ideal for performing many organic syntheses. In particular, the syntheses of heteroaromatics are top candidates to profit from this interplay. Heteroaromatics synthesized in HTW to date include pyrazolones, perylene bisimides,[1] benzimidazoles,[2] and quinoxalines.[3] The Debus-Radziszewski synthesis of lophines, i.e., 2,4,5-triphenylimidazoles, in HTW has also been reported at 210 °C in presence of ammonium acetate.[4] The reported conditions are limited to very high concentrations, which in fact rather correspond to liquid starting compounds in which a small amount of H_2O is dissolved than vice versa. Here, we present an in-depth study of the reaction parameter space to synthesize lophines in HTW. We found reaction conditions capable of overcoming the use of highly concentrated aqueous solutions. The herein presented synthesis features high yields of products and a broad scope of starting materials with a high diversity of functional groups. We present particular examples where our conditions outperform classical approaches, i.e., standard reported syntheses using volatile organic solvents and acid catalysts. Overall, we showcase the potential of HTW to synthesize conjugated heteroaromatic compounds in a green and efficient fashion.

Keywords: High-temperature water, Heteroaromatics, Lophines, Imidazoles.
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Acknowledgements: We thank the Vienna Science and Technology Fund (WWTF) under grant number LS17-051 and the Austrian Science Fund (FWF) under grant No. START Y1037-N28

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WEDNESDAY – SEPTEMBER 13th, 2023

Room Dr. Luis de Mercado – Sustainability

12:15 - 12:30 ORAL PRESENTATION 80424

FABRICATION OF POROUS MATERIALS USING FLUORESCENT WASTE LAMPS BY HYDROTHERMAL HOT PRESSING (HHP)

Zully Matamoros-Veloza[1], Yolanda Del Rosario Gutiérrez-Velázquez[1], Juan Carlos Rendon-Ángeles[2], Kazumichi Yanagisawa[3], Epsylon E. Mejia-Martinez[1]

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Hydrothermal hot-pressing (HHP) is a low-temperature sintering method that uses for the recycling of waste glass by the reaction of glass dissolution-precipitation that occurs under hydrothermal conditions [1]. Initially, the experiments of the preparation of hydrothermal compacts were carried out using starting raw fluorescence glass powder with particles size <38 mm at different temperatures (150 and 200 °C) and adding different wt. % (5, 10, and 15 wt. %) of water as a solvent. The reactivity of the glass particles during hydrothermal compaction was studied by means of SEM micrographs, it was observing the formation of a “new glass phase”, which incorporates a certain amount of water in its structure, the apparent density of the new glass was measured by helium psychometry. Also, the hydrothermal hot press-treated glass compacts were characterized by X-ray diffraction (XRD) and Fourier transform IR spectroscopy (FTIR). It was found that during compaction, the reactivity of the particles increases with increasing temperature. Subsequently, the hydrothermally prepared compacts were heated at different temperatures (450, 500, and 550 °C) for 1h in the air atmosphere. To evaluate the porosity and expansion of porous glasses obtained after heat treatment. The density (Helium pycnometer) was determined, and the size of the pores was examined using (SEM). Additionally, x-ray diffraction patterns were used to study the effect of the temperature after the heat treatment.

Keywords: Porous glass, hydrothermal hot pressing, recycling glass, fluoresce glass

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Acknowledgements: ZMV thanks TECNM for the "financial support granted through the key project 13533-22-P.2022, and project IT16D550.P-2023, which made it possible to conduct this study.

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Room Dr. Luis de Mercado – Sustainability

12:30 - 12:45 ORAL PRESENTATION 80116

DEVELOPING A SOLVOTHERMAL REACTION CELL FOR IN SITU NEUTRON SCATTERING OF CRYSTALLISATION

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Despite solvothermal synthesis being one of the most versatile methods for the synthesis of metal oxides, little is known of the chemistry that occurs during the process due to the closed nature of a solvothermal reaction. Although a range of X-ray techniques have been used to follow solvothermal crystallisations, the benefits of neutron diffraction have not been exploited in the *in-situ* study of the formation of materials. This includes the penetration of bulky reaction vessels, sensitivity to low atomic number elements, and, potentially, study of magnetic materials.

In this contribution I will explore the potential of a new cell design which is composed of a null-scattering titanium zirconium alloy ($Ti_{0.676}Zr_{0.324}$) with an aim for the cell to be easily transportable and adaptable to a variety of neutron instruments depending on suitability for the reactions being studied. The cell has been deployed in the study of the synthesis of the strontium ruthenate $SrRu_2O_6$ on Polaris at ISIS and D20 at the ILL for the real time monitoring of its crystallization at different temperatures. This material is of particular interest for its potential as a new semiconductor material while also possessing antiferromagnetic ordering with a Néel point above the synthesis temperature (T_N = 565 K). It has also been reported that with minor changes to the synthesis conditions of $SrRu_2O_6$, two additional strontium ruthenate phases can be produced. This makes the study of this material ideal to explore the potential of the cell in monitoring synthesis routes, magnetic structure formation in real time and reaction kinetics. The cell has also been used to study the formation of zeolite A (LTA) and its conversion under basic conditions to hydrosodalite (SOD) on NIMROD at ISIS. This allows for studying the impact of temperature on the rate of formation of the zeolite and the rate of conversion to the sodalite with an opportunity to use the cell to study disordered materials and its suitability for PDF analysis *in situ*.

Keywords: Neutrons, Diffraction, in situ

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12:45 - 13:00 ORAL PRESENTATION 79913

SUPERCRITICAL WATER IMPREGNATION OF ZINC OXIDE NANOPARTICLES ON CARBON SUPPORT

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The use of supported metal oxides has been found to be beneficial in the new technologies using supercritical water (scH_2O) as a green reaction medium for the oxidation and/or gasification of biomass, municipal solid wastes or wastewater [1]. The impregnation process in a batch scH_2O reactor has been proven to be effective in obtaining carbon-supported metal oxides. This technique allows for the production of composite materials in a single-step, without the need for mineralizers or seeds [2].

In the present work, we use the continuous flow tubular reactor of the NISA (*Neutron Imaging Supercritical-water Analysis*) equipment [3] for the impregnation of zinc oxide on activated carbon fibers with a monolithic structure [3]. Three synthesis parameters were studied to understand their influence on the composite's formulation in terms of crystallinity, size and morphology. First it was the impregnation temperature at working pressure of 250 bar. The reactor was operated at 648K and 668K. Second parameter was the concentration of the aqueous solutions of zinc nitrate (0.0041 M and 0.0082 M) used as the Zn source. The third parameter was the flow rate used to feed the solution into the reactor, which was set at 2.5mL/min and 5mL/min. All the obtained samples were characterized by X-ray diffraction and scanning electron microscopy.

The XRD analysis revealed that ZnO with hexagonal structure is formed at both temperatures. By SEM we observed that ZnO particles with 1D morphology are formed at 648 K. Such particles are only attached to the carbon fibers surface, while for the sample obtained at 668 K, uniformly distributed ZnO nanoparticles, with cubic morphology, are covering the carbon fibers surface. It is to note that uniform distribution of ZnO nanoparticles on C support is attained at low precursor concentration and high flow rate.

The results show that scH_2O impregnation of ZnO on carbon support is a promising approach for the composite materials preparation. This one-step synthesis method in a continuous flow uses neither seed layer nor mineralizer, and needs substantially lower preparation times than the conventional impregnation methods.

Keywords: Zinc oxide, Supercritical water, Continuous flow tubular reactor, Supercritical hydrothermal impregantion.

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Acknowledgements: This work was supported by the Romanian Ministry of Research, Innovation and Digitization, grant number PN-III-P4-ID-PCE-2020-1241. The work with NISA at the Romanian institution is possible due to the Research Collaboration Agreement with Paul Scherrer Institute, Switzerland, group of Prof. C. Ludwig. The authors thank Dr. C. Contescu retired from ORNL, USA for providing the monolith samples and to Dr. I. Atkinson for performing the XRD analysis.

A. Applications & Products

Biorefinery and Separations

KEYNOTE LECTURE

ORAL PRESENTATIONS

WEDNESDAY – SEPTEMBER 13th, 2023

Room Claudio Moyano – Biorefinery and Separations

11:30 - 12:00 KEYNOTE LECTURE 81273.

New Vinegar Production from Vinegar Processing Residue by the Subcritical Water Hydrolysis and Acetic Acid Fermentation

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The food industry generates a large amount of solid residues in its manufacturing process and the disposal of these residues cause economical and environmental problems. The authors have focused on the development of novel processes for converting food processing and agricultural solid residues to value-added functional components with an environmentally benign manner. Subcritical water treatment is one of promising processes for biomass liquefaction and hydrolysis to produce nutrient components. In this work, the authors employed sake lees and rice bran as food processing residues and liquefied them in subcritical water using a stirred-tank reactor whose inner volume was 521 mL (MMJ-500, OM labotech., Tochigi, Japan) at various temperatures, reaction times and solid/water ratio. First, we found that the liquefaction rate was relatively high (70-75wt%) at 180-220oC, but the total amount of amino acids formed via the hydrolysis of protein was not so high and detected bitter smell due to the formation of furan derivatives.1 For improving these problems, another series of liquefaction experiments of these starting materials at lower temperatures were carried out. As a result, we succeed to produce the liquefied aqueous solution with high content of amino acids from sake lees at 140oC for 4 h, and with high content of minerals from rice bran at 180oC for 30 min. Vinegars were prepared from the hydrolyzates obtained by subcritical water treatment by acetic acid fermentation treatment and also their properties were compared with commercially available vinegars.

Keywords: Subcritical water liquefaction, sake lees, rice bran, acetic acid fermentation, vinegar.

[1] *K. Yamato, D. Murakami, S. Hirayama, Y. Hoshino, M. Hoshino, M. Sasaki*, "Food-Grade Vinegar Production from the Extract of Sake lees obtained by Subcritical Water Treatment", J. Food Nutr., 2021, 7, 1-12.*

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Room Claudio Moyano – Biorefinery and Separations

12:00 - 12:15 ORAL PRESENTATION 80895

POLYURETHANE ADHESIVES FROM PINUS RADIATA LIGNIN BIOPOLYOLS

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Polyurethanes (PUs) are widely used synthetic materials. Typically, they are synthesised using petroleum-derived isocyanates and polyols. However, there is growing interest in utilising renewable resources, such as lignin, to produce polyols for PUs. Lignin, with its phenolic nature and abundance of hydroxyl groups, is a promising candidate for polyol production. To overcome the steric hindrance of lignin's hydroxyl groups, one commonly studied approach is liquefaction using polyhydric alcohols like polyethylene glycol and glycerol or crude glycerol as solvents [1]. In this study, polyurethane adhesives were synthesised using biopolyols derived from *Pinus radiata* organosolv lignin formulated with commercial glycerol and crude glycerol. The synthesised PU adhesives were then characterised to determine their chemical structure (FTIR), shear strength (ABES), and the thermal degradation kinetic and estimated lifetime was studied through TGA analysis employing the Ozawa-Flynn-Wall method [2]. The FTIR analysis revealed that PU synthesised with crude glycerol had a higher degree of phase separation and a lower proportion of hard segment compared to the PU synthesised with commercial glycerol. The shear strength at 120 s was significantly higher for the PU synthesised with crude glycerol (6.08 MPa) compared to the PU synthesised with commercial glycerol (2.21 MPa). The thermal degradation kinetics showed similar activation energies (Ea) at 5% conversion for both PUs, with the PU synthesised with commercial glycerol having a slightly higher Ea (145.0 kJ/mol) compared to the PU synthesised with crude glycerol (141.2 kJ/mol). Consequently, the estimated lifetime of the former PU was slightly longer.

Keywords: Lignin, Biopolyol, Polyurethane, Adhesive

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Acknowledgements: The authors acknowledge the financial support of the University of the Basque Country (project COLAB20/04) and the grant received from the Environmental Department of the Diputación Foral de Gipuzkoa.

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Room Claudio Moyano – Biorefinery and Separations

12:15 - 12:30 ORAL PRESENTATION 81576

HYDROLYSIS OF THE TRIGLYCERIDES OF SUNFLOWER SEED OIL USING SUBCRITICAL AND SUPERCRITICAL WATER

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Biodiesel is currently a fraction of fuels and is likely to increase in the future. The main production technology is transesterification. Nowadays, the reaction involves vegetable oils or animal fats and methanol in the presence of base a catalyst (NaOH or KOH). The reaction is carried out below 100 ºC with reaction times of hours. Glycerol is a by-product of the reaction. Can this reaction be carried out in shorter reaction times and with lower reaction volumes? We have investigated this possibility using supercritical fluids, which have demonstrated to possess unique properties that make them highly suitable as solvents and reaction mediums for diverse chemical applications[1]. In fact, supercritical water has given excellent results for the fractionation of lignocellulosic biomass in different fields, such as hydrolyzation of cellulose and beet pulp[2], depolymerization of lignin[3] and generating new products from grape seeds[4].
From a chemical point of view, it has already been demonstrated that the hydrolysis of an ester can be achieved using subcritical and supercritical water without the use of an acid or base[5]. This work presents the fundamentals of a continuous hydrolysis system in subcritical and supercritical water that converts sunflower oil triglycerides to diglycerides, monoglycerides, fatty acids and glycerol. The results showed a high conversion of triglycerides and no other by-products were formed. Our research studied the influence of reaction time (0.6 to 20 s), temperature (250 to 400 °C), pressure (180 to 250 bar), inlet concentration, ionic product and density. Results show that at temperatures around 375 °C and 250 bar, it is possible to obtain 41.1% fatty acids 20.2% monoglycerides, 29.8% diglycerides and less than 2% glycerol. Under subcritical water conditions 250°C and 220 bar, fatty acids, monoglycerides, diglycerides, and glycerol hydrolyzation is much lower respectively 1%, 0.2%, 2.1% and 0%, respectively, while triglycerides 94.6% is not fully hydrolyzed.
The oral presentation will encompass a comprehensive discussion of all experimental data and the conducted kinetic study.

Keywords: biodiesel, hydrolysis, triglycerides, fatty acids, supercritical

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Acknowledgements: This work was supported by Ministry of Science and Innovation & FEDER for funding the project PID2019-105975GB-I00 and the Regional Government of Castilla y León & FEDER for funding the program CLU-2019-0.

WEDNESDAY – SEPTEMBER 13th, 2023

Room Claudio Moyano – Biorefinery and Separations

12:30 - 12:45 ORAL PRESENTATION 81551

SYNTHESIS OF LAYERED DOUBLE HYDROXIDES FOR SORBING PHARMACEUTICALS FROM WASTEWATER

Amy-Louise Johnston[1], Edward Lester[1], Orla Williams[1] and Rachel Louise Gomes[1]

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Layered Double Hydroxides (LDHs) are increasingly emerging as successful sorbents for wastewater treatment. They are particularly attractive due to their low cost and simple synthesis. Further, LDHs, also known as anionic clays, have tuneable physiochemical properties, which can be harnessed to design bespoke high performing sorbent materials.
Most synthesised LDH materials have been binary LDHs, including a varying divalent metal and aluminium as the trivalent metal. This work has expanded the pool of LDHs synthesised in the continuous system beyond this traditional binary system to include ternary LDHs, including but not limited to LDHs containing Mg, Fe and Al.
Whilst a large body of literature is available for LDH performance for the removal of conventional pollutants (dyes, metals) from waters, their capability for removal of emerging contaminants, such as pharmaceuticals, under real environmental conditions is limited.
Lab-scale experiments were conducted to explore the removal of antibiotic pharmaceuticals from wastewater effluent (750,000 p.e) by a MgAl-LDH, under realistic conditions (pollutant concentration 100 µgL-1 and temperature 20 ˚C). Findings show sorption behaviour to be greatly impacted by the composition of the wastewater effluent. For example, equilibrium removal of amoxicillin decreased from 94.5 % (SD=0.1) in ultrapure water to 0 % in wastewater effluent. This inhibitory effect is due to multiple competing ions present in effluent, which preferentially sorb to the LDH.
It is concluded that pollutant characteristics and nature of the aqueous matrix play a significant role in sorption performance of LDH for the removal of organic pollutants. This talk will concentrate on how the LDH is made hydrothermally and how how both pollutant and aqueous matrix complexity need to be considered early in the development stages of new sorbent materials to ensure the possibility of future widespread applications.

Keywords: LDH synthesis, effluent, water beneficiation

[1]A.-L. Johnston, E. Lester, O. Williams and R. L. Gomes, Understanding Layered Double Hydroxide properties as sorbent materials for removing organic pollutants from environmental waters, J. Environ. Chem. Eng., 2021, 9, 105197.

Acknowledgements: Engineering and Physical Sciences Research Council for funding of the EPSRC Centre for Doctoral Training in Sustainable Chemistry (Grant number EP/L015633/1).

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Room Claudio Moyano – Biorefinery and Separations

12:45 - 13:00 ORAL PRESENTATION 80877

CO2-INTENSIFIED HYDROTHERMAL CLEAVAGE OF GLYCOSIDIC BONDS IN CITRUS BIOFLAVONOIDS

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Hydrolysis of naturally available compounds into more bioactive and bioavailable materials are gaining popularity in food and pharmaceutical industries. However, conventional method employs harmful catalysts such as sulfuric acid with low yield, while separation of the target compounds from the reaction products requires rather tedious approaches. To overcome these problems, this research aims to develop, optimize and evaluate by experimental approaches the cleavage of glycosidic bonds to separate sugar moieties by employing hydrothermal method intensified with supercritical carbon dioxide. The application of this novel approach to hydrolysis of citrus bioflavonoids (hesperidin, HPD) into its aglycones (hesperitin, HPT) was elucidated. Using a batch reactor, we were successful in hydrolyzing HPD into HPT under hydrothermal conditions with supercritical CO_2. The highest yield of HPT of about 40.0 % was obtained at T=160 ^oC, P=15 MPa and t=4 h. The combined reaction and separation process was also investigated using a semi-batch reactor system employing the mixture of supercritical CO_2 and subcritical H_2O. After the reaction, extraction of HPT was carried out by passing supercritical CO_2 through the reaction products. Results indicated the possibility of separating HPT from the mixture, and higher yield can be obtained by manipulating the pressure and temperature of the CO_2-H_2O mixture.

Keywords: Hydrothermal, Supercritical CO_2, Bioflavonoids, Glycosidic Bond

Acknowledgements: The authors gratefully acknowledge the financial support from JSPS Grant-in-Aid for Scientific Research (Grant Numbers 17KK0118 and 18K05202), the Japan Science and Technology Agency via the e-ASIA joint research program in the field of Bioenergy (SICORP Grant Number JPMJSC18E2) and JSPS Bilateral Joint Research Program with Chulalongkorn University (Thailand) and Valladolid University (Spain).

LIST OF POSTERS

MONDAY – SEPTEMBER 11th, 2023

11:00 - 11:30

TUESDAY – SEPTEMBER 12th, 2023

11:00 – 11:30

15:45 – 16:15

WEDNESDAY – SEPTEMBER 13th, 2023

11:00 - 11:30

Room Cardenal Mendoza

80881 Taisei Nagamine	Deamination of bio-oil using hydrothermal liquefaction intensified with supercritical carbon dioxide
79880 Daiki Takahashi	Degradation of CeO2 nanocatalyst under hydrothermal condition and durability enhancement by assembly control
81572 Teresa Sanz	Effect of maillard reactions on sugar degradation in subcritical water
80855 Siqi Xu	Growth Control of BaTiO3 by Supercritical Water Hydrothermal Synthesis
79521 Jyh-Ming Ting	High entropy layered double hydroxide for ultra-stable oxygen evolution reaction
81013 Tadafumi Adschiri	Holistic understanding of reaction kinetics in supercritical water
80797 Herminia Domínguez	Hydrothermal extraction of ulvan from Ulva sp.
80169 Jacob Oyarzabal	Hydrothermal synthesis of cerium hydroxy carbonates as precursors for oxygen deficient ceria
79911 Yuki Makinose	Hydrothermal synthesis of iron oxide nanoparticles and analysis of monodispersed nanoparticle conditions by machine learning
81517 Adrian Sanz Arjona	Hydrothermal synthesis of rutile IrxSn1-xO2 for Electrocatalytic Applications
80178 Shuyu Lin	Hydrothermal treatment of Ti-bearing blast furnace slag with dilute sulfuric acid
82083 Izaskun Dávila Rodríguez	Influence of the ultrasounds during the sequential extraction of oligosaccharides from apple pomace

80791	Maurício de Souza Ribeiro	Microwave aqueous extraction of shrimp shell proteins
81520	Adrian Sanz Arjona	Mild Hydrothermal Synthesis of Zircon-type Silicates (MSiO4) as Analogues to Radioactive Species
83067	Daniela Andrea Ramírez Espinosa	Obtaining energy vectors and developing materials for their sustainable storage
80801	Aránzazu Redondo Hernangómez	PMMA foaming in scCO2 and water
80778	Fei Li	Recovery of Valuable Materials from Microalgae Extraction Residue by Hot Compressed Water
80179	Shuyu Lin	Selective Methane Sensing Based on ZnO/Pd@ZIF-8
82715	Lisa Bernhard	Shape-Anisotropic Palladium Nanoparticles synthesized hydrothermally on Polyurethane sponges for heterogeneous catalysis
81718	Laura S. Junkers	Studying the Non-Crystalline Stages of Hydrothermal Bismuth Molybdate Formation through In Situ Total Scattering
81570	Rodrigo Melgosa	Subcritical water hydrolysis of fish protein fractions – techno-functional properties
79623	Hinako Kimura	Synthesis of CNT conjugates with sub-micron size spherical porous as cores
79763	Ayano Taniguchi	Synthesis of high-entropy porous metal oxides and their superior catalytic activity
80160	Katie Pickering	The solution crystallisation and characterisation of basic magnesium chloride salts studied in situ using a laboratory SAXS/WAXS instrument
81621	Vesna Leontijevic	Wetting properties of lignin-cellulose composites obtained after supercritical water hydrolysis of birch wood determined by contact angle measurement

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A.3. Biorefinery: materials and energy

82083. INFLUENCE OF THE ULTRASOUNDS DURING THE SEQUENTIAL EXTRACTION OF OLIGOSACCHARIDES FROM APPLE POMACE

Molares, A.[1] , Erdocia, X.[2] , Sillero, L.[3] , Hummel-Régis, F.[1] , Labidi, J.[1] Dávila-Rodríguez, I.[3] .

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Apple pomace is a highly abundant byproduct with a rich polysaccharide content, ranging from 60% to 70%. This makes it a promising source of oligosaccharides, which are compounds of great interest to the pharmaceutical and food industries due to their prebiotic activity.

The conventional method for obtaining oligosaccharides involves autohydrolysis treatment. However, their composition can vary depending on the specific conditions used in the process. Therefore, this study proposes a sequential extraction approach to isolate the oligosaccharides present in apple pomace. The sequential treatment consists of a hydrothermal step conducted at 60 ºC for 1 hour, using a solid-to-water ratio of 1/10 (g/g), followed by a microwave-assisted autohydrolysis step performed at 180 ºC for 10 minutes, using the same solid-to-water ratio.

To optimize the energy and time requirements of the initial hydrothermal treatment, the assistance of this process using ultrasounds was evaluated. The ultrasound-assisted hydrothermal treatments were conducted at 60ºC with an ultrasound amplitude set to 50%, for durations of 5, 10, and 20 minutes. Furthermore, the influence of the ultrasound-assisted treatments on the subsequent autohydrolysis step was assessed.

To evaluate the efficacy of the sequential extraction and the ultrasound-assisted techniques, the monosaccharide content of the liquid phases obtained after each treatment were quantified using high-performance liquid chromatography (HPLC). The oligosaccharide content was determined through a posthydrolysis treatment. Furthermore, to evaluate the efficiency of the extraction of the polysaccharides, the solids obtained after the different sequential treatments were chemically characterized.

Keywords: Apple pomace, oligosaccharides, ultrasounds, autohydrolysis

References: 1G.S. Dhillon, S. Kaur, S.K. Brar. Renew. Sust. Energ. Rev., 2013, 27, 789-805.

Acknowledgements: The authors would like to acknowledge the Department of Economic Development, Sustainability and Environment of the Basque Government (PA23/04) for the financial support.

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A.4. Food and cosmetics

80797. HYDROTHERMAL EXTRACTION OF ULVAN FROM *ULVA* SP.

Rodríguez-Iglesias, P.[1], Flórez-Fernández, N.[1], Torres, M.D[1], Domínguez, H.[1]

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Ulvans are sulfated cell-wall polysaccharides, mainly composed of rhamnose, uronic acids and xylose, found in the intercellular space of the cell wall, bound to proteins, cellulose and other polysaccharides[1]. Ulvans exhibit gelling properties and a number of biological healthy characteristics, including antioxidant, anticoagulant, anti-inflammatory, antimicrobial, antiviral, antihyperlipidemic, immunomodulating, antitumor and healing[2, 3]. Their high biocompatibility and low toxicity makes them suitable for biomedical and pharmaceutical materials[1,2,4].
The composition, especially the monosaccharide profile and sulfate content, as well as the structural features of ulvan, mainly the molecular weight and spatial conformation, determine its bioactivity. Those properties depend on the species, life cycle, origin and season of collection but also the extraction conditions may affect the yield and characteristics of the resulting ulvan[1,2]. The precipitation agent and conditions can be determinant since conformation of ulvan in solution is pH dependent and is influenced by the presence of counter-ions[1,5].
The present work is aimed at optimizing the operational conditions during hydrothermal treatment of *Ulva* sp. in order to maximize the overall and ulvan extraction yields and the physicochemical and biological properties of the recovered biopolymer, which will be used in formulations for topical use. Both conventional and microwave assisted heating during extraction will be tested and different purification strategies, including precipitation with conventional and alternative agents and membrane processing, will be considered.

Keywords: Hydrothermal treatment, sulphated oligosaccharides, rheology

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Acknowledgements:
Authors acknowledge Ministry of Science, Innovation and Universities of Spain (PID2021-124017-B-I00) and Consellería de Cultura, Educación e Universidade da Xunta de Galicia (GRC-ED431C 2022/08). M.D.T. thanks the Ministry of Science, Innovation and Universities of Spain for her postdoctoral grant (RYC2018-024454-I) and Xunta de Galicia (ED431F 2020/01).

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81570. SUBCRITICAL WATER HYDROLYSIS OF FISH PROTEIN FRACTIONS – TECHNO-FUNCTIONAL PROPERTIES

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Fish meal is an essential ingredient in aquaculture and pet-food industry since it contains valuable proteins, polyunsaturated fatty acids (PUFAs), essential amino acids, vitamins, and minerals[1]. However, the rise of new sources of protein (plant-based, microorganisms, insects, etc.) force fish meal producers to look for more valuable alternatives. Moreover, the growing demand for high-quality protein urge food producers to explore new protein sources and alternative processing methods to obtain new products with functional and healthy properties.
In this work, Subcritical Water Hydrolysis (SWH) has been used as a green, efficient method to prepare fish protein hydrolysates. Compared to chemical and enzymatic hydrolysis, SWH provides higher-purity extracts without need of reprocessing. Higher extraction yield than enzymatic hydrolysis and potentially better functional properties as a result of higher degree of hydrolysis are also important benefits of SWH technology[2].
Hydrothermal treatment of fish protein has been carried out in a batch-type reactor, at different temperatures (140180 ºC), and using N_2 and CO_2 as pressurization agents. Different protein sources have been also tested: fish meal (FM) from tuna (*Thunnus* sp.), its water-soluble fraction (WSP) and its non-water-soluble fraction (NSP). The extraction yield and the release of small peptides and amino acids have been followed over time. The highest amino acid yield was found at 180 ºC, with 275 ± 3 mg aa/g WSP and 344 ± 5 mg aa/g WSP for N_2 and CO_2, respectively[2]. Alanine, glycine, and proline were the major free amino acids, accounting for 81 (N_2) and 74 % (CO_2) of total amino acids[2]. The SWH extracts were lyophilized and used as emulsifiers in O/W nanoemulsions. The NSP fraction showed the best emulsifying properties of the studied hydrolysates, likely due to its higher surface hydrophobicity and intermediate peptide size. The emulsions stabilized with the NSP hydrolysate showed a droplet size centred around 150 nm (D[4,3] = 155 nm), which was stable after 14 days of storage at 4 ºC.

Keywords: Fish meal; Subcritical Water; Small peptides, Amino acids, Extraction

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Acknowledgements: Agencia Estatal de Investigación (AEI) [grant numbers PID2019-104950RB-I00/AEI/10.13039/501100011033 and PID2020-116716RJ-I00/AEI/10.13039/501100011033]. AEI, MICINN, UE NextGenerationEU [grant numbers TED2021-129311B-I00 and PDC2022-133443-I00] and by the Junta de Castilla y León (JCyL) and the European Regional Development Fund (ERDF) [grant number BU050P20]. R. Melgosa contract to Beatriz Galindo Research Fellowship [BG20/00182]. A.E. Illera contract to TED2021-129311B-I00.

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A.5. Nanomaterials and nanofluids

79623. Synthesis of CNT conjugates with sub-micron size spherical porous as cores

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Carbon nanotube (CNT) conjugates, in which CNTs are grown uniformly from substrates such as metals and ceramics, have attracted much interest in recent years.[1] We have succeeded in obtaining submicron-sized spherical porous aggregates composed of metal oxide nanoparticles by a one-pot solvothermal reaction.[2] Then, we thought these aggregates could be applied as spherical cores for CNT conjugates. So far, most of these CNT conjugates have been developed on spherical cores with sizes larger than 1 μm, and there are a few examples of growing CNTs from submicron-sized core spherical catalysts.[3] Our spherical porous aggregates have a characteristic nano-concave-convex surface structure and a large number of pores, making it possible to support metal nanoparticles on submicron-sized spherical porous aggregates uniformly.[4] In this paper, we applied the spherical porous metal oxide as the core catalysts for CNT conjugates with the isotropic growth of CNTs.[5]

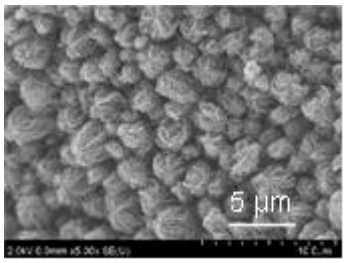

Fig 1. SEM image of CNT conjugates.[5]

FeO_x, CoO_x, and NiO_x were selected as catalysts for CNT growth. TiO_2, ZrO_2, SnO_2, and CeO_2 spherical porous aggregates were chosen as catalyst supports. FeO_x, CoO_x, and NiO_x catalyst supported on TiO_2, ZrO_2, SnO_2, and/or CeO_2 porous spheres were prepared by solvothermal reaction of the precursor solution including metal alkoxide and/or metal nitrate as metal sources, acetylacetone as an additive, and ethanol as a solvent at 300°C. Thermal chemical vapor deposition (CVD) technique using ethyne was applied to the CNT growth. Among these catalysts, a combination of FeO_x–ZrO_2 resulted in the best growth of CNT, where 2–3 μm long CNTs grew in all directions to afford like “CNT-hair” morphology (Fig. 1). Structures and properties of the CNT conjugate will be discussed.

Keywords: Spherical metal oxide catalysts, Carbon nanotube conjugate

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79763. SYNTHESIS OF HIGH-ENTROPY POROUS METAL OXIDES AND THEIR SUPERIOR CATALYTIC ACTIVITY

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High-entropy oxides, containing five or more non-oxygen elements in equimolar ratios, have been paid much attention as catalysts in this decade. To homogeneously mix multiple elements, high-temperature processes at around 1000 °C such as solid-state synthesis,[1] solution combustion synthesis[2] and spray pyrolysis[3] are typically employed. Therefore, crystallite sizes of the products are large and their specific surface areas are low. Then, we considered that the solvothermal method using organic solvents can be applied to the preparation of the high-entropy oxides with small crystallites, since the reaction is performed at relatively low temperatures (~300 °C) as compared with the above mentioned high-temperature processes. In this study, we developed a new approach to synthesize high-entropy oxides $CoCrFeMnNiO_x$ with small crystallites and porous structures by the solvothermal method and evaluated their catalytic performances.
Nitrates were used as the metal sources, and reaction conditions including solvents, additives and heating conditions were optimized. Porous $CoCrFeMnNiO_x$ successfully obtained through the reaction in a methanol/acetonitrile mixture with triethylene glycol has beautiful spherical secondary morphology. Although the as-synthesized product was amorphous judging from its XRD pattern, calcined product at 500 °C for 1 h exhibited the XRD peaks corresponding to the single-phase of spinel structure with a crystallite size of ~6 nm. STEM/EDX analysis revealed that the five metal elements were uniformly distributed in the porous spheres. The obtained porous $CoCrFeMnNiO_x$ spheres were applied as a catalyst for the reverse water-gas shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$) at 700 °C for 15 h. As a result, $CoCrFeMnNiO_x$ spheres exhibited superior catalytic activity and durability over a long time period.

Keywords: Solvothermal, High-entropy oxides, Porous, Reverse water-gas shift reaction

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Acknowledgements: This work was supported by the JSPS KAKENHI (grant number 22J14894, 22KJ2634).

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82715. SHAPE-ANISOTROPIC PALLADIUM NANOPARTICLES SYNTHESIZED HYDROTHERMALLY ON POLYURETHANE SPONGES FOR HETEROGENEOUS CATALYSIS

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Elemental Palladium (Pd) is an extremely useful hydrogenation catalyst.[1,2] Of particular relevance for catalysis are Pd nanoparticles (NPs), as they provide a higher portion of surface atoms, which enable said activity in hydrogenation, than bulk Pd. Synthetically one typically reduces Pd salts, commonly Na2PdCl4, in solution in the presence of ligands or surfactants, which stabilize the formed NPs through coordinating to their surface. As for any metal NPs used for catalysis, catalytic selectivities of Pd NPs can be tuned through the particle morphology, i.e., through growing particles that feature a higher proportion of the catalytically highly active nanocrystal loci vs. the less active facets, in other words: by generating shapeanisotropic Pd NPs. For synthesizing shape-anisotropic Pd NPs, one typically employs seed particles in the presence of surfactants and capping agents, which block crystal growth on specific facets.[1] Furthermore, for technical application, the Pd NPs have to be anchored on a support (e.g., metal oxides)[2] in order to (i) enable reusability (especially compared to the difficult recovery of NPs dispersed in solution), and (ii) enable operation in flow (by loading into a reactor). We have recently developed a hydrothermal synthesis of near-spherical noble metal NPs anchored on a polyurethane foam (PUF).[3]

Here, we expand on the reported Pd NP@PUF systems, specifically with respect to accessing shape-anisotropic Pd NPs. We show that under hydrothermal conditions anchored anisotropic Pd NPs can be generated using different surfactants in the presence of the PUF. Inductive coupled plasma - optical emission spectroscopy (ICP-OES) were employed to characterize the amount of Pd on the PUF support, while transmission electron microscopy (TEM) was used to determine size and shape of the NPs. Furthermore, for assessing the catalytic properties of the Pd NP@PUF materials, we determined the turnover number (TON) and frequency (TOF) for a model hydrogenation, which was performed in a fully automated setup and its progress was monitored by UV-Vis spectroscopy. Particular attention has been placed on evaluating the effect of Pd NPs' size and morphology on the reaction kinetics. Furthermore, we tested the Pd NP@PUF materials as cross-coupling catalysts and monitored their functioning via nuclear magnetic resonance (NMR) spectroscopy. We here provide an environmentally friendly alternative for generating anisometric Pd NPs on porous supports and evaluate their use as recyclable catalyst.

Keywords: Palladium Nanoparticles, Shape-anisotropic Nanoparticles, Heterogenous Catalysis, Cross-Coupling Reactions, Hydrothermal Synthesis.

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Acknowledgements: We acknowledge both the Austrian Science Fund (FWF) under grant No. START Y1037-N38 and the Natural Science and Engineering Research Council of Canada (NSERC) (Discovery Grant program and CGS D) for financial support of this project

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79880. DEGRADATION OF CeO2 NANOCATALYST UNDER HYDROTHERMAL CONDITION AND DURABILITY ENHANCEMENT BY ASSEMBLY CONTROL

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To improve the activity of catalyst, particle size ultrafine refinement, morphology control, metal loading/doping have been conducted. In particular, size control of CeO_2, which is oxidative catalysts for hydrocarbon (biomass, waste plastics, etc.) reforming, has succeeded in recent years in reducing the particle size to less than 5 nm[1] . However, it is known that when catalytic reactions are carried out at high temperature, the particles change their shape and sinter with surrounding particles, resulting in a decrease in activity. In this study, we investigated the effect of reaction condition on CeO_2 degradation, by TG (Thermogravimetry) analysis and X-ray diffraction, in order to realize a highly efficient oxygen carrier design. As a result, it is found that, by assembly with Pt or ZrO_2, the durability of CeO_2 nanocatalyst was enhanced.

At first, 5 nm-sized CeO_2 was heated at 500℃ under various gas conditions such as Ar, H_2, H_2O, O_2, CH4, and CO_2. In this result, H_2 and H_2O conditions mostly promoted CeO_2 nanocatalyst degradation by crystallite size enlargement. It is suggested that sintering induced by hydroxide formation is one of the dominant mechanisms on CeO_2 degradation. 1 wt% Pt loading on 5 nm CeO_2 (Pt/CeO_2) was performed. In the case of Pt/CeO_2, the crystallite size was kept small, indicating that Pt loading greatly improved the stability. This may be due to the stabilization of the CeO_2 surface crystalline structure by Pt loading and the suppression of sintering by the presence of other materials such as Pt in the spaces between the CeO_2. To prove the effect of inserting other materials on sintering inhibition, ZrO_2 nanoparticles were mixed with CeO_2. The increase in crystallite size, after thermal treatment under H_2O atmosphere, was suppressed. It should be noted that, Pt adsorbed on to the surface of CeO_2, but ZrO_2 is simply mixed, similar stability enhancement was obtained. Thorough, this study, it is indicated that loading of noble metal enhances nanocatalyst stability, as well as catalytic activity. Especially, this improvement in stability is thought to depend on the mixing state of CeO_2 and other substances, so achieving high dispersibility and high mixing state will be a future challenge.

Keywords: CeO_2, nanoparticle, stability, mixing

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Acknowledgements: This study was supported by the grants from the Japan Society for the Promotion of Science (JSPS); KAKENHI (Grant Number JP22H01845, and JP20K21856)

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A.6. Polymers, composites, hybrid and industrial materials

81621. WETTING PROPERTIES OF LIGNIN-CELLULOSE COMPOSITES OBTAINED AFTER SUPERCRITICAL WATER HYDROLYSIS OF BIRCH WOOD DETERMINED BY CONTACT ANGLE MEASUREMENT

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Due to its complex structure, lignin biopolymer, as the most abundant aromatic polymer in nature, has a wide range of potential applications. Isolation of lignin from different sources has become a highly researched topic. As a result, several most common methods for lignin extraction can be found in the literature. However, it is shown that the properties of extracted lignin are highly affected by the method used for extraction[1] . Wettability is one of the tools used for studying material structure. Additionally, it is a commonly tested property when the application of material is proposed. For direct measurement of surface wettability, contact angle (CA), a quick, inexpensive, and relatively simple, technique is frequently used[2] .

In this work wettability behavior of the five lignin and lignin-containing samples was compared. Two tested samples were obtained in our laboratory after supercritical water hydrolysis (SCWH) of the birch wood (hereafter called SCWL1 and SCWL2). The product is composed mostly of lignin. However, depending on the hydrolysis conditions, polysaccharides, primarily cellulose, can be found in the product after the process. The contact angle was measured on raw birch wood for comparison. Additionally, two commercially available lignin, sulfonated kraft lignin (SKL) and indulin are used as a reference. To perform the experiments, all tested samples were formed into pellets using a hydraulic press. The measurements were performed using High-Pressure View Cell coupled with a high-resolution CCD camera. The sessile drop method was used at a temperature of 22 - 25 °C. The time dependence of contact angle was monitored over a period of approximately 10 min. The roughness of the tested pellet surface was measured to examine the influence of the surface structure. Furthermore, a crystallinity test for samples containing cellulose was also performed.

The results showed that CA could not be measured on the raw birch wood due to swelling which appears immediately after the droplet is placed on the pellet surface. Further, considering the generally accepted rule that solid surfaces with CA < 90° are considered hydrophilic, while surfaces with CA > 90° are considered hydrophobic, the results showed that all tested samples are hydrophilic[3] . Although there was no significant difference between the CA of different lignin samples, different trends in the change of contact angle with time could be noticed. SKL, indulin, and SCWL2, sample from our process without cellulose had similar behavior where the biggest change in CA appeared in the first 60 seconds from the moment when the droplet was deposited on the polymer surface. On the other side, SCWL1, with higher cellulose content, shows a more linear profile of change.

Keywords: Lignin, Contact angle, Supercritical water hydrolysis

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Acknowledgments: This work is funded by FEDER, Ministry of Science and Innovation projects PID2019-105975GB-100, and Junta de Castilla y Leon CLU-2019-04. V Leontijevic thanks JCYL for the predoctoral contra

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83067. OBTAINING ENERGY VECTORS AND DEVELOPING MATERIALS FOR THEIR SUSTAINABLE STORAGE

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Renewable hydrogen is currently a sustainable solution for the decarbonization of the economy and has great potential for energy storage. It is a valuable energy carrier in hydrogen-intensive industries, for high-temperature processes, long-distance heavy transport, maritime, rail and air transport.[1]
The MATENERGYH2 project addresses H2 generation and storage from an innovative point of view by developing new catalytic systems and polymers, as well as less energy-demanding processes than the current ones. The project addresses two main challenges facing the industry that are related to energy sustainability. On the one hand, the generation of alternative energy carriers to fossil fuels from biomass and low added-value waste. In this sense, the highly selective obtaining of H2 by means of two thermochemical treatment processes assisted by catalysts. On the other hand, modified polymeric and nanoporous materials will be designed and modified to separate and store different energy vectors efficiently, which will reduce weight and improve the tightness of tanks.

Keywords: hydrogen, sustainable storage, revalorization, capture, energy.

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Acknowledgements: The project was realised thanks to the collaboration of companies such as UBE, Keraben, Stadler, E22, Greene Waste to Energy and BluePlasma Power. The consortium is grateful to the Instituto Valenciano de Competitividad Empresarial (IVACE), for funding the project

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80801. Poly (methyl methacrylate) foaming in scCO$_2$ and water

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Poly(methyl methacrylate) (PMMA) is a synthetic and amorphous polymer that belongs to the acrylate family. It is an optically clear polymer with a glass transition temperature range of 100ºC to 130ºC. It presents high resistance to sunshine exposure, high impact strength, high scratch and shatter resistance, good optical properties, good degree of compatibility with human tissue, is a lightweight and exhibits favorable processing conditions and a reasonable resistance to chemicals [1]. Very promising application have been developed with PMMA in recent years through the polymer foaming with CO_2. The produced foams present very low thermal conductivity, which make them a great insulation material [2].

This work study foaming of PMMA with supercritical CO_2 in different conditions to obtain nanoporous polymers. Also, it is focused on the effect of aqueous media in the foaming process to improve the cell number and reduce the cell size.

PMMA Plexiglas® 7N was supplied by EVONIK in the form of pellets. Foaming was carried out in High-Pressure foaming unit HPF-700. A given amount of PMMA was placed in a 65 mL high pressure tube autoclave. CO_2 was also introduced in the system by pneumatically driven gas booster and the temperature was controlled by a PID loop connected to a jacket heater. The experiments were analyzed at different conditions. Also, different water/polymer ratios were selected to do the assays. The system was depressurized by pneumatic ball valve.

The results show difference between the experiments which are carried out with and without water. The polymer shape in both cases was completely changed, increasing the volume of the sample and changing to a white color. Therefore, the foaming was achieved.

It is worth emphasizing that foaming is appeared in both mediums. Further experiments will be conducted to study this effect to reach the best foaming conditions.

Keywords: PMMA, scCO$_2$, water, foaming, polymers.

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A.7. Inorganics, surface

80179. Selective Methane Sensing Based on ZnO/Pd@ZIF-8

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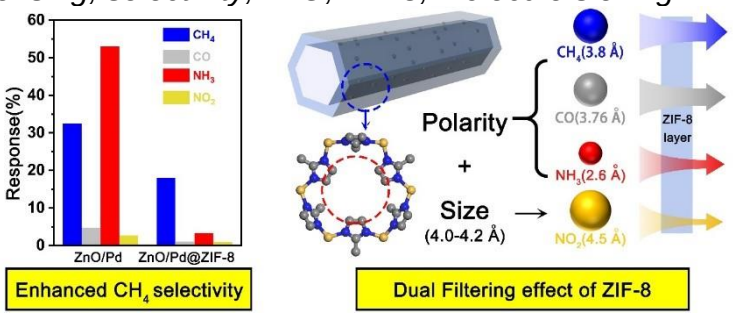
Methane(CH_4) sensing selectivity remains one of the biggest challenge for metal oxide conductive sensors due to the low reactivity and non-polar structure of CH_4 compared with other gases(CO, NH_3 and NO_2). In this work, the core-shell ZnO/Pd@ZIF-8 sensing composites with urchin-shaped hierarchical ZnO/Pd as the core sensitive material and ZIF-8 as gas sieve were designed for selective CH_4 sensing against CO, NH_3 and NO_2. There existed dual sieving mechanism of ZIF-8: size-sieving: the diffusion resistance of NO_2 (kinetic diameter: 4.5 Å) was larger than CH_4 (kinetic diameter: 3.8 Å) in ZIF-8 (aperture size: 4.0-4.2 Å); 2) polarity-sieving: the diffusion resistances of polar CO and NH_3 in ZIF-8 were larger than that of nonpolar CH_4. The response to 500 ppm CH_4 of ZnO/Pd@ZIF-8 was 20.6, 11.8 and 113.1 times higher than those to 50 ppm CO, 50 ppm NH_3 and 5 ppm NO_2 at 210 °C.

Keywords: Methane sensing, selectivity, ZnO, ZIF-8, molecule sieving.



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Acknowledgements: This work was supported by the National Science Foundation of China (51774191, 52274410 and 51802123)

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80178. HYDROTHERMAL TREATMENT OF TI-BEARING BLAST FURNACE SLAG WITH DILUTE SULFURIC ACID

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Titanium-bearing blast furnace slag (TBFS) formed during the smelting of Vanadium-titanium magnetite ore. Around 8 million tons of TBFS are produced every year in China. Currently, only a small part of the slag is used to prepare cheap building materials such as slag cement, sanitary porcelain plate, alkali-resistant slag, etc., and most of TBFS is still not used yet. This work investigates the hydrothermal treatment of TBFS with dilute sulfuric acid (20wt%), which is a by-product in the commercial production of TiO_2 from ilmenite, with the aim of utilizing TBFS.
X-ray fluorescence (XRF) and x-ray diffraction (XRD) analyses indicated that TBFS was rich in Ti (TiO_2: 20-22%), and the main Ti-bearing ores were perovskite ($CaTiO_3$), Ti-bearing diopside [(Ca, Mg, Ti, Fe, Mn)$(Al, Si)_2O_6$], and Ti-rich diopside [(Mg, Fe, Ca, Mn)$(Al, Ti, Si)_2O_4$].
TBFS was first treated in 20wt% sulfuric acid at 80 °C to extract the Ti-bearing components. The experimental results indicated that Ti-bearing diopside and Ti-rich diopside were completely decomposed after 6.0 hours of reaction at 80°C. The slurry was then treated at hydrothermal condition in the temperature range of 100-160°C. The effects of hydrothermal conditions as temperature and reaction time on the change of the components were investigated.

Keywords: Conversion of TBFS, Dilute sulfuric acid, Ti-bearing composites

Acknowledgements: This work was supported by the National Natural Science Foundation of China (No.21978153 and No.52274410).

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B.2. Green solvents: Supercritical fluids, ionic liquids, deep eutectic solvents and others

81572. EFFECT OF MAILLARD REACTIONS ON SUGAR DEGRADATION IN SUBCRITICAL WATER

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The variability of the substrates in the hydrolysis of lignocellulosic biomass results in multiple reactions. Different compounds are released into the medium that can interact with each other and suffer different reaction process making difficult the overall understanding of the process. Brewer's spent grain (BSG) is a lignocellulosic solid by-product generated in the brewing industry. In a discontinuous configuration, at 170ºC and 22 minutes of subcritical water (subW) treatment, 56 % of the total polysaccharide fraction, but also 64 % of the protein fraction was released into the reaction medium. Therefore, in this reactive medium, Maillard reactions can be initiated due to the presence of a reducing-end carbonyl group, coming from the hydrolysis of the polysaccharide fraction, and a free primary amine group, coming from free amino acids and small peptides. The presence of different compounds might affect the mechanism and pathway of the reactions of the components released, being worth the investigation with model compounds to better understand the behavior of sugars and amino acids in subW.
In this work degradation kinetics of pure sugars (glucose and xylose), amino acids (proline and aspartic acid) were determined and compared with the degradation kinetic profile of binary systems sugar + amino acid in the temperature range from 150 to 200ºC in a discontinuous reactor at 50 bar. At all temperatures studied in this work, a faster depletion rate was observed for all the compounds in the binary sugar + amino acid systems indicating that both compounds were used as reactants in the Maillard reactions. According to the browning development, it has been shown, that xylose presented a higher propensity to produce Maillard reactions compared to glucose. The effect of Maillard reactions on the main sugar degradation reaction products profile, HMF and furfural as dehydration products from glucose and xylose, respectively, was clearly observed by showing a retard in its production as sugar conversion increased, supporting the fact of Maillard reactions between sugar and amino acids in the early stages of the process[1]. Furthermore, lower maximum concentrations of furfural were obtained for xylose+amino acid systems compared to xylose-systems supporting previous results of higher browning degree due to higher tendency of pentoses to be involved in Maillard reactions.

Keywords: Sugars; Amino acids; Degradation routes, Maillard reactions, Subcritical Water

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Acknowledgements: Agencia Estatal de Investigación (AEI) [grant numbers PID2019-104950RB-I00 / AEI / 10.13039/501100011033 and PID2020-116716RJ-I00/ AEI / 10.13039/501100011033]. AEI, MICINN, UE NextGenerationEU [grant numbers TED2021-129311B-I00 and PDC2022-133443-I00] and by the Junta de Castilla y León (JCyL) and the European Regional Development Fund (ERDF) [grant number BU050P20]. R. Melgosa contract to Beatriz Galindo Research Fellowship [BG20/00182]. A.E. Illera contract to TED2021-129311B-I00.

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B.3. Hydrothermal liquefaction, gasification, carbonization.

80881. DEAMINATION OF BIO-OIL USING HYDROTHERMAL LIQUEFACTION INTENSIFIED WITH SUPERCRITICAL CARBON DIOXIDE

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Fossil fuels are used in many aspects of everyday life and are necessary for people's lives. However, fossil fuels are finite substances and will eventually be depleted. In addition, the use of fossil fuels emits large amounts of carbon dioxide, which is a greenhouse gas. Recently, biomass-based fuels have attracted attention as an alternative to fossil fuels. One of the advantages of biomass-derived fuels is that they are more sustainable than other renewable energies in terms of supply. Another advantage is that they are not affected by weather conditions, as is the case with solar and wind power. In addition, the combustion of biomass-based fuels does not significantly increase carbon dioxide emissions by virtue of the carbon cycle, thus making them an environment-friendly energy source. However, the existing refining processes for this type of fuels are costly. In this study, we propose the use of hydrothermal liquefaction (HTL) in the deamination of bio-oil as an alternative to the conventional expensive process of hydrogenation. Deamination is an essential step in the refining process because it reduces the amount of the pollutant NOx released after the combustion of fuels. As an intensification strategy to HTL, supercritical carbon dioxide was introduced into the system to generate an acidic environment necessary to remove the amino-groups in the various compounds that are present in bio-oil. The main products in the bio-oil produced by HTL treatment with aspartic acid were found to be long-chain alkenes and nitrogen-containing heterocyclic compounds, and GC-MS results showed that the use of supercritical CO_2 suppressed the formation of nitrogen-containing heterocyclic compounds.

Keywords: Deamination, Bio-oil, Hydrothermal liquefaction, Carbon dioxide

Acknowledgements: The authors gratefully acknowledge the financial support from JSPS Grant-in-Aid for Scientific Research (Grant Numbers 17KK0118 and 18K05202), the Japan Science and Technology Agency via the e-ASIA joint research program in the field of Bioenergy (SICORP Grant Number JPMJSC18E2) and JSPS Bilateral Joint Research Program with Valladolid University (Spain).

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80778. Recovery of Valuable Materials from Microalgae Extraction Residue by Hot Compressed Water

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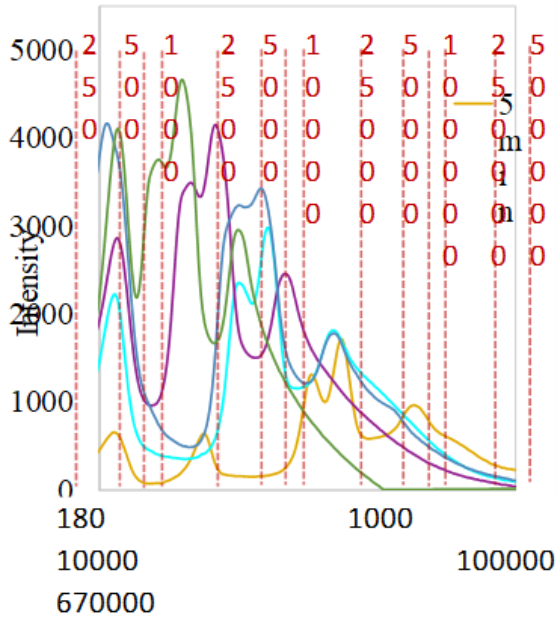
Microalgae is rich in proteins, lipids and carbohydrates and it has been recognized as one of the most promising feedstocks for bio-oil production.[1] However, the large amount of residue generated during bio-oil extraction process is of great concern.[2] This study aims to recover valuable products from lipid-extracted microalgae residue by hot compressed water. The effects of reaction variables (temperature, time, microalgae concentration) on the solubilization degree and the extract composition distribution (especially saccharides) were investigated.

A low-lipid chlorella was selected as a model for oil-extracted microalgae residue. 5 g of chlorella with 5 mL of deionized water were treated in a batch reactor at 175℃, 200℃, 225℃, 250℃ and 300℃ for 5 min to 90 min. The solubilization degree was evaluated by the dissolved total organic carbon (TOC) ratio (ratio of TOC content in the aqueous extract to total carbon content in the sample). The contents of saccharides in the extract and the original sample were determined by phenol-sulfuric acid method and two-step sulfuric hydrolysis followed by HPLC, respectively. The molecular weights of polysaccharides were confirmed by HPLC.



Results show that the solubilization degree at 175℃ was low, only about 34.9% in 90 min and it increased up to 65% at 225℃, while there was no significant improvement of solubilization degree above 225℃ due to the generation of gas at 250℃ and 300℃. On the other hand, the highest recovery rate of saccharides could be achieved at 200℃ in 15 min, where over 50% of saccharides could be retained in the aqueous extract compared to the original saccharides content in chlorella. Above 200℃, degradation of saccharides occurred quickly, leading to the decrease of saccharides contents. At 200℃, the molecular weight of polysaccharides was lower than 5000 after 5 min, and it continued to decrease till 30 min. After that, the molecular weight of polysaccharides increased with reaction time until 90 min accompanying with the increase of disaccharides, indicating that the repolymerization and hydrolysis of polysaccharides occurred simultaneously. In addition, the effect of microalgae concentration was investigated by adding 0.1 g, 0.25 g, 0.75 g, 1 g of chlorella with 5 mL of deionized water and treating at 200℃ for 5 min to 60 min.

Results show that the solubilization degree and the yield of saccharides could be promoted by loading lower concentrations of chlorella. While at 200℃, with higher concentrations of chlorella, the molecular weight of polysaccharides was smaller. A possibility is that the hydrolysis of polysaccharides is facilitated by the presence of certain product.

Keywords: Microalgae residue, Valuable product recovery, Hot compressed water.

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Acknowledgements: This study was supported by JST OPERA JPMJOP1832.

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B.4. Material synthesis

80169. HYDROTHERMAL SYNTHESIS OF CERIUM HYDROXY CARBONATES AS PRECURSORS FOR OXYGEN DEFICIENT CERIA

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Given the effect greenhouse gases have on our climate which are fueling the current climate crisis, methods of reducing greenhouse gas emissions are of key importance. The use of heterogeneous catalysts is one such method, and one of the most commonly used, and industrially relevant, of these materials are ceria and ceria-based materials. The redox chemistry of cerium allows these materials to be used for oxygen storage in applications such as the three-way catalytic converter, which help to reduce emissions from vehicles.[1]

This work aims to synthesise and characterise cerium-based precursors, which can be decomposed in the presence of various gases to produce cerium oxide materials, with higher than usual concentrations of cerium(III). Of particular interest are cerium hydroxy carbonates, $Ce(OH)CO_3$, where different polymorphs of the material can be synthesised using either a microwave assisted hydrothermal method, with urea as the carbonate source, or a more traditional hydrothermal synthesis using sodium carbonate.

With cerium already in its +3 oxidation state in these materials, these materials are ideal as precursors to be decomposed into materials with higher than typical amounts of cerium(III). These decompositions have been studied using variable-temperature XRD under various gas atmospheres, and the resultant materials further characterised using SQUID magnetometry and EPR spectroscopy.[2] The aim of using these techniques is to determine the amount of Ce(III) incorporated into the materials, moving towards developing in situ techniques (e.g. EPR) to characterise these materials during catalytic conditions.

Keywords: in situ, decomposition, magnetism

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81520. MILD HYDROTHERMAL SYNTHESIS OF ZIRCON-TYPE SILICATES ($MSiO_4$) AS ANALOGUES TO RADIOACTIVE SPECIES

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The long-term, safe, storage of nuclear waste materials poses a major challenge; however, storing radiological waste in natural landscapes is the most common way to dispose of this waste. The potential release of radioactive materials due to the corrosion of the containers, may lead to the formation of secondary phases. Repositories (such as planned in European policies1) are placed near water and silica-rich grounds. As a result of this, radioactive silicates are reported as possible products of the release of nuclear waste. These silicates include coffinite (USiO4) and thorite (ThSiO4). Although they have been reported to be found in nature, every attempt to obtain them synthetically in the lab seems to result in mixed phases, limiting the information which can be gleaned on these systems (thermodynamics, structure, kinetics, etc.). An easy and reproducible synthetic approach for the formation of these silicates is essential in order to predict their properties and potential behaviour arising from the storage of radiological waste materials from natural landscapes.

Hydrothermal synthesis is a versatile method to replicate mineralization in water-rich grounds, which is crucial to understand the possible reactions in the already mentioned repositories. This synthesis technique can reproduce the geological processes of different metals reacting with a silicon-rich solution to obtain the corresponding silicate minerals. Here we report the development and optimisation of a soft hydrothermal (100-250 °C) route to obtain zircon type silicates. These mild hydrothermal conditions have proven successful in yielding Zircon (ZrSiO4), Stetindite (CeSiO4), and thorite (ThSiO4). Additionally, mixed-metal silicates (CexZr1- xSiO4) have been synthesised, though the formation of the corresponding oxides present a competitive path. The obtained products were analysed by XRD, FTIR and TEM, and show significant differences in the apparent nucleation and growth pathway these materials follow.

Keywords: Mineralisation, Silicates, Nuclear Fuel

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79911. HYDROTHERMAL SYNTHESIS OF IRON OXIDE NANOPARTICLES AND ANALYSIS OF MONODISPERSED NANOPARTICLE CONDITIONS BY MACHINE LEARNING

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Iron oxide nanoparticles have been applied for hyperthermia and drug delivery systems,[1,2] and monodispersed nanoparticles are desirable for these applications. Monodispersed nanoparticles are defined by a coefficient of variation (CV) of <10%. The uniform distribution of precursors in the reaction solution and the separation of nucleation and growth are important factors for decreasing the CV.[3] The hydrothermal method has advantages such as low cost and environmental friendliness, and the reaction occurs in oxidative polar solvents. Recently, we reported the synthesis of near-monodispersed iron oxide nanoparticles using an alkaline-treated Fe oleate precursor by the hydrothermal method.[4] Alkaline treated Fe oleate precursor,which showed well dispersibility in aqueous solution, were used in the synthesis. The CV of the synthesized monodispersed iron oxide nanoparticles was 15.7%. In this study, CV values were obtained at different conditions by varying the hydrothermal temperature, time, ammonia content, and oleate/metal ion ratio to explore the conditions for monodispersed nanoparticlesand utilize machine learning. Iron chloride (II) and sodium oleate solutions were mixed by stirring. The resulting precipitate was separated and washed with water by vacuum filtration. Subsequently, the precipitate was mixed with an ammonia solution, and the separated supernatant was added to the Fe oleate mixture. Finally, the mixture was hydrothermally treated by varying temperature and time. The obtained samples were centrifuged, dried overnight, and then dispersed in cyclohexane. Subsequently, these were washed several times with HCl solution and dried. The obtained nanoparticles were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and dynamic light scattering (DLS). The XRD patterns of all the samples corresponded to the magnetite (Fe3O4) and maghemite (γ-Fe2O3) phases. DLS and TEM results showed that the nanoparticles have good dispersibility in cyclohexane. The size distribution was measured using the TEM images. The CV was 11.4% using 3 mL of NH3 at 220 °C for 24 h. The CV at varying hydrothermal temperature and time exhibited different trends depending on the NH3 content and oleate/metal ion ratio. For low CV, the optimal NH3 content was in the range of 3–5 mL. At lower NH3 content, the CV was less correlation with temperature and time. At higher NH3 content, The CV was higher than 30%. The machine learning results will be presented at the conference.

Keywords: Hydrothermal method, Iron oxide nanoparticles, Monodisperse, Machine learning
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Acknowledgements: This study was supported by the "FY2022 Shimane University Internal Competitive Grants Project B", "Hosokawa research grants," and "Tokuyama International grants".

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81517. Hydrothermal synthesis of rutile IrxSn1-xO2 for Electrocatalytic Applications

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The increasing population along with the climate change crisis has pushed researchers to find new ways to satisfy the current and future energy demand. Currently, there are many alternatives being projected as “greener” surrogates for energy production. Hydrogen has attracted great attention as an energy source as it encompasses the highest energy density per gram compared to others.[1] Nonetheless, the formation of H2 in a great majority of the cases still relies on the steam methane reforming method with a high generation of “greenhouse “ gases within the process. An alternative approach is the water splitting reaction (oxygen evolution reaction (OER) and hydrogen evolution reaction (HER)) in acidic conditions. Nonetheless, due to the slow kinetic of the OER in the anode, noble metals such as Ru and Ir are often used as electrocatalysts.[2] The stability and activity of these materials are mainly hindered by their dissolution into higher oxidation states species. A common way to solve this problematic is by doping this metal into a more stable oxide matrix that acts as stabiliser and surrogate in reaction.

Here we propose the hydrothermal synthesis of Ir doped rutile SnO2 in mild conditions for their application as electrocatalysts. The gelation and crystallisation by hydrothermal means accounts for a great structure and size control of the particles,3 essential to avoid instability during catalysis. The synthesis was performed at different conditions such as dopant concentration, time and temperature. Additionally, due to the nanometric size of the particles, total scattering measurements, pair distribution function (PDF) analysis, was performed to acknowledge their local structure. The presence of iridium was corroborated by XRF and the composition calculated by ICP measurements. Their electrochemical performance is projected to be studied and correlated to the different synthetic conditions and structure observed from the scattering data to optimise the oxides performance.

Keywords: Electrocatalysis, Total Scattering, PDF, Nanomaterials

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80855. GROWTH CONTROL OF BATIO3 BY SUPERCRITICAL WATER HYDROTHERMAL SYNTHESIS

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Supercritical water hydrothermal synthesis has emerged as a promising technique for the synthesis of nanostructured materials with unique properties. Barium titanate (BaTiO3) is a well-known ferroelectric material with applications in electronics. Since the size effect and the influence of crystal defects, controlling the size of nanoparticles and reducing crystal defects will be essential in the synthesis of barium titanate nanoparticles. Matsui et al.[1] has successfully prepared nano-size BaTiO3. But the methods of eliminating internal defects have not been studied. This study aims to reduce crystal point defects and control the particle size of nano BaTiO3 by changing experimental conditions.

Experiments were conducted by using a continuous-flow reactor. Titanium sources, Ba(NO3)2 and KOH were feed by pumps and mixed with heated distilled water to react in reactor at 400 °C and 30 MPa in reactor. The pressure of the system was regulated by a back-pressure valve. Samples' crystal structures and sizes were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Ba and Ti ion concentrations of BaTiO3 were determined by ICP-AES after acid digestion, thus Ba defect rate could be calculated.

Titanium sources include a titanium dioxide colloid named TiO2-sol and an organic titanium compound. The results showed that the two reactions brought about similar particle sizes, both around 25 nm, but the Ba defect rate in the case of using organic titanium compound was 18.7%, which was smaller than 23.1% in the case of using TiO2-sol. Such discrepancy could likely be explained by the homogeneity difference of the titanium sources, in which TiO2-sol was heterogeneous while organic titanium compound was homogeneous. In homogeneous reactions, Ba and Ti ions could be distributed in reactor more uniformly. So, the organic titanium compound was used in the following experiments.

Initially, the effect of residence time was explored. As the residence time increased from 0.18 s to 18 s, the size of the products continued to grow, increasing from 25 nm to 36 nm. Such increase probably resulted from growth of coalescence, which increases the size due to the collision of small domains after nucleation[2] . The Ba defects rate continued to decrease from 21% to 13%. Also, in order to understand the effect of hydroxide ion, the concentration of KOH was altered from 0.025 mol/L to 0.1 mol/L. In this case, BaTiO3 switched from an amorphous form to crystal when the concentration was above 0.03 mol/L. The smallest size was achieved when the concentration was 0.05 mol/L, and the size increased when the KOH concentration was below or above 0.05 mol/L. When KOH concentration increased, Ba defect continued reducing, from 22% to 11%. Hydroxide ion increased the supersaturation and accelerated precipitation. On the other hand, it also speeded up the reaction and promoted crystal growth.

Keywords: barium titanate, size control, barium defect rate. References: [1]Matsui, K. et al. J. Cryst. Growth., 2008, Vol. 310, 2584-2589. [2]Yoko, A. et al. J. Nanopart., 2014, Res. 16, 2330

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81718. STUDYING THE NON-CRYSTALLINE STAGES OF HYDROTHERMAL BISMUTH MOLYBDATE FORMATION THROUGH IN SITU TOTAL SCATTERING

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Bi3+ and Mo6+ both exhibit rich cluster chemistry that may influence the hydrothermal formation of BixMoyOz phases. Bi3+ has a unique coordination chemistry and ability to stabilise highly charged clusters, [1] while aqueous solutions of Mo6+ are known for their variety of discrete polyoxometalate (POM) clusters.[2] This makes classical nucleation theory unlikely to fully explain the formation mechanisms of BixMoyOz catalysts[3] . To facilitate the targeted synthesis of BixMoyOz nanoparticles with tailored properties we therefore aim to further our understanding of the early stages of their formation. [4] In this study, we investigate the non-crystalline structures involved in the hydrothermal formation of bismuth molybdates using in situ X-ray total scattering. Pair Distribution Function (PDF) analysis allows us to probe the local atomic structure of particles as they evolve during the synthesis, even before crystallinity occurs.[4] This enables us to investigate how the known impact of pH and Bi:Mo ratio variations[5] influences the emerging product prior to its crystallisation. Here, we show insights into the non-crystalline BixMoyOz species observed in the initial stages of synthesis as well as their transformation into more ordered bismuth molybdate phases. We observe precursor structures that differ from those occurring when only Bi3+ or Mo6+ are present.

Keywords: Mechanistic Formation Study, Hydrothermal, Bismuth Molybdates, PDF analysis, Non-crystalline structures.

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80160. THE SOLUTION CRYSTALLISATION AND CHARACTERISATION OF BASIC MAGNESIUM CHLORIDE SALTS STUDIED IN SITU USING A LABORATORY SAXS/WAXS INSTRUMENT

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We demonstrate a method for monitoring the in situ solution crystallisation of basic magnesium chloride salts Mgx+y(OH)2xCl2y·zH2O using a laboratory based SAXS/WAXS instrument. Although laboratory-based SAXS/WAXS instruments have limitations compared to synchrotron based sources, we have demonstrated how they can provide new insights into the formation of these materials.[1]

The salts were synthesised using a mixture of MgCl2 aqueous solution and nano-sized MgO. The reagent mixture was transferred to a disc-shaped reaction cell, consisting of a circular metal washer with internal diameter of 4 mm and thickness 0.5 mm sealed, each side using Kapton® tape. The cell was heated to temperatures between 28-120 °C. Although the synthesis of basic magnesium chloride salts has been reported,[2-3] by monitoring their synthesis using simultaneous SAXS and WAXS we are able to obtain time resolved data showing the phase evolution of the material and particle size.

Using the in situ WAXS data, a two-phase Rietveld refinement was carried out to quantify the progress of the reaction over time. The extracted phase fraction allows the decay of the MgO starting material and growth of product phase(s) to be observed directly over a period of several hours. Avrami kinetics were fitted to the data from which we suggest that there are two competing mechanistic processes in the formation of Mg3Cl(OH)5·4H2O. This was then compared to the SAXS data, analysed using combined sphere and Porod gradient model. With SAXS being sensitive to particle size below 160 nm, we observe a reduction in the volume fraction of the primary MgO particles during the initial stages of the reaction and, at later stages of the reaction, the emergence of larger crystalline material. Considering the SAXS and WAXS data we observed an offset between the consumption of crystalline MgO in the WAXS and reduction in the sphere volume fraction in the SAXS. We suggest this is due to the formation of an amorphous Mg(OH)2 intermediate during the synthesis of Mg3Cl(OH)5·4H2O. In conclusion, by simultaneous acquisition of both SAXS and WAXS, new mechanistic insights and quantitative kinetic information has been obtained for the formation of basic magnesium chloride salts.

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B.7. Separation, extraction and impregnation

80791. MICROWAVE AQUEOUS EXTRACTION OF SHRIMP SHELL PROTEINS

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Shrimp production generates the exoskeleton as one of the waste products due to the moulting process of the arthropods[1]. This shell can be valorised by the recovery of chitin, but it also has a high protein content (20-40%)[2] with interest to be isolated. During the conventional chitin extraction process, these obtained proteins cannot be reused, due to the use of inorganic alkaline solvents[3]. In this context, this study aimed to use water as solvent for the extraction of proteins from shrimp molt shells by microwave assisted extraction. The variables temperature (T: 175 and 225 °C), isothermal time (t: 0 and 10), and solvent-feed ratio (S/F: 10, 20 and 40 mL/g) were studied to understand their effects in the extraction of the proteins and co-extraction of other compounds. According to the obtained results, the highest protein extraction yield with low degradation into free amino acids, minimizing the co-extraction of other compounds, was obtained at T = 225 °C, t = 0 min, and S/F = 40 mL/g (protein content: 8.0 ± 0.3%, free amino acids: 0.97 ± 0.02%, and co-extraction yield: 19.8 ± 1.4%), while the lowest protein extraction yield was achieved at T = 225 °C, t = 0 min, and S/F = 10 mL/g (protein content: 2.7 ± 0.7%, free amino acids: 1.103 ± 0.014%, and co-extraction yield: 19.3 ± 1.4%). These results suggest that S/F is a controlling parameter in the extraction of proteins and do not promote neither the co-extraction of other compounds nor the complete hydrolysis of proteins during the microwave assisted aqueous extraction process. Thus, these parameters are being considered in the process optimization study under development nowadays.

Keywords: Amino acids, Molt shell, Protein, Non-conventional process, Microwave process.

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Acknowledgements: This work/project (project PID2020-119481RA-I00) was supported by the Regional Government of Castilla y León and the EU-FEDER program (CLU-2019-04). M.M. de-Souza-Ribeiro thanks the Department of Education of the Regional Government of Castilla y León and the European Social Fund Plus (ESF+) for his doctoral grant.

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C.1. Sustainability, Environment and Green policies

79521. High entropy layered double hydroxide for ultra-stable oxygen evolution reaction

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High entropy layered double hydroxide (LDH) consisting of five different non-noble transition metals of Fe, Ni, Co, Mn, and Cr (denoted as FeNiCoMnCr) is reported. The high entropy LDH was grown on nickel foam using a simple hydrothermal method. The catalyst demonstrates outstanding OER performance, with a low overpotential of 218 mV to achieve a current density of 50 mA cm^{-2} and a small Tafel slope of 47.1 mV dec^{-1}, outperforming its binary, ternary, and quaternary metal counterparts, and many reported electrocatalysts. At a very high current density of 400 mA cm^{-2}, the electrocatalytic performance of FeNiCoMnCr is well maintained for an ultra-long duration of 600 h. The interaction among the multi-metal components along with the electronic structure modulation accelerates the formation of high-active high valency Ni species, drastically boosting the electrocatalytic activity. DFT calculation also shows that the modification of electronic structure leads to the shift of d-band center, resulting in superior OER performance. In summary, we have prepared a high entropy LDH rooted on Ni foam of FeNiCoMnCr, as high-efficient and superior-stability electrocatalyst for OER in water splitting.

Keywords: High-entropy, layer double hydroxide, oxygen evolution reaction

Acknowledgements: This work was supported by the Ministry of Science and Technology in Taiwan under Grant Number MOST 111-2224-E-006-005.

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D.1. Advanced measurements, properties of fluids and fluid phase equilibria

81013. HOLISTIC UNDERSTANDING OF REACTION KINETICS IN SUPERCRITICAL WATER

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This paper reviews more than 30 years of research of Tohoku University on reactions in SCW and the commercialization of the proposed processes: Supercritical hydrothermal synthesis of NPs, and Supercritical Chemical Recycling. It is known that around the critical point, drastic change of kinetics (critical abnormality) occurs because of the significant variation of the solvent effect on kinetics due to the change of dielectric constant of water. In this paper, how to understand the solvent effect is explained by demonstrating the use of Kirkwood equation for hydrolysis of metal salts (inorganic reaction) and of cellobiose (organic reaction). By taking into account of dielectric constant and the concentration of reactant (chemical species, H+, OH- , Water etc.) under high temperature high pressure condition for Kirkwood equation (solution theory), observed reaction rate could be fairly well explained. The polarity change through the hydrolysis reaction was also evaluated by the DFT calculation, which fairly well matched with the experimentally evaluated results