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協賛：台灣觸媒學會（Catalysis Society of Taiwan）

IL01

Understanding microwave-enhanced catalytic reactions by in situ / operando analyses

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Abstract.

Decarbonizing the chemical industry is strongly desired to mitigate climate change and achieve sustainable development. Renewable energies such as solar and wind power generation are expected to be utilized to recycle carbon resources such as biomass, waste plastics, and carbon dioxide. Microwave-driven catalytic processes are expected to contribute as a key technology to replace conventional industrial processes that consume large amounts of fossil resources. Microwaves enable the efficient conversion of renewable energy into heat necessary to drive the reaction. In addition, microwaves can afford on-demand material production in small-scale and distributed chemical plants.

Unlike conventional electric furnaces, microwaves penetrate the gas phase and heat the catalyst bed directly. Previous literature estimated the formation of localized high-temperature reaction fields at the active sites of the catalysts. We can achieve an ideal catalytic reaction if energy can be applied directly to the catalyst's active sites without heating the entire reaction system. On the other hand, it is not easy to understand the temperature distribution during microwave irradiation. To solve such problems, we have developed various in situ XAFS [1], XRD [2], SAXS [3], Raman [4], and so on. We can also utilize resonance frequency to monitor the catalyst oxidation state under microwaves [5]. We can estimate the local temperature in a material-selective way by analyzing the temperature-dependent spectral changes. Based on the mechanism of local heat generation, we can rationally design various microwave catalytic reactions, such as biomass conversion processes.

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Hydrotreatment of Vegetable Oil for Biofuel with Ni-Mo Bimetallic Catalysts Supported on Zeolite ZSM-5

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Abstract. The hydrotreatment processes of vegetable oil with Ni-Mo/ZSM-5 catalysts for biofuel were studied with a semi-batch reactor (Parr Model 4561). To prepare Ni-Mo/ZSM-5 catalysts, the incipient wetness impregnation method was used to load Ni and Mo onto zeolite ZSM-5 supports that were first modified priorly through hydrothermal and alkali treatments. The catalysts in oxide forms had to be activated by reduction in H_2 atmosphere at 550°C prior to the hydrotreatment process [1,2]. The hydrotreatment of soybean oil was performed using decalin as the solvent and various catalysts in a semi-batch reactor for 6 h. The products were analyzed quantitatively by GC-FID and qualitatively by FTIR and GC-MS. The objective is to achieve the maximum yield while operating within the reaction pressure fixed at 40 bar of hydrogen, and reaction temperatures from 300°C to 350°C. (Figure 1 and Figure 2). The selectivity of liquid hydrocarbon products towards more carbon numbers increased notably with more concentrated alkali solution used to treat zeolite ZSM-5 supports. To attain more sustainable aviation fuel (SAF) as possible, the focus of this research work was shifted towards products with medium carbon numbers. Despite the burgeoning development of alternative energy sources, the aviation industry, reliant on liquid fuels with high-enough energy density, commonly fossil liquid fuels, to carry passengers and goods over a long distance, still necessitates them. Hence, ZSM-5 is subjected to hydrothermal treatment to promote the formation of MCM-41/ZSM-5 composite materials, augmenting catalyst surface area and mesopore volume. This augmentation facilitates the diffusion and reaction of triglycerides, thus improving selectivity towards medium carbon numbers. Finally, recyclability tests of the catalyst probe whether the nickel-molybdenum bimetallic catalysts retain good deoxygenation capabilities after catalysis.

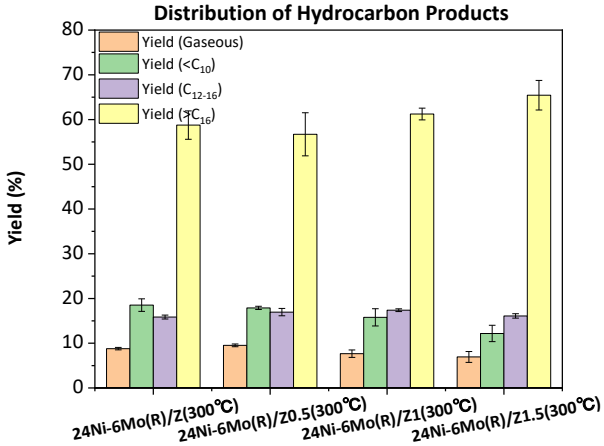

Figure 1. Effects of catalysts on the yields of hydrocarbon products.

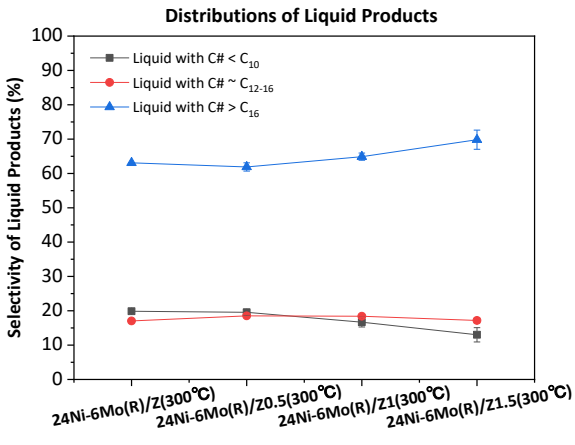

Figure 2. Effects of catalysts on the selectivity of hydrocarbon products.

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IL03

Phase Controlled Metal Nanoparticles and their Catalytic Applications

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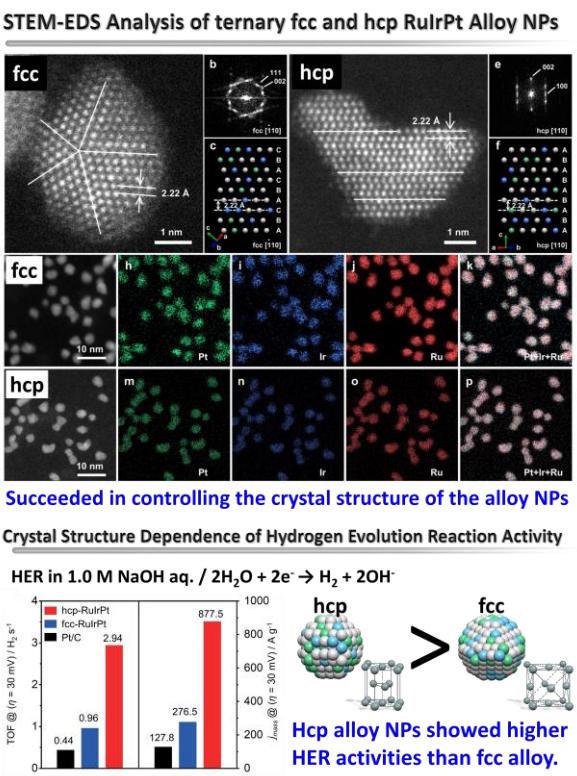
Inorganic nanoparticles such as metal nanoparticles synthesized in a liquid phase usually have a three-dimensional atomic arrangement same as their bulk forms. For example, nanoparticles of a metal element with a hexagonal close-packed (hcp) structure in bulk have the hcp structure, and alloy nanoparticles have a phase-separated structure with an immiscible alloy system. This is because the nanoparticles with an equilibrium phase are formed through the self-assembly of atoms during chemical reduction synthesis. Therefore, it is common that we can select elements as we like when we design metal nanoparticles, but we cannot easily control their crystal structures. Properties of metal nanoparticles such as catalytic properties are significantly influenced by their electronic structure and surface structure. Therefore, if we could control the crystal structure of materials regardless of elemental species, we would be able to obtain a new direction to design functional nanomaterials since the electronic structure and atomic arrangement of the surface depend on the crystal structure. In this presentation, some examples of phase-controlled metal nanoparticles and their catalytic applications will be introduced. We have successfully controlled crystal structures of monometallic and alloy nanoparticles by utilizing their surface energy or precisely tuning the reduction speeds of precursors during the reactions[1, 2, 3, 4]. As an example, we succeeded in selectively synthesizing fcc and hcp RuIrPt ternary alloys at a certain composition and found that the hcp one had higher catalytic activity for electrochemical hydrogen evolution reaction (Figure)[4]. The details of how to control the atomic self-assembly in the synthesis of metal nanoparticles and their catalytic properties will be discussed.



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CONSTRUCTION ARCHIMEDEAN TILING PATTERNS BASED ON POROUS ORGANIC POLYMERS

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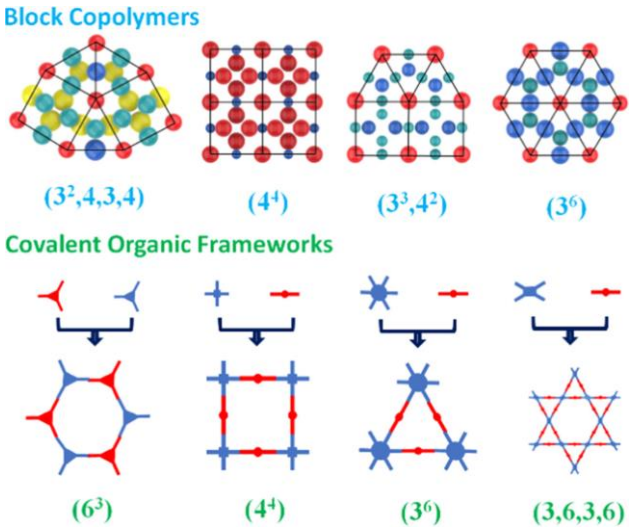
Abstract. Soft materials based on block copolymers or covalent organic frameworks (COFs) that exhibit Archimedean tiling patterns have attracted significant interest due to their potential applications in nanopatterning, nanocomposites, and shape selectivity. Additionally, researchers have widely investigated the corresponding microporous or mesoporous materials with Archimedean tiling from COF or block copolymers as templates with high surface area and pore volume, or tunable porosity with different length scales, in separation, energy storage, drug delivery, photo-catalysis, photovoltaic solar cells, and chemical sensing. This talk highlights recent progress in constructing Archimedean tiling patterns based on the creation of ordered structures from block copolymers by self-assembly and the direct synthesis of COF materials with various topologies



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Ba-Al Oxyhydride Promoting Cobalt Catalyst in Ammonia Synthesis

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Abstract. Catalytic ammonia synthesis is vital for production of fertilizer, which is needed to produce food for the world's expanding population. Ru has been regarded as the best metal for ammonia synthesis due to its suitable nitrogen adsorption ability but its problems of severe hydrogen poisoning and low natural abundance make Ru less attractive for industry. Non-noble metal Co is considered as a promising alternative to Ru. However, the weak Co-N interaction at mild conditions makes Co inactive for ammonia synthesis using conventional supports especially under mild reaction conditions. On the other hand, electride materials, such as C12A7:e^- and Ca_2N:e^-, have been studied as very effective supports for Ru catalysts because their strong electron injection to Ru lowers the energy barrier of N_2 dissociation, leading to the high activity in ammonia synthesis[1-3].

In the present study, we report a novel oxyhydride electride, $BaAl_2O_{4-x}H_y$, in which electrons are located at interstitial cage sites and serve as anions individually rather than combining with other atoms. The $BaAl_2O_{4-x}H_y$ functions as efficient and stable support of Co catalysts in ammonia synthesis at low reaction temperatures [4].

$BaAl_2O_{4-x}H_y$ oxyhydride has a monoclinic structure (space group $P2_12_12_1$) and anionic electrons and H^- ions are accommodated in the interstitial cage sites (Fig. 1). The existence of anionic electrons is confirmed by iodometric titration and magnetic susceptibility measurements, and H^- ions are confirmed by TPD and DRFTIR measurements. DFT calculations reveal that the interstitial cage sites play a pivotal role to stabilize anionic electrons or H^- ions. Various elemental analyses revealed that the chemical composition is determined to be $BaAl_2O_{3.66}H_{0.40}$:$e^-_{0.28}$.

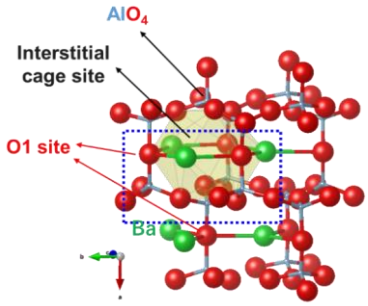

Figure 1. Crystal structure of $BaAl_2O_4$.

Co-loaded $BaAl_2O_{4-x}H_y$ achieved significant activity (500 mmol g_{Co}^{-1} h^{-1}) under mild conditions (340°C, 0.90 MPa) with a very low apparent activation energy (49.6 kJ mol^{-1}), which is in complete contrast to the catalytic performance of $Co/BaAl_2O_4$ (0.7 mmol g_{Co}^{-1} h^{-1}, 100 kJ mol^{-1}) (Figure 2). The $Co/BaAl_2O_{4-x}H_y$ outperformed the Co/C12A7:e^- and state-of-the-art Co catalysts in terms of activity per gram of Co. Isotope N_2 exchange reaction experiments reveal that the energy barrier of N_2 cleavage is largely lowered due to the strong electron donation. Furthermore, the lattice H^- ions further boost ammonia synthesis by accelerating the N−H bond formation. These properties make this catalyst even comparable to the latest Ru catalysts at 300°C. It is well known that the most of reported hydride-based catalysts are deactivated after exposure to air because of irreversible oxidation. On the other hand, the activity of $Co/BaAl_2O_{4-x}H_y$ could be recovered by simple annealing in H_2 flow. This is because the three-dimensional AlO_4-based network in the stuffed tridymite structure has strong chemical stability and protects anionic electrons and H^- ions from the oxidation. Such robustness and reusability are distinct advantages over the reported hydride-based Co catalysts for ammonia synthesis.

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Non-Reductive Conversion of CO_2 Mediated by Surface Oxygen Vacancy of CeO_2 Catalysts

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Carbon dioxide (CO_2) has been regarded an inexpensive, safe, and renewable carbon resource [1]. Non-reductive conversion of CO_2 into value-added products such as organic carbonate [2] has recently received considerable attention as it may provide an economic incentive to valorize CO_2 largely produced from human activities. Nevertheless, the high stability of CO_2 has limited its utilization as a chemical feedstock [1]. Accordingly, the development of catalysts that are capable of CO_2 activation is essential to exploit the potential of CO_2 as the alternative feedstock. CeO_2 catalyst has been shown its high efficiency to catalyze the direct copolymerization of CO_2 and alcohol into dialkyl carbonate and polycarbonate oligomers [2]. The promotional role of surface oxygen vacancy has been proposed as an active site in the heterogeneous catalysis of CeO_2-based materials [3]. Upon interactions with adsorbed species, the surface oxygen vacancy is dynamically annihilated (due to adsorption) and created (due to desorption) under the reaction conditions. In this presentation, I will introduce our studies on the non-reductive activation of CO_2 on CeO_2 catalysts using in-situ infrared spectroscopy [4, 5] and X-ray absorption spectroscopy [6]. It is found that the surface oxygen vacancy of CeO_2 catalysts effective for the non-reductive conversion of CO_2 can be readily recognized using the in-situ spectroscopies combined with CO_2 as the probe molecule. The bidentate carbonate identified by infrared spectroscopy is proposed as the key intermediate for the non-reductive conversion of CO_2 on CeO_2 catalysts.

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IL07

Proposal of Methanol Society -From basic research to application-

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Scientific research has confirmed that climate change is driven by anthropogenic CO_2 emissions. To combat this, urgent measures are needed to capture CO_2 at emission sources and implement renewable energy efficiently worldwide, requiring global cooperation among scientists, engineers, and policymakers. A key solution is converting captured CO_2 into an energy carrier. Among various options, methanol emerges as the most suitable carrier. This conclusion is based on 30 years of dedicated research into methanol synthesis catalysts from CO_2. Catalytic chemistry plays a critical role in producing sustainable energy fuels, replacing cheap fossil fuels.

In this presentation, I will discuss why methanol is an effective energy carrier. True innovation involves technology that can be utilized in any country, including those with limited resources. Methanol synthesis from CO_2 is feasible globally, using inexpensive copper as a catalyst. The energy required for this process at 250°C and 50 atm is relatively low. Additionally, methanol offers advantages such as easy handling, suitability as fuel for internal combustion engines and fuel cells, and utility in chemical synthesis processes like the MTO process. Above all, it is an ideal energy carrier that facilitates CO_2 recycling.

I also introduce model catalyst studies of methanol synthesis over Cu/ZnO [1-4]. In the 1990s, we have reported that CuZn alloy sites form active sites in model catalysts using Cu(111) with deposited Zn [4]. It has been found that that the CuZn site promotes the hydrogenation of formate ($HCOO_a$) on Cu, while Cu sites play a role to produce formate from CO_2 and adsorbed H_a via Eley-Rideal type mechanism. When the bending mode of the linear CO_2 molecule is excited, its reactivity as an acid increases due to the reduction in the LUMO level. This allows CO_2 to react with hydrogen on the Cu surface without the need to heat the catalyst [1]. Understanding the mechanism of heterogeneous catalysis is equivalent to creating a potential diagram of the reaction intermediates. A potential diagram for methanol synthesis from CO_2 using Cu-based catalysts is being created [2].

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IL08

Cooperative dual single atom Ni/Cu catalyst for highly selective CO_2-to-ethanol reduction

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Abstract

The electrochemical CO_2-to-C2 conversion bargains a promising approach to lowering CO_2 emission while yielding valuable chemical products. Despite the unique advantages of single-atom catalysts, molecular dual-active sites facilitate the C-C coupling reaction for C2 products toward the CO_2 reduction reaction (CO_2RR). The Ni/Cu proximal dual-active site catalyst (Ni/Cu-PASC) is developed, which is a harmonic catalyst with dual-active sites [1,2]. Here, we report the NiCu-SACs catalysts with cooperative dual heteroactive sites that achieve by far the highest catalytic activity for yielding ethanol with the unprecedented Faradaic efficiency of 92.2 % at the potential of − 0.6 V versus RHE. The catalyst exhibits the lowest onset potential of − 0.4 V versus RHE to catalyze CO_2-to-ethanol conversion. In-operando X-ray absorption spectroscopy provides an interesting observation of restructuring behavior of dynamically generated Cu clusters from atomically distributed Cu single-atoms and reversible structural changes or oxidation states of Cu sites while Ni sites remain unchanged during the catalytic reactions. Our experimental analysis and DFT computation suggest that CO produced on Cu-N_4/Ni-N_3 cooperative single atom sites undergoes C-C coupling, which is further reduced into ethanol. This strategy provides a new route to design selective and efficient catalysts for CO_2-to-ethanol conversion.

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Chemical recycling of polyolefins to valuable chemicals over heterogeneous Ru catalysts

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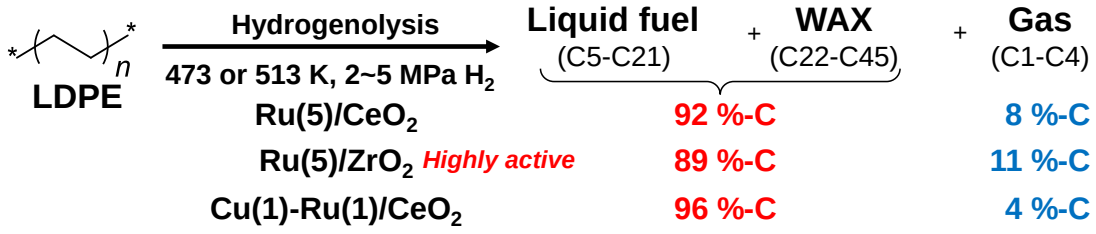
Abstract. In recent years, the development of plastic recycling technologies has been increasingly required due to issues such as plastic wastes and the depletion of fossil resources. Among these technologies, chemical recycling is considered one of the most effective methods in terms of carbon recycling. Polyolefins like PE and PP comprise a large portion of plastics. Therefore, their conversion to valuable chemicals is expected to have a significant impact. Pyrolysis is commonly known as a transformation method for the chemical recycling of polyolefins to liquid oils. However, it typically requires harsh conditions, such as high temperatures above 673 K, resulting in a high yield of gases, and produces a mixture of various compounds, including aromatic compounds. Therefore, the development of effective catalysts that can provide target products in high selectivity under low-temperature conditions is desirable, and hydrogenolysis, a method that cleaves C-C bonds using H_2, has attracted much attention.

Our research group has investigated the heterogeneous catalysts for the transformation of olefinic plastic wastes such as PE and PP with various supported hydrogenation-active metals catalysts and found that Ru was the most active metal for the hydrogenolysis of polyethylenes. Through the studies, we found that CeO_2- and ZrO_2-supported Ru (Ru/CeO_2 and Ru/ZrO_2) catalysts were highly efficient for the hydrogenolysis of polyolefins by suppressing the formation of gas products (C1-C4), and these catalyst systems could be applied to the reaction of plastic bags and waste polyethylenes [1,2]. These catalyst systems can be operated even at a low reaction temperature of 473 K and a low hydrogen pressure of 2 MPa, providing about 90% total yield of valuable products, including liquid chemicals (C5-C21 alkanes) and waxes (C22-C45 alkanes). However, about 10% of low-cost gaseous products (C1-C4) are produced, decreasing the yield of valuable chemicals. To overcome the problem, we explored the potential of solid catalysts with reduced Ru particle sizes by decreasing the Ru loading amount and introducing a second metal species to Ru. We found that CeO_2-supported Cu-doped Ru (1 wt%) catalyst, $Cu\text{-}Ru/CeO_2$, is effective for the hydrogenolysis of PE, suppressing the formation of gas products (yield: ~4%) and providing valuable chemicals with high yields (96%). In this presentation, we will introduce the background of the development of these catalysts.



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IL10

From Plastic to Valuable MOF Materials: Catalytic PET-to-BHET-to-MOF Conversion over Efficient Solid Catalysts

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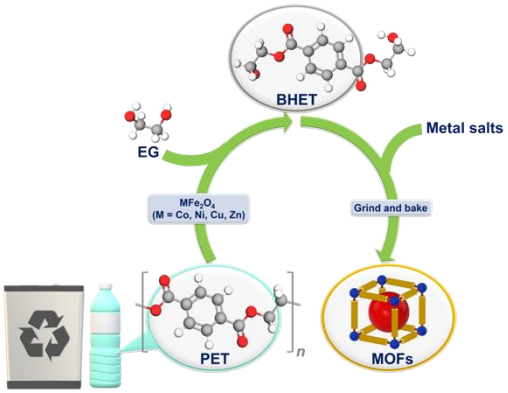
Owing to the rapid upsurge in plastic production in the last five decades, which has resulted in a dramatic increase in global plastic pollution, the development of sustainable techniques for plastic recycling and upcycling is indispensable in an attempt to decrease global plastic pollution and to attain a sustainable cycle. In response to this, the present author performed the development of heterogeneous catalysts for the chemical recycling of polyester plastics, i.e., polyethylene terephthalate (PET) via glycolysis and polycarbonate (PC) via methanolysis, and the conversion of PET and the glycolysis product of PET, namely bis(2-hydroxyethyl) terephthalate (BHET), into valuable metal-organic frameworks (MOFs).



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Switching the Selectivity of CO_2 Hydrogenation Over Supported Metal Catalysts by Phosphorous Loading

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Extensive efforts are needed to develop CO_2 utilization (Carbon recycling) technologies by using green hydrogen. Both the Sabatier reaction ($CO_2+4H_2 \rightarrow CH_4+2H_2O$) and the reverse water-gas shift (RWGS) reaction ($CO_2+H_2 \rightarrow CO+H_2O$) proceed competitively at ambient pressure [1]. To achieve the selective formation of CH_4 or CO by CO_2 hydrogenation, it is necessary to reveal the dominant factor for changing the selectivity in CO_2 hydrogenation. We found that the RWGS reaction proceeds selectively by phosphorus-loaded Rh catalyst. In contrast, the Sabatier reaction proceeds mainly on Rh/TiO_2 (Fig. 1). To elucidate the role of phosphorus in CO_2 hydrogenation, phosphorus-loaded supported metal catalysts were prepared and the relationship between structure and catalysis (activity and selectivity) was investigated. We found that the RWGS reaction proceeds selectively by phosphorus-loaded metal (various 3d, 4d, and 5d metals) catalysts while the Sabatier reaction proceeds mainly on TiO_2-supported metal catalysts [2].

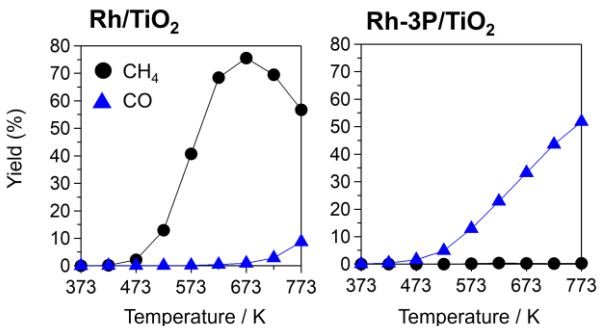

Fig. 1. CO_2 hydrogenation over Rh/TiO_2 and $Rh\text{-}3P/TiO_2$. $CO_2/H_2/N_2/He$ = 10/40/5/45 mL min^{-1}, GHSV = 60000 mL g_{cat}^{-1} h^{-1}.

The catalysts were reduced with H_2 at 673 K for 1 h prior to reaction and structural analysis. Rh K-edge XAFS analysis indicated that Rh phosphide (Rh_2P) was formed on $Rh\text{-}3P/TiO_2$. In addition, TEM and XRD results indicate that Rh_2P NPs were highly dispersed on $Rh\text{-}3P/TiO_2$. In Rh 3d XPS of catalysts reduced at 673 K, the binding energy for $Rh\text{-}3P/TiO_2$ is higher than that for Rh/TiO_2, indicating that the state of Rh in $Rh\text{-}3P/TiO_2$ and in Rh/TiO_2 are cationic and metallic, respectively. The band due to linearly adsorbed CO in the CO-DRIFT spectra was observed on Rh/TiO_2 (2082.3 and 2095.9 cm^{-1}) and (2085.5 and 2098.9 cm^{-1}), respectively. The peak position indicates that the C-O bond distance in adsorbed CO on $Rh\text{-}3P/TiO_2$ is shorter than that on Rh/TiO_2 by decreasing the π back-donation of the d-electron of Rh to the π* orbital in the C-O bond. Therefore, the cleavage of C-O bond of CO molecule was strongly suppressed on $Rh\text{-}3P/TiO_2$. No CO hydrogenation took place on $Rh\text{-}3P/TiO_2$. The H_2/D_2 exchange reaction was performed at 298 K to evaluate the H_2 activation ability. $Rh\text{-}3P/TiO_2$ exhibited a higher exchange rate than Rh/TiO_2. Based on the kinetic analysis, the reaction orders of H_2 and CO_2 were estimated to be 0.7 and 0.0 for $Rh\text{-}3P/TiO_2$, and 0.0 and 1.3 for Rh/TiO_2, respectively. These results indicate that the rate-determining step (RDS) of CO_2 hydrogenation to CO over $Rh\text{-}3P/TiO_2$ would be the reaction process involving CO_2 (adsorption or activation). In the case of Rh/TiO_2, the activation of H_2 or the bond formation (C-H or O-H) processes is the RDS to form CH_4.

Product selectivity in CO_2 hydrogenation by supported metal catalysts was switched by phosphorous-loading. RWGS reaction proceeds selectively by supported metal phosphide (Rh, Ru, Pd, and Pt) catalysts.

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IL12

Operando understanding the dynamic behavior of electrocatalysts during CO_2 reduction

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Abstract.
Electrochemical reduction of CO2 is heavily pursued as a potential solution of CO2 recycling and realizes the high-density renewable energy storage. Among numerous types of catalysts, copper-based catalysts have been shown to perform interesting nature toward hydrocarbon products. Nevertheless, achieving practical CO2RR selectivity toward desired products on the state-of-the-art copper-based catalysts is still facing great challenges. The great challenge for promoting the CO2RR selectivity may arise to a fact that this electrochemical process is a multiple proton-electron-transfer step and highly surface-sensitive, implying that the surface state of electrocatalyst may be dynamic and unpredictable under practical situations. By employing the comprehensive in-situ techniques we developed during past few years[1,2], we validate potential-driven dynamic low-coordinated Cu centers for performing significantly high selectivity and activity toward CO product over the well-known four N-coordinated counterparts[3]. Additionally, we have demonstrated the first empirical demonstration to track the dynamic structural reconstruction/transformation in a model bimetallic system, which establishes a good understanding of the correlation between catalyst surface structure and catalytic selectivity[4,5]. Furthermore, we also realized a very important achievement to develop an operando seconds-resolved X-ray absorption spectroscopy to uncover the chemical state evolution of working catalysts[6]. We aim to establish an indispensable in situ research model for future studies and offers exciting research prospects for catalytic scientists.

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Photobiocatalytic Conversion of Solar Energy to NH_3 and H_2 from N_2 and H_2O under Ambient Condition

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Abstract. NH_3 is an important chemical fertilizer and now expecting as H_2 carrier. Several methods have been investigated for eco-friendly NH_3 synthesis under mild conditions instead of Haber-Bosch process using 400 ℃, 20 MPa. In this study, cyanobacterial Anabaena variabilis was utilized as a nitrogenase-producing biocatalyst that converts N_2 and H_2O to form NH_3 and H_2 under ambient conditions. NH_3 formation rate of the hybrid system was increased by 82 times with the maximum rate of 4.06 $\mu M \cdot g^{-1} \cdot h^{-1}$.

Currently, most NH_3 is produced by the Haber-Bosch process, in which hydrogen (H_2) and nitrogen (N_2) gases are converted into NH_3 under severe condition, high temperatures and pressure (typically 350–550°C and 150–300 atm). NH_3 is an important chemical fertilizer and chemical intermediate for industrial production. However, the process consumes around 2 % of global energy annually and is responsible for roughly 3 % of all anthropogenic greenhouse gas (GHG) emissions. Due to growing concern and awareness about global warming, new environmental-friendly process under more mild conditions is strongly required. Nitrogenase is the only biocatalytic enzyme to fix and break the strong N≡N bond of N_2 to NH_3 as follows:

$N_2 + 16MgATP + 8H^+ + 8e^- \rightarrow$(Nitrogenase) $\rightarrow 2NH_3 + H_2 + 16MgADP$

According to the biological properties of cyanobacteria, this study aims to establish the photobiocatalytic system for NH_3 production using light energy. TiO_2 is served as a light-absorbed photocatalyst, while an N_2-fixing cyanobacterium Anabaena variabilis acts as a whole-cell biocatalyst. The development of TiO_2:cyanobacteria hybrid systems operating under ambient conditions is a promising strategy for sustainable NH_3 production from N_2 to H_2O.

During the reaction of photobiocatalytic NH_3 production, H_2 production and N_2 consumption were simultaneously determined. Fig. 1 shows time course of NH_3 formation under various condition. Among various conditions, lower yields of H_2 were observed in the systems using cyanobacteria cultivated in Allen & Arnon medium (CyaAA) and the systems lacking one of each component (Fig. 1), i.e., glycerol, MV^{2+} and TiO_2. The complete system of whole-cell CyaAA produced H_2 at the rate of 3.71 ± 0.39 μmol/h, while the lack of components showed lower H_2 production rate. In addition, it was found that the addition of MSX (L-methionine sulfoximine), as a glutamine synthetase inhibitor, showed similar results to the MSX-free complete system suggesting MSX did not affect the activity of nitrogenase or hydrogenase. At 48-h reaction time, the complete system of CyaAA extract showed the maximum NH_3 production rate of 2.03 μmol/h that significantly increased 81.59 times higher compared to the capacity of CyaAA itself (without other components), while lower rates were found in the complete system of CyaAA without MSX.

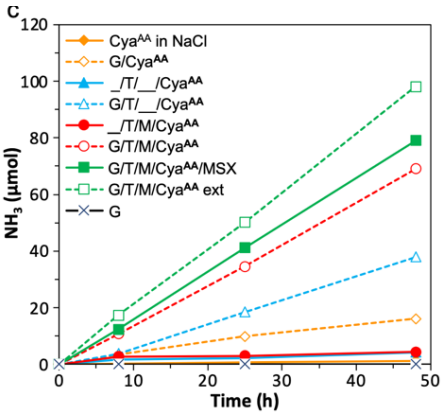

Fig.1 NH_3 production from the combination of cyanobacterium *A. variabilis* coupled to TiO_2 under various conditions.
Cya^{AA}, cyanobacterium cultivated in Allen & Arnon medium; G, glycerol; T, TiO_2; M, methyl viologen (MV^{2+}); MSX, L-methionine sulfoximine.

Photocatalytic Reforming of Methanol and CO_2 into H_2 and C_2 Compounds

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Photocatalytic reforming of CO_2 and other C_1 compounds into value-added C_2 compounds with/without simultaneous H_2 production under solar illumination is considered a promising strategy to address the global warming problem. The presence of co-catalysts substantially improves the separation of the photogenerated charges and therefore the reaction rates. The present study demonstrates that co-catalysts CoP and Pt facilitates the production of ethylene glycol and acetate, respectively, in addition to H_2 evolution, from photocatalytic methanol reforming in alkaline solutions. When performing coupled CO_2-CH_3OH reforming over a photocatalyst deposited with Pt, our study demonstrates that, performing the photocatalytic reforming under a high concentration of CH_3OH for electron donation, the large amount of photoelectrons in the conduction band of the catalyst effectively convert CO_2 into the $\cdot CO_2^-$ radical, which then swiftly transforms into formate or proceeds with self-coupling into acetate. When the CH_3OH concentration is close to the CO_2 concentration, the coupling reaction between the donor and acceptor-derived $\cdot CH_3OH$ and $\cdot CO_2^-$ radicals to form acetate becomes dominant. The present work demonstrates that increasing donor concentration speeds up the rate of CO_2 conversion, but at the expense of reduced product selectivity.

Visible-light driven polymer precursor synthesis from gaseous CO_2 with hybrid catalytic system

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While various plastics are inexpensive, lightweight, durable, and multifunctional materials with excellent ductility, the issue of environmental pollution caused by plastic waste has been attracting attention in recent years. Biodegradable plastics are attracting attention as a way to solve serious environmental problems such as the marine floating plastic debris. Biodegradable plastics are typically produced from renewable raw materials, petrochemicals, and are broken down by living organisms into water, CO_2 and biomass. Among these biodegradable plastics, poly-3-hydroxybutyrate (PHB)-based or polybutylene succinate (PBS)-based plastics are attractive materials because they are compostable, made from renewable feedstocks, and biodegradable. A new biodegradable plastics precursor synthesis from gaseous CO_2 using visible-light driven catalytic system consisting of triethanol amine (TEOA), zinc porphyrin (ZnP), $[Cp^*Rh(bpy)(H_2O)]^{2+}$ (Cp^*: 1,2,3,4,5-pentamethylcyclopentadien, bpy: 2,2'-bipyridine), NAD^+ and various biocatalysts is a candidate for a useful green process method (Figure 1).

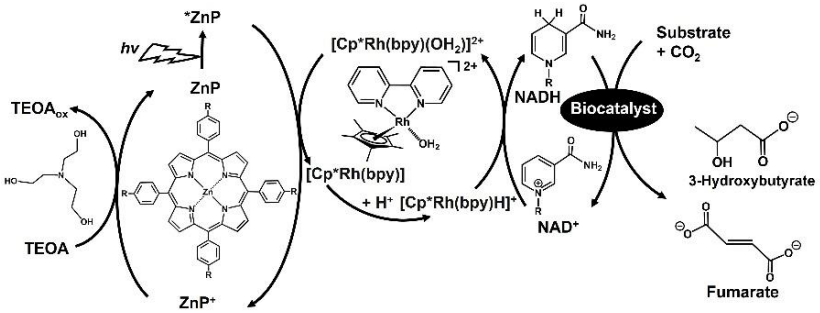

Fig. 1. Visible-light driven plastics precursor synthesis from gaseous CO_2 and substrate with the system of NADH regeneration and biocatalyst.

In this lecture, an enzyme extract containing acetone carboxylase and 3-hydroxybutyrate dehydrogenase from a purple nonsulfur photosynthetic bacterium was applied as the biocatalysts for the visible light-driven 3-hydroxybutyrate synthesis from acetone and gaseous CO_2 system was introduced as an example for a PHB-based plastic precursor production with the hybrid catalytic system [1-4]. In addition, the visible light-driven fumarate synthesis from pyruvate and gaseous CO_2 system consisting of TEOA, ZnTPPS, $[Cp^*Rh(bpy)(H_2O)]^{2+}$, NAD^+ and dual biocatalysts consisting of malic enzyme and fumarase also was introduced as an example for a PBS-based plastic precursor production with the hybrid catalytic system [5-8].

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Catalyst-Support Interaction for Practical Water Electrolysis

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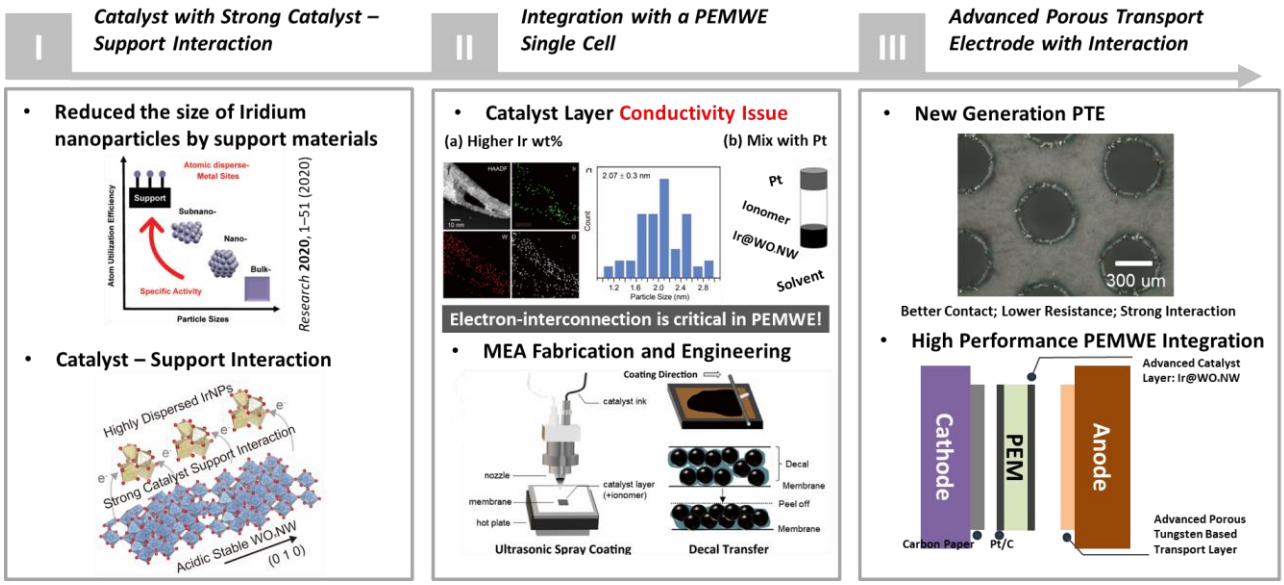
Abstract. Polymer electrolyte membrane water electrolysis (PEMWE) is a promising technology to produce green hydrogen due to its high power density and fast start-up/shut-down characteristics. However, the scarcity of the anode iridium (Ir) catalyst impedes the mass deployment of PEMWE. To solve this problem, ultra-low Ir loaded anodes are developed with the aid of an acid-stable support material, *i.e.*, tungsten/tungsten oxides. Leveraging the reducible nature of tungsten oxides (WO_x), strong catalyst-support interaction between Ir and WO_x can be created in various scenarios. In this presentation, we will summarize our research findings in recent years on developing WO_x-supported Ir and PGM-free catalyst to drive the oxygen evolution reaction (OER). Our roadmap from model catalyst development to the implementation in practical membrane electrolyzers will also be revealed in this presentation.



Scheme 1. Illustration of our roadmap to achieve low-Ir PEMWE by catalyst-support interaction.

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Charge Carrier Dynamics for the Development of Highly Active Photocatalysts

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Photocatalytic water splitting has attracted much attention as an environment-friendly way to produce hydrogen gas as energy resources. Photocatalysts are usually used in powder form in view of their low cost and large surface area. Powder particles are rich in surface defects. It has been widely believed that defects work as electron-hole recombination centers and decrease the photocatalytic activity. Nevertheless, in fact, photocatalytic reactions proceed well with powders. Moreover, it has been reported that introducing more defects can sometimes elongate the photocarrier lifetime and improve the photocatalytic activity. However, the effects of powder defects on photocarrier dynamics have not been fully understood yet. Herein, we studied the effects of defects on photocarrier recombination processes by comparing powder and a defect-less single-crystalline $SrTiO_3$. We also compared photocarrier dynamics in undoped and Na-doped $SrTiO_3$ to investigate the roles of defects on photocatalytic reaction.

A broadband time-resolved absorption spectroscopy was conducted to observe the photocarrier dynamics. In the case of the single-crystalline $SrTiO_3$, most of the photoexcited electrons survive as free electrons without being trapped by defects. The absorptions by free electrons hardly decayed in the picosecond region. However, the absorption decayed almost single-exponentially in the nanosecond region, and the intensity decreased to less than one-hundredth the original value by 150 ns. On the other hand, in the case of the powder $SrTiO_3$, a large portion of the photogenerated carriers are trapped by defects. The free and trapped electrons decayed rapidly even within a few picoseconds, where trapped electrons decreased more rapidly than free electrons. This result indicates that defects accelerate the recombination just after the excitation. However, the electrons in the powder decayed not in a single-exponential but a multi-exponential manner, and their decay decelerated gradually. Especially, the decay of the trapped electrons became slower than that of free electrons within ~200 ps. Some of the photocarriers survive into the millisecond region. When the decay of electrons in the single-crystalline and powder $SrTiO_3$ were compared, the lifetime of photocarriers in the single crystal was longer than that in powder in a few nanoseconds. However, the photocarrier lifetime in powder became longer in the nanoseconds to milliseconds region than that in the single crystal.

These results suggest that defects in powders initially accelerate the photocarrier recombination, but later they decelerate it. This dualistic property of defects in powder is considered to depend on whether electrons and holes are trapped in the vicinity or far away from each other. Powders contain a lot of defects, and most of the photoexcited carriers in powder are captured by these defects. Since the charge separation is not proceeded enough just after the excitation, electrons and holes will tend to be captured when in the vicinity of one another. The closely trapped electrons and holes can hop to approach each other. Therefore, the recombination will be accelerated in the picosecond region. However, once the electrons and holes escape from this initial recombination process, they can spread and get separated by longer distances. In this case, the electrons and holes need to travel long distances by repeated hopping or tunneling for recombination to come closer. This makes the photocarrier lifetime in powder longer than that in single crystal after the nanosecond region.

Metal oxide-based 3D-printed catalyst support used for photocatalytic reactions

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Abstract. In this work, Al_2O_3-based 3D-printed catalyst supports were prepared to integrated with carbon-bridged g-C_3N_4 for the photocatalytic oxidation of tetracycline. Different carbon-containing linkers, oxamide (OD), malonamide (MD), and succinamide (SD) were used to react with melamine and urea to produce carbon-bridged g-C_3N_4. Computational calculations were also employed, and Bader charge analysis supported the charge redistribution and transfer of the carbon-bridged g-C_3N_4 samples. The 3D-printed Al_2O_3-supported carbon-bridged g-C_3N_4 exhibited high stability for photocatalytic tetracycline oxidation and can be reused for at least 10 cycles (**Fig. 1**). The tetracycline oxidation followed step-by-step oxidation, deamination, and mineralization to form CO_2 and H_2O. Moreover, self-supported TiO_2-based 3D-printed catalyst was fabricated and employed for photocatalytic hydrogen evolution (**Fig. 2**). The self-supported TiO_2-based 3D-printed catalyst can be prepared in a very short time and exhibited extremely high stability for photocatalytic H2 production. Our work suggested that the metal oxide-based 3D-printed catalyst support is an efficient and effective system for photocatalytic reactions.

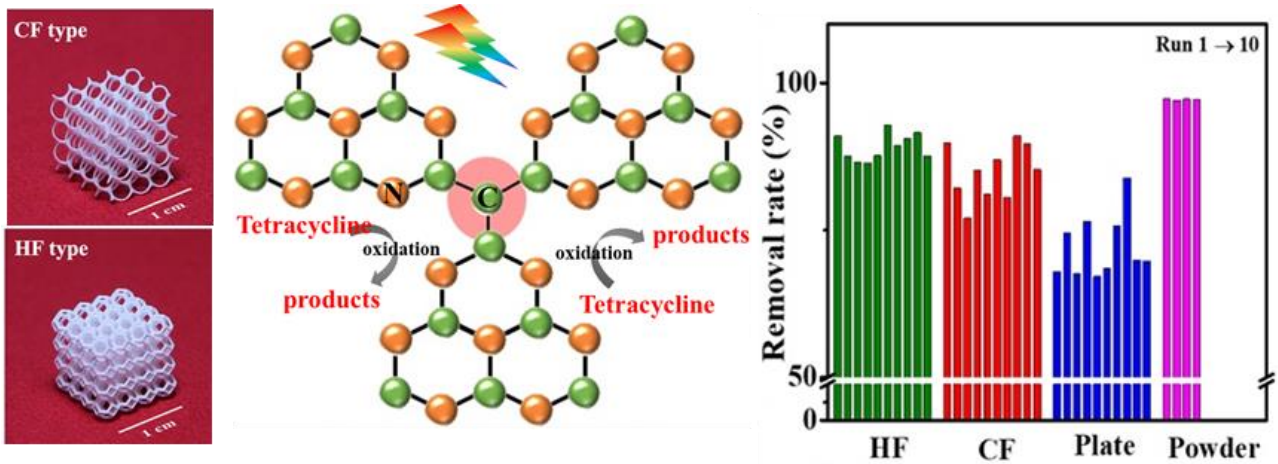

Fig. 1 Al_2O_3-based 3D-printed catalyst support, structure of carbon-bridged g-C_3N_4, and the tetracycline oxidation efficiency using these samples.

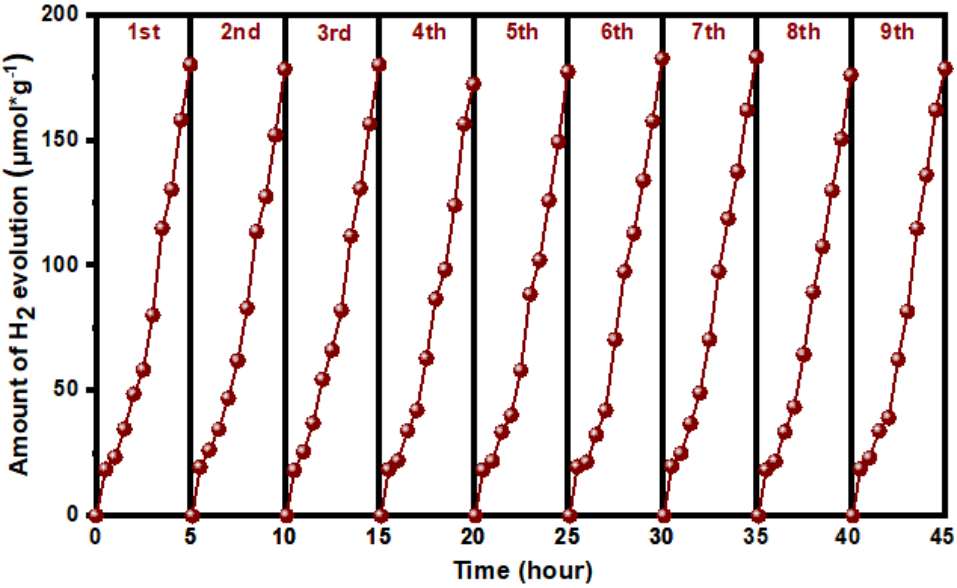

Fig. 2 Photocatalytic H_2 production using a self-supported TiO_2-based 3D-printed catalyst in the presence of TEOA solution (5 vol%) under light irradiation. 0.5 wt% of Pt was used as a cocatalyst.

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IL19

Theoretical Study of Surface Reactions from a Molecular Science Perspective

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The nonoxidative coupling of methane (NOCM) is a process that converts two methane molecules into ethane and hydrogen. A major competing reaction for this is the carbon deposition due to the dehydrogenation of methane [1,2]. In organometallic chemistry, the cleavage of C–H bonds and the formation of C–C and H–H bonds on catalyst surfaces are referred to as oxidative addition and reductive elimination, respectively. We have sought to understand these reactions on a Pt surface from a molecular perspective, applying the Walsh diagram, or orbital correlation diagram, from molecular science, to the bands (crystal orbitals) in surface science [3,4].

In general, reductive elimination is less favorable in dinuclear complexes but more likely in mononuclear complexes. The same principle applies to surface reactions. On a Pt surface, the reductive elimination of two CH_3 species adsorbed on adjacent top sites requires a substantial amount of energy. However, when the two CH_3 species are adsorbed on the same Pt atom, the reductive elimination process is much more facile. In mononuclear reactions, the CH_3 species can strongly interact with the surface orbitals in the transition state, while in dinuclear reactions, the orbital overlap is weaker, resulting in a less stable transition state.

Compared to Au, Pt has a higher d-band and a lower Fermi level, making it particularly effective at stabilizing the C–H bond. Consequently, the C–H bond cleavage capability of the Pt surface is superior to that of Au. Additionally, the H atom generated from C–H bond cleavage is effectively stabilized by the triangular Pt–Pt–Pt ensemble present on the Pt surface.

While Pt(111) is not optimal for preventing carbon deposition and facilitating reductive elimination, it is still essential to break the first C–H bond in methane. To balance these conflicting requirements, we have proposed the Pt_1/Au(111) single-atom alloy (SAA), in which one Pt atom replaces a Au atom in the Au(111) surface. The Pt dopant provides a highly reactive site capable of cleaving the first C–H bond in methane, while the lack of the Pt–Pt–Pt ensemble prevents overoxidation. At the same time, the mononuclear Pt site is favorable for promoting the reductive elimination of ethane and hydrogen [4].

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Next-Generation Molecular Design: Integrating Uncertainty into AI-Based Predictions

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Machine learning (ML) has become an integral tool in material designs, yet its performance is often constrained by data limitations and inherent uncertainties. This work introduces a novel approach that integrates uncertainty quantification (UQ) into optimization tasks, enabling a more reliable and insightful molecular design process. By combining advanced surrogate models with UQ techniques, the framework not only enhances prediction accuracy but also provides a granular understanding of uncertainty through atomic-level attributions. Our methodology employs the Tartarus platform [1] for property validation and leverages direct message-passing neural networks (D-MPNN) [2] for surrogate modeling. UQ techniques, such as deep ensembles and evidential learning, are used to characterize both aleatoric and epistemic uncertainties, guiding single- and multi-objective optimization tasks. Additionally, an explainable UQ framework is developed [3], attributing uncertainty to specific atoms and improving interpretability as shown in Fig. 1. The results demonstrate that UQ-integrated optimization significantly improves property distributions and top-k hit rates across diverse molecular design tasks, including organic emitters and reaction substrates. For multi-objective optimization, UQ-guided methods reliably explore design spaces to meet practical constraints, enhancing the design process's reliability and robustness. By embedding UQ into molecular optimization workflows, this research transforms uncertainty from a limitation into a strategic asset, fostering breakthroughs in computational molecular design. These innovations address real-world application challenges and provide a versatile platform for advancing molecular discovery across various scientific domains.

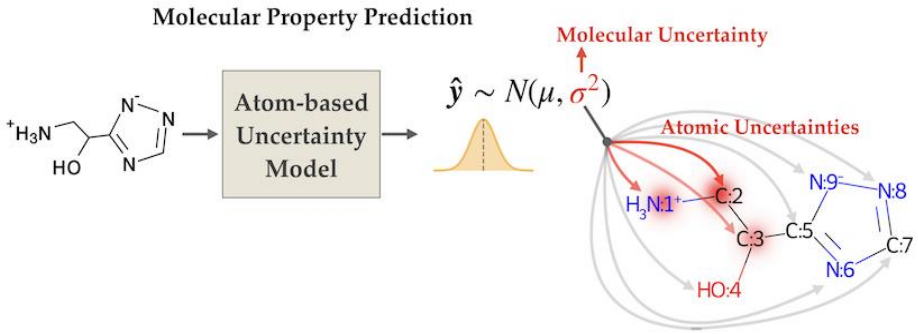

Figure 1. An explainable UQ framework for deep learning-based molecular property prediction. This atom-centric approach enhances chemical insight by attributing uncertainties to individual atoms, enabling the identification and diagnosis of specific molecular components that contribute to prediction variability [3].

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Development of heterogeneous Mo-based catalysts for H_2-driven deoxydehydration

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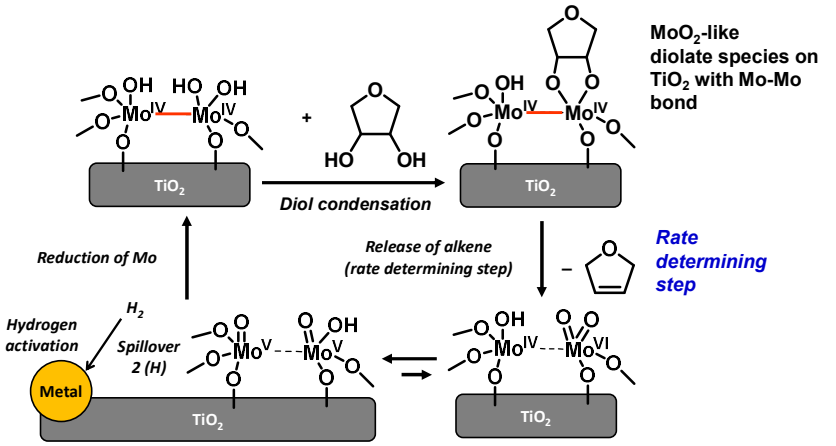
Abstract. Hydrodeoxygenation is one of the important reactions for the production of biomass-derived chemicals. The deoxydehydration (DODH) reaction converts vicinal OH groups to the carbon-carbon double bond and is promising as a selective approach to converting biomass to olefinic compounds, where suitable catalysts and reducing agents are needed. Regarding the reducing agent, H_2 is one of the feasible reductants, however, H_2 is not suitable reductant for homogeneous DODH catalysts. Therefore, we have been developing the heterogeneous DODH catalysts enabling H_2 as a reductant, which is called as H_2-driven DODH and the reaction is regarded as hydrodeoxygenation, by the combination of DODH catalytically active species fixed on the oxide support surface with metal modifiers for the activation of H_2. We have reported ReO_x-M/CeO_2 (M = Pd, Au, Ag) and ReO_x/CeO_2 + Ni/CeO_2 (physical mixture) as effective catalysts for H_2-driven DODH (+hydrogenation of C=C). The disadvantage of these catalysts is the utilization of noble metals. We recently attempted to develop cheaper heterogeneous DODH catalysts by the substitution of Re by Mo, and MoO_x-Au/TiO_2 catalyst is found to be effective [1]. An interesting point is that the direct Mo-Mo in the MoO_x species on the anatase TiO_2 was detected by EXAFS. In the case of ReO_x/CeO_2, monomeric Re species is catalytically active has been proposed, in contrast, in the case of MoO_x/TiO_2, MoO_2-like structure or dimeric species is suggested to be important. DFT studies also suggest that monomeric Mo species is not so active because of higher barrier of the reduction of the Mo species [2]. The proposed reaction mechanism is shown as below. In addition, we have also reported MoO_x-Cu/TiO_2 catalysts as non-noble metal H_2-driven DODH catalysts. In particular, the use of a small amount of the basic Mo precursor Na_2MoO_4 (MoO_x-Cu-Na/TiO_2) enhanced the selectivity to DODH products, achieving the highest yield of 2,5-dihydrofuran at 81% from 1,4-anhydroerythritol. This catalyst maintained its performance through at least three reuse cycles without significant drops in the con version or selectivity when the spent catalyst was calcined before each run. The catalyst displayed broad substrate scope including both linear and cyclic diols. In particular, this catalyst also worked well for tartaric ester, which is difficult to be converted to the corresponding DODH product in the reported catalysts with H_2 as the reductant.



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Vibrational Spectroscopy at Electrified Interfaces: Electrochemical Catalytic Reaction and Li-ion Batteries

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Abstract. The solid-liquid interfacial reactions play a crucial role in controlling the performance and stability of electrocatalysts and battery materials [1-4]. In situ vibrational spectroscopy techniques such as Raman and surface-enhanced infrared absorption spectroscopy (SEIRAS) are the powerful tools for examining the surface-adsorbed intermediates on the solid-liquid interfaces. In this talk, we report on our use of in situ SEIRAS, Raman, and X-ray absorption spectroscopy to investigate the electrochemical CO_2 reduction mechanism over the Cu-based electrocatalysts and the reaction mechanism of Li-rich layered oxide cathode in Li-ion/Li metal batteries. The Cu-based electrodes with different oxidation states result in the formation of various CO intermediates such as CO_{atop} and CO_{bridge}. The co-existence of CO_{atop} and CO_{bridge} corresponds to the selectivity of CO_2-to-C_2H_4 reaction. Also, the bimetallic electrocatalysts are developed for efficient CO_2-to-HCOOH and CO_2-to-CO conversion processes. We found that the surface-adsorbed COO species with different binding structures play crucial role in the reduction process. The electronic structures of Cu-based electrocatalysts are associated with the formation of surface-adsorbed intermediates and electrocatalytic properties. The formation of surface-adsorbed intermediates and reaction mechanism associated with CO_2-to-HCOOH and CO_2-to-CO reactions over the bimetallic electrocatalysts will be discussed in detail.

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Nanocatalysts for a low-carbon society: upgrading chemicals through electrochemical hydrogenation

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Hydrogenation reactions using green hydrogen are indispensable for the energy storage and material synthesis without a great deal of CO_2 emission. Electrochemical CO_2 reduction (eCO_2R) using H_2O as a hydrogen source attracts much attention as a technology for carbon circulation on the earth and the selective eCO_2R for the production of high value-added chemicals is increasingly demanded.[1, 2] Hydroxide-derived copper (OH/Cu) electrodes exhibit excellent performance for eCO_2R. In this study, we have quantitatively evaluated surface OH and established a direct correlation between the OH amount and selectivity for the production of CH_4 and C_{2+} on OH/Cu and demonstrated valuable selectivities using OH/Cu electrodes.[3] The eCO_2R in acidic electrolytes would have various advantages due to the suppression of carbonate formation. Here, we designed an optimal architecture of a gas diffusion electrode (GDE) employing a copper-based ultrathin superhydrophobic macroporous layer (Cu-GDE), in which the CO_2 diffusion is highly enhanced and demonstrated Faradaic efficiency of 87% for C_{2+} products.[4]

To date, only a few studies have evaluated eCO_2R of CO_2 feeds containing O_2. Therefore, the development of systems that enable efficient eCO_2R in the presence of O_2, is critical to the establishment of DAC-U technology.[5] Recently, we achieved eCO_2R by direct introduction of 60% air containing CO_2 using a porous Cu network formed on a hydrophobic gas diffusion layer. Even in the presence of 12% O_2, Faradaic efficiency for the C_{2+} production reached 85% at a partial current density of 132 mA cm^{-2}.[6]

This presentation will also discuss highly efficient hydrogenation reactions using a structure controlled TiO_2 catalysts.[7-9]

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Stable and Electrochemically "Inactive" Sulfonate-Functionalized Metal–Organic Framework for Electrocatalysis

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Abstract

Metal–organic frameworks (MOFs) with ultrahigh surface areas and interconnected porosity have been considered as attractive materials for electrocatalysis and other electrochemical applications. But the poor stability in water and low electrical conductivity of most MOFs strongly restrict the design and direct use of structurally robust and electrochemically active MOFs. The development of stable group(IV) metal-based MOFs, such as Zr-based MOFs (Zr-MOFs), has allowed the use of MOFs in aqueous media while preserving their structures, but the poorly conducting nature of these MOFs still limits their performances as electrocatalysts.

Herein, a unique concept of utilizing electrochemically "inactive" and "non-catalytic" MOFs in electrocatalytic reactions is proposed. The porous and stable MOF thin film can modulate the microenvironment near the underlying surface of the electrocatalyst and thus adjust the selectivity of complicated electrochemical reactions. The underlying electrocatalytic material with a high electrical conductivity and a high catalytic activity, and the highly porous MOF capable of turning the microenvironment near the electrocatalyst, can thus be designed separately.

To demonstrate this concept, a water-stable Zr-MOF, MOF-808, was selected to post-synthetically immobilize the sulfonate-based ligands. By coating a thin film of this "anionic MOF" on the surface of another state-of-the-art electrocatalyst, the selectivity and reaction rates of electrocatalytic processes can be remarkably enhanced. This talk will cover two recent examples from our group. In the first example, the Zr-MOF thin film can enhance the selectivity for electrochemical dopamine sensing occurring on the surface of graphene-oxide electrocatalyst against the interference from both ascorbic acid and uric acid, and it can even outperform the conventionally used Nafion thin films (Figure 1(a)). In the second example, the Zr-MOF coating can concentrate protons and thus promote the nine-proton-coupled reduction of nitrate to produce ammonia occurring on the underlying copper electrocatalyst; the two-proton side reaction of nitrite formation can thus be suppressed (Figure 1(b)). Findings here shed light on the use of such porous and ionic MOFs as advanced alternatives to Nafion for adjusting the selectivity and reactivity of complicated electrocatalytic processes.

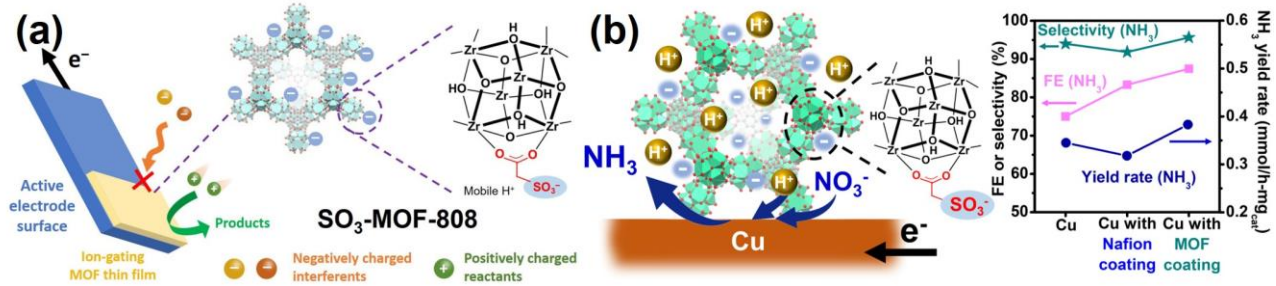

Figure 1. Sulfonate-functionalized stable MOF coating to enhance the (a) selectivity of catalysis-based electrochemical sensors and (b) selectivity of electrocatalytic nitrate reduction to produce ammonia.

Reductive decomposition of nitrous oxide over supported iridium catalysts at low temperature

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It has been pointed out that anthropogenic greenhouse gases cause global warming, and nitrous oxide (N_2O) is one such gas. Although emission of N_2O is small comparing with CO_2, its impact on global warming is significant because its global warming potential is about 300 times larger than that of CO_2. Recently, research on the development of high-performance N_2O adsorbents is actively underway, and in fact, several adsorbents have been developed with performance almost applicable for practical use [1]. In the process for the removal and decomposition of N_2O, the adsorbent that adsorbs N_2O is heated in gas flow and the released N_2O is decomposed in a reactor located downstream. From energy saving perspective, the adsorbent should release N_2O at as low temperature as possible. Therefore, a catalyst is needed to decompose N_2O at low temperatures, preferably near room temperature. In this study, aiming to develop such catalysts, we searched for supported metal catalysts that promote reductive decomposition of N_2O using H_2 as reductant ($N_2O + H_2 \rightarrow N_2 + H_2O$).

Fig. 1 shows catalytic performances of Al_2O_3-supported metal catalysts for N_2O reduction with H_2 at 50°C. Most catalysts were inactive or only slightly active at this temperature, while the catalysts with fifth and sixth periods metals, except for Ag and Au, showed decent activity at 150°C. In contrast to them, it should be noted that Ir/Al_2O_3 showed high activity for the reaction even at 50°C. Reaction mechanism study with the supported Ir catalyst have shown that the reaction proceeded via a redox mechanism, where N_2O was reduced by the reaction with metallic Ir site to give N_2 and oxidized Ir site, followed by the reduction of the oxidized Ir site with H_2. The activity of the Al_2O_3-supported metal catalysts showed a volcanic-type trend with respect to the d-band center of the metals (Fig. 2). Thus, the high catalytic activity of Ir was assumed to be due to its moderate oxygen affinity derived from the moderate d-band center.

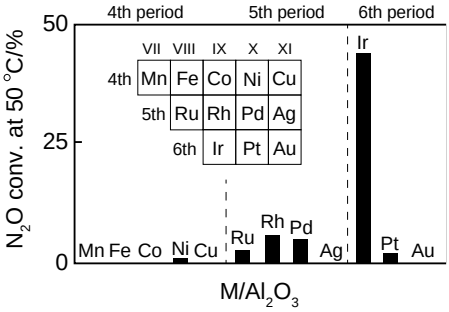

Fig. 1 Catalytic performance of Al_2O_3-supported metal catalysts for reductive decomposition of N_2O with H_2 at 50°C.

The support effect of the Ir catalyst was then investigated to improve catalyst performance. The activity varied greatly depending on the support, with Ir/SiO_2 and Ir/ZrO_2 exhibiting particularly high catalytic activity among the catalysts examined, which were about twice as high as that of Ir/Al_2O_3. To clarify the reason for the support effect, the surface area of Ir particles was estimated from the amount of CO chemisorption. The catalytic activity was increased with increase in the surface area of Ir particles. In other words, the reaction rate per surface Ir atom was almost independent for these catalysts. Therefore, it was concluded that the high activity of Ir/SiO_2 and Ir/ZrO_2 was due to the high Ir dispersion. The Ir/SiO_2 showed catalytic activity for the reaction even at room temperature and there was little decrease in activity over reaction time in long-term reaction test at the temperature.

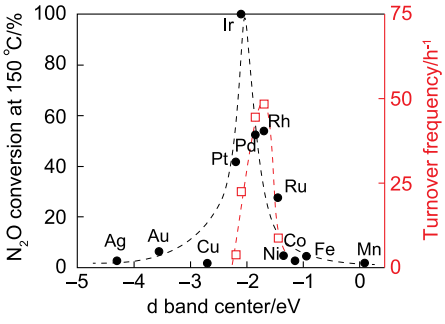

Fig. 2 Relationship between d band center and catalytic activity of Al_2O_3-supported metal catalysts.

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The Structure Transformation of Transition Metal Oxide as Electrocatalysts in Anodic Oxidation Reaction

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Abstract. The impact of structural transformations on electrocatalytic reactions is significant and can greatly influence the efficiency and performance of electrochemical processes. Structural transformations refer to changes in the composition, morphology, and configuration of the catalyst material. Revealing structural transformations could involve changes in surface morphology, active sites exposure, or electronic structure modification, resulting in enhancing the catalytic activity of materials, leading to optimize electrocatalytic performance. Moreover, changes in the catalyst's structure may influence electron transfer pathways, affecting the kinetics of the electrocatalytic reaction. Optimizing these pathways can enhance electron transport and reduce energy losses, leading to improved overall efficiency. Recently, we found that under electrochemical reaction, the structure of various materials, including metal-organic framework (MOF) and amorphous binary metal oxide are so sensitive to be changed in alkaline electrolytes, which were characterized by in-situ synchrotron techniques, including high-resolution X-ray diffraction and X-ray absorption spectroscopy, etc. In water splitting reaction, Co-Mo-MOFs as electrocatalysts for oxygen evolution reaction (OER) will be reacted in alkaline electrolyte to form highly porous gyroid morphology with large surface area, resulting in demonstrating a superior OER electrocatalytic activity with a low overpotential of 210 mV at a current density of 10 mA cm^{-2} and small Tafel slope of 50 mV dec^{-1} in alkaline solution. In other case on urea electrooxidation reaction, High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), corresponding energy-dispersive X-ray spectroscopy (EDS), and in-situ X-ray absorption spectra (XAS) were employed to elucidate the structural transformation from Co-Ni hydroxide to blending CoOOH-$Ni(OH)_2$ nanoclusters during the reaction. The blending CoOOH-$Ni(OH)_2$ nanoclusters exhibited superior electrocatalytic activity for UOR in alkaline environment, achieving low onset potential of 1.24 V (vs. RHE) in 1M KOH with 0.5M urea. Overall results indicated that the impact of structural transformations on electrocatalytic reactions is multi-faceted, influencing catalytic activity, durability, selectivity, and overall performance. Controlled and strategic modifications of catalyst structures are essential for advancing the field of electrocatalysis and developing more efficient energy conversion technologies.

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Artificial photosynthesis by heterogeneous photocatalysts -Photocatalytic reduction of CO_2 by H_2O as an electron donor-

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The reduction in human-induced emissions of CO_2 from automobiles, factories, power stations etc., over the next 15 years is currently one of the most important issues facing the planet. We should therefore attempt to develop industrial processes using CO_2 as a feedstock to build a sustainable society. Linear CO_2 molecules adsorbed on the surface of the solid bases are converted into unique structures, such as bicarbonate and carbonate species possessing lattice oxygen atoms. These days, we succeeded in designing highly selective photocatalytic conversion of CO_2 by H_2O as the electron donor, by the simultaneous use of an inhibitor of the production of H_2 and a material for CO capture and storage as shown in Table 1. An isotope experiment using $^{13}CO_2$ and mass spectrometry clarified that the carbon source of the evolved CO is not the residual carbon species, but the CO_2 introduced in the gas phase. In addition, stoichiometric amounts of O_2 were generated together with CO. Consequently, Ag@Cr/CaO/$CaGa_4O_7$/Ga_2O_3 reported in 2020 exhibits the highest photocatalytic activity (835 μmol h^{-1} of CO) with much better selectivity (94.5%) than the pristine Ag/Ga_2O_3 photocatalyst which had been found by our group in approximately 10 years ago. In addition, we found that Mg–$SrTiO_3$ showed relatively high activity with approximately 100% selectivity for the photocatalytic conversion of CO_2 to CO using H_2O as the electron donor under monochromatic UV-light irradiation at 365 nm.

Table 1. Summary of our photocatalysts tested for the photocatalytic reduction of CO_2 by H_2O in our research group. Ag co-catalyst loading: 0.25–1.0 wt%; light source: 400 W high-pressure Hg lamp; water volume: 0.2-1.0 L; CO_2 flow rate: 30 mL min^{-1}; additive: 0.1 M $NaHCO_3$

Sample	Cat. / g	Formation rate / μmol h^{-1}			Selec. to CO (%)	e^-/h^+	*Ref.*
		H_2	O_2	CO			
Ag/$ZnGa_2O_4$/Ga_2O_3	1.0	16.9	70.1	117	87.4	0.96	[1]
Ag/$ZnGa_2O_4$	1.0	8.5	74.3	155	94.8	1.10	
Ag/$Sr_{1.6}K_{0.37}Na_{1.43}Ta_5O_{15}$	1.0	16.0	53.7	94.6	85.5	1.03	
Ag@Cr/Ga_2O_3	0.5	91.6	326	525	85.2	0.95	[2]
Ag@Cr/CaO/$CaGa_4O_7$/Ga_2O_3	0.5	48.9	402	835	94.5	1.10	[3]
Ag-Co/Al-$SrTiO_3$	0.5	0.1	25.8	52.7	99.8	1.02	[4]
Ag-Co/Mg-$SrTiO_3$	0.2	0.05	8.9	19.7	99.7	1.12	[5]

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Optimizing TiO_2-Bi_2WO_6 Composites for CO_2 Photoreduction

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Abstract. The morphology of bismuth tungstate (Bi_2WO_6) was tuned by incorporating various amounts of cetyltrimethylammonium bromide (CTAB) as a surfactant during the hydrothermal synthesis process. Sodium tungstate dihydrate and bismuth nitrate aqueous solutions, mixed in a fixed molar ratio, were combined with CTAB to achieve this control. Additionally, commercial TiO_2 was introduced in varying amounts to fabricate TiO_2-Bi_2WO_6 heterojunctions for photocatalytic CO_2 reduction. Scanning electron microscopy (SEM) revealed that CTAB concentration significantly influenced the morphology of Bi_2WO_6 (Fig. 1), while UV-Vis spectroscopy indicated only a limited improvement in light absorption. Morphological variations affected the material's CO_2 affinity and the generation rate of reactive radicals (Fig. 2). The TiO_2-Bi_2WO_6 composites demonstrated superior photocatalytic performance compared to pure TiO_2 and pristine Bi_2WO_6, primarily due to enhanced charge carrier separation and improved light utilization efficiency.

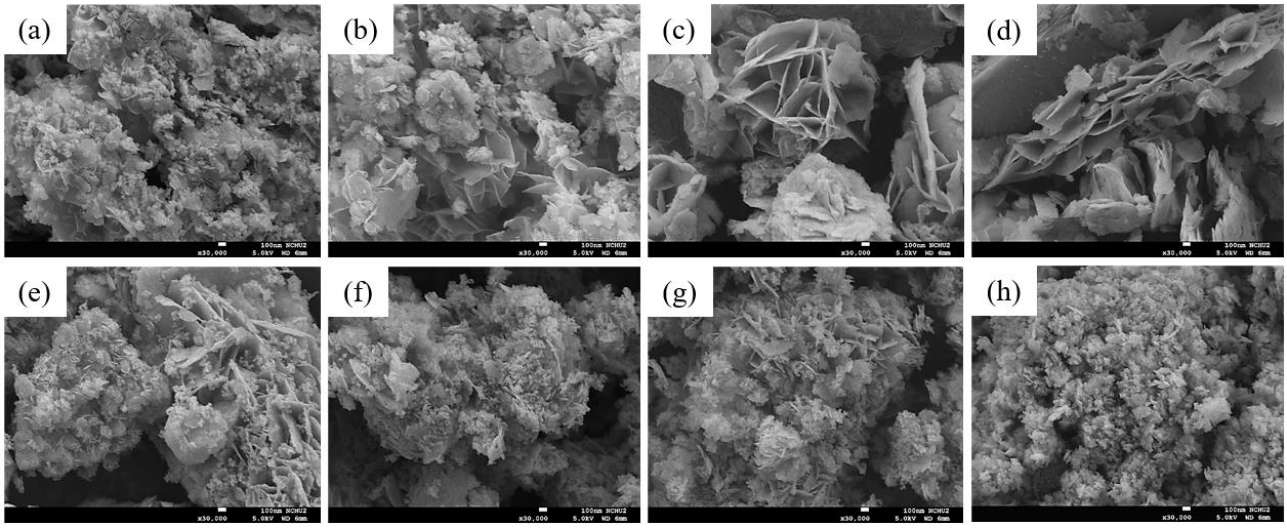

Figure 1. SEM images : (a) Bi_2WO_6 , (b) 0.015C_Bi_2WO_6 , (c) 0.05C_ Bi_2WO_6 , (d) 0.1C_ Bi_2WO_6 , and (e) 10% (f) 20% (g) 30% (h) 40%_Ti_0.05C_Bi_2WO_6.

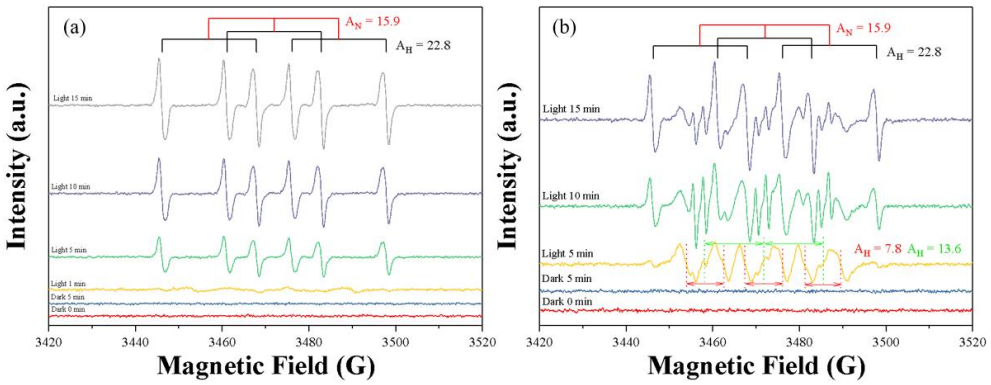

Figure 2. EPR spectra of DMPO-adducts from illuminated samples: (a) 0.05C_ Bi_2WO_6 and (b) 30%Ti_0.05C_ Bi_2WO_6.

Z-scheme Water Splitting Systems using Prussian Blue Analogues as Effective Surface Modifiers on Semiconductor Photocatalysts

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The construction of Z-scheme-type water splitting (Zs-WS) systems (Fig. 1), which consist of two different photocatalysts and an electron mediator, is an effective approach toward harvesting a wide portion of the solar light spectrum. We for the first time demonstrated Zs-WS and then have been applying various photocatalyst materials [1]. However, the success has often depended on the affinity between photocatalyst surfaces and electron mediator. This drawback is typified by the limited choice of efficient H_2 evolution photocatalysts (HEPs) (e.g., Rh-doped $SrTiO_3$) for Zs-WS using Fe^{3+}/Fe^{2+} redox couple. The majority of visible light-responsive materials shows low activity for H_2 production with Fe^{2+} electron donors, despite having suitable band levels, probably due to the absence of an effective site for oxidizing Fe^{2+} on their surfaces. Herein, an effective strategy for overcoming this issue is demonstrated: activation of originally inactive materials via surface modification with metal hexacyanoferrate (MHCF) nanoparticles. MHCFs are a class of 3D coordination polymers (see Fig. 2(a)), where M and Fe cations are bridged by cyanide (CN) ligands. As seen in Fig. 2(b), the surface modification of RCO/TaON (RCO represent Rh-Cr mixed oxide cocatalyst) with InHCF nanoparticles triggered the H_2 evolution under visible light in the presence of Fe^{2+} electron donor. Various characterization revealed that the InHCF promotes Fe^{2+} oxidation to Fe^{3+} in the solution utilizing the holes photogenerated in TaON *via* Fe^{III}/Fe^{II} redox cycles in InHCF. The InHCF modifier eventually enables Zs-WS with the Fe^{3+}/Fe^{2+} redox mediator coupled with an O_2 evolution photocatalyst under visible light. It is also disclosed that InHCF function as a solid electron mediators for achieving interparticle Zs-WS (Fig. 2(c)) even in the absence of redox mediator dissolved in the aqueous solution [2]. The redox potential of Fe^{III}/Fe^{II} cycles in MHCFs changes based on M cations, implying a possibility of improving the efficiency *via* tuning the redox potential tailored for the band levels of photocatalysts. We successfully controlled the H_2 evolution rates on a TaON by using different MHCF modifier and different polyoxometalates (POMs) redoxes, testifying the effectiveness of potential control for improving the efficiency of Zs-WS systems [3].

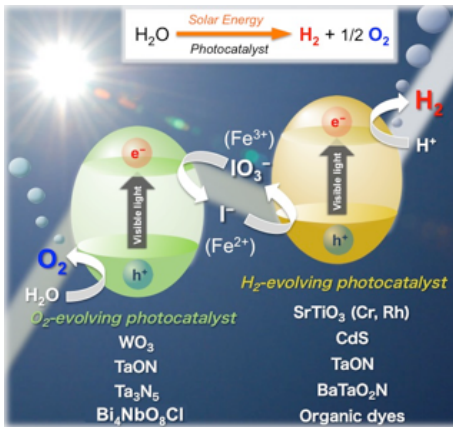

Fig. 1: Conceptual scheme for Z-scheme-type water splitting systems.

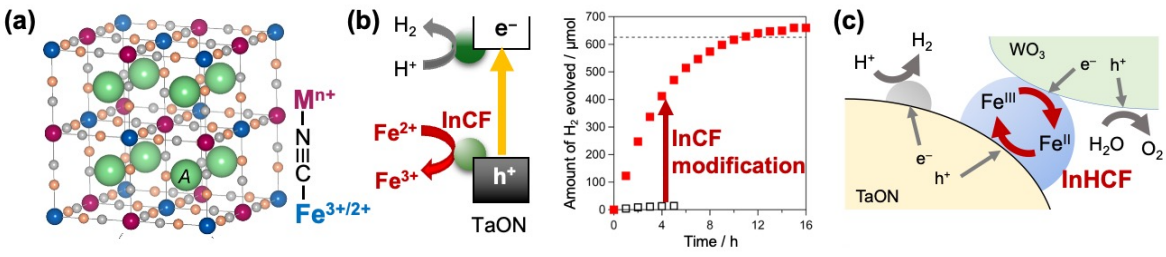

Fig. 2: (a) Structure of MHCF, (b) H_2 evolution on TaON, (c) Interparticle Z-scheme.

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Core@Shell and Yolk@Shell Nanocrystals for Hydrogen Production

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Abstract. With the inherently high degree of complexity, heterostructures composed of two or more materials joined in unique architectures may exhibit superior synergetic properties that are difficult or impossible to acquire from their individual constituents. For semiconductor heterostructures, the relative band alignment of the constituents promotes effective charge separation to bring them desirable properties for photocatalysis applications. Among the different types of heterostructures, core@shell and yolk@shell nanocrystals have received particular interest due to their fascinating properties. Several representative works from our lab will be introduced to demonstrate the promising potentials of core-shell and yolk-shell nanocrystals for hydrogen production applications [1-6].

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Structural Analysis of Deactivated Rh/γ-Al_2O_3 Using Rh K-edge HERFD-XANES Spectroscopy

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Durability is a critical factor in automotive catalysts which are subjected to harsh operating conditions such as high temperatures, fluctuating gas compositions, and exposure to impurities. To improve durability, understanding the deactivation behavior of automotive catalysts is essential. Rh/γ-Al_2O_3 is known as one of the highly active automotive three-way catalysts; however, it deactivates under high-temperature lean conditions due to formation of RhAlOx. Thus, in order to understand the deactivation behavior of Rh/γ-Al_2O_3, it is necessary to quantitatively assess the formation of RhAlOx under reaction conditions. However, in situ evaluation of RhAlOx formation under practical reaction conditions is challenging. Although RhAlOx can be analyzed using X-ray photoelectron spectroscopy or atomic resolution electron microscopy, these techniques require vacuum conditions. X-ray absorption spectroscopy (XAS) using synchrotron radiation hard X-rays is an effective approach for in situ analysis of solid catalysts. In fact, in situ Rh K-edge XAS has been applied for investigation of the redox behavior of Rh species in Rh/γ-Al_2O_3 during automotive three-way catalyst reactions [1]. However, it is difficult to distinguish and quantitatively evaluate RhAlOx and RhOx due to their similar spectral features [2]. Here, we hypothesized that high-energy resolution fluorescence detected (HERFD)-X-ray absorption near edge structure (XANES) spectroscopy could enable us to distinguish between RhAlOx and RhOx. HERFD-XANES has higher energy resolution than conventional XANES because of the longer core-hole lifetime. Figure 1 compares the HERFD-XANES spectrum of Rh foil with its conventional XANES spectrum, which clearly demonstrates higher energy resolution of the HERFD-XANES spectrum than the conventional one. Therefore, we analyzed a deactivated Rh/γ-Al_2O_3 using HERFD-XANES. As a result, we successfully distinguished and quantified RhAlOx and RhOx in the deactivated Rh/γ-Al_2O_3. Furthermore, in situ Rh K-edge HERFD-XANES measurements revealed differences in the redox properties of RhAlOx and RhOx.

Acknowledgement: The HERFD-XANES spectra were obtained on the SPring-8 BL12XU (NSRRC Taiwan Beamline, SPring-8 proposal nos. 2023A4263; 2022B4253; 2022A4256).

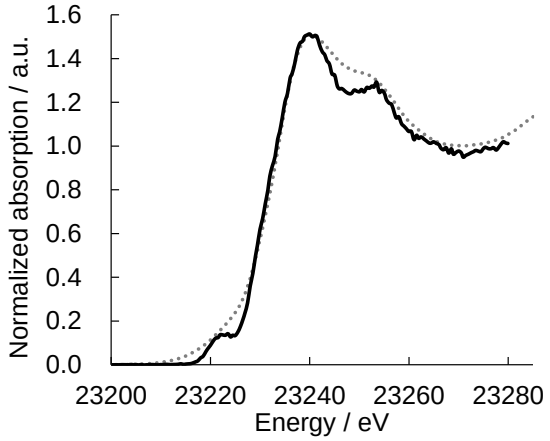

Figure 1. Rh K-edge HERFD XANES spectrum of Rh_2O_3 (black solid) together with a conventional XANES spectrum of Rh_2O_3 taken from the SPring-8 BENTEN database (gray dotted) for comparison.

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Phosphorus-modified small pore zeolite catalysts with enhanced thermal and hydrothermal stability

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Small-pore zeolites with 8-membered ring windows and large cavity, such as CHA, AEI, LEV, and AFX zeolites, have received gained attention owing to their excellent catalytic abilities in the selective catalytic reduction of NOx by ammonia (NH_3-SCR) and alcohol (methanol and ethanol) conversion. Thermal and hydrothermal resistances of the small-pore zeolites are crucial for these catalytic applications due to the high reaction temperatures in the presence of steam. The impregnation of phosphorus (P) compounds such as H_3PO_4 is effective for the enhancement of the thermal/hydrothermal stability of zeolites. However, the narrow pore size of small-pore zeolites typically inhibits such post-modification due to the limited diffusion of the P species. Recently, we achieved the direct P modification by using alkylphosphonium as a phosphonium modifying agent (P-MA). Fig. 1 illustrates the scheme of the direct P modification. During the zeolite hydrothermal synthesis, P-MA is introduced into the zeolite pore system. After calcination, P-MA is decomposed and oxidized into the phosphoric acid or phosphorus oxide interacted with the zeolite framework. The obtained P-modified small-pore zeolites retained high catalytic activity in the NH_3-SCR even after the severe hydrothermal treatment at 900 °C for 8 h in the presence of 10 vol% of H_2O [1-3]. We also found the high catalytic stability of the phosphorus-modified zeolites on alcohol conversion [3]. Further, the zeolite framework obtained in this P-modification can be altered according to the multiple-templating strategy selecting the combination of P-MA and co-existing alkylammonium as an organic structure directing agent (OSDA) [2-4]. Herein, we introduce the recent synthetic progress of the P-modified small-pore zeolites and their catalytic applications.

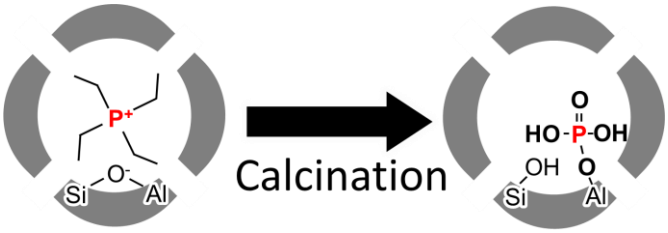

Fig 1. Direct phosphorus modification

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Reactive Forms of Oxygen in Ethylene Epoxidation: Insights from Operando Raman Spectroscopy and DFT Calculations

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Abstract. Ethylene (C_2H_4) epoxidation by reactions with molecular oxygen over silver (Ag) catalysts is the largest-scale epoxidation process in industry, producing more than 30 million metric tons of ethylene oxide (EO) in 2022. Practically, trace amount of promoters (e.g., ppm-level of chlorine species and transition metals) are employed to increase EO selectivity against the undesired carbon dioxide (CO_2) formation from the complete oxidation of C_2H_4. However, the mechanisms of the promotion effects remain elusive, which impedes technical development to further improve the EO selectivity and reduce the CO_2 emission from this industry. This is because even for the unpromoted system, the reactive forms of oxygen, the catalytic surfaces, and the reaction pathways for the formation of EO have yet to be addressed at industrial relevant conditions [1,2].

Here, by performing *operando* Raman spectroscopy and steady-state and transient kinetic measurements, we demonstrate that the surface of Ag catalysts restructures to form a partially oxidized layer that binds atomic oxygens (O*), diatomic oxygens (O_2*), and ethylene-derived intermediates [3]. The coverages of surface species change with the partial pressures of ethylene and oxygen gas, and the rate and selectivity to EO positively correlates with the coverages of surface peroxo species (O_2^{2-}). DFT calculations suggested a peroxametallacycle-mediated pathway that favors EO formation at high oxygen coverages. In addition, the peroxo species can be regenerated through the recombination of 2O* at rates comparable to surface reactions. Consequently, insights from this unpromoted system suggest that coverage of O_2^{2-} on the promoted Ag catalysts may increase when the promoters (e.g., Cl) oxidize the Ag surface, leading to a higher EO selectivity.

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Catalytic decomposition of methanethiol in an electric field

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Introduction

The handling of sulfur species has increased attention due to the higher sulfur content in fossil resources and the utilization of renewable biogas (CH_4 + CO_2). Generally, sulfur species are removed before the chemical process in desulfurization steps. On the other hand, we have tried to aggressively utilize these sulfur species as feedstocks to develop a new route for CO_2 utilization [1]. In our proposed process, CO_2 and CH_4 were converted to C_2H_4 and aromatics via CH_3SH as an intermediate. The advantage of the process is that these reactions proceed at ambient pressure thermodynamically. In the process, the sulfur species are necessary to be recycled; for example, CH_3SH and CH_3SCH_3 in the outlet gas should be decomposed to H_2S. The problem with the recycling process is that the catalyst is easily sulfurized by the sulfur species. In this study, we tried to apply an electric field to the CH_3SH decomposition to suppress the sulfurization by the electrical activation. As the catalyst, a Pt/CeO_2 catalyst, which was well-known to be adaptive for the electric field [2], was utilized in the process.

Experimental

The Pt/CeO_2 catalyst (500 mg) was charged into the reactor, and two electrodes were inserted into both ends of a flow reactor to apply the electric field. The concentration of CH_3SH was 1,000 ppm balanced by N_2, and the total flow rate was 50 mL min^{-1}. The DC voltage was applied to the catalyst to form the electric field, and it was controlled by current cutoff. The outlet gas was analyzed by a GC-FID/FPD.

Results and Discussion

Fig. 1 shows the current dependency on the CH_3SH decomposition over the Pt/CeO_2 catalyst in the electric field. In all results, the CH_3SH conversion reached 100%. Although CH_3SH easily decomposed into CH_4 without the electric field, sulfur species were not observed, indicating the adsorption on the catalyst. Compared to the result, H_2S was formed at a high current of over 20 mA. The result showed that the electric field changed the surface properties of the catalyst, resulting in the release of the sulfur species. Actually, the formation of the Ce_2O_2S phase was observed on the catalyst after the reaction without the electric field, whereas the catalyst in the electric field was stable without sulfurization. The result showed the possibility of the application of the electric field to the sulfur recycling process.

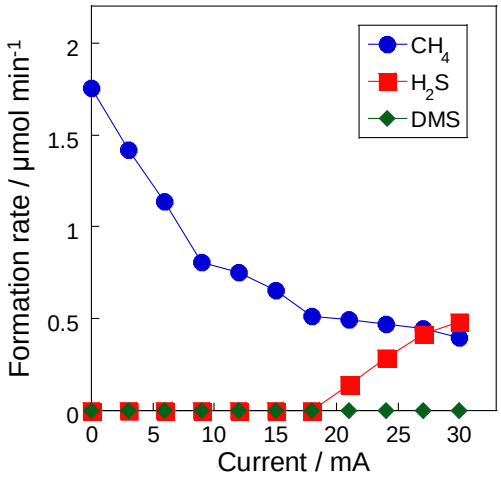

Fig. 1 CH_3SH decomposition over Pt/CeO_2 in the electric field.

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CPC Advanced Catalysis Center: Transforming Captured CO_2 into Methanol with Catalysis

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Abstract. CPC Corporation, Taiwan is the largest petrochemical energy company in Taiwan. Its primary business includes the import, exploration, development, refining, storage, transportation, and sale of oil and gas, as well as the supply of petrochemical raw materials. With the growing global demand for energy conservation and carbon reduction, and in alignment with domestic and international policies, CPC is actively engaged in various research projects to achieve carbon reduction goals.

In 2021, CPC established the Advanced Catalysis Center, focusing on three major tasks: carbon reduction economy, energy conservation and environmental protection, and green products. One of its key missions is to develop carbon reduction technologies which are generally categorized into carbon capture, storage, and utilization. Reportedly, carbon utilization involves hydrogenating CO_2 to produce methanol, methane, or synthetic fuels [1], often using renewable energy sources for hydrogen production [2].

Given the inherent stability of CO_2, converting it into valuable chemicals remains a significant challenge. However, CO_2 can be hydrogenated to form methanol through thermo-catalytic reactions with hydrogen. Cu-Zn-based catalysts are widely used in the conversion of CO or CO_2 into methanol [2]. In Cu-Zn-based catalysts, copper activates hydrogen and ZnO facilitates CO_2 adsorption. In our work, we have developed a Cu-Zn-based catalyst for the hydrogenation of CO_2 to produce methanol.

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Catalyst Characterization using the Synchrotron Beam Line at Kyushu University

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Abstract.

The Synchrotron Radiation Research Center at Kyushu University is a university-wide organization, and it has established a beamline (KU-BL06) at the Saga Synchrotron Light Research Center (SAGA-LS) to support the development and research of environmental and energy materials both within and outside the university. KU-BL06 is a hard X-ray beamline equipped with various cells, chambers, and gas distribution lines, and it regularly conducts XAFS measurements in a vacuum or under He gas flow. In addition, KU-BL06 is equipped with a hazardous gas removal tower that processes toxic gases such as hydrogen sulfide, and in situ measurements are possible while these gases are being circulated. Here, we introduce some of the research results related to the development of catalyst materials and the analysis of catalytic reaction mechanisms that make use of these characteristics.

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Insights into MOF Chemical Biology: Biocatalysts Encapsulated within MOFs

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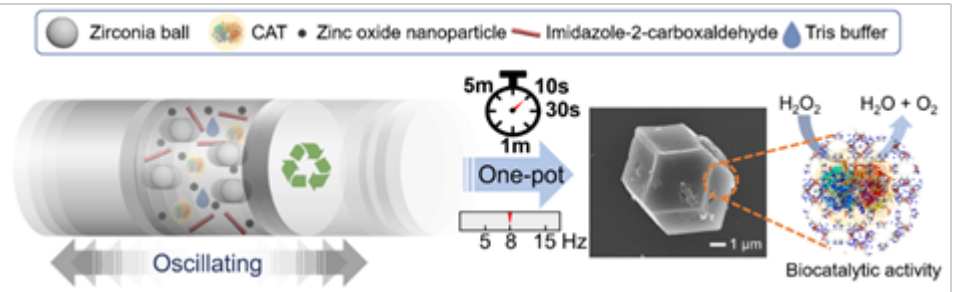
Metal-organic frameworks (MOFs) have found diverse applications in bio-sensing, biomass utilization, and catalysis. This study introduces a novel concept in material biology known as MOF Chemical Biology. It focuses on investigating the impact of containing biomolecules, such as protein enzymes, within synthetic MOF biocomposites, referred to as enzyme@MOFs. These biocomposites are prepared using a *de novo* biomineralization synthesis route, conducted under mild and aqueous conditions. The framework of these biocomposites possesses apertures that enable the free movement of substrates, while the encapsulated enzymes or bacteria remain confined within the structure, thereby shielding them against most structural changes.

Furthermore, we present the first successful demonstration of encapsulating enzymes into robust Zirconium-based MOFs, specifically UiO-66, using a solid-state mechanochemical process. The enzymes encapsulated through this method retain their desired functionality and exhibit resistance to proteases, even under acidic conditions. These innovative approaches provide an alternative system, exploiting the structural confinement effect, for expanding the application of MOFs in studying the biochemical functionalities of prokaryotes, eukaryotes, mammalian cells, and more.[1-6]



***Green and Ultrafast One-Pot Mechanochemical Approach for Efficient Biocatalyst Encapsulation in MOFs*[3]**

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