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 / operando* spectroscopy to gain solid comprehension of the active sites and the transformation pathways. Currently our major attentions are given to the conversion of CO_2 and CO_2-derived chemicals into fuels and useful chemicals and also to the production of hydrogen, the important molecule for CO_2 reduction. Also, powerful *in situ* / operando 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_2 conversion

Convincing and overwhelming scientific evidence shows that CO_2 emissions caused by human activities using fossil fuels have caused the climate to change. Considering the release of nearly 30 billion tons of CO_2 (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 21st century scientists to find solutions and implement them on a global scale. Recent worldwide efforts have advanced the technologies for CO_2 capturing and storage (sequestration), and they are already at pilot to production scale. The amount of CO_2 sequestration is still minor; approximately some million tons of CO_2 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_2 into useful substances such as transportable fuels and chemicals is another, probably the most important technology to be developed for the mitigation of CO_2 from the atmosphere. A successful conversion of CO_2 into fuels can lead to closure of the carbon cycle by recycling the carbon taken originally from fossil fuels. Finding alternative energy sources, energy carrier and CO_2 conversion technologies has become 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_2 conversion processes.

Catalysis plays a pivotal role in the success of CO_2 chemical transformation by lowering and optimizing the barrier of the highly energetic process (Fig. 1). Nature does it even at room temperature; CO_2 and H_2O 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_2. Therefore, deeper knowledge, novel ideas and innovation of efficient catalytic CO_2 conversion processes are demanded.

Our group works on the development of CO_2 conversion catalytic materials and processes using (i) high-pressure approach, (ii) unsteady-state operation, (iii) electrochemical approach, and (iv) photocatalytic reduction. Also, using the approaches (iii) and (iv), hydrogen production based on renewable/natural energy sources are being studied.

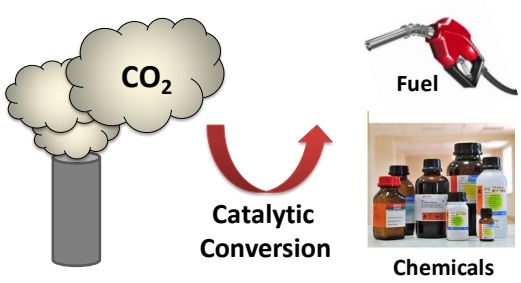

Fig. 1 – *The goal of our research activities on heterogeneous catalytic CO_2 conversion process*

High-pressure CO_2 hydrogenation to methanol

We utilize high pressure approach to achieve high efficiency in catalytic CO_2 conversion. CO_2 has relatively low critical temperature (304 K) and low critical pressure (74 bar). 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_2 shows high-diffusivity and low viscosity, which can enhance the mass transfer of CO_2 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_2 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.

Previously, we have reported that using the high pressure approach and tuning the reaction conditions towards thermodynamically more favorable ones, we achieved a nearly full one-pass conversion of CO_2 (>95 %) into methanol with high methanol selectivity (>98 %) at CO_2:H_2 molar ratio of 1:10. Although the process is extremely efficient, there is still an issue related to the recovery of unreacted H_2 due to excess amount of H_2 was added in the feed. This recovery (recycle) process is energetically costly. Ideally, we perform the reaction at the stoichiometric ratio of CO_2:H_2, which is 1:3.

We have systematically evaluated high-pressure advantages (up to ca. 500 bar of reaction pressure) and reactions conditions such as

space velocity to achieve high CO_2 conversion with high methanol productivity at the stoichiometric CO_2:H_2 ratio. At high pressure conditions (reactant pressure of 442 bar, Fig. 2) and carefully avoiding the mass transfer limitations, we could achieve 88% CO_2 conversion with high methanol productivity (>2 g_{MeOH} g_{cat}^{-1} h^{-1}). Upon increasing the space velocity, the productivity went up to 15.3 g_{MeOH} g_{cat}^{-1} h^{-1} at the expense of lower CO_2 conversion (65%) which is still considered excellent. The productivity value is by far the highest reported to date.

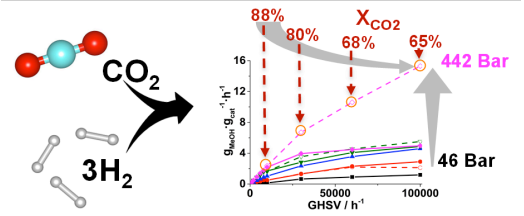

Fig. 2 – *High-pressure stoichiometric hydrogenation of CO_2 to methanol.*

Combined CO_2 capture and reduction in one process

Albeit a variety of available strategies for CO_2 conversion to useful chemicals and fuels, most technologies require relatively pure CO_2, especially without oxygen and water. This requires additional steps of CO_2 capture and purification of flue gas before its efficient conversion. This necessity increases energy requirement, leading to poorer carbon footprints and higher capital expenditures lowering the viability of overall CO_2 conversion processes. We have developed an effective technology which combines CO_2 capture and reduction processes (thus we call it CCR) using isothermal unsteady-state operation and a catalyst consisting of earth-abundant chemical elements such as Cu, K and Al as the major constituting chemical elements to convert diluted CO_2 to highly pure syngas consisting of CO and H_2 (Fig. 3).

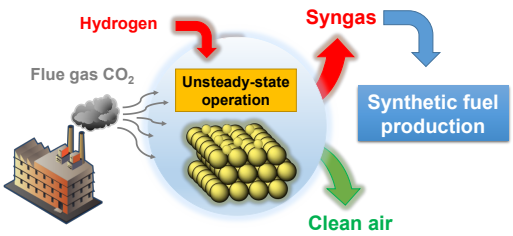

Fig. 3 – *Concept of CO_2 capture and reduction (CCR) process for syngas production.*

More than 99% of CO_2 could be captured and converted efficiently to CO at the catalyst temperature of 350-550 °C. The process and a unique CCR catalyst were developed in collaboration with Repsol.

To understand the key roles of the catalyst components such as Cu and K, *operando* spectroscopic studies (DRIFTS, XAFS, XRD) were performed with space- and time-resolution to understand the varying chemical gradients along the axial direction of the catalyst bed (Fig. 4) and thus to rationally optimise the CCR catalyst and process conditions.

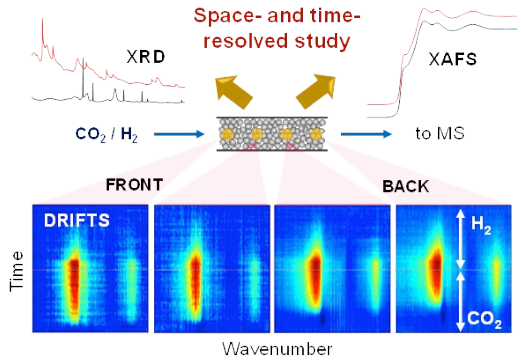

Fig. 4 – *Space- and time-resolved operando spectroscopic study of CCR catalysts.*

Photocatalytic water splitting

Production of one of the most promising future chemical energy carriers, hydrogen, from water via photocatalytic reaction using sunlight as the activation energy source is an attractive path for sustainable development. The use of semiconductor metal oxide as catalyst promoted by specific chemical elements is a widespread approach. An extraordinary boosting of activity has been recently reported by Zn (promoter) and Rh–Cr (co-catalyst) promotion to Ga-oxide-based photocatalysts and we investigated the general applicability of the promotion strategy used for Ga oxides to Ta and Ti oxides in water splitting under UV irradiation using a slurry reactor. Photophysical characterization was used to clarify the specific roles of Zn and Rh–Cr and their synergetic promotional action. It was indicated that Zn acts as a booster of charge separation lifetime. Zn promotion alone, however, does not trigger a great boost in catalytic activity in the absence of Rh–Cr. It is only when Rh–Cr is added that the charge separation boost is fully exploited and driven within the catalyst towards overall water splitting. Effective wavelength ranges of the excitation UV light source were also investigated in detail, leading to questioning

the dominant semiconductor bandgap model for this class of catalysts.

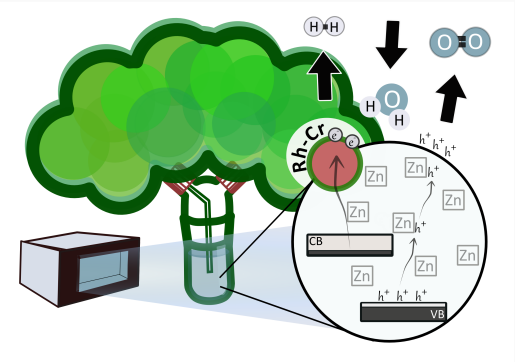

Fig. 5 – *Understanding the synergetic effects of Zn and Rh-Cr in photocatalytic water splitting reaction.*

Articles

"High-pressure advantages in stoichiometric hydrogenation of carbon dioxide to methanol"
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R. Gaikwad, A. Bansode, A. Urakawa

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