

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 CO₂ and CO₂-derived chemicals into fuels and useful chemicals and also to the production of hydrogen, the important molecule for CO₂ 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 CO₂ conversion

Convincing and overwhelming scientific evidence shows that CO₂ emissions caused by human activities using fossil fuels have caused the climate to change. Considering the release of nearly 30 billion tons of CO₂ (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 CO₂ capturing and storage (sequestration), and they are already at pilot to production scale. The amount of CO₂ sequestration is still minor; approximately some million tons of CO₂ per year, but the worldwide concern about climate change will advance the technological development and implementation very rapidly.

On the other hand, conversion of CO₂ into useful substances such as transportable fuels and chemicals is another, probably the most important technology to be developed for the mitigation of CO₂ from the atmosphere. A successful conversion of CO₂ 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 CO₂ 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 CO₂ conversion processes.

Catalysis plays a pivotal role in the success of CO₂ chemical transformation by lowering and optimizing the barrier of the highly energetic process (Fig. 1). Nature does it even at room temperature; CO₂ and H₂O 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 CO₂. Therefore, deeper knowledge, novel ideas and innovation of efficient catalytic CO₂ conversion processes are demanded.

Our group works on the development of CO₂ 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 studied.

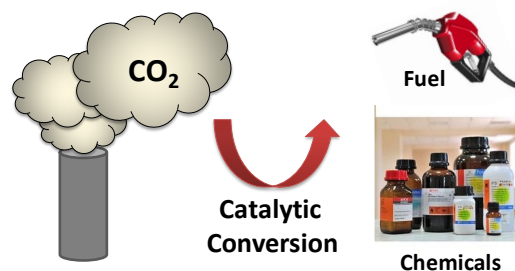
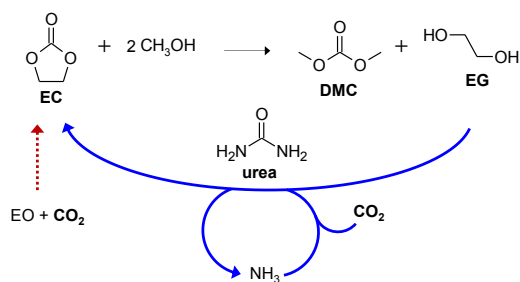


Fig. 1 – The goal of our research activities on heterogeneous catalytic CO₂ conversion process

Urea as CO₂-derived starting chemical: Transesterification of ethylene glycol with urea

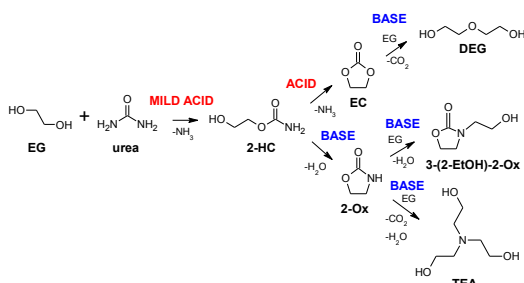
Organic carbonates are the family of commercially important chemicals widely employed as intermediates for a variety of synthetic and industrial applications and also as solvents. Ethylene carbonate (EC) is a reactive starting and intermediate chemical for selective alkoxylation, carbamate formation, and transesterification to produce glycerol carbonate (GC) and linear carbonates such as dimethyl carbonate (DMC) which has drawn great attention as green solvent, phosgene replacement and a fuel additive.

DMC can be obtained with high yield via the transesterification reaction of EC with methanol. In this reaction, an equimolar amount of ethylene glycol (EG) is produced along with DMC (Scheme 1). This feature could be disadvantageous because of the different market demands for these two products (EG and DMC). One approach to balance the amount of the two products at a desired ratio is to convert EG back to EC via transesterification of EG with urea where NH₃ is co-produced. The EC synthesis in this route is advantageous for the mild operating pressure and for low toxicity and ease of handling of starting chemicals besides high EC yield and selectivity, compared to the commercialized path of EC production by cycloaddition of CO₂ with ethylene oxide (EO) (Scheme 1). In addition, the transesterification of EG with urea, synthesized from CO₂ and NH₃, can be considered as one important path for indirect CO₂ utilization (Scheme 1)



Scheme 1 – Urea transesterification with EG to produce EC and to close the cycle of DMC synthesis.

The performance of the transesterification reaction is known to be influenced by both acidic and basic sites and we investigated the catalytic performance of single and mixed metal oxide materials consisting of Zn, Mg, Al and/or Fe with distinct acid-base properties. Binary mixed metal oxides were prepared via hydrotalcite precursors to achieve high surface area and homogeneous mixing of the resulting, typically-nanosized metal oxide phases after calcination treatment. The reaction network influencing the yield of EC was identified and every reaction path in the network was separately studied (Scheme 2) to elucidate the role of acidic and basic sites of the catalysts in every reaction path using a rational approach (*vide infra*).



Scheme 2 – Full reaction paths of urea transesterification with EG.

Rational and statistical approach in catalyst and process design

The catalytic tests were performed with simultaneous monitoring of concentration evolutions of chemical species by means of a dip-in IR probe and multivariate analysis to extract kinetic information of every reaction path. The kinetic parameters, the yield of products, and acid-base properties of the materials determined by NH_3 - CO_2 -TPD, respectively, were holistically evaluated to elucidate the function of acid-base sites on the identified reaction paths, giving a comprehensive view on

the strategies to rationally maximize EC yield. Besides, optimization of the reaction conditions was attempted with the best performing catalyst by applying a contrasting method, namely a statistical method, design of experiments (DoE). The results enlighten the usefulness of such mathematical approaches to maximize the selectivity and/or the yield of the target product influenced by each path in the complex reaction network (Fig. 2).

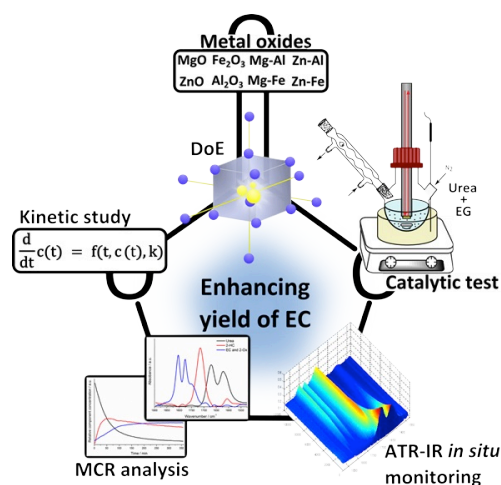


Fig. 2 – Rational and statistical approaches used to maximize the EC yield.

High-pressure synchrotron XRD: Detecting accelerated methane hydrate formation

We have shown previously that the electronic state and structure of active Cu metal in high-pressure CO_2 hydrogenation can be studied by X-ray absorption spectroscopy under working (*operando*) conditions. Continuous *operando* studies up to 200 bar had been demonstrated using a simple home-made capillary cell shown in Fig. 3, which could be used also for Raman spectroscopic study.

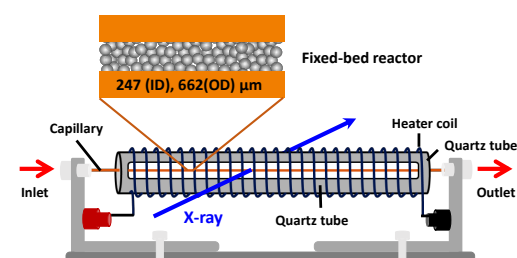


Fig. 3 – High-pressure capillary cell for *in situ* XRD studies

The capillary cell with a small inner diameter was also well suited and employed for

synchrotron X-ray diffraction studies. The capability was demonstrated successfully by carbon materials compared to unconfined conditions as found in nature. This finding is of great importance to show that chemical energy

monitoring the accelerated formation of methane hydrate in a confined nano-sized cavity of (methane) can be stored more efficiently using such nano-pores under mildly pressurized conditions.

Articles

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