

## Urakawa Research Group



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### Abstract

We develop novel heterogeneous catalysts and catalytic processes with the aim to minimize the energy usage and negative impacts of such processes on environment while achieving high product yield and selectivity. We take a multi-disciplinary approach based on material science, reaction engineering, and *in situ* spectroscopy to gain solid comprehension of the active sites and

the transformation pathways. Currently our major attentions are given to the conversion of CO<sub>2</sub> into fuels and useful chemicals and also to the production of hydrogen, the important molecule for CO<sub>2</sub> reduction. Also, powerful *in situ* spectroscopic tools for studying solid materials and gas-solid and solid-liquid interfaces are being developed and applied to shed light on catalytic reaction mechanisms.

### Catalytic CO<sub>2</sub> conversion

Convincing and overwhelming scientific evidence shows that CO<sub>2</sub> emissions caused by human activities using fossil fuels have caused the climate to change. Considering the release of nearly 30 billion tons of CO<sub>2</sub> (the so-called 'greenhouse gas' because of its high infrared radiation absorption) into the atmosphere each year by human activities, particularly by burning fossil fuels, its current and future devastating impacts on the earth's energy circulation and recovery systems can be easily anticipated. Such a temperature rise can induce various serious consequences influencing human activities such as agricultural yields, glacier retreat, and species extinctions. It is the task of 21<sup>st</sup> century scientists to find solutions and implement them on a global scale. Recent worldwide efforts have advanced the technologies for CO<sub>2</sub> capturing and storage (sequestration), and they are already at pilot to production scale. The amount of CO<sub>2</sub> sequestration is still minor; approximately a few million tons of CO<sub>2</sub> per year, but the worldwide concern about climate change will advance the technological development and implementation very rapidly.

On the other hand, conversion of CO<sub>2</sub> into useful substances such as transportable fuels and chemicals is another, probably the most important technology to be developed for the mitigation of CO<sub>2</sub> from the atmosphere. A successful conversion of CO<sub>2</sub> into fuels can lead to closure of the carbon cycle by recycling the carbon taken originally from fossil fuels. Finding alternative energy sources, carrier and CO<sub>2</sub> conversion technologies has become more urgent due to the expected exhaustion of fossil fuels in near future. It is indeed the time to put worldwide focus and efforts together into the development of CO<sub>2</sub> conversion processes.

Catalysis plays a pivotal role in the success of CO<sub>2</sub> chemical transformation by lowering and optimizing the barrier of the highly energetic process (Fig. 1). Nature does it even at room temperature; CO<sub>2</sub> and H<sub>2</sub>O are converted into carbohydrate (glucose) as an energy carrier in plants via complex catalytic pathways of photosynthesis. The rate of photosynthesis is, however, not sufficiently high to be used on a production scale to convert captured CO<sub>2</sub>. Therefore, deeper knowledge, novel ideas and innovation of efficient catalytic CO<sub>2</sub> conversion processes are demanded.

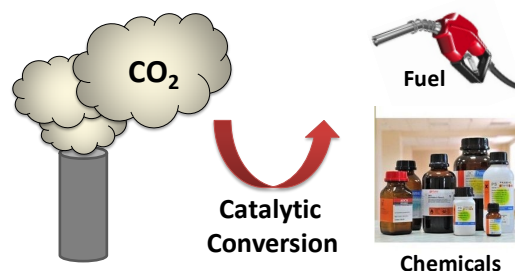


Fig. 1 – The goal of our research activities on heterogeneous catalytic CO<sub>2</sub> conversion process

### Continuous high pressure catalytic CO<sub>2</sub> conversion

We utilize high pressure approach to achieve high efficiency in catalytic CO<sub>2</sub> conversion. CO<sub>2</sub> has relatively low critical temperature (304 K) and low critical pressure (74 bar), which renders it a unique medium and reactant under technically relevant and achievable conditions. Above the critical temperature, the phase transition from the gas to supercritical state is continuous, leading to high compressibility, allowing density variation in a wide range and fine-tuning of reaction conditions. Supercritical CO<sub>2</sub> shows high-diffusivity and low viscosity, which can enhance the mass transfer of CO<sub>2</sub> itself and products. Its relatively high thermal conductivity under supercritical state leads to a good dissipation and control of heat during reactions. Moreover, supercritical CO<sub>2</sub> is known to dissolve well organic and reducing molecules such as hydrogen, which can lead to a drastic enhancement of reaction rates. It is also important to note that high pressure processes are not necessarily energy demanding; the reactor size, thus the energy requirements, can be greatly reduced at the same or better productivity.

We currently focus on CO<sub>2</sub> hydrogenation reaction to produce fuels and chemicals under supercritical conditions. The main working tool of this project is the high-pressure microreaction system where CO<sub>2</sub> and other fluids are passed into a tubular microreactor containing heterogeneous catalysts (fixed-bed reactor) at a controlled, low flow-rate. Reactions up to 500 bar, 700 °C can be tested. This small scale, yet high productivity thanks to the dense medium, allows minimizing the risk of the high pressure operation and also quickly screening various experimental conditions. One of the major target products is methanol, which can be used as fuel and also as a C1 building block.

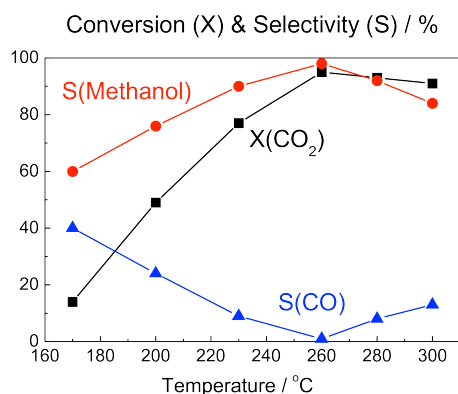


Fig. 2 – CO<sub>2</sub> conversion and selectivity to methanol and CO in CO<sub>2</sub> hydrogenation using a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst at 360 bar with a feed molar ratio of CO<sub>2</sub>:H<sub>2</sub> = 1:10.

Notably, using the high pressure approach and tuning the reaction conditions towards thermodynamically more favorable directions, we achieved a nearly full one-pass conversion of CO<sub>2</sub> (>95 %) into methanol with high methanol selectivity (>98 %) under optimized reaction conditions (Fig. 2). A clear optimum in the reaction temperature was observed and above this temperature the reaction reaches the equilibrium conversion and is thus thermodynamically controlled.

The effluent stream of methanol, rich in H<sub>2</sub> and water, from the reactor could be directly fed to a reactor containing acidic H-ZSM-5 catalyst for selective production of dimethyl ether (89 %), alkane (85 %) or alkene (42 %), showing the great potential of the process in direct transformation of *in situ* generated methanol to valuable bulk chemicals.

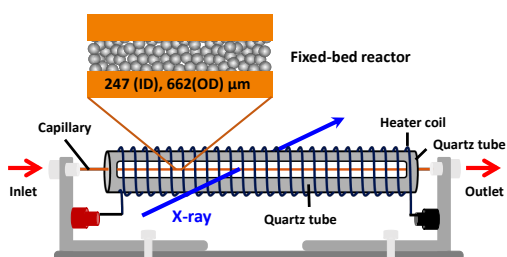


Fig. 3 – High-pressure capillary cell for operando XAFS studies

It is of great challenge to identify active state of catalyst (e.g. Cu oxidation state) under such extreme reaction condition, especially under working, *operando*, condition. We have built a spectroscopic cell using readily commercially available components without complex

machining (Fig. 3). Using a small diameter capillary made of fused silica we could monitor the electronic state of catalysts up to 300 °C and 300 bar. One of the major advantages of the design is the tunable length of the capillary reactor, thus reproducing the catalytic performance using the high pressure laboratory reactor and enhancing the practical relevance of the *operando* study.

Another important chemical which can be produced from CO<sub>2</sub> and has gained attention as fuel additive is dimethyl carbonate (DMC). In theory, DMC can be synthesized by the reaction between CO<sub>2</sub> and methanol. Although the reaction is known to be catalyzed by ZrO<sub>2</sub> and CeO<sub>2</sub>, the reaction is severely limited thermodynamically, even under favourable high pressure conditions (ca. 1% conversion at 400 bar). In order to shift the equilibrium effectively, a recyclable organic dehydrating agent has been used to remove water from the reactor. Combination of this with our high pressure approach resulted in very high methanol conversion (>95%) and high DMC selectivity (>99%). The values are by far the best reported for the continuous DMC synthesis to date.

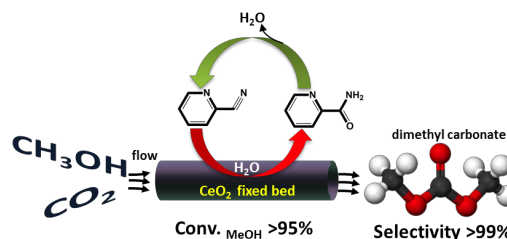


Fig. 4 – Continuous DMC synthesis using a recyclable organic dehydrating agent.

### Heterogeneous photo- and electrocatalysis for H<sub>2</sub> production and CO<sub>2</sub> reduction

Three major energy forms, thermal, solar, and electric, energies are inter-convertible; therefore it is important to develop CO<sub>2</sub> and catalytic conversion processes based on a different kind or a combination of energy forms. Taking solar energy as an example, it can be readily converted to electric energy by photovoltaic solar cells or to thermal energy by a solar furnace. This flexibility and inter-convertible nature of energy form needs to be carefully considered when a chemical process is designed based on even one form of a primary energy.

Solar energy can be used directly to reduce and convert CO<sub>2</sub> into fuels and chemicals taking

hydrogen atoms from H<sub>2</sub>O. An electron at a conduction band and a positively-charged hole created by photon absorption reduce CO<sub>2</sub> (or produce H<sub>2</sub>) and oxidize water to form H<sup>+</sup>. Ti- and Ga-based oxide materials have shown prominent catalytic performance in CO<sub>2</sub> reduction and H<sub>2</sub> production, respectively. For electrocatalysis, we employ polymeric electrode membrane (PEM) to separate two electrodes (anode and cathode). The home-made electrochemical cell and the working principle are shown in Fig. 5.

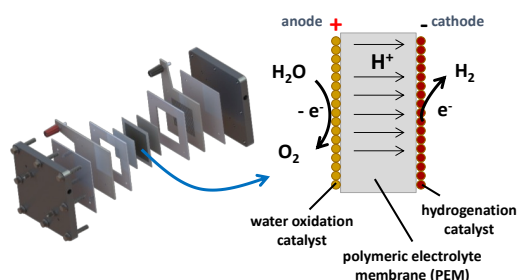


Fig. 5 – Electrochemical cell for PEM electrolysis and electrolysis-assisted reduction reactions.

Noble metals such as Pt and Ir are the popular electrode catalysts for water oxidation (anode) and hydrogen evolution reaction (HER, cathode). However, their low abundance on Earth's crust and high price render them unsustainable for future use and alternative materials have to be identified. We found that molybdenum disulphide (MoS<sub>2</sub>) and cobalt oxides can be promising alternative HER catalysts when modified with carbon materials such as active carbon and graphene-based materials (Fig. 6).

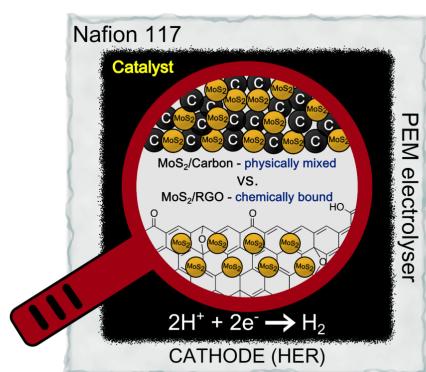


Fig. 6 – Efficient, economic, and earth-abundant catalysts, MoS<sub>2</sub>-carbon composites, for HER

### Towards efficient analysis of temporally varying spectroscopic data

In *in situ* and *operando* spectroscopy, identification of chemical species, structure, and/or sites inducing specific spectral features is of central importance. However, in reality this is not trivial since generally there are more than one spectroscopically active components present in the system. Even worse, often these species and structures are present transiently under specific reaction conditions and, therefore, there is neither reference sample available for structural determination nor quantification.

To solve this problem, we are employing a multivariate analysis method on spectroscopic data. Particularly, we have demonstrated that multivariate curve resolution (MCR) can be employed for different types of spectroscopic data set. For XAFS data we have shown full separation of spectroscopic fingerprints and characteristics from the kinetic differences of the spectral features without reference measurements (Fig. 7). This method is gaining popularity due to its high efficiency and capability to simplify complex data into pure component spectra and their concentration profiles.

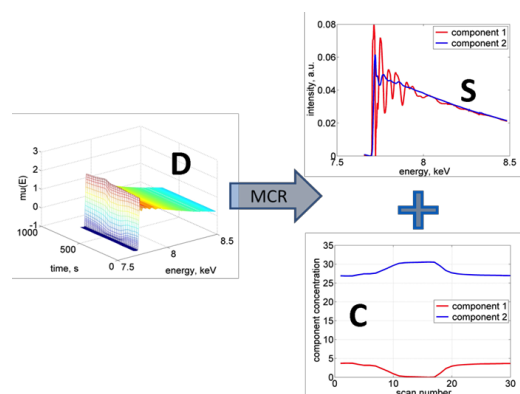


Fig. 7 – Efficient analysis of XAFS using MCR.

## Articles

“Towards full one-pass conversion of carbon dioxide to methanol and methanol-derived products”

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(Highlighted as Editor's choice in *Science*)

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