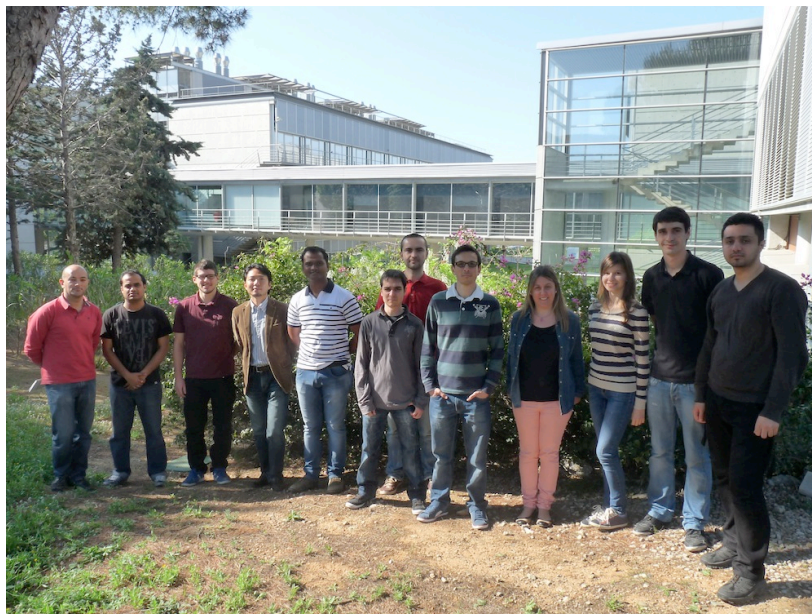


Urakawa Research Group



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Abstract

Our research aim is the rational improvement and design of heterogeneous catalysts and catalytic processes in order to minimize the energy usage and the damage 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 attention is given to the conversion of CO₂ into fuels and useful chemicals. 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 seek 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 a pilot to production scale. The amount of CO₂ sequestration is still minor; approximately a few 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, the chemical and catalytic conversion of CO₂ into useful substances such as transportable fuels and chemicals forms 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. The need for alternative energy sources, carrier and conversion technologies have become more urgent due to the approaching expected exhaustion of fossil fuels. 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.

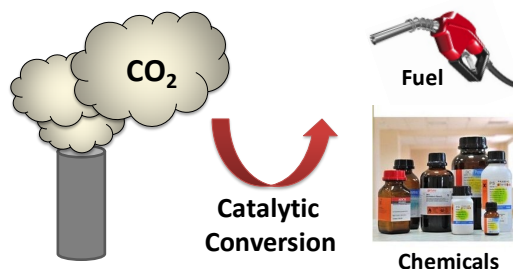


Fig. 1 – The goal of our research activities on heterogeneous catalytic CO₂ conversion process

Continuous high pressure catalytic CO₂ conversion

We utilize high pressure approach to achieve high efficiency in catalytic CO₂ conversion. CO₂ exhibits a 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 CO₂ shows high-diffusivity and low viscosity, which can enhance the mass transfer of CO₂ itself and products. Its relatively high thermal conductivity under supercritical state leads to a good dissipation and control of heat during reactions. Moreover, supercritical CO₂ 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 CO₂ hydrogenation reaction to produce fuels and chemicals under supercritical conditions. The main working tool of this project is the high-pressure microreaction system where CO₂ and other fluids are admitted into a tubular microreactor containing heterogeneous catalysts at a controlled, low flow-rate. 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. Fig. 2 shows the scheme of our continuous, high-pressure CO₂ hydrogenation setup. Reactions up to 400 bar, 700 °C can be tested. Products are analyzed by on-line GC. One of the major target products is methanol,

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which can be used as fuel and also as a C1 building block.

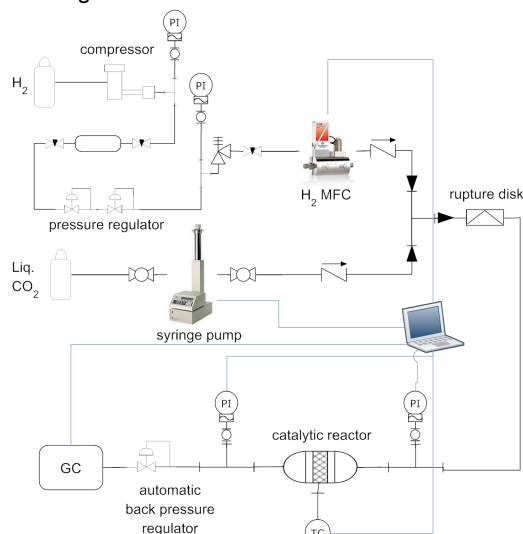


Fig. 2 – Scheme of the high pressure reaction setup

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 CO₂ (>95 %) into methanol with high methanol selectivity (>98 %) under optimized reaction conditions (Fig. 3). A clear optimum in the reaction temperature was observed and above this temperature the reaction reaches the equilibrium conversion and is thus thermodynamically controlled.

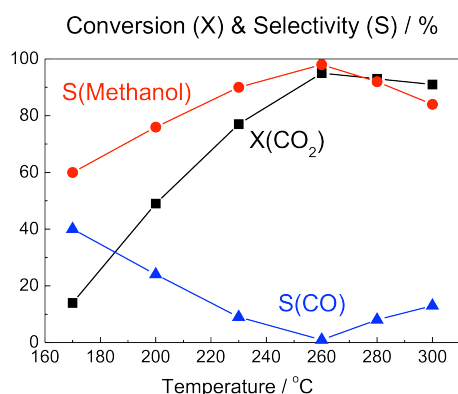


Fig. 3 – CO₂ conversion and selectivity to methanol and CO in CO₂ hydrogenation using a Cu/ZnO/Al₂O₃ catalyst at 360 bar with a feed molar ratio of CO₂:H₂ = 1:10.

The effluent stream of methanol, rich in H₂ 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.

Furthermore, K and Ba promoter effects on Cu/Al₂O₃ catalyst have been investigated under low to high pressure conditions. XRD, temperature-programmed reduction, and *in situ* IR study clarified the roles of promoters (Fig. 4). K, highly dispersed over the Al₂O₃ as well as Cu surfaces, preferentially promotes the formation of surface formates which act as the precursor for CO formation. In contrast, Ba neutralized the acidity of Al₂O₃ surface while keeping the Cu surface uncovered, thus promoting methanol production. The promoter effects are in the entire pressure range investigated (1-360 bar).

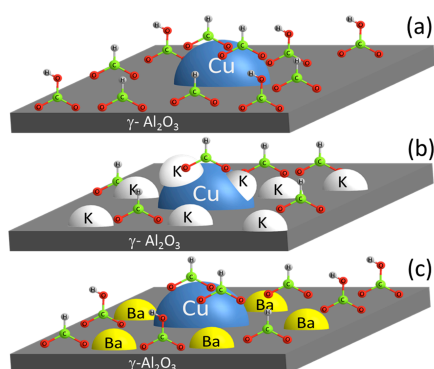


Fig. 4 – Promoter effects identified by *in situ* IR study for (a) unpromoted, (b) K-promoted, and (c) Ba-promoted catalysts.

Heterogeneous photo- and electrocatalytic CO₂ reduction

Three major energy forms, thermal, solar, and electric, energies are inter-convertible; therefore it is important to develop CO₂ conversion processes based on a different kind or a combination of energy forms. Taking solar energy as an example, solar energy 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 CO₂ into fuels and chemicals taking hydrogen atoms from H₂O. An electron at a conduction band and a positively-charged hole created by photon absorption reduce CO₂ and oxidize water to form H⁺, respectively.

We have investigated both H₂O-splitting process and consecutive or simultaneous CO₂ reduction, using TiO₂-based materials in the continuous gas-phase photocatalytic reactor shown in Fig. 5.

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The major advantage of the reactor configuration is the high time-resolution (in the order of seconds) for the detection of products (H_2 and CH_4) by means of mass spectrometry and the possibility to identify activation and deactivation process upon irradiation.

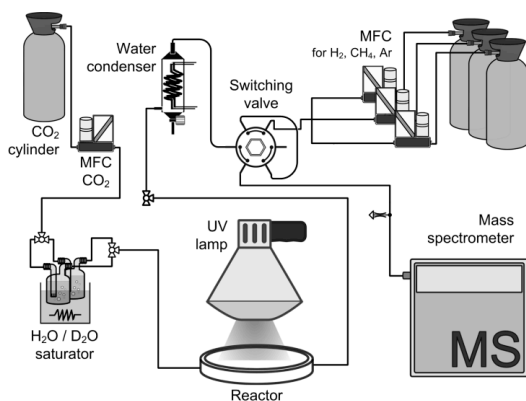


Fig. 5 – Scheme of the continuous photocatalytic CO_2 reduction setup.

With this reactor setup, two distinct photocatalytic activities, namely steady-state and transient activities, were identified. The former is active at the lower temperature and only for H_2 production, whereas the latter was found to dominate for CH_4 production.

Very interestingly, the transient activity was recovered during dark time (i.e., the light is off) in the reaction mixture, with the magnitude of recovery proportionally increasing with the duration of the dark time (Fig. 6). Higher

temperature was found to be kinetically more effective for the recovery process. The nature of deactivation and reactivation mechanisms were gained by *in situ* IR spectroscopy, clarifying the growth of surface species formed by CO_2 and H_2O during the dark time, which are decomposed to CH_4 and H_2 under UV-light irradiation.

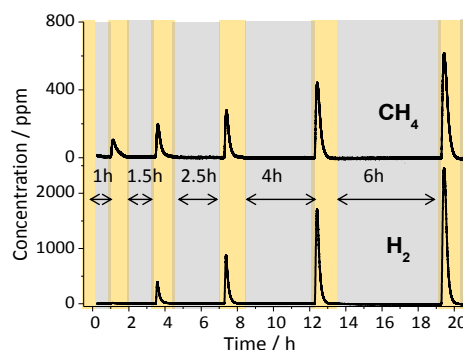


Fig. 6 – Effect of dark-time length showing the recovery of transient photocatalytic activity for CH_4 and H_2 production.

Articles

“Modulation Enhanced Diffraction: Theory and Applications”

ACA Transactions (2013) 137-148

R. Caliendo, D. Chernyshov, H. Emerich, W. van Beek, M. Milanese, L. Palin, D. Viterbo, A. Urakawa

“Impact of K and Ba promoters on CO_2 hydrogenation over Cu/Al_2O_3 catalysts at high pressure”

Catal. Sci. Technol. (2013) 3, 767–778

A. Bansode, B. Tidona, P. Rudolf von Rohr, A. Urakawa

“High pressure plant for heterogeneous catalytic CO_2 hydrogenation reactions in a continuous flow microreactor”

Chem. Eng. Process (2013) 65, 53-57

B. Tidona, A. Urakawa, P. Rudolf von Rohr

“ CO_2 hydrogenation to methanol at pressures up to 950 bar”

J. Supercrit. Fluids (2013) 78, 70-77

B. Tidona, C. Koppold, A. Bansode, A. Urakawa, P. Rudolf von Rohr

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Proc. SPIE (2013) 8811, 881106

“Origin of Photocatalytic Activity in Continuous Gas Phase CO_2 Reduction over Pt/TiO_2 ”

ChemSusChem (2013) 6, 2095–2102

A. Bazzo, A. Urakawa

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

J. Catal. (2014) 309, 66-70

A. Bansode, A. Urakawa

(Highlighted as Editor’s choice in *Science* (2013) 6 Dec.)