

Development of CO₂ + Ethanol and Dimethyl Ether Extraction Technologies for Extraction of Natural Products – A NZ Perspective

Owen Catchpole^{a,*}, Jolin Morel^a, Stephen Tallon^b, Teresa Moreno^b, Andrew MacKenzie^b,
Kirill Lagutin^b, Stephen Bloor^b

^aCallaghan Innovation, Auckland, New Zealand

^bCallaghan Innovation, Lower Hutt, New Zealand

*Corresponding author: owen.catchpole@callaghaninnovation.govt.nz

Commercial scale supercritical extraction has been carried out in New Zealand since the 1990s and has mostly been focused on production of high value extracts for use foods and beverages, nutraceuticals and dietary supplements. Extracts were made primarily with supercritical CO₂, but processing technologies now include CO₂ + ethanol co-solvent, propane and dimethyl ether (DME). The development of CO₂ + ethanol co-solvent and dimethyl ether extraction technologies are discussed from a theoretical and experimental perspective including integration into overall processing suites. The application of these technologies to extraction of partially processed biomass are discussed with reference to two current collaborative R&D projects in New Zealand – the Bioresource Processing Alliance (BPA) and the Cyber-Marine project. The BPA seeks to add value to by-product streams arising from primary processing of biological materials and the Cyber-Marine project aims to develop the ‘fish and aquaculture processing factory of the future’ utilizing AI and a suite of advanced processing technologies to maximize value from landed catch and aquaculture species. Recent work on CO₂ + co-solvent has extended to the Gas-eXpanded Liquid (GXL) region i.e. high levels of co-solvent in the range 30 – 50 %. Such high levels allow for rapid extraction of phospholipids from marine biomass at moderate extraction pressures. Recent work in dimethyl ether extraction has expanded to low temperatures and partially freeze-dried biomass as a means to avoid endogenous enzymatic degradation of marine biomass; and the extraction of oil and chlorophyll from seeds to give high protein content residues.

New Technology and Product Application of Supercritical CO₂ Foaming Polymer

Ling ZHAO*

State Key Laboratory of Chemical Engineering, East China University of Science and Technology,
Shanghai 200237, China

*Corresponding author: zhaoling@ecust.edu.cn

Lightweight materials have broad application prospects in aerospace, automotive, and construction fields. Traditional methods for preparing lightweight materials often involve high energy consumption and significant environmental pollution. As a novel green preparation method, supercritical fluid foaming technology offers unique advantages, such as low energy consumption, high efficiency, and environmental friendliness.

However, there are still challenges in the supercritical fluid foaming of polymers, such as the narrow foaming temperature range of semi-crystalline polymers, shrinkage of thermoplastic elastomers after foaming, and poor foaming performance and difficult molding of engineering plastics. Based on these issues, and building on over two decades of related work in our laboratory, we will introduce the following key topics: based on the interaction between supercritical fluids and polymers, we will explore their effects on polymer crystallization behavior, melting behavior, dissolution and diffusion behavior, and rheological behavior, thus revealing the general principles of supercritical fluid foaming of polymers.

From the perspective of molecular chain structure design, we will use methods such as in-situ polymerization and reactive extrusion modification to prepare modified polymers with excellent foaming performance. From the perspective of improving process efficiency, reducing process energy consumption, and enhancing product quality, we have designed a series of innovative foaming strategies, including (1) pressure swing saturation, mixed gas foaming, dynamic aging in molding foaming, (2) polymer beads production without water as suspension medium and (3) microwave-assisted foaming. In addition, we will introduce the functional applications of polymer microcellular materials in fields such as high-frequency communication, electromagnetic shielding, infrared stealth, and etc.

Particle Design of Active Pharmaceutical Ingredient using the Supercritical CO₂ Process

Chie-Shaan Su*

Department of Chemical Engineering and Biotechnology, National Taipei University of Technology

*Corresponding author: cssu@ntut.edu.tw

The active pharmaceutical ingredient (API) is the central ingredient that shows therapeutic effects in drug products. The control of solid-state properties and formulation design of API is crucial to meet the drug efficacy, especially for the BSC (biopharmaceutical classification system) class II or IV drugs, which show a poorly water-soluble nature. Supercritical fluid technology, especially adopting supercritical CO₂ as the solvent or antisolvent, has been successfully adopted for the particle design of API. This study presents several case studies that adopted the supercritical CO₂ process in particle design of API, including the generation of micron to nano-sized API particle, preparation of cocrystal, and design of amorphous solid dispersion microparticle via the RESS (rapid expansion of supercritical solution), SAS (supercritical antisolvent) and CSS (cocrystallization with supercritical solvent). Regarding the producing micron to nano-sized API particles, several API candidates were investigated, such as haloperidol, p-toluenesulfonamide, sulfasalazine, and allopurinol. The quasi-spherical crystal habit of API powder with a mean size ranging from a few microns to 300 nm was successfully prepared. In addition, by adopting supercritical CO₂ as the solvent or antisolvent, the preparation of cocrystal of pirfenidone-fumaric acid and p-toluenesulfonamide-4,4'-bipyridine was also demonstrated. By adopting the supercritical CO₂ process, cocrystal with high purity and total powder recovery can be achieved. Furthermore, the supercritical CO₂ process was also efficient in designing and preparing amorphous solid dispersion (ASD) microparticles of various sulfonamides using a polymeric excipient, polyvinylpyrrolidone (PVP). Among these case studies, the dissolution rate of the processed APIs was also investigated, and the dissolution of APIs can be improved considerably. Moreover, by systematically investigating the effect of operating parameters, the supercritical CO₂ process can meet the engineering requirement with high throughput and satisfactory recovery under optimized conditions.

Keywords: Supercritical CO₂ process, Particle design, Active pharmaceutical ingredient

Continuous Flow Hydrothermal Synthesis of Ultra-Small Metal Oxide Nanoparticles

Akira Yoko^{a,b,*}

^aInternational Center of Synchrotron Radiation Innovation Smart (SRIS), Tohoku University, Sendai, Japan

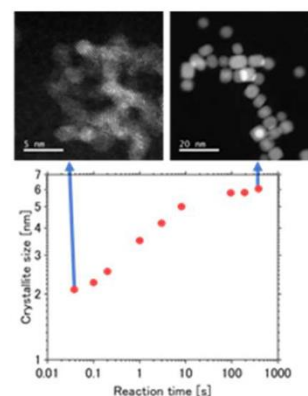
^bWPI-Advanced Institute for Materials Research (WPI-AIMR), Sendai, Japan

*Corresponding author: akira.yoko.c7@tohoku.ac.jp

Continuous flow hydrothermal synthesis is the methodology of synthesizing metal oxide nanoparticles by mixing starting solution with super-heated water rapidly. This method is suitable for large-scale synthesis of nanomaterials utilizing turbulent mixing flow. Also, in situ organic modification is possible because of the phase behavior of high temperature compressed water. In this study, synthesis of ultra-small (< 5 nm) metal oxide nanoparticles, which has not been explored before for metal oxides, was studied.

For the control of the organic-inorganic reactions in high temperature compressed water, metal organic complex was used for the starting materials. By the rapid hydrolysis of metal organic complex, which can be controlled by reaction temperature and concentration of organic modifiers, high supersaturation degree was obtained. Residence time was controlled based on the reaction design and reactor design with enhanced mixing. As a result, precisely controlled synthesis of metal oxides was enabled.

Figure 1 shows the reaction time dependence of particle size with corresponding TEM images of the obtained particles [1]. Owing to the precise control of the reaction route, mixing state, and reaction time, high controllability of the products was achieved including ultrasmall size (< 5 nm). Formation mechanism was intensively studied, and fusion growth of small particles was elucidated. In addition, largely distorted local structure and corresponding unusual electronic state was observed by utilizing synchrotron spectroscopy methods. The synthesis of the ultrasmall metal oxide nanoparticles opens a new research field with the emergence of the new property such as magnetic, optical, catalytic, and adsorption properties, by controlling particle size precisely. In addition, this method is widely applicable for various metal oxides [1].



Reference [1] A. Yoko, et al., J. Am. Chem. Soc. 2024, 146, 23, 16324–16331. Figure 1 Ultrasmall metal oxides

Biomass Utilization using Sub- and Supercritical Fluids

Jaehoon Kim^{a,b,c,*}

^aSchool of Chemical Engineering, Sungkyunkwan University, 2066 Seobu-Ro,
Jangan-Gu, Suwon, Gyeong Gi-Do, 16419, South Korea

^bSchool of Mechanical Engineering, Sungkyunkwan University, 2066 Seobu-Ro,
Jangan-Gu, Suwon, Gyeong Gi-Do, 16419, South Korea

^cSKKU Advanced Institute of Nano Technology (SAINT), Sungkyunkwan University,
2066 Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do, 16419, South Korea

*Corresponding author: jaehoonkim@skku.edu

Because of current global warming, production of carbon-neutral and renewable fuels and chemicals from renewable and sustainable resources have received a considerable attention recently. Owing to their beneficial physicochemical properties such as zero surface tension, fast reaction rates, deoxygenation ability, and suppression of coke formation, biomass conversion in sub- and supercritical fluids is considered one of most promising approaches in utilizing effectively technologically challenging feedstocks. This talk consists of three parts; first, extraction of bioactive compounds from various types of biomass will be discussed in sub- and supercritical fluids. Then, traditional hydrothermal and solvothermal liquefaction of various types of biomass such as woods, microalgae, and sewage sludge will be discussed. Under supercritical ethanol condition, complete conversion of biomass into liquids and gases could be achieved. During the liquefaction, some fraction of ethanol reacted with reactants and intermediates. A sophisticated separation of the products results in higher bio-oil yields, which let us to think again the process efficiency. The third part of this talk will cover solvent participation during catalytic conversion of biomass constituents. Over heterogenous catalysts, water and ethanol molecules donated their hydrogen to reactants (such as furfural) to change the reaction pathways. The solvent-mediated product selectivity will be discussed.

CO₂ Transformation into Valuable Chemicals

Zhimin Liu*

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

*Corresponding author: liuzm@iccas.ac.cn

CO₂ is an abundant, readily available, nontoxic and renewable C1 resource in the earth. The chemical transformation of CO₂ into valuable chemicals and fuels meets the requirements of green chemistry and sustainable development and is of great significance for achieving carbon neutrality. Our research group has long been dedicated to developing green reactions and preparing green materials using green solvents. In recent years, we have conducted extensive work on the clean and efficient chemical transformation of CO₂ [1-7]. We designed and synthesized various types of high-performance catalysts, such as task-specific ionic liquids, functional organic polymers, and supported nano-catalysts, developed novel reactions and strategy for CO₂ transformation in supercritical conditions, and realized several CO₂-involved atom-economic reactions under metal-free and mild conditions. We also adopted photocatalytic and electrocatalytic reactions to achieve CO₂ conversion into useful chemicals, and revealed the activation and transformation mechanism of CO₂ in different reaction processes.

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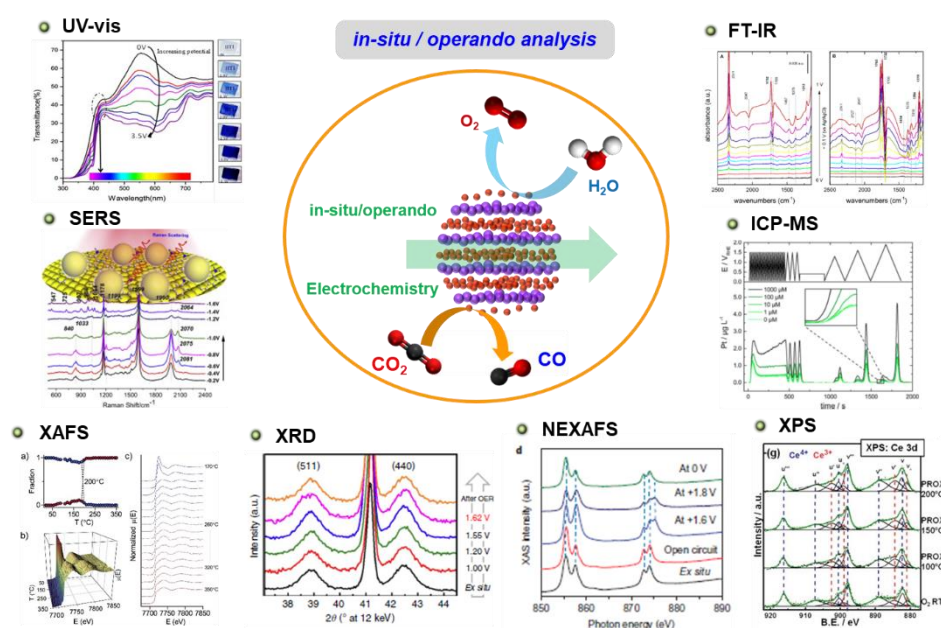
Developing Efficient and Stable Membrane Electrode Assembly (MEA) for CO₂ Electrolysis

Hyung-Suk Oh*

Korea Institute of Science and Technology, Seoul, South Korea

*Corresponding author: hyung-suk.oh@kist.re.kr

Nanoscale catalytic materials are key components of various electrochemical devices for storing and converting renewable energy, such as fuel cells, water splitting and CO₂ electrolysis system. Their successful development and optimization require insight into the relations between atomic-scale structure of the catalytic interface and their electronic structure to improve the catalytic activity and stability. Furthermore, optimization of the membrane-electrode assembly (MEA) is necessary for the commercialization of electrochemical CO₂ conversion research. MEAs are where the actual electrochemical reactions take place, where electrons, ions, and electrolytes are actively transported for CO₂RR. In this talk, I will present recent findings on the design and understanding of CO₂ reduction reactions (CO₂RRs) from a MEA perspective. In particular, I will describe the observation of fluid dynamics and local pH evolution under CO₂ electrolysis operating conditions using *in-situ/Operando* analytical platforms, such as XAFS, Raman and CT. These results can provide direction for the design of electrocatalysts as well as the preparation of MEAs for CO₂RR.



Effect of Cannabis Supercritical CO₂ Extract of Smart-Farmed Hemp on the Suppression of Geriatric Diseases

Youn-Woo Lee^{a,c,*}, Ki Won Lee^{b,c}

^aSchool of Chemical and Biological Engineering, Institute of Chemical Processes
Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, South Korea

^bFood Science & Biotechnology Major, College of Agriculture and Life
Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, South Korea

^cSNU HEMP lab., Korea Advanced Institutes of Convergence Technology
864-1, Iui-dong, Yeongtong-gu, Suwon-si, Gyeonggi-do 16229, South Korea

*Corresponding author: ywlee@snu.ac.kr, kiwon@snu.ac.kr

The contents of CBD and CBDA, which are the main components of the hemp samples obtained by various extraction processes, were compared. Various hemp samples cultivated at home and abroad. Before extraction, samples, cultivated at home and abroad, were prepared by grinding followed by decarboxylation at 140 °C for 1 hour. The decarboxylated samples were extracted using various solvents such as water, ethanol, and supercritical CO₂ or their mixture using a batch type extractor, a soxhlet extractor, and a flow type supercritical extractor.

The total polyphenol content and total flavonoid content of the extracts were measured, and antioxidant activity was evaluated through dpph assay. In addition, mouse neurons and muscle cells were used to investigate the effect of Cannabis Supercritical CO₂ Extract (CSCE) on memory and muscle strength improvement in the cell model. The CSCE inhibits the death of nerve cells caused by oxidative stress, inhibits the death of myoblasts, and is effective in promoting muscle differentiation as the formation of the myotube. It was also found that the CSCE suppressed neuronal cell death by oxidative stress.

How Supercritical Hydrothermal Reactions Contribute to Innovation?

Tadafumi Adschiri*

Tohoku University, Sendai, Japan

*Corresponding author: tadafumi.ajiri.b1@tohoku.ac.jp

We started the research on reactions in supercritical water 35 years ago. In this lecture, first the characteristics of supercritical hydrothermal reactions will be summarized, followed by an explanation of their potential for various applications: The expansion of this academic field will be discussed from the number of academic papers, and the development in industry will be discussed from the number of patent applications; In relation to SDGs and Carbon Neutral, I will explain the possibility of contribution to waste plastics, biomass degradation, and recovery of chemicals as the substitute of petroleum (revolution in chemical industries), and also new science research of nanomaterials (basic research and designing basis), which we believe contributes to the innovations in materials industries.

Research Advances in the Application of Hydrothermal Leaching Technology for Lithium-Ion Battery Recycling

Masaru Watanabe*, Qingxin Zheng

Research Center of Supercritical Fluid Technology, Department of Chemical Engineering,
Graduate School of Engineering, Tohoku University, Japan

*Corresponding author: masaru.watanabe.e2@tohoku.ac.jp

With a rapid growth in EV sales, the demand for lithium-ion batteries (LIBs) is surging, which is leading to a massive consumption of critical materials in LIBs (e.g., Li, Co, Ni, and Mn). On the other hand, spent LIBs are considered a hazardous solid waste and must be disposed of properly. Therefore, recycling of spent lithium-ion batteries (LIBs), especially recovering critical metal components from spent LIB cathode materials such as LiCoO_2 (LCO), LiNiO_2 (LNO), LiMn_2O_4 (LMO), LiFePO_4 (LFPO), $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ (NMC), is an urgent task and would be beneficial to conserve natural resources, reduce environmental damage, maintain resource stability and security, and bring economic benefits.

As one of popular LIB recycling processes, hydrometallurgy mainly involves two steps of acid leaching and metal isolation (Fig. 1). Metal ions in spent LIB cathode materials are leached by acid and then each metal component is isolated. In a traditional leaching step, high-concentration inorganic acids and reductants are necessary, and a long reaction time is required for complete leaching, which increases the costs and causes environmental pollution and acid corrosion.

To resolve these problems, a method of ‘hydrothermal leaching’ using organic acids as the leaching agents was proposed (Fig. 2). Compared to the traditional leaching method, hydrothermal leaching shows many advantages such as low chemical consumption and high leaching rate. Here, the applicant aims to introduce the research development of hydrothermal leaching technology for LIB recycling in recent years.

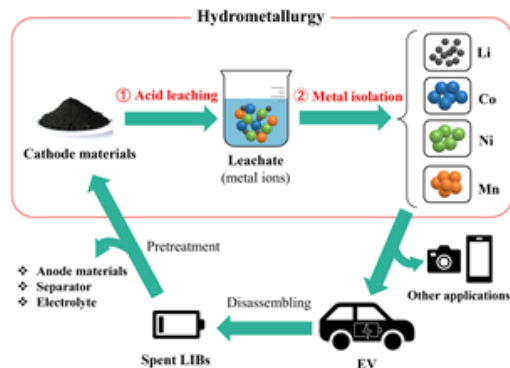


Fig. 1. Hydrometallurgical LIB recycling.

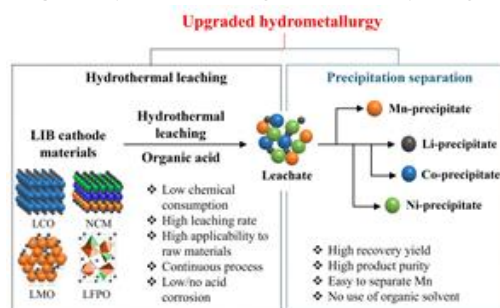


Fig. 2. Proposed LIB recycling process.

Supercritical CO₂-Assisted Scalable Exfoliation of Graphite into Graphene via Ball Milling

Huijun Tan, Rahul Navik, Yaping Zhao*

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University,
800, Dongchuan Road, Minghang District, 200240, Shanghai, China

*Corresponding author: ypzhaos@sjtu.edu.cn

Graphene is a two-dimensional crystal nanomaterial composed of a single layer of carbon atoms arranged in a hexagonal pattern. Due to its excellent electrical, thermal, and mechanical properties, as well as its high specific surface area, graphene holds broad application prospects in various fields such as energy, environment, and materials. The preparation of graphene can be categorized into two main approaches: top-down exfoliation and bottom-up synthesis. The former is the primary method for preparing graphene powders and functional composites, employing techniques such as oxidation-reduction, electrochemical methods, and solvent-based liquid phase exfoliation. However, these methods often result in either poor electrical properties, and low yields of graphene or involve the use of large amounts of strong acids and oxidizers, leading to significant environmental challenges that hinder the development and application of downstream graphene products. Therefore, the scalable production of high-quality graphene remains a pressing challenge. Supercritical CO₂ is a unique and environmentally friendly fluid that has already been industrially applied in fields such as extraction, separation, foaming, and drying. This report presents a supercritical CO₂-assisted, scalable method for the production of graphene from graphite via ball milling and explores its applications. The effects of the process parameters on graphene yield, structure, and properties, as well as the performance of graphene-polymer composites, are discussed. Future outlooks for this technology are also explored.

Keywords: Supercritical CO₂, ball milling, graphite, graphene, exfoliation.

Boosting CO₂ Electrolysis in Green Solvents

Xiaofu Sun*

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

*Corresponding author: sunxiaofu@iccas.ac.cn

Achieving CO₂ conversion with high efficiency is very important and meaningful. Our group has focused on highly efficient electrochemical conversion of CO₂ to value-added chemicals and fuels in green solvents,[1] and proposed a new strategy to implement electrochemical conversion of CO₂ process via the promotion of green solvent electrolyte. Aiming at the key scientific issues such as high selective conversion and clarifying the mechanism, we did comprehensive research in catalyst and electrolyte design. Green catalysis systems have been constructed, and several routes have been developed for CO₂ electroreduction to chemicals and fuels with high selectivity and stability, including CO, methanol and C₂ products.[2-6] The effect of electrolyte, the structure-activity relationship of catalyst, the synergistic effect between electrolyte and catalyst, as well as the mechanism for the enhanced CO₂ conversion has been also discussed thoroughly.

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Operando Spectroscopic Analysis in Photo/Electro-Catalysis

Wooyul Kim*

Department of Energy Engineering

Korea Institute of Energy Technology (KENTECH)

200 Hyeoksin-ro, Naju 58330, Republic of Korea

*Corresponding author: wkim@kentech.ac.kr

Direct observation of key intermediates on the catalyst surface is one of the biggest challenges in various photo/electro-catalysis including CO₂ reduction reaction O₂ reduction reaction, etc. For a rational understanding of the reaction mechanism, combined studies encompassing complementary tools such as electrochemical characterization, computational calculations and operando spectroscopies should be conducted. Among various operando spectroscopies, the time-resolved attenuated total reflection-surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) is particularly suitable for the investigation of various electrochemical reaction as it allows observation of interfacial processes in real-time owing to its high surface sensitivity. In addition, time-resolved analysis would reveal the kinetic relevancy of intermediates and their relationship with the reactants and the products based on their dynamic behavior during the reaction. Lastly, a combination of the operando spectroscopic studies with material characterization would enable a correlation of the behavior of the intermediates and the catalyst conditions. Herein, I will introduce *in situ* time-resolved FT-IR (or ATR mode) spectroscopic techniques to acquire the isotopically labeled products and key intermediates from the various photo/electro-catalysis.

Multi-Phasic Nature of Supercritical Fluids

Tae Jun Yoon^{a,b,*}

^aSchool of Transdisciplinary Innovations, Seoul National University, Seoul 08826, Republic of Korea

^bSchool of Chemical and Biological Engineering, Institute of Chemical Processes, Seoul National University,
Seoul 08826, Republic of Korea

*Corresponding author: tyoon124@snu.ac.kr

Supercritical fluid, a state of matter beyond the critical temperature and pressure, has been widely used in chemical processes as a separation and reaction medium. This versatility is believed to stem from its instantaneous tunability. A slight change in operating conditions makes it possible to continuously change its thermophysical behavior from gas-like to liquid-like to solid-like states without any discontinuities. This ever-changing nature of supercritical fluids casts us with the following profound questions. What is liquid? What is gas? What is a solid?

In this talk, I will present my studies on the structural and dynamic transitions of supercritical fluids across the Widom line and Frenkel line, which are believed to be related to gas-like to liquid-like and gas-like (ballistic) to solid-like (vibrational) transitions in supercritical fluids. Based on molecular simulation results, I first show how the structural characteristics evolve from gas-like to liquid-like states near the critical point. These results are analyzed based on data scientific algorithms and neural network classifiers to quantify the gas-like nature of supercritical fluids in terms of the local density. This quantification of gas-likeness in supercritical fluids enables us to find a universal power-law dependence of the pressure-density-temperature relation in supercritical fluids.

Second, I explore how the dynamic nature of supercritical fluids changes when they become close to the solid-supercritical fluid transition line. Exploiting the diffusional and topological nature of supercritical fluids, I show that the dynamic transition from translational to vibrational modes is deeply related to the local topology (solvation structure) of supercritical fluids, enabling us to conclude that the dynamic transition of simple supercritical fluids can be expressed as a single function of the residual entropy. These endeavors ultimately provide a theoretical basis for the supercritical fluid polyamorphism and have the potential to be applied to the design and optimization of the supercritical fluid processes.

Development of Extended Supercritical Extraction Processes for Waste Valorization

Hong-shik Lee^{a,*}, Ji Sun Lim^{a,b}, Seung Eun Lee^{a,c}, Bonggeun Shong^b, Young-Kwon Park^c

^aKorea Institute of Industrial Technology, Cheonan, Republic of Korea

^bHongik University, Seoul, Republic of Korea

^cUniversity of Seoul, Seoul, Republic of Korea

*Corresponding author: leehongshik@kitech.re.kr

Supercritical extraction (SFE) has been practicalized in various industry such as food, pharmaceutical, cosmetics, and fine chemicals. These cases show that the SFE is a competitive process owing to its high efficiency and characteristic performance. However, still in many cases, the requirement of high capital cost which is inevitable due to the operation pressure has been regarded as the biggest hurdle for wider application of SFE process. In this study, the extension of SFE by the hybridization with other novel technologies was focused on for the improvement of economic feasibility of SFE process. While the use of cosolvent in SFE makes the extraction of more various compounds possible, it requires the additional energy consumption to separate cosolvent from extracts. The application of membrane distillation to concentrate the extract solution could reduce the energy requirement for recovery of cosolvent. In the extraction of phytochemicals such polyphenols or flavonoids, the extraction yield generally stays at around 10 % so that large amount of residue is remained. For the valorization of residues from SFE, the transition to biofuel and porous biochar by hydrothermal treatment was tried, and it was found that the quality of biofuel and biochar from SFE residue could be controlled by the extraction conditions.

Production of Silk Fibroin Self-sustaining Hydrogels by Hydrothermal Gelation

Mitsumasa Osada*, Hayata Matsushita, Kenta Mizushima

Department of Chemistry and Materials, Faculty of Textile Science and Technology, Shinshu University,
3-15-1, Tokida, Ueda, Nagano 386-8567, Japan

*Corresponding author: osadam@shinshu-u.ac.jp

The ultimate biomaterial will be able to be prepared using only a biomass resource and water, without additional chemical modification. Although chemical modification is a useful way to control the shape and strength of biomaterials, there are concerns that chemical additives harmful to the human body may remain. If chemical modification is not performed, and no chemical additives are used, the production of biomaterials requires the use of simple attractive forces. One possible means of accomplishing this is wet pulverization with a water jet, which can disintegrate biomass particles into nanofibers (NFs) and/or nanoparticles [1, 2]. We have proposed hydrothermal gelation as a means to confer shape stability to NF dispersions after disintegration. Polysaccharides such as cellulose and chitin NF dispersions can be gelled by simply heating them in a sealed reactor [3]. This is referred to as hydrothermal treatment, as it uses water in the pressurized liquid phase (above 100 °C).

In this work, we apply hydrothermal gelation to a protein, namely silk fibroin, rather than polysaccharides such as cellulose and chitin in previous research [1–3]. Conventional methods for obtaining silk fibroin self-sustaining hydrogels have a high environmental impact, such as using high concentrations of lithium bromide (LiBr), and there is also the problem of LiBr remaining in medical materials. We propose a new method of preparing silk fibroin self-sustaining hydrogels using only water. At first, silk fibroin dispersions in water were prepared by the wet pulverization process with a water jet at 25 °C from raw silk fibroin powder. Next, the silk fibroin dispersion can be converted by hydrothermal gelation (100–180 °C, 10–120 min) to a mechanically strong hydrogel that can maintain its shape. In addition, the gelation mechanism and physicochemical properties of the silk fibroin hydrogels were elucidated.

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Chemical Looping Steam Methane Reforming Process using Nano CeO₂

Gimyeong Seong^{a,*}, Akira Yoko^{b,c}, Takaaki Tomai^d, Tadafumi Adschiri^{b,e}

^aDepartment of Environmental & Energy Engineering, The University of Suwon, Hwaseong, Republic of Korea

^bWPI-Advanced Institute for Materials Research, Tohoku University, Sendai, Japan

^cInternational Center for Synchrotron Radiation Innovation Smart, Tohoku University, Sendai, Japan

^dInstitute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan

^eNew Industry Creation Hatchery Center, Tohoku University, Sendai, Japan

*Corresponding author: soppua4@suwon.ac.kr

In this study, the goal was to significantly reduce the operating temperature of methane steam reforming, typically conducted at temperatures above 900 °C, by introducing the Chemical Looping Steam Methane Reforming (CL-SMR) process. This was achieved through leveraging the strong methane activation and carbon adsorption properties of {001} facet-exposed cubic CeO₂ (cubic CeO₂), leading to the discovery of a novel reaction pathway. Unlike conventional chemical looping cycles where synthesis gas is obtained during the CH₄ conversion step and pure hydrogen during the steam flow step, this process generates pure hydrogen during the CH₄ conversion step.

The low-temperature activity for methane and carbon carrier properties of cubic CeO₂ were analyzed, and the CL-SMR process was executed under isothermal conditions at 500 °C. During the methane flow step, pure hydrogen was generated by the active oxygen sites of cubic CeO₂. In the steam flow step (steam gasification), CO₂ is desorbed while creating oxygen-deficient sites. At these oxygen-deficient sites, steam is converted to regenerate oxygen, and simultaneously, hydrogen is produced. This cycle fulfilled stoichiometric methane conversion.

Furthermore, the feasibility of the CL-SMR process was validated through periodic cycle reactions. Pure hydrogen generation was observed in all methane flow steps, while consistent production of hydrogen and CO₂ was observed in all steam gasification steps. Methane conversion and hydrogen production via steam remained relatively stable from the mid-process onwards.

These results highlight the potential of the CL-SMR process in achieving methane steam reforming at low temperatures, thereby contributing to future clean energy production saving energy consumption.

Ionic Liquids-Mediated Valorization of CO₂ and Spent Polyesters into Value-Added Chemicals

Yanfei Zhao*, Zhimin Liu*

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

*Corresponding author: lianyi302@iccas.ac.cn; liuzm@iccas.ac.cn

As renewable and recyclable carbon resources, the chemical transformation of CO₂ and spent polyesters to useful chemicals is of great significance for green chemistry and sustainable development. Ionic liquids (ILs) provide new opportunity for developing high-performance catalysts for clean transformation of these carbon resources due to their unique properties.

My research work mainly focuses on developing ILs-based catalytic system for the green transformation of these carbon resources under mild conditions [1-6]. We synthesized several CO₂-reactive ILs that can chemically capture and activate CO₂ via forming anion-based carbonate/carbamate intermediates, thus further accomplishing its chemical transformation under metal-free conditions [1, 3-5]. We realized the upcycling of hydroxyl carboxylic acid-derived polyesters to various chemicals via hydrolysis, alcoholysis and aminolysis using hydroxyl carboxylate ILs under metal-free and mild conditions [2]. Additionally, we also developed some IL-metal catalyst systems, and realized the selective reduction transformation of CO₂ with H₂ [6, 7]. Notably, Pd/C in 1-butyl-3-methylimidazolium tetrafluoroborate works well for the reaction of cyclic amines with CO₂/H₂, selectively producing N-formamides and N-methylamines in high yields just by varying the reaction temperature [6]. Moreover, 1,2-bis(N-heterocyclic)ethanes were for the first time obtained from cyclic amines and CO₂/H₂ via McMurry reaction of formamides coupled with subsequent hydrogenation.

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Selective Production of Ethanol over Co-Based Catalyst by Electrocatalytic Reduction of CO₂ at Supercritical Conditions

Sheraz Ahmed^a, Jaehoon Kim^{a,b,c,*}

^aSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^bSKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

^cSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

Electrochemical carbon dioxide reduction reaction (CO₂RR) is a promising approach to mitigate CO₂ concentration and generate carbon feedstock. Although grain boundaries (GBs) have been tailored to tune the binding energies of reaction intermediates and consequently accelerate the CO₂RR, it is challenging to exclusively clarify the correlation between GBs and enhanced reactivity in nanostructured materials with small dimensions (<10 nm). In this study, we design nitrogen-doped cobalt oxide nanoparticles (N/CoO_x-NPs) having GBs exposed to the surface, which are effective in overcoming the reaction barrier to improve the kinetics and FE. Furthermore, the competent HER and mass transfer limitations have been improved under supercritical CO₂ conditions. Herein, the effect of supercritical conditions on N/CoO_x-NPs was studied, which increased the CO₂RR activity significantly in H-type cells and maintained the selectivity of ethanol at low overpotential. The impact of nitrogen dopant at higher pressure, activation mechanism, and formation of ethanol from CO₂RR are elucidated by experimental studies. Various parameters were compared through comprehensive analyses, including GG-TOF/MS, HPLC analysis, HR-TEM, and X-ray absorption spectroscopy. These results highlight the potential of controlled particle size in directing electrochemical reaction selectivity and the design of highly optimized catalytic materials. The results of this study provide novel insights and open promising opportunities for the advancement of CO₂RR.

Electrochemical Reduction of CO₂ to CO in Zero Gap Electrolyzer at High Pressure

Muhammad Shakir Hussain^a, Jaehoon Kim^{a,b,c*}

^aDepartment of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^bSKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

^cSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

Electrochemical conversion of CO₂ offers a promising approach to utilize CO₂ and simultaneously store excess renewable energy. Electrochemical conversion of CO₂ to CO requires high energy efficiency to minimize electrical input. To be economically feasible, the CO₂ electrolyzer needs high product selectivity and low hydrogen evolution reaction at low cell voltages with corresponding industrial level current density. Herein, zero-gap membrane electrode assembly (MEA) electrolyzer using pristine silver nano particles (< 150 nm) catalyst for Carbon dioxide conversion to CO is reported. Significant improvements in CO selectivity and cell energy efficiency are demonstrated with the pressure increment up to 15 bar maximum. High alkaline environments (2 M KOH) enhance the kinetics with reduced ohmic losses across the membrane. The combination of high pressure with alkaline conditions resulted in 350 mA cm⁻² current density at -2.33 V (IR-compensated) with more than 40% CO energy efficiency. Furthermore, the high-pressure CO₂ reduction reduces the hydrogen generation due to abundance of CO₂ presence on catalyst surface and thus enhancing CO selectivity. This study reports industrial level current density at the lowest applied potential so far.

Electrochemical Property of Nanoporous Au Electrode in Hydrothermal CO₂ Reduction Reaction (CO₂RR) System

Takaaki Tomai^{a,b,*}, Kazuyuki Iwase^b, Ryusei Takayanagi^b

^aFrontier Research Institute for Interdisciplinary Sciences (FRIS), Tohoku University, Sendai, Japan

^bInstitute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai, Japan

*Corresponding author: takaaki.tomai.e6@tohoku.ac.jp

Electrochemical CO₂ reduction reaction (CO₂RR) has attracted attention as a key reaction that can convert CO₂ into valuable chemical products using renewable electricity. However, high overvoltage derived from the slow reaction rate has prevented its social implementation.

We propose using hydrothermal conditions to address the challenges of CO₂RR. Practically, most industrial electrolysis system, such as water electrolysis, are operated at elevated temperatures (R.T. < T < 100 °C) to enhance the reaction rate. Although the decrease in CO₂ solubility in water at higher temperatures negatively impacts the selectivity of CO₂RR, we found it can be compensated for by pressurizing CO₂ and the energy-efficient CO₂RR can be performed by applying hydrothermal condition [1].

Moreover, the enhanced mass transfer of CO₂ due to high solubility and high diffusivity in hydrothermal condition facilitates the effective use of the nanoporous electrode in CO₂RR. Nanoporous electrode is a promising strategy to improve the reaction rate due to its high specific surface area. However, it has been reported that too small pore size of nanoporous electrode leads to insufficient diffusion of ions and formation of electrochemically inactive regions in the porous channel [2].

Our recent study revealed that by applying hydrothermal condition, the inactive regions in nanoporous structure were reduced, and the current density for CO₂RR was enhanced by decrease in the averaged pore size in nanoporous Au cathode. Changes in product selectivity associated with nanoporous structure will also be discussed on Supergreen 2024.

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Effect Of Reduction Temperature on the Interaction of Cobalt-Manganese Bimetal and its Impact on CO₂ Conversion for Long-Chain Hydrocarbon

Heuntae Jo^a, Jaehoon Kim^{a,b,c,*}

^aSchool of Mechanical Engineering, Sungkyunkwan University

2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 16419, Republic of Korea

^bSchool of Mechanical Engineering, Sungkyunkwan University

2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 16419, Republic of Korea

^cSchool of Chemical Engineering, Sungkyunkwan University

2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 16419, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

This study reveals the effect of reduction temperature on the CO₂ direct hydrogenation to long-chain hydrocarbon using a cobalt-manganese (Co-Mn) bimetallic catalyst. The catalyst first converts the CO₂ to CO by reverse water-gas shift reaction (RWGS) and further converts it to C₂₊ hydrocarbons by the Fischer-Tropsch (FT) mechanism. As the reduction temperature increased, C₅₊ long-chain hydrocarbon yield significantly decreased due to the segregation between cobalt and manganese with increasing reduction temperature. In the end, the highest reduction temperature (600 °C) entirely reduced the bimetal catalyst, and cobalt and manganese were segregated. In this case, the product is predominantly changed to methane, reducing the overall CO₂ conversion efficiency. Our findings indicate that Co-Mn interaction significantly impacts the CO₂ conversion to long-chain hydrocarbon, and controlling the reduction temperature is essential for CO₂ utilization.

Application of Simulated Moving Bed to the Separation of Enantiomers: A Comparison of Liquid Solvent and Supercritical Fluid Eluents

Xiaoqing Bao, Ming-Tsai Liang*

JOPE Technology Co., Ltd., Yanchao Dist., Kaohsiung City, TAIWAN

*Corresponding author: mtliang@jope-smb.com

In this study, an enantioseparation was investigated by using simulated moving bed (SMB) with liquid methanol, abbreviated as LQ-SMB, and with supercritical fluid, abbreviated as SF-SMB. The effects of operating parameters, such as temperature, pressure, and the weight percent of methanol in supercritical fluid were evaluated by single column chromatography. Langmuir adsorption isotherm and van Deemter equations for the enantiomers were also investigated. For liquid methanol, it was found the relative retention is about 2.2. For supercritical fluid, it was found that the relative retention decreased from 1.59 to 1.21 as the weight percent of methanol increased from 5 wt% to 30 wt%. Consequently, the operating conditions of 120 bar, 40 °C, and 15 wt% methanol in supercritical fluid were used for the SF-SMB. Both LQ-SMB and SF-SMB were conducted in the same SMB, which is equipped with eight columns, three HPLC pumps for methanol, three HPLC pumps with Coriolis mass flow meter for carbon dioxide, and two UV detectors at the ports of raffinate and extract. A closed loop design with four sections of SMB was used for LQ-SMB, and an open loop design with three sections was used for SF-SMB. The experimental results showed that LQ-SMB and SF-SMB can achieve complete separation, yielding extract and raffinate streams of nearly 100% purity and recovery. In this presentation, a comparison of KKD and solvent usage between LQ-SMB and SF-SMB will also be discussed. It was also observed that the UV absorption intensities at the outlet ports exhibited periodic repetition, and this will help to develop automatic process control based on real-time UV monitoring in the future.

Comparative Study of the Chemical Properties and Bioactive Potential of Subcritical Water Extracts from Different Parts of *Undaria pinnatifida*

Jin-Seok Park, Ji-Min Han, Sang-Min Lee, Sin-Won Park,
Jang-Woo Kim, Min-Seok Choi, Byung-Soo*

Department of Food Science and Technology, Pukyong National University,
45 Yongso-Ro, Nam-Gu, Busan 48513, Republic of Korea

*Corresponding author: bschun@pknu.ac.kr

This study evaluates the bioactive potential of *Undaria pinnatifida* (wakame) using subcritical water extraction (SWE) across different parts of the seaweed, including the blade, sporophyll, and root. The extracts were analyzed for their chemical composition and biological activities to explore their application in functional foods, pharmaceuticals, and cosmetics. The root extract exhibited the highest phenolic (43.32 ± 0.19 mg/g) and flavonoid (31.54 ± 1.63 mg/g) content, correlating with superior antioxidant activity, with IC_{50} value of 1.51 ± 0.12 mg/mL (DPPH), 3.31 ± 0.24 mg/mL (ABTS⁺), 2.23 ± 0.13 mg/mL (FRAP) and α -glucosidase inhibitory activities, with IC_{50} value of 5.07 ± 0.45 mg/mL. In contrast, the blade extract demonstrated significant antihypertensive potential (IC_{50} of 0.62 ± 0.01 mg/mL), while the sporophyll extract was rich in polysaccharides, especially fucose (41.99%) and sulfate (7.76%), highlighting its potential in industrial and biomedical applications. The findings demonstrate the selective utility of SWE for maximizing bioactive compound recovery, suggesting a novel approach for enhancing the value of marine biomass waste. This research underscores the potential of *U. pinnatifida* as a versatile resource for developing health-promoting products, addressing growing demand in sustainable industries.

Recovery of Valuable Bioactive Compounds from Wet Mandarin Pomace using Liquid Dimethyl Ether

Aye Aye Myint^{a,b}, Sabrina Wulandari^a, Ruqian Cao^b, Jongho Choi^b, Jeong Jaeryeong^c,
Jaehoon Kim^{a,b,c*}

^aSchool of Chemical Engineering, Sungkyunkwan University, Suwon, South Korea

^bSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, South Korea

^cSKKU Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon, South Korea

*Corresponding author: jaehoonkim@skku.edu

Efficient and eco-friendly “green” strategy to recover value-added products from agri-food industrial wastes towards a circular and sustainable bioeconomy is crucial to minimize their serious environmental impacts. Mandarin (*Citrus unshiu*) is the most cultivated in Northern Jeju Island, South Korea, and a popular *Citrus* fruit worldwide thanks to its ease of peeling by hand, seedlessness, sweet flavor, and high nutritional value. During industrial processing, a vast amount of mandarin pomace (MPM) is generated as a main by-product that accounts for >50% of the total fruit weight. Notably, MPM presents abundant bioactive molecules including phenolic compounds, flavonoids, carotenoids, vitamins, fragments, and essential oils (terpenes/terpenoids), and hence exhibits beneficial physiological functions in the human body such as antioxidant, anti-inflammatory, anti-cancer and neuroprotective. Therefore, in this study, a green solvent “liquified dimethyl ether (*L*-DME)” was employed for recovering the valuable bioactive chemicals directly from the wet MPM without involving high-energy-intensive and costly processes of drying and solvent separation from the extracted substances and residual solids. Response surface methodology was applied to evaluate optimal *L*-DME extraction conditions such as temperature, pressure, retention time, and flow rate of *L*-DME for achieving high extraction efficiency and recovery of the high-value-added bioactive compounds. The *L*-DME extract obtained at an optimized conditions (45 °C/ 4 MPa/ 120 min/ 20 mL min⁻¹) possessed relatively higher total phenolics (3.1–1.3 folds), total flavonoids (1.6–1.5 folds), antioxidant activities (1.2–2.2 folds) as compared to these of Soxhlet extracts using *n*-hexane and ethanol as solvents for 4 h extraction of freeze-dried MPM. Beneficially, the *L*-DME extract has noticeably high levels of bioactive phenolic flavonoids such as hesperetin, naringenin, narirutin, hesperidin, quercetin, nobiletin, and tangeretin, which can find its potential applications in nutraceutical, pharmaceutical and cosmeceutical industries.

Co-production of Bio-crude, Bioactive Extract, and Bio-solid Fuel from Wet Spent Coffee Grounds using Liquefied Dimethyl Ether

Ruqian Cao^a, Aye Aye Myint^{a,b}, Jaehoon Kim^{a,b,c,*}

^aSchool of Mechanical Engineering, Sungkyunkwan University

2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong gi-Do 16419, Republic of Korea

^bSchool of Chemical Engineering, Sungkyunkwan University

2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong gi-Do 16419, Republic of Korea

^cSKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University

2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong gi-Do 16419, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

Spent coffee grounds (SCG) are the waste grinds remaining after the brewing process of coffee beans. SCG is rich in lipids, sugars, antioxidants, and other valuable compounds, making it a potential resource of energy and functional food. This study introduces a low-energy consumption and environmentally friendly technique for extracting lipids, bioactive compounds, and moisture from wet SCG using liquefied dimethyl ether (l-DME). The l-DME extraction processes were performed under various operating conditions, including temperature, pressure, and time, to optimize bio-crude yield, dewatering rate, and recovery of bioactive compounds. Furthermore, the chemical compositions and molecular weights of the original wet SCG, dry SCG powder, dewatered bio-solids, extracted bio-crude and removed water were studied. The results were then compared with those obtained from conventional Soxhlet extraction with hexane.

Elimination of Impurities from Cotton Textiles using Compressed Liquid CO₂ Combined with Co-Solvents

Jaeryeong Jeong^a, Aye Aye Myint^b, Jaehoon Kim^{a,b,c,*}

^aSKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

^bSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^cSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

Dry cleaning is an essential process for removing organic contaminants, such as sebum and cooking oil, from textiles and clothing using solvents other than water. Traditionally, perchloroethylene (PER) has been the most commonly used solvent due to its effectiveness and non-flammability. However, PER poses significant environmental and health risks, being classified as a Class 2A carcinogen and a persistent pollutant. As a safer and more sustainable alternative, liquid carbon dioxide (L-CO₂) has gained attention due to its non-toxic, non-flammable, and environmentally friendly properties. This study explores the optimization of the L-CO₂ cleaning process, with a focus on selecting the appropriate co-solvent and evaluating its efficacy at different temperatures and flow rates. The use of isopropanol (IPA) and water as co-solvents significantly enhanced cleaning performance, particularly in the removal of water-soluble contaminants. The analysis revealed that L-CO₂ effectively eliminated fat-soluble substances, including sterols, fatty acids, and alkenes, without causing damage to fabric fibers. However, potential recontamination during cleaning remains a concern, highlighting the need for further research.

Simultaneous Material and Chemical Recycling of Waste PET/PE Multi-Layer Films under Hydrothermal Conditions

Qingxin Zheng^{a,*}, Yoshiki Suga^b, Masaru Watanabe^{a,*}

^a Research Center of Supercritical Fluid Technology, Department of Chemical Engineering,
Graduate School of Engineering, Tohoku University, Japan

^b Department of Chemical Engineering, Graduate School of Engineering, Tohoku University

*Corresponding author: qingxin.zheng.a2@tohoku.ac.jp; masaru.watanabe.e2@tohoku.ac.jp

The overuse and improper disposal of plastics have led to a severe environmental problem with a global concern [1]. Plastic waste clogs landfills and oceans, harms wildlife, and poses a threat to human health. Compared to incineration and landfilling, recycling is an environmentally friendly approach to managing plastic waste and mitigating its negative impact [2]. Among current recycling methods, material and chemical recycling processes targeting regenerated polymers and depolymerized monomers can shorten the route from plastic waste to plastic products, in line with the needs for a green circular economy [3].

Multi-layer plastic films have a wide range of applications, in which PET/PE (PET: Polyethylene terephthalate; PE: Polyethylene) films possess a market share of more than 50%. The recycling of PET/PE films is vital in mitigating the environmental impact of plastic waste and achieving the global goal of reducing plastic packaging. However, because of complex composition, it is challenging to recycle PET/PE films through traditional methods.

In this study, we proposed a new hydrothermal process for recycling PET/PE films using a semi-batch system equipped with two filters [4]. PE plastic and PET monomers including terephthalic acid (TPA) and ethylene glycol (EG) were collected separately, indicating the simultaneous material and chemical recycling of PET/PE films was firstly achieved. The effects of parameters were investigated, and mechanism and kinetic studies were conducted. This research opened up a new and sustainable pathway to recycle multi-layer plastic films in both lab and industry.

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Revolutionizing Alkali-Ion Batteries with 2D Ultrathin A_2FeSiO_4 Nanosheets

Lalit Kumar Singh^a, Jaehoon Kim^{a,b,c,*}

^aSKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon, Republic of Korea

^bSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^cSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

The scarcity and rising costs of lithium resources have spurred interest in alternative rechargeable batteries utilizing more earth-abundant elements, such as sodium and potassium, for grid-scale energy storage. However, the larger ionic radii of Na^+ and K^+ ions pose significant challenges in developing universal host materials that can accommodate these alkali metal ions while maintaining structural stability. This study explores the potential of A_2FeSiO_4 (AFS) ($A = Li, Na, K$) as a promising cathode material for sodium-ion batteries (SIBs) and potassium-ion batteries (KIBs) due to its low cost, non-toxicity, and abundant Fe resources. A facile solvothermal technique was employed to fabricate ultrathin 2D AFS nanosheets, which were subsequently exfoliated using oxalic acid to enhance their electrochemical performance. The resulting nanosheets exhibited specific discharge capacities of 149 mAh g^{-1} for Li^+ , 99 mAh g^{-1} for Na^+ , and 88 mAh g^{-1} for K^+ at a current density of 100 mA g^{-1} . Additionally, the nanosheets demonstrated excellent capacity retention, with rates of 75% for Li^+ , 99% for Na^+ , and 65% for K^+ after 100 charge/discharge cycles. This study highlights the efficacy of 2D nanosheets in stabilizing silicate-based cathode materials against structural and volume changes, thus improving their electrochemical performance in SIBs and KIBs, and underscores their potential as viable alternatives for sustainable energy storage solutions.

Conversion of Soybean Oil to Bio-Oils with Hydrothermal Reaction

Jongho Choi^a, Aye Aye Myint^b, Jaehoon Kim^{a,b,c,*}

^aSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^bSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^cSKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

This study aimed to decompose the triglycerides in soybean oil into ranges of biofuel hydrocarbons using a sub-/supercritical water reaction without the use of any catalysts, on the degree of decarboxylation in soybean oil. Decarboxylation plays a significant role in the process of transforming soybean oils into biofuels, eliminating oxygen content. To find optimal conditions, the reactions were carried out in a batch reactor under various conditions, temperatures of 380–440 °C, pressures of 2.5–22.5 MPa, soybean oil-to-water ratios of 1:1–6:1, and reaction times of 10–30 min. Various parameters were compared through comprehensive analyses, including GGXGC-TOF/MS, elementary analysis, simulated distillation, and total acid value. The optimum conditions were determined to be at 420 °C, an autogenous pressure of 4.5 MPa, a 6:1 ratio of soybean oil to water, and a reaction time of 10 min. Despite not using a catalyst, the oxygen contents were removed up to 5.1 wt% from 11.6 wt% and the selectivity of gasoline, jet fuel, and diesel was 26.4, 61.7, and 90.3%. The results of this study not only present novel challenges, but also open up promising avenues for the advancement of commercial biofuels.

Enhancing Dispersibility and Stability in ZrO₂ Colloidal with Yttria Doping and Crystalline Phase

Hee-Seon Lee, Kyuyoung Heo*

Reliability Assessment Center, Korea Research Institute of Chemical Technology,
Daejeon 34114, Republic of Korea

*Corresponding author: kheo@kriict.re.kr

The dispersibility and stability of colloids are essential for enhancing functional properties such as visibility, refractive index, and reactivity in display applications. Despite the wide use of zirconia (ZrO₂) nanoparticles (NPs) in optical fields, their tendency to aggregate poses challenges. This study explores how the crystalline structure of ZrO₂ NPs and yttrium doping influence dispersion stability. ZrO₂ NPs were synthesized in tetragonal (T-ZrO₂) and amorphous (Am-ZrO₂) forms, and surface modification was performed using TMSPM, a silane coupling agent. As a result, the TMSPM–T–ZrO₂ NPs demonstrated exceptional stability, maintaining dispersion for up to a year, while the TMSPM–Am–ZrO₂ still showed agglomeration. Moreover, to further enhance dispersion, yttrium-doped ZrO₂ NPs were examined, and it was found that the acetate precursor (A-3YSZ) offered superior dispersibility compared to the ZrO₂ NPs due to its electrostatic repulsion. This indicates significant potential for improving the refractive index in optical coatings, suggesting promising applications in the field of optical coating solutions.

Bismuth/Zinc Oxide Composite as a New Anode Material for Li Storage

Anith Dzhanxinah Mohd Sarofil^a, Jaehoon Kim^{a,b,c,*}

^aSKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

^bSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^bSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

The development of Bismuth (Bi) alloy-based anode nanomaterials is a promising strategy to address the severe volume variation of Bi alloys during cycling and enhance the overall electrochemical performance for next generation Li-ion batteries (LIBs). However, conventional fabrication methods are often complex and fail to consider the tap density of the material, which is crucial for maintaining the high volumetric capacity of Bi (3765 mAh cm⁻³). In this study, we introduce a hierarchical micro-nano structured Bi/ZnO composite, leveraging ZnO, a conversion-based material, that not only improves the low specific capacity of Bi (385 mAh g⁻¹) but also allows for high nanomaterial density (1.94 g cm⁻³). The composite's unique architecture, featuring nano-sized particles intimately positioned and encapsulated within a thin carbon layer with heterointerfaces, helps cushion localized mechanical stress and promotes rapid ion/charge transfer. The Bi/ZnO composite electrode exhibited a high gravimetric capacity of 797 mAh g⁻¹, corresponding to a remarkable volumetric capacity of 1546 mAh cm⁻³ after 180 cycles at 0.1 A g⁻¹, along with excellent long-term cyclability, achieving 379 mAh g⁻¹ at 1.0 A g⁻¹ after 1000 cycles. Comprehensive kinetic analyses, ex situ microscopic techniques, and DFT simulations reveal that the enhanced electrochemical performance stems from improved reaction kinetics, reduced volume changes, reinforced structural stability, and increased Li⁺-ion adsorption capability. This work not only showcases the exceptional Li storage performance of the Bi/ZnO composite but also provides valuable insights for the future development of high-energy Bi-based anode materials.

Green Preparation of Biodegradable Polyester Foams with Supercritical Fluid

Dongdong HU*, Ling ZHAO*

State Key Laboratory of Chemical Engineering, East China University of Science and Technology,
Shanghai 200237, China

*Corresponding author: hudd@ecust.edu.cn, zhaoling@ecust.edu.cn

The preparation of low-density biodegradable polyester foams with uniform fine cell morphology and dimensional stability is very challenging. The foaming behavior of biodegradable polyesters with different chain structures and different blends was investigated by using supercritical fluid as the blowing agent. The interactions between biodegradable polyesters and CO₂, as well as the rheological properties of biodegradable polyesters, were explored. The effect of chain expansion and blending modification on foaming process was carefully studied. Then the key influence factors on cell morphology and shrinkage performance of foamed biodegradable polyesters were analyzed. Based on insights into the interaction between polymer and supercritical fluid, we carried out a series of explorations on suitable raw materials and additives. Introducing a suitable aromatic content obtained higher strength to improve the cell stability on the premise that the strong degradability can be maintained, which provides an effective strategy to prepare PBAT and PBST foams with good degradability and favorable mechanical properties. Combines the advantages of tunable molecular structure of in-situ copolymerization with the high efficiency of melt blending, it also provides an effective strategy for the preparation of biodegradable functionalized foams. These findings can serve as valuable insights for the large-scale production of lightweight biodegradable foams.

High-power Organic Redox Supercapacitors with Reduced Interfacial Resistance Effect by Supercritical CO₂ Impregnation

Yuta Nakayasu^{a,b,*}, Shu Sokabe^b, Chie Ooka^b, Tomoya Yamada^b,
Naoka Nagamura^c, Masaru Watanabe^b

^aFrontier Research Institute for Interdisciplinary Sciences, Tohoku University, Sendai, Japan

^bGraduate School of Engineering, Tohoku University, Sendai, Japan

^cNational Institute for Materials Science, Tsukuba, Japan

*Corresponding author: nakayasu@tohoku.ac.jp

As the demand for energy storage rapidly expands, our research group is developing organic redox supercapacitors using activated carbon (AC) impregnated with quinones, aimed at fast-charging and environmentally sustainable energy storage. Using supercritical carbon dioxide (sc-CO₂) to impregnate the cathode material chloranil (CHL) [1], we achieved increased loading and enhanced specific capacity compared to conventional liquid impregnation methods [2]. Additionally, the rate performance significantly improved, indicating distinct differences in quinone adsorption between the methods.

In this study, we further utilized sc-CO₂ to impregnate 1,5-dichloroanthraquinone (DCAQ), the anode active material with an entrainer, into AC and evaluated its electrochemical properties. Impregnation states on the AC surface were analyzed using Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy.

Cathodes and anodes produced via sc-CO₂ impregnation exhibited a 37% and 83% increase in specific capacity, respectively. Full-cell measurements showed an energy density of 21 Wh/kg, a 1.4-fold improvement over previous studies [2]. Durability tests over 1000 cycles demonstrated a 95% retention rate, indicating superior long-term stability.

The C K-edge NEXAFS spectra revealed that the transition peak to the 1s→π* orbital for CHL and DCAQ was observed at a higher energy in sc-CO₂-impregnated samples, suggesting stronger interactions with AC. This shift, indicating an increase in π-bond components and effective oxidation state, is believed to contribute to the enhanced electrochemical performance of the sc-CO₂ impregnated electrodes by decreasing interfacial resistance.

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The High Carbon Silicon Oxycarbide (HC-SiOC) Encapsulated Porous Silicon (PSi) Particles for Lithium-Ion Batteries (LiBs) Anode Materials

Dongho Nam^a, Jaehoon Kim^{a,b,c,*}

^aSKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon, Republic of Korea

^bSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^cSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

The lithium-ion batteries (LiBs) are one of the practical energy storage materials due to its high power and durability. However, graphite, which has been used as a basic anode material, has relatively lower capacity (372 mAh g⁻¹) and is hard to satisfy increasing energy demand. To improve energy density of LiBs, silicon (Si) could be excellent substitute because of its high capacity (3579 mAh g⁻¹), low operating voltage (< 0.2 V), and natural abundance. Despite variable advantages, enormous volume expansion (< 300%) during lithiation caused continuous capacity fading, impeding stable LiBs lithiation and delithiation. For decades, numerous coating materials were recommended to buffer volume expansion of Si, and achieved enhanced stability compared to bare Si particles. Nevertheless, accommodation of volume expansion during cycling has been challengeable due to instability during cycling. Herein, high carbon silicon oxycarbide (HC-SiOC) is recommended for coating material. The HC-SiOC synthesized using silicone oil (Si Oil) and divinyl benzene (DVB) exhibited enhanced electrical conductivity and stability compared to SiOC using Si Oil without DVB. Therefore, HC-SiOC could cover mechanical strength caused by volume expansion. These porous silicon (PSi) particles coated with HC-SiOC (PSi@HC-SiOC) proved enhanced electrochemical properties compared to bare PSi particles in LiBs. Furthermore, PSi@HC-SiOC blended with graphite for practical use and maintained capacity (536 mAh g⁻¹) at 200 cycles and 70% of initial capacity (108 mAh g⁻¹) in full cell at 50 cycles within NCM 523 cathode material.

Preparation and Structure Regulation of Microcellular Foams and Devices with Low Dielectric Properties

Yichong Chen*, Jiabao Yu, Wenyu Zhong, Dongdong Hu, Ling Zhao

State Key Laboratory of Chemical Engineering, East China University of Science and Technology,
Shanghai 200237, China

*Corresponding author: chenyc@ecust.edu.cn

High-frequency and high-speed communications impose stringent requirements on low-dielectric materials with exceptional comprehensive properties. The development of low dielectric materials holds significant value in reducing interconnect delay, power consumption, and crosstalk in high-frequency communication. While, the low dielectric loss lens antenna with signal gain effect is also a device that needs to be developed urgently for the next generation of communication technology.

In this work, polyphenylene oxide (PPO), were chosen as the base material. Modified polymers with a long-chain branched structure were prepared using the multi-epoxy modifier ADR-4468. Consequently, a series of microcellular modified foams with high expansion ratio (from 10.18 to 14.12), small average cell size (from 31.00 μm to 13.43 μm), and large cell density (from 5.78×10^7 cell/ cm^3 to 7.33×10^8 cell/ cm^3) exhibiting low dielectric properties (with a dielectric constant as minimal as 1.09 and a dielectric dissipation factor as low as 0.0006) were prepared using supercritical CO_2 foaming.

Concurrently, the dielectric properties of microcellular foams were examined at 10 GHz, revealing that the foam's dielectric properties were minimally impacted by the properties of the raw materials. Based on water absorption analysis, an improved equation for calculating the dielectric dissipation factor was proposed, comprehensively analyzing the influencing factors on the foam's dielectric dissipation factor, which shows that water absorption significantly affects the foam's dielectric dissipation factor, and under high expansion ratios, water absorption's impact on the dielectric dissipation factor exceeds that of air introduction.

Finally, based on the above material, a lens antenna with dielectric constant gradient distribution was prepared through a supercritical fluid gradient foaming process. At a frequency of 40 GHz, only a 15mm lens antenna can increase the signal strength by about 7 dBi. These microcellular foams and devices hold promise for wide applications in the realm of high-frequency and high-speed communications.

Superior Oxygen Storage Capacity of Mn-CeO₂ Nanoparticles in a Non-Equilibrium State

Chunli Han^{a,*}, Akira Yoko^{a,b}, Tadafumi Adschiri^{a,c}

^aWPI-Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Sendai, Japan

^bInternational Center for Synchrotron Radiation Innovation Smart, Tohoku University, Sendai, Japan

^c New Industry Creation Hatchery Center, Tohoku University, Sendai, Japan

*Corresponding author: han.chunli.a6@tohoku.ac.jp

Oxygen carriers are crucial for energy conversion and storage processes, where their performance is highly dependent on precise control of composition and local structure. Continuous-flow hydrothermal synthesis offers distinct advantages in this regard due to its excellent heat and mass transfer capabilities, which enable fast initiation and quenching of particle formation process and allow the capture of nanoparticles in non-equilibrium states. On this basis, we revealed the dynamic doping behavior of Mn in CeO₂ nanoparticles from both kinetic and thermodynamic perspectives. We also explored the relationship between the particle microstructure and oxygen storage capacity (OSC) of Mn-CeO₂ nanoparticles, as well as the activation mechanism of the Mn dopant for low- (<300 °C) and high-temperature (≥300 °C) OSC. The flow supercritical hydrothermal technique shows great potential for the controllable synthesis and large-scale production of low-temperature oxygen carriers for energy conversion applications.

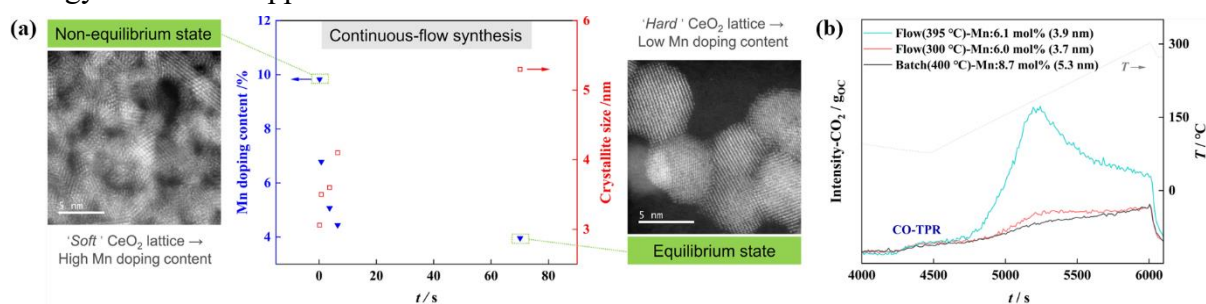


Fig. 1. (a) Non-equilibrium Mn doping to CeO₂ nanoparticles in continuous-flow hydrothermal synthesis. (b) Superior oxygen migration ability of Mn-CeO₂ oxygen carrier synthesized under flow supercritical condition.

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Direct Conversion of Biomass to Sustainable Aviation Fuel Components over ZrO₂-Doped Cu-Pd Alloy Catalyst in Sub- and Supercritical Methanol

Deepak Verma^{a,b}, Jaehoon Kim^{a,b,c,*}

^aSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^bSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^cSKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

The direct conversion of cellulose into specific chemicals is challenging because of its resistant structure and high oxygen content. In this study, we present a strategy for selectively producing 2,5-dimethylfuran (2,5-DMF) and 2,5-hexadione (2,5-HDN) directly from cellulose, achieving yields of 33.8% and 17.2%, respectively. This was accomplished using multifunctional heterogeneous ZrO₂-doped bimetallic Cu–Pd nanoparticles supported on an HY(5.1) catalyst (CuPdZr/Y) under supercritical methanol (scMeOH) conditions. The catalyst's acidic and metallic sites facilitated a series of cascade reactions, including solvolysis, dehydration, hydrogenation (HD), and hydrogenolysis (HDO). Preferential adsorption of reaction intermediates on oxygen vacancy sites of ZrO_x, located near the metallic sites, enhanced both HD and HDO. H–D exchange experiments showed that the hydroxyl hydrogens of methanol acted as active hydrogen atoms involved in HD and HDO. After three runs, the yields of 2,5-DMF and 2,5-HDN only slightly declined, demonstrating that CuPdZr/Y remained highly stable under scMeOH conditions.

Direct Conversion of Succinic Acid to 1,4-butanediol over Rhenium-Promoter-free Ruthenium–Zirconia Catalyst in Water

Neha Karanwal^{a,b}, Jaehoon Kim^{a,b,c,*}

^aSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^bSKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

^cSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

The direct conversion of succinic acid to 1,4-butanediol (1,4-BDO) in water was investigated using Ru deposited on oxygen-vacant zirconia (Ru–O_vZrO_x) as the catalyst. 1,4-BDO was produced in high yield (89.5%) and space–time yield (0.19 h⁻¹) at 200 °C. Ultrasmall Ru⁰ nanoparticles were deposited on the O_vZrO_x surface, and certain Ru species were incorporated into the ZrO_x domain by forming a Ru_xZr_yO_z solid solution. The proximity of Ru to O_vZrO_x stabilized the nanosized Ru⁰ particles, enabled hydrogen spillover, increased the acidity of the catalyst, and achieved intermediate adsorption. The Zr^{δ+} center (2 ≤ δ < 4)—which featured abundant Lewis acid sites and was adjacent to the O_v sites—activated the γ -butyrolactone ring-opening reaction via a route involving 2-hydroxytetrahydrofuran formation. The electron-rich Ru⁰ center facilitated heterolytic hydrogen dissociation, and the dissociated H⁻ and H⁺ ions traveled to the Zr^{δ+} sites and water molecules via hydrogen-shuttling mechanism. Moreover, the weakly bonded hydrogen actively participated in the hydrodeoxygenation and hydrogenation of intermediates to 1,4-BDO. Notably, the SA conversion and 1,4-BDO yield achieved after the four subsequent runs using the reactivated catalyst were almost similar to those of the fresh catalyst, thereby establishing the high stability and reusability of the catalyst.

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Facet Dependent Pt Adsorption on Rutile TiO₂ Surface for Efficient Photocatalytic VOCs Removal

Ardiansyah Taufik^{a,*}, Akira Yoko^{a,b}, Chunli Han^a, Wahyudiono^c,
Satoshi Ohara^c, Tadafumi Adschiri^{a,c,*}

^aWPI – Advanced Institute for Materials Research (WPI-AIMR), Tohoku University,
2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan

^bInternational Center for Synchrotron Radiation Innovation Smart (SRIS), Tohoku University,
Aramaki Aza-Aoba, Aoba-ku, Sendai, 980-8572, Japan

^cNew Industry Creation Hatchery Center, Tohoku University, Sendai 980-8579, Japan

*Corresponding author: ardiansyah.taufik.d2@tohoku.ac.jp, tadafumi.ajiri.b1@tohoku.ac.jp

Removing volatile organic compounds (VOCs) from the environment via photocatalytic reactions is highly effective for achieving clean air. While Pt deposition on TiO₂ surfaces is recognized as a viable catalytic method, understanding Pt interaction, dispersion, and facet optimization remains incomplete, leading to suboptimal performance and cost inefficiencies. This study investigates Pt adsorption on rutile TiO₂ surfaces, focusing on the (101) and (110) facets. It reveals that Pt attachment is strongly influenced by surface facet and Pt ion type. The (101) facet exhibits superior adsorption for Pt ions, such as Pt(OH)₂ and PtCl₅⁻, due to its higher surface energy which leads to higher adsorption energy for chemical adsorption of Pt species. Higher adsorption of Pt(OH)₂ than PtCl₅⁻ is attributed to stronger hydrogen bonding with the (101) surface. The photocatalytic result revealed that the higher Pt density on the (101) surface exhibits higher photocatalytic reaction for toluene degradation. Moreover, the high crystallinity of TiO₂ leads to further improve electron mobility which improve the electron transfer to Pt species and drastically improve toluene degradation per unit area with 9.2 times higher performance than Pt adsorb on lowest crystallinity sample. These findings suggest the control of facet orientation of TiO₂ and structure optimization is important for optimizing Pt deposition, which will benefit future photocatalytic research and development.

Volatile Organic Compounds (VOCs) Removal from Polypropylene (PP) Waste using Supercritical CO₂

Sabrina Wulandari^a, Jongho Choi^b, DaeSung Jung^c, Aye Aye Myint^{a,b}, Jaehoon Kim^{a,b,d,*}

^aSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^bSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^cSustainable Materials Research Team, Hyundai Motor Group, Uiwang, Republic of Korea

^dSKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

Waste polypropylene (PP) pellets originated from car bumpers containing high concentrations of volatile organic compounds (VOCs). These compounds are hazardous to human health and need to be kept under certain thresholds to be reused. In this study, supercritical carbon dioxide (scCO₂) is used for VOCs removal from waste PP. The effect of process parameters including pressure, temperature, and reaction time were studied by varying its value in the range of 313–353 K, 10–25 MPa, and 1–6 h, respectively. Response surface methodology (RSM) was used to determine the optimized conditions for VOCs removal. Waste PP pellets with VOCs content lower than the allowed amount was produced after the VOCs extraction using scCO₂. Chemical, thermal, and rheological properties of the scCO₂-treated waste PP were analyzed to observe if change was induced by treatment using scCO₂.

Two Step Process for High Yield of Phenolic Monomers from Lignocellulosic Biomass in Water Methanol Mixture

Yasora Liyanage^a, Seoyeon Kim^a, Neha Karanwal^{b,c}, Jaehoon Kim^{a,b,c,*}

^aSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^bSKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon, Republic of Korea

^cSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

Lignin is emerging as a valuable feedstock that can be utilized to produce fuels and chemicals. A highly efficient 2-step approach was developed to produce aromatic monomers from the lignocellulosic biomass. Birch wood was first solvolysed in different methanol/water ratios (v/v) at a flow rate of 3 ml/min for 3h at 225 °C, 8 MPa in a flow through reactor. The product stream was depolymerized in a batch reactor at 290°C for 3h with Pd/C catalyst and 3 MPa of H₂. A methanol/water mixture of 8:2 v/v yielded a maximum degree of delignification of 96% in solvolysis with a cellulose retention of 94.7 wt% in the pulp rich solid. Monomer yield of 69.3 C% was achieved in depolymerization step. 4-n-propanol syringol was the highest selective monomer in the given optimum conditions. Development of the 2-step approach could lead insights into how the solvent affects in solvolysis and depolymerization steps separately. The spent catalysts in methanol/water (8:2, v/v), methanol and water were characterized to investigate the effect of solvent on Pd during the reaction.

Keywords: solvolysis, depolymerization, 2-step method, Lignin derived monomers, Pd/C

Different SnBi Alloy Composites via Controlling Cooling Rate for High Performance Lithium-Ion Battery Anode

Hyeon So Park^a, Winda Devina^b, Anith Dzhanxinah Mohd Sarofil^a, Jaehoon Kim^{a,b,c,*}

^aSKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University,

2066, Seobu-ro, Jangan-Gu, Suwon, Gyeonggi-Do 16419, Republic of Korea

^bSchool of Mechanical Engineering, Sungkyunkwan University,

2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeonggi-Do 16419, Republic of Korea

^cSchool of Chemical Engineering, Sungkyunkwan University,

2066 Seobu-Ro, Jangan-Gu, Suwon, Gyeonggi-Do, 16419, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

Alloy-based materials, such as tin (Sn) and bismuth (Bi), have been considered as potential anode materials for lithium-ion batteries (LIBs) due to their high theoretical volumetric capacities of 1991 and 3765 mAh cm⁻³, respectively. However, these materials tend to exhibit volume expansion upon full lithiation, such as Li_{4.4}Sn (260%) and Li₃Bi (215%), which is a critical challenge for practical implementation. To overcome this issue, the use of two metal alloys is an effective strategy to maintain the energy density and integrity of the electrode in each cycle. The different working voltages of Bi (0.78–0.69V) and Sn (0.65–0.1V) inhibit the extreme structural collapses that occur during cycling. At the initial discharge stage, the unreacted Sn phase acts as a buffer during the lithiation of Bi. Meanwhile, the Lithiated state of Bi (Li_xBi) will suppress the expansion when Sn is Lithiated with Li-ions. However, the definition and mechanism of the buffering effect between active-active metals are still unclear. Therefore, the tin-bismuth (SnBi) alloys with different phase scale are designed by controlling the cooling rate to form micro-phase alloys (SnBi_M) and nano-phase alloys (SnBi_N). The SnBi nano-phase alloy anode (BiS_{NN}) exhibits a better buffering effect and stable cyclability over 300 cycles and achieves a superior discharge capacity of 550 mAh g⁻¹ at 0.1 A g⁻¹ and 320 mAh g⁻¹ at 2 A g⁻¹.

Impact of Additional Phase in SnSb Alloy Anodes for Lithium-Ion Battery

Taewan Ko^a, Anith Dzhanxinah Mohd Sarofil^b, Hyeon Seo Park^b, Jaehoon Kim^{a,b,c,*}

^aSchool of Mechanical Engineering, Sungkyunkwan University,

2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeonggi-Do 16419, Republic of Korea

^bSKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University,

2066, Seobu-ro, Jangan-Gu, Suwon, Gyeonggi-Do 16419, Republic of Korea

^cSchool of Chemical Engineering, Sungkyunkwan University,

2066 Seobu-Ro, Jangan-Gu, Suwon, Gyeonggi-Do, 16419, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

Graphite has long been the standard anode material for Li-ion batteries, but its theoretical capacity is limited to 372 mAh g⁻¹, which presents a significant limitation. As a result, there has been growing interest in exploring alloy-based materials such as Sn, Si, Sb, and Ge for high-capacity secondary batteries, given their much higher theoretical capacities (Li_{4.4}Sn: 993 mAh g⁻¹; Li₂₂Si₅: 4200 mAh g⁻¹; Li₃Sb: 660 mAh g⁻¹; Li₂₂Ge₅: 1624 mAh g⁻¹). However, these alloy materials face a major challenge due to substantial volume expansion, which undermines their stability. In response to this issue, we propose the use of intermetallic SnSb, known for its high theoretical capacity (829 mAh g⁻¹), synthesized via planetary ball milling. While prior research has largely focused on fully alloyed SnSb compositions to improve battery performance, our study explores the impact of both fully alloyed (SnSb-FA) and partially alloyed (SnSb-PA) structures on cyclic stability. Our results show that SnSb-PA exhibits superior stability compared to SnSb-FA, with a capacity close to the theoretical capacity. This enhanced capacity was maintained over 100 charge-discharge cycles, demonstrating excellent retention even in the absence of a carbon source. The improved performance of SnSb-PA is likely due to the presence of separated phases (Sn and Sb) and the natural formation of oxidation layers. These results provide fundamental insight into the design of intermetallic alloy-based anodes for high-capacity secondary batteries.

High-Capacity, High-Rate Nanosized Bismuth-Antimony Embedded in N-doped Carbon Matrix via Facile Pyrolysis as Anodes for Advanced Li Storage

Sun Chi Rong^a, Anith Dzhaxinah Mohd Sarofil^b, Winda Devina^b, Jaehoon Kim^{a,b,c,*}

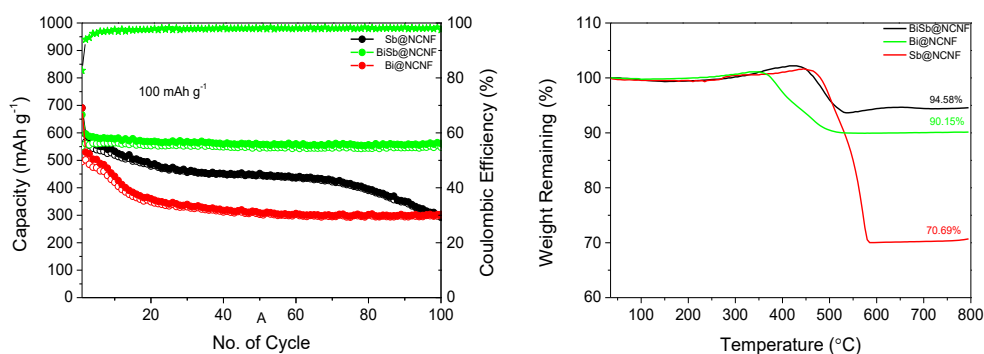
^aSchool of Mechanical Engineering, Sungkyunkwan University, 2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeonggi-Do 16419, Republic of Korea

^bSKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, 2066, Seobu-ro, Jangan-Gu, Suwon, Gyeonggi-Do 16419, Republic of Korea

^cSchool of Chemical Engineering, Sungkyunkwan University, 2066 Seobu-Ro, Jangan-Gu, Suwon, Gyeonggi-Do, 16419, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

Antimony (Sb) is an attractive anode material for lithium-ion batteries (LIBs) because of its high theoretical capacity (660 mAh g⁻¹). Nevertheless, it suffers from huge volume expansion and severe particle pulverization during lithiation/delithiation processes, which leads to poor cycling performance. Herein, to address this matter, a composite of bismuth-antimony alloy nanoparticles embedded in N-doped-carbon coating (BiSb@NC) is fabricated via a simple pyrolysis method. The design of bimetallic Bi-Sb solid solutions is possible at any molar ratio. The coupled pair, metallic Bi itself, does not only provide high volumetric capacity (3765 mAh cm⁻³) and low working potential (0.8 V hereafter vs. Li⁺/Li) but could also synergistically buffer the volume fluctuation due to the different working potentials between the two alloys. Nanosized BiSb alloys can enhance the reaction kinetics through shortened Li⁺-ion diffusion pathways. Additionally, the N-doped carbon coating also effectively cushions the volume changes of BiSb and maintains effective conductive networks during extended alloying/dealloying reactions with Li⁺ ions. As a result, the BiSb@NC anode achieves a high reversible capacity of 550 mA h g⁻¹ after 100 cycles at 100 mA g⁻¹ and superior high-rate performance of 350 and 220 mA h g⁻¹ at 2 and 5 A g⁻¹, accordingly despite its high BiSb loading (82 wt%).



Keywords: Bismuth antimony alloy; N-doped carbon; Long-Term; Solid Solution

Silicon Oxycarbide-Encapsuled Bismuth as Anodes in Lithium-Ion Batteries

Anith Dzhanxinah Mohd Sarofil^a, Jaehoon Kim^{a,b,c,*}

^aSKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

^bSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^cSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

The search for high-energy-density anode materials in lithium-ion batteries highlights bismuth (Bi) as a promising candidate due to its suitable reaction potential (~ 0.8 V) and high volumetric capacity (3765 mAh cm^{-3}). However, Bi experiences significant volume fluctuation during cycling, which constrains battery performance and limits practical application. Herein, a silicon oxycarbide (SiOC) coating is introduced onto Bi nanoparticles through a straightforward process involving the dispersion of bismuth hydroxide in silicone oil followed by calcination, aimed at improving the alloy's reversibility. The robust SiOC matrix not only mitigates mechanical stress from continuous Li⁺-ion insertion/extraction but also contributes to Li storage via a conversion mechanism, enhancing the composite's overall capacity. In half-cell testing, Bi@SiOC achieved high performance (507 mAh g^{-1} at 50 mA g^{-1} after 150 cycles), high volumetric capacity (872 mAh cm^{-3}), excellent cyclic stability (380 mAh g^{-1} at 500 mA g^{-1} after 500 cycles), and maintained cell integrity. In a full-cell configuration (Bi@SiOC||LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂), the cell demonstrated gravimetric and volumetric energy densities of 343 Wh kg^{-1} and 607 Wh L^{-1} , respectively. Comprehensive kinetic and postmortem microscopic analysis underscored the advantages of amorphous SiOC as a protective coating, effectively suppressing thick solid electrolyte interface passivation and preserving electrode integrity for prolonged reaction kinetics.

Effect of Precursor Morphology on the Electrochemical Performance of Porous Si Anodes Prepared by Magnesiothermic Reduction

Dongho Nam^a, Jaehoon Kim^{a,b,c,*}

^aSKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon, Republic of Korea

^bSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^cSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

For Si particles synthesis, the magnesiothermic reduction of SiO₂ is a practical process to prepare porous structure in the particles. This unique structure in Si enhanced electrochemical properties of Lithium-ion batteries (LiBs). However, it was unclear that the effect of SiO₂ precursor morphology in the electrochemical properties of Si after magnesiothermic reduction. Herein, porous Si (PSi) particles were synthesized from various morphologies of SiO₂ precursors within different diameters and porous structures. The spherical SiO₂ particles with different diameters of 300 nm (denoted SiO₂-0.3) and 20 μm (denoted SiO₂-20), fumed SiO₂ powder (denoted SiO₂-F), and hyper meso-porous structure SiO₂ particles KIT 6 (denoted SiO₂-K). The PSi particles exhibited polycrystalline phase following magnesiothermic reduction and acid leaching process. Consequently, PSi from SiO₂-0.3 maintained its original morphology from SiO₂ precursors within well-defined porous structures, whereas other PSi particles from three precursors except SiO₂-0.3. Among the four different PSi particles, those synthesized from SiO₂-0.3 exhibited the highest reversible capacity (1427 mAh g⁻¹ at 0.1 A g⁻¹) after 50 cycles. The enhanced electrochemical properties of PSi from SiO₂-0.3 came from the well-defined porous structure in the particles to accommodate volume expansion of Si, suppressing the thickness expansion below 140 %. Furthermore, the stability of PSi synthesized from SiO₂-0.3 was enhanced compared to three other PSi particles synthesized from SiO₂ except SiO₂-0.3.

Thermocatalytic CO₂ Conversion into Carboxylic Acid under High Pressure Conditions

Jiyeon Lee^a, Wonjoong Yoon^a, Jaehoon Kim^{a,b,c,*}

^aSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Korea

^bSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Korea

^cSKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Korea

*Corresponding author: jaehoonkim@skku.edu

For decades, substantial efforts have been directed toward reducing carbon dioxide (CO₂), a key greenhouse gas, in the atmosphere. One effective approach is converting CO₂ into valuable fuels rather than releasing it into the air. For instance, research has been actively exploring the use of CO₂ in the Fischer-Tropsch process to synthesize long-chain hydrocarbons, traditionally reliant on syngas (CO + H₂).

Currently, CO₂ hydrogenation via thermal conversion is primarily aimed at producing olefins. Cobalt and iron are recognized as highly active catalytic metals in this reaction, often combined with an alkali metal promoter to enhance activity and selectivity.

In this study, we investigated CO₂ hydrogenation over a simple iron catalyst under high-pressure conditions and observed the formation of carboxylic acids. The objective was to evaluate the impact of pressure on an Fe₂O₃ catalyst doped with potassium (K) as a promoter. The Fe₂O₃ catalyst was synthesized by co-precipitating iron nitrate and ammonium carbonate, followed by the addition of 3% potassium using the wet impregnation method to create an Fe₂O₃-3% K catalyst. Hydrogenation of CO₂ was carried out at 330 °C, with a H₂/CO₂ ratio of 3 and GHSV of 6200 mL g⁻¹h⁻¹, under pressures ranging from 35 to 100 bar. The catalysts, both before and after the reaction, were characterized using various analytical methods.

Investigating the Role of Cerium Oxide Promoter for the Hydrogenation of CO₂ to Higher Hydrocarbons over Fe-Based Catalysts

Muhammad Kashif Khan^{a,b}, Sheraz Ahmed^b, Jaehoon Kim^{a,b,c,*}

^aSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^bSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^cSKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

CO₂ conversion plays a crucial role in reducing greenhouse gas emissions and mitigating climate change which involved a process of transforming CO₂ into useful chemicals, fuels, or materials, thereby preventing it from accumulating in the atmosphere. Herein, we report a multifunctional sodium promoted-FeCeO_x-9 catalyst to produce liquid hydrocarbons. The sole Na-Fe₃O₄ catalyst showed intrinsic limitations of low CO₂ conversion and long-chain hydrocarbons (C₅₊) selectivity with a great tendency of quick deactivation at harsh reaction conditions (300–350 °C, and 3–4 MPa) in the presence of redox media (H₂O and CO₂). To overcome these limitations, CeO₂ was incorporated in Fe-based catalyst to enhance the catalytic properties of the catalysts. At 350 °C, 3.5 MPa, CO₂/H₂ ratio of 1:3 and at a space velocity of 4000 mL h⁻¹ g⁻¹, CO₂ conversion and C₅₊ selectivity was 36.7 and 49.1% whereas, CH₄ and CO selectivity were 18.7 and 18.4% respectively. The sole Na-Fe₃O₄ catalyst was deactivated after 100 h time on stream (TOS) whereas, addition of CeO₂, enhanced the catalyst stability up to 200 h TOS. Moreover, the promotional role of CeO₂ was also elucidated with DFT calculations and it revealed that CeO₂ proved to be an excellent electronic promoter which hindered the excessive surface oxidation of active Fe-phase, leads to more stable and active catalyst during CO₂ hydrogenation.

Revolutionizing CO₂-FTS: The Impact of Alkali promoter Introduction on Iron Catalysts

Wonjoong Yoon^a, Jiyeon Lee^a, Jaehoon Kim^{a,b,c,*}

^a School of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^b SKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

^c School of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

The objective of our research is to enhance the efficacy of iron-based catalysts in CO₂ Fischer-Tropsch synthesis (CO₂-FTS) by developing an optimal approach for incorporating the alkali metal promoter on the prepared iron-aluminum oxide (FeAlO_x)-based catalysts. Two methods of introducing an alkali promoter are employed: wet impregnation (Na(W)) and physical mixing (Na(MM)). The distribution of sodium on the catalyst surface was found to result in differing performance outcomes when each method was compared. The CO₂-FTS reaction was conducted under the following conditions: pressure of 3.5 MPa, temperature of 330 °C, and ratio H₂/CO₂ = 3. The Na(W)-FeAlO_x catalyst exhibited superior CO₂ conversion, a higher yield of liquid hydrocarbons (C₅₊), and a lower CO selectivity in comparison to the Na(MM)-FeAlO_x catalyst. In particular, the Na(W)-FeAlO_x catalyst exhibited a uniform distribution of Na by wet impregnation, which promoted the formation of Fe₅C₂ and enhanced the CO₂ conversion performance. In contrast, the Na(MM)-FeAlO_x catalyst exhibited a predominantly localized distribution of Na on the surface, which resulted in a comparatively lesser level of catalytic performance. This study offers a comprehensive insight into the influence of Na introduction methods on catalyst performance and presents a novel approach for optimizing catalyst design in CO₂ conversion reactions.

Influence of Alkali promoter in Cobalt-Manganese Catalysts for direct CO₂ hydrogenation to long chain hydrocarbon

Heuntae Jo^a, Jaehoon Kim^{a,b,c,*}

^aSchool of Mechanical Engineering, Sungkyunkwan University

2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 16419, Republic of Korea

^bSchool of Mechanical Engineering, Sungkyunkwan University

2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 16419, Republic of Korea

^cSchool of Chemical Engineering, Sungkyunkwan University

2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 16419, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

In this study, we investigated the performance differences of cobalt-manganese catalysts in the direct CO₂ hydrogenation reaction using various alkali promoters. Our findings reveal that the type of alkali promoter significantly influences the product distribution, shifting from methane to C₅₊ hydrocarbons. Through comprehensive analysis, we observed a transition from direct methanation to a coupled Reverse Water-Gas Shift and Fischer-Tropsch (RWGS-FT) process. The catalyst's structural evolution was characterized by the formation of a core-shell structure during this transition. We found that the oxidation state of the catalyst varies according to the O* removal energy, which in turn affects the reaction mechanism. This mechanistic shift was confirmed through in-situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) analysis. Our results demonstrate the critical role of alkali promoters in tuning the selectivity and reaction pathways of CO₂ hydrogenation over cobalt-manganese catalysts.

Revealing the New Role of ZrO_x in CO₂ Hydrogenation to High-Yield C₅₊ with Long-Term Stability over Fe-Based Catalysts

Sheraz Ahmed^a, Muhammad Kashif Khan^a, Jaehoon Kim^{a,b,c,*}

^a School of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^b SKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

^c School of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

Liquid hydrocarbons such as olefins and paraffins are indispensable chemicals that are used widely as transportation fuels and as feedstocks to synthesize numerous commodity chemicals. Carbon dioxide can be considered an alternative feedstock to fossil resources for producing liquid hydrocarbons, which can contribute not only to reducing the high concentration of CO₂ in the atmosphere but also to providing a sustainable solution to depleting fossil fuel reserves. The metal oxide promoter decisively influences the performance of Fe catalysts in the direct hydrogenation of CO₂ to C₅₊ hydrocarbons. However, the roles of metal oxide promoters for Fe catalysts particularly ZrO₂, have rarely been investigated. To overcome this gap, a new Fe catalyst promoted with Na and partially reduced ZrO_x (Na–FeZrO_x-9) was developed in this study; the catalyst helped produce C₅₊ hydrocarbons in remarkably high yield (26.3% at 360 °C). In contrast to ZrO_x-free Fe-oxide, Na–FeZrO_x-9 exhibited long-term stability for CO₂ hydrogenation (750 h on-stream). The findings revealed multiple roles of ZrO_x. Notably, ZrO_x decorated the Fe-oxide particles after calcination, thereby suppressing excess particle aggregation during the reaction and acting as a “coke remover” to eliminate the carbon deposited on the catalyst surface. Additionally, oxygen vacant (O_v) sites in ZrO_x and electron transfer from ZrO_x to Fe sites facilitated the adsorption of CO₂ at the Zr–Fe interface. Moreover, ZrO_x acted as both the structural and electronic promoter to boost CO₂ conversion and reduce CO selectivity.

Enhanced CO₂ Hydrogenation to Hydrocarbon Fuels: The Role of Metal Oxide Promoters in Cobalt-Based Catalysts

Syeda Sidra Bibi^a, Heuntae Jo^b, Sheraz Ahmed^b, Jaehoon Kim^{a,b,c,*}

^aSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^bSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^cSKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

Catalytic carbon dioxide (CO₂) conversion into hydrocarbon fuels is a significant strategy for mitigating climate change and confronting issues with the sustainability of energy sources. In this study, a bimetallic Cobalt-metal oxide catalyst (CoMO_x) is synthesized, and it is investigated how promoter influences the catalyst's structure and activity in the Fischer-Tropsch Synthesis (FTS). At a low temperature of 270 °C and a CO₂ conversion of 69.8%, the CoMO_x catalyst exhibits a high C₅₊ yield of 26.9% and favorable for less production of undesired methane. In the H₂/CO₂ ratio of 3:1, the bimetallic oxide generates active sites that can initiate chain-growth reactions at a space velocity of 4000 mlg⁻¹h⁻¹ and showed an excellent long-term stability reaction of up to 2100 h. Evidence from multiple in situ/ex situ technologies including HR-TEM, EDS mapping, X-ray Absorption analysis (XAS) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) disclose that the synergistic effect of the metal oxide and Co catalyst is accountable for creating a conducive environment for high C₅₊ selectivity and stability.

Recycling of Polyamide Composite Materials: A Solvent Extraction Approach for Polymer Recovery

Jaeryeong Jeong^a, Aye Aye Myint^b, Jongho Choi^c, Sabrina Wulandari^b,
Daesung Jung^d, Jaehoon Kim^{a,b,c,*}

^aSKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

^bSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^cSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^dSustainable Materials Research Team, Hyundai Motor Group, 37, Cheoldobangmulgwan-ro, Uiwang-si,
Gyeonggi-do 16082, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

The automotive industry has increasingly been subject to stringent regulations regarding the use of recycled polymers in the production of new vehicles. As a result, it has become critical to develop effective and efficient recycling technologies for complex polymer composites and multilayer materials, which are widely used in automotive manufacturing. Among these, polyamide (PA) composites, such as glass fiber-reinforced PA and silicone-coated PA materials, present unique challenges in terms of selective recycling due to their complex chemical and physical properties. Thus, there is a growing need for novel approaches to improve the recycling process for these materials. The primary objective of this study was to develop a solvent extraction technology for the selective extraction and recovery of PA from automotive composite materials.

Hansen Solubility Parameters (HSP) were used to select the most suitable solvent for the selective extraction of PA from glass fiber reinforced composites and silicone-coated PA materials. Furthermore, the study determined the optimal conditions for the solvent extraction process by varying several key parameters, including solvent-to-sample ratio, solvent concentration, temperature, pressure, and dissolving time. The physical properties of the recovered polymer (molecular weight, composition, thermal properties, etc.) were evaluated, and it was confirmed that there was no difference in physical properties before and after recovery. Further research is needed to explore the recycling potential of other polymer types used in automotive components.

Removal of Chemical Residue from Gelatin-based Microparticles using Supercritical CO₂

Truc Cong Ho^a, Jang-Woo Kim^b, Jin-Seok Park^b, Byung-Soo Chun^{b,*}

^aPL Micromed Co., Ltd., 1F, 15-5, Yangju 3-gil, Yangsan-si, Gyengsangnam-do 50620, Republic of Korea

^bDepartment of Food Science and Technology, Pukyong National University, 45 Yongso-ro Nam-gu, Busan 48513, Republic of Korea

*Corresponding author: bschun@pknu.ac.kr

Some chemicals are commonly used as a cross-linker to form covalent bonds between biopolymer molecules such as proteins and chitosan. In embolization therapy, a high amount of cross-linker residue in an embolic agent might cause side effects on patients. Therefore, the content of cross-linker residue in the final product must be minimized using modern extraction techniques. Regarding advanced extraction techniques, supercritical carbon dioxide (SC-CO₂) has been widely used. SC-CO₂ has liquid-like solvent power and gas-like diffusivity; therefore, it is an ideal solvent because it can easily penetrate the sample matrix and remove the target compound. Fish gelatin is one of the most popular biopolymers, and is widely used in food, pharmaceutical, and cosmetic fields because of its biodegradation and biocompatibility. Fucoidan, obtained from seaweed, is a sulfated polysaccharide with promising ferrous ion chelating effects which is useful for embolization therapy for cancer treatment. Gelatin-based microparticles (GMs) are an embolic agent developed by PL Micromed Co., Ltd. The degradation rate of the GMs is controlled by varying gelatin molecular weight which was modified by the subcritical water hydrolysis technique. This study aimed to minimize the content of cross-linker residue in GMs using SC-CO₂ at different temperatures, time, and pressures. The cross-linker content in the treated GMs was measured using high-performance liquid chromatography. GMs' morphology is characterized by using a scanning electron microscope. The results showed that the cross-linker content was significantly reduced while the GMs' surface was maintained after SC-CO₂ treatment. SC-CO₂ treatment proved to be a promising technique for removing the cross-linker from GMs.

Utilization of Hydrolyzed Rice Husks as an Eco-Friendly Polymer Additive

Sung Hyun Kim^{a,b}, Seung Eun Lee^{a,c}, Gun Woo Sin^{a,d}, Chul-jin Lee^b, Young-Kwon Park^c,
Hong-shik Lee^{a,*}

^aKorea Institute of Industrial Technology, Cheonan, Republic of Korea

^bChung-Ang University, Seoul, Republic of Korea

^cUniversity of Seoul, Seoul, Republic of Korea

^dSun Moon University, Asan, Republic of Korea

*Corresponding author: e-mail. leehongshik@kitech.re.kr

As the demand for sustainable alternatives to petroleum-based plastic additives increases, the development of bioplastics is progressing, yet there are still limitations in replacing the durability of conventional plastics. This study investigates the potential of rice husk-derived bio-based additives as replacements for chemical-based additives in polymer coatings. Hydrothermal decomposition of rice husks was performed under various parameters, including temperature, reaction time, and sample-to-solvent ratio, to optimize the process. As a result, under the reaction conditions of 1 g of sample, 10 mL of solvent, 473.15 K, and 45 minutes, a solid yield of 71.74 % and a liquid yield of 22.43 % were obtained. The liquid yield increased as the temperature rose or as the sample-to-solvent ratio decreased, with the maximum liquid yield corresponding to the optimal condition for the complete removal of hemicellulose. Structural modifications were characterized using elemental analysis and Fourier-transform infrared spectroscopy, while polymer compatibility was assessed through blending experiments.

Enhancing Food Drying Efficiency using Supercritical CO₂: A Study on Process Parameter Optimization

Ji Sun Lim^{a,b}, Seung Eun Lee^{a,c}, Gun Woo Shin^{a,d}, Bonggeun Shong^b,
Young-Kwon Park^c, Hong-shik Lee^{a,*}

^aKorea Institute of Industrial Technology, Cheonan, Republic of Korea

^bHongik University, Seoul, Republic of Korea

^cUniversity of Seoul, Seoul, Republic of Korea

^dSunmoon University, Asan, Republic of Korea

*Corresponding author: leehongshik@kitech.re.kr

Drying is a widely used method in the food industry to inhibit microbial growth and preserve nutritional components, thereby facilitating long-term storage while maintaining the quality and characteristics of food[1]. Supercritical drying offers several advantages over conventional methods such as hot-air drying or freeze-drying, including the preservation of quality without thermal damage, shorter drying times, and lower energy consumption[2,3]. To minimize the effects of surface tension, the process was designed to first exceed the critical pressure and then the critical temperature, preventing surface shrinkage caused by liquid-gas interface formation and reducing structural deformation. This study aimed to maximize drying efficiency by effectively removing moisture from food using supercritical fluid extraction equipment. The extraction pressure and temperature were maintained at 10 MPa and 40 °C, respectively. Before extraction, the food samples were immersed in gaseous CO₂, allowing the gas molecules to penetrate and diffuse sufficiently across the surface, thereby enabling efficient moisture removal in the supercritical state. Additionally, the flow rate and Reynolds number were identified as key parameters to assess their impact on moisture removal and drying efficiency. The experimental results demonstrated that, under optimal flow rate and Reynolds number conditions, up to 99.7 % of moisture could be effectively removed while preserving the shape of the food.

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Unraveling Characteristics of Mandarin Pomace for its Potential Value-added Applications

Aye Aye Myint^{a,b}, Sabrinna Wulandari^a, Ruqian Cao^b, Jongho Choi^b,
Jeong Jaeryeong^c, Jaehoon Kim^{a,b,c,*}

^aSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^bSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^cSKKU Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

The valorization of biowaste from agro-fruit industries is pivotal role of circular economy and especially for maintaining a sustainable green environment. For this regard, the development of green strategies to the efficient utilization of the whole waste biomass for not only recovering valuable bioactive compounds but also producing biorefinery products are highly needed. In this work, we demonstrate a green solvent, liquified/subcritical dimethyl ether (*L*-DME) for efficient extraction of valuable phytochemicals from the wet mandarin pomace (wet MPM), a waste residue leftover mandarin orange fruit juice production industry for the first study. The nutritive values and antiradical activities of the *L*-DME extract were evaluated to imply its value-added applications as in medicines and functional foods. In addition, the chemical compositions of solid residue obtained after *L*-DME extraction of wet MPM were characterized using HPLC, GC-FID, EA, FTIR, FE-SEM, and GCxGC-TOF/MS for the aspect of its potential applications in bioenergy and bioproduct processing. On the other hand, we performed conventional Soxhlet exactions of freeze-dried MPM powder with n-hexane and ethanol for assessing the extraction performance of *L*-DME process on the wet MPM. Besides, the interaction and solubility of bioactive compounds in *L*-DME under the examined extraction conditions (temperature and pressure) was elucidated using Hansen solubility parameters and their relative energy differences analysis.

Enhanced High-Yield Recovery of Bioactive Compounds from Red Ginseng Marc using CO₂-Assisted Subcritical Water Extraction

Ruqian Cao^a, Aye Aye Myint^{a,b}, Jaehoon Kim^{a,b,c,*}

^aSchool of Mechanical Engineering, Sungkyunkwan University, 2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 16419, Republic of Korea

^bSchool of Chemical Engineering, Sungkyunkwan University, 2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 16419, Republic of Korea

^cSKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, 2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 16419, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

Subcritical water extraction (SWE) is recognized as an efficient, eco-friendly technique for isolating bioactive compounds from red ginseng marc (RGM). This study introduces CO₂ into the SWE system as a green catalyst to further improve extraction efficiency and optimize the recovery of reactive bioactive compounds from RGM. A range of extraction parameters including temperatures (140–180 °C), pressures (10–20 MPa), and times (10–60 minutes) were systematically evaluated to maximize the hydrolysate yields and bioactive recovery. For comparison, Soxhlet extraction with water and 80% ethanol, as well as conventional SWE under N₂ were performed. The in situ formation of carbonic acid under the hydrothermal conditions enhanced the hydrolysate yields, rare ginsenoside content, total phenolic content, Maillard reaction product levels, and antioxidant activity of the RGM extracts under optimal conditions (172 °C, 10 MPa, 10 min). CO₂-SWE thus emerges as a safe, sustainable technique with strong potential applications in the pharmaceutical, cosmeceutical, and functional food industries.

Synthesis of Astaxanthin/ β -cyclodextrin Microparticles using Supercritical Antisolvent (SAS) Process

Sabrina Wulandari^a, Aye Aye Myint^{a,b}, Jaehoon Kim^{a,b,c,*}

^aSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^bSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^cSKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

Astaxanthin, a type of carotenoid, has many health benefits and high antioxidant content, but unfortunately it has low availability and stability. Encapsulation is one of the ways to increase astaxanthin stability. The encapsulation material chosen in this study was β -cyclodextrin. Supercritical CO₂ as the antisolvent was used for the encapsulation, which is called supercritical antisolvent (SAS) process. Precipitation of astaxanthin/ β -cyclodextrin microparticles was finished in short time and without the need for another solvent removal step. The effect of process parameters including pressure, temperature, solution concentration, solution flow rate and mole ratio on the encapsulation efficiency and particle sized were examined. The properties of the microparticles were further investigated, including the antioxidant activity and the residual DMSO content.

One-Pot Conversion of Mucic Acid to Hexanedioic Ester over Bimetallic Disperse Ru-Re, Ru-Mo, and Ru-W on Activated Carbon Catalyst

Rizky Gilang Kurniawan^a, Jaehoon Kim^{a,b,c,*}

^aSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^bSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^cSKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

One of the most important monomers in the polymer industry is adipic acid (AA) which is mostly utilized in nylon-6.6 monomer. Recently, there has been a lot of research done on sustainable and renewable energy methods to make AA from mucic acid (MA). Here, we developed three distinct catalysts, 0.8Ru₂Re/AC-P, 0.8Ru₂Mo/AC-P, and 0.8Ru₂W/AC-P, which able to convert MA to AA in this work with the yield of 88.2, 48.9, and 14.3% respectively. Ru⁰ nanocluster aided in the generation of hydrogen, which turn reduced Re⁷⁺/Mo⁶⁺/W⁶⁺ to active forms that adsorbed mucic acid and generated trans-trans muconic acid as an intermediate product. After additional hydrogenation, this intermediate molecule will adsorb on the Ru⁰ surface, producing AA as the final product. A density functional theory (DFT) study confirmed that the first deoxydehydration (DODH) step was the rate-determining step in the MA conversion for all three catalysts. among these three catalysts, Re based catalyst shows lowest activation energy barrier compared to Mo, and W based catalyst in DODH step. The Isotope labelling study also validates the reaction mechanism, demonstrating that solvent acts as hydrogen source in the reaction.

Production of Hydrocarbon-Rich Fuel via Hydrothermal Deoxygenation of Triglycerides in a Continuous Flow Reactor

Do Hui Kwon^{a,b}, Sung Hyun Kim^{a,c}, Bonggeun Shong^b, Chul-Jin Lee^c, Hong-shik Lee^{a,*}

^aKorea Institute of Industrial Technology, Cheonan, Republic of Korea

^bHongik University, Seoul, Republic of Korea

^cChung-ang University, Seoul, Republic of Korea

*Corresponding author: leehongshik@kitech.re.kr

The primary objective of this study is to investigate the production process that converts triglycerides, including saturated and unsaturated fatty acids, into hydrocarbon products that can be used as fuels like biodiesel, sustainable aviation fuel (SAF), and marine fuel. The study explored the effects of reaction mechanisms and deoxygenation through hydrothermal decomposition. Soybean oil was selected as the model feedstock for triglycerides. The continuous hydrothermal processing reactions were conducted at temperatures above 400 °C, pressures ranging from 5 to 10 MPa, and residence times between 0.5 to 2 hours, with a small amount of water added. Additionally, basic compounds were introduced to examine their impact and changes in the main products. As a result, various straight-chain hydrocarbons were generated in the liquid phase, and at the same time, short-chain fatty acids were observed to form. This indicates that the deoxygenation reaction proceeded via a decarboxylation mechanism. Furthermore, the presence of unsaturated bonds led to cracking at allylic C=C bonds, resulting in the formation of hydrocarbons and short-chain fatty acids.

Electrocatalytic Cleavage of α -O-4, β -O-4 and 4-O-5 Linkages using Pd/C Catalyst

Seoyeon Kim^a, Neha Karanwal^{b,c}, Jaehoon Kim^{a,b,c,*}

^aSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^bSKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

^cSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

With the emergence of 2050 carbon neutrality around the world, interest in biomass is increased as a renewable energy source. Lignin, which accounts for 20–30% of wood, is considered highly promising feedstock for producing transportation fuels and highly value-added chemicals. The goal of this study is to convert lignin through an electrochemical approach that can confirm the reaction under relatively economical and mild conditions. Using a Pd/C catalyst, C–O bond cleavage of lignin dimer model compounds including diphenyl ether, p-Tolyl ether (4–O–5 linkage) and benzyl phenyl ether (α -O–4 linkage), and hydrogenation of oxygen-containing intermediates were investigated. The experiment was conducted at 70 °C with varying reaction times and currents in a perchlorate buffer. The conversion of the dimers to their respected monomers was achieved. The 4–O–5 bond cleavage was achieved by parallel hydrogenolysis and reductive hydrolysis, while the C–O bond of the α -O–4 was mainly cleaved by hydrogenolysis.

Fuel-Range Hydrocarbons via Non-Catalytic Sub-/Supercritical Water Reaction of Waste Oils

Jongho Choi^a, Aye Aye Myint^b, Jaehoon Kim^{a,b,c,*}

^aSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^bSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^cSKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

Global bio-jet fuel consumption currently ranges from 20,000 to 30,000 tons annually, representing only 0.1% of total jet fuel consumption. However, the International Energy Agency (IEA) forecasts a rapid increase, with demand projected to reach 60 million tons per year by 2040. South Korea's current share in global bio-jet fuel consumption is about 2%, with significant growth anticipated as international aviation trends increasingly favor sustainable fuels. In this study, we examine the decarboxylation of waste oils under subcritical and supercritical water (subH₂O and scH₂O) conditions, which is essential for producing oxygen-free bio-jet fuel from waste oils. Liquid products were characterized by GCXGC-TOF/MS, elemental analysis, simulated distillation, ICP-OES and Karl Fischer titration. Additionally, the decarboxylation reaction mechanism under subH₂O and scH₂O conditions was explored and discussed.

Electrocatalytic Conversion of Lignocellulose Biomass into Biochemicals

Neha Karanwal^{a,b}, Jaehoon Kim^{a,b,c,*}

^aSchool of Mechanical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

^bSKKU Advanced Institute of Nano Technology, Sungkyunkwan University, Suwon, Republic of Korea

^cSchool of Chemical Engineering, Sungkyunkwan University, Suwon, Republic of Korea

*Corresponding author: jaehoonkim@skku.edu

Numerous catalytic strategies, both homogeneous and heterogeneous, have been explored to depolymerize lignin into smaller fragments suitable for upgrading. However, the harsh reaction conditions typically required, and the challenge associated with catalyst recovery make these methods difficult to apply practically. To overcome these limitations, electrochemical depolymerization has emerged as a promising alternative, offering the potential for milder reaction conditions, ideally at ambient temperature and pressure. This approach is not only simple, cost effective but also waste-free, and environmentally friendly, as it relies solely on the transfer of electrons and protons. A key advantage of electrochemical processes is the utilization of electricity—an energy source that can be generated from renewable sources such as solar, wind, hydro, or nuclear power without relying on the combustion of carbon-based fuels. While electro-oxidative depolymerization of lignin has been extensively reported, usually involving various types of metal or high-cost electrodes, reductive processes have received less attention. Here, we demonstrated the electroreduction of birch wood lignin using a Pt catalyst on nitrogen-doped carbon as cathode and PW12 as a mediator, successfully producing lignin-derived monomers.

Bubble Pressure Measurement of Carbon Dioxide Dissolution in Propylene Carbonate, Dimethyl Carbonate, and Acetonitrile

Bomin Kim^a, Dongho Yoo^b, Tae Jun Yoon^{a,c,*}

^aSchool of Chemical and Biological Engineering, Institute of Chemical Processes,
Seoul National University, Seoul, 08826, Republic of Korea

^bDepartment of Chemical Engineering & Applied Chemistry, Chungnam National University,
Daejeon, 34134, Republic of Korea

^cSchool of Transdisciplinary Innovations, Seoul National University, Seoul, 08826, Republic of Korea

*Corresponding author: tyoon124@snu.ac.kr

The widespread use of lithium-ion batteries (LIBs) is expected to generate a huge amount of battery waste in the near future. However, a standardized method to recycle electrolytes in waste batteries has not yet been established due to the fire hazard and economic limitations. In this study, we aim to build the thermodynamic database for the supercritical fluid extraction process, which is considered one of the promising candidates for electrolyte recycling.

We selected carbon dioxide and propylene carbonate as a non-flammable solvent and a model electrolyte solute. As cosolvents, we chose dimethyl carbonate, one of the electrolyte components, and acetonitrile, which is commonly used for its amphiphilic properties. After measuring the bubble pressure of binary and ternary systems at 20, 40 and 60 °C, we used cubic equations of state and a quadratic mixing rule to fit the experimental data. The average absolute relative deviation between the model and experimental data was less than 10 %, showing the reliability of the experimental data and the thermodynamic model.

The thermodynamic data generated from this work will contribute to optimizing the supercritical carbon dioxide extraction process, leading to the reduction of raw materials and the improvement of process efficiency.

Prediction of the Solid Solubility of Anthraquinone Derivatives in Supercritical CO₂ by the Solution Model with Melting Temperature Estimated from Message-Passing Neural Network

Yu-Chiao Chu^a, Salal Hasan Khudaida^b, Yung-Ho Chiu^c,
David Shan-Hill Wong^{a,*}, Chie-Shaan Su^{b,*}

^aDepartment of Chemical Engineering, National Tsing Hua University

^bDepartment of Chemical Engineering and Biotechnology, National Taipei University of Technology

^cTaiwan Supercritical Technology Co., Ltd.

*Corresponding author: dshwong@che.nthu.edu.tw; cssu@ntut.edu.tw

Understanding the solid solubility in supercritical fluid is a crucial task for developing supercritical fluid technology. This study aims to demonstrate a total predictive approach to estimate the solid solubility in supercritical CO₂ for structure-related compounds only from its molecular structure. Anthraquinone derivatives (AQDs) were selected as the model compounds since they provide versatile applications such as dyeing agents, pharmaceutical ingredients, and organic photocatalysts. The solid solubility data of 28 anthraquinone derivatives (AQDs) in supercritical CO₂ were collected, and a solution model was used to develop a generalized model for solubility prediction. First, the generalized solution model shows the capability for predicting the solubility within order consistency. The only required physical property for solubility prediction was the melting temperature of AQD. Then, different extrapolation tests were investigated to validate the robustness of the solution model. Finally, a total prediction approach was developed by generalizing the solution model using the melting temperature predicted from the message-passing neural network (MPNN). In this total prediction case, about 90% of the data points can be predicted within order consistency, and the crossover phenomena were also described reasonably. In summary, the solution model with melting temperature predicted from MPNN is an efficient approach for solubility order prediction and shows the potential to screen or design new molecules for supercritical fluid application.

Keywords:

Solid solubility prediction, Supercritical CO₂, Order consistency, Anthraquinone derivative, Solution model, MPNN

Theoretical Study of the Depolymerization of Lignin Model Compound over Pd and Ni with Different Sizes

Junjung Rohmat Sugiarto^a, Jaehoon Kim^{a,b,c,*}

^aSKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, 2066, Seobu-ro, Jangan-Gu, Suwon, Gyeonggi-Do 16419, Republic Korea

^bSchool of Mechanical Engineering, Sungkyunkwan University, 2066, Seobu-ro, Jangan-Gu, Suwon, Gyeonggi-Do 16419, Republic Korea

^cSchool of Chemical Engineering, Sungkyunkwan University, 2066, Seobu-ro, Jangan-Gu, Suwon, Gyeonggi-Do 16419, Republic Korea

*Corresponding author: jaehoonkim@skku.edu

Biomass structure, such as high dimers lignin, conversion into high energy biofuels or valuable chemical compounds had been investigated. Noble metal catalysts, like palladium (Pd), have been proven effective in generating valuable lignin-derived chemicals. In this study, density functional theory (DFT) is used to examine the reaction pathways involved in lignin depolymerization. A key step in this process is breaking the C-O bond in the β -O-4 linkage, which has a dissociation energy of 2.83 eV. Pd catalysts showed relatively low energy barriers for β -O-4 bond cleavage: 1.8 eV on Pd (111), 0.58 eV on Pd nanoclusters, and 1.16 eV on Pd single atoms. These low energy values suggest that Pd catalysts, regardless of their size, can effectively promote lignin depolymerization. In contrast, nickel (Ni) catalysts had higher energy barriers for β -O-4 bond cleavage: 0.6 eV on Ni (111), 2.75 eV on Ni nanoclusters, and 2.47 eV in Ni single atoms. The higher energy barriers for Ni at low loading levels make them less effective for lignin depolymerization compared to their bulk forms.

Synthesis of Silicalite-1 by Hydrothermal Method Applied for Steam-Resistant Cobalt Catalyst in Propane Dehydrogenation

Shokhboz Muxamadqulov^{a,b}, Yong Ki Park^{a,b}, Dae Sung Park^{a*}

^aKorea Research Institute of Chemical Technology, Daejeon, South Korea

^bSchool of KRICT, University of Science and Technology (UST), Daejeon, South Korea

*Corresponding author: dpark@kRICT.re.kr

Silicalite-1 (S-1), a pure silica-based zeolite, is an MFI structure that can be used for heterogeneous catalysts in various chemical reactions. MFI structure zeolites are known to be very efficient in the production of light olefins, which are basic chemical monomers in the petrochemical industry. Herein, various sizes of silicalite-1 with high crystallinity were synthesized using a hydrothermal synthetic method and applied to the propane dehydrogenation to produce propylene. The as-prepared silicalite-1 was used as a support for the cobalt-based catalyst. The prepared Co/S-1 catalyst was highly dispersed in the silicalite-1 crystal and did not form clusters or nanoparticles of cobalt. The pure silica-based zeolite showed high steam resistance compared to silica-alumina blends or alumina-based catalysts. This is due to the inhibition of water adsorption at high temperatures and the ability to remove some adsorbed hydroxyl groups on the surface of silicalite-1, which is much better than alumina.

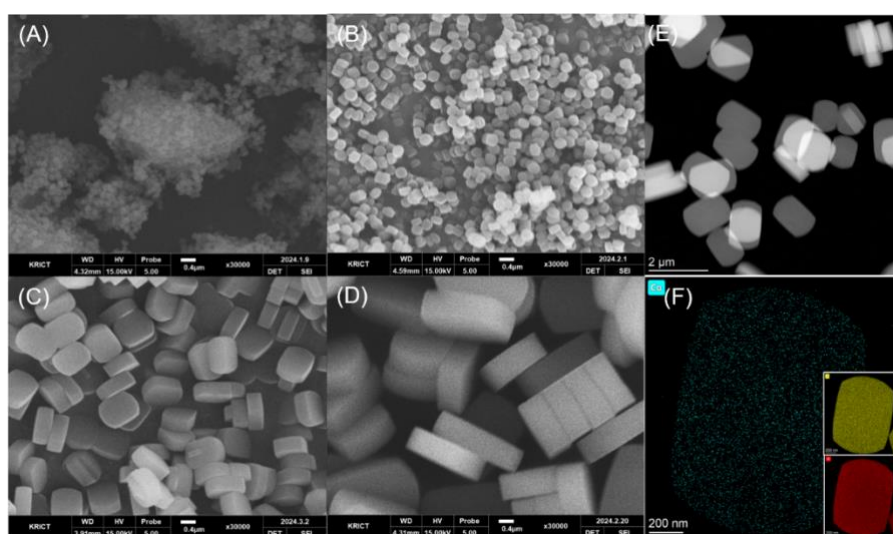


Figure 1. SEM images of various sized silicalite-1 (A~D), HAADF-STEM image of Co/S-1 (E) and EDS mapping (F).