

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 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* / *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 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. 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 being studied (Fig. 1). In this year, we summarised our views and work in two perspective articles (ChemPhysChem and ChemSusChem) and one review article (Chemical Reviews) describing the state of the art in CO₂ activation and methanol/formate syntheses.

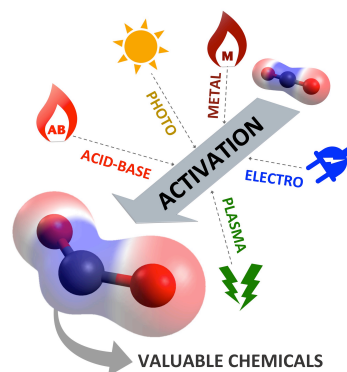


Fig. 1 – Activation of CO₂ over catalytic surfaces using various activation methods

Operando visualization – DMC synthesis from CO₂ and methanol

Besides CO₂ hydrogenation to methanol, we actively investigate the synthesis of dimethyl carbonate (DMC) from CO₂ and methanol. Although the reaction is known to be catalysed by ZrO₂ and CeO₂, 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. However, the most active catalyst, CeO₂, is also known to deactivate noticeably in the time-scale of days during the continuous operation. Thus we aimed to understand the origin of the deactivation by visual information of the catalyst under *operando* conditions by

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means of an optically transparent, fused quartz reactor resistant to high-pressure (<70 bar). The visual inspection was further combined with IR and Raman spectroscopic studies to identify the origin of the catalyst deactivation and establish an efficient catalyst reactivation protocol (Fig. 2).

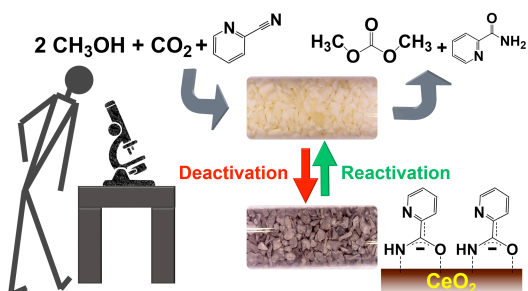


Fig. 2 – *Operando* visualisation of DMC synthesis from CO₂ and methanol over CeO₂ in the presence of 2-cyanopyridine.

Novel materials for electrocatalytic water splitting

For electrocatalytic water splitting and electrolysis-assisted catalytic reactions, we employ polymeric electrode membrane (PEM) electrolyser to separate two electrodes (anode and cathode). The home-made electrochemical cell and the working principle are shown in Fig. 3.

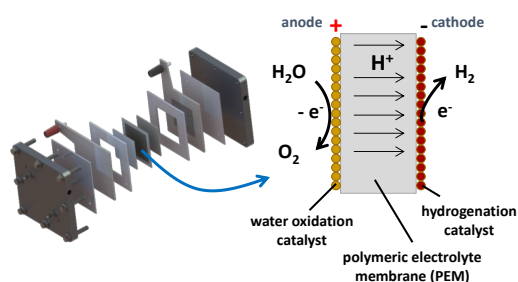


Fig. 3 – *Electrochemical cell for PEM electrolysis and electrolysis-assisted reduction reactions.*

Precious metals such as Pt and Ir are the popular electrode catalysts for water oxidation at anode and hydrogen evolution reaction at cathode. However, their low abundance on Earth's crust and high price render them unsustainable for future use. Particularly, water oxidation at anode is known to be more difficult and iridium based materials are the state-of-the-art anode catalysts for PEM water electrolysis thanks to their unmatched stability and performance in the acidic environment of common PEMs like Nafion. To improve their

wider utilisation, identifying a synthesis method of nano-structured iridium oxide with high dispersion and high active surface area is of great importance. For this aim, we developed a one-step and cost effective solution combustion synthesis (SCS) method to prepare nano-structured IrO₂ and IrO₂-based materials suitable for PEM electrolysis. Among various materials prepared, the iridium oxide incorporated and dispersed in amorphous alumina (Fig. 4) showed high surface area (131 m² g⁻¹) and the current density of 1.78 A cm⁻² at 1.8 V which is comparable to the performance of the state-of-the-art commercial MEA made of IrRuO_x (1.8 A cm² at 1.8 V) under PEM water electrolysis. Importantly, the dispersion of the material in the catalyst ink used for the preparation of membrane electrode assembly (MEA) was significantly superior compared to commercial IrO₂ nanoparticles and the amount of the precious metal in the catalyst made by SCS could be reduced by 45 wt% compared to that in the commercial MEA.

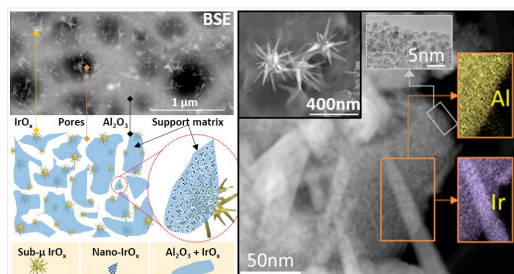


Fig. 4 – *Nanostructured IrO₂-Al₂O₃ anode catalyst made by solution combustion synthesis for water oxidation*

Operando IR study of gas sensing mechanisms

In our group, by mean of *operando* spectroscopic tools, we actively investigate surface reaction mechanisms including those taking place under gas-sensing conditions. In collaboration with other expert groups, we studied the surface species and elementary steps responsible for NO₂ gas sensing over indium oxide by *operando* DRIFTS coupled to a multivariate spectral analysis. It revealed the important roles of surface nitrites on the temperature-dependent gas sensing mechanism and the interaction of such nitrites with surface

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hydroxyls. A highly hydroxylated surface with high concentration of surface adsorbed H₂O is beneficial to enhance the concentration of adsorbed NO₂, present as nitrites, thus explaining superior sensing response at lower operating temperatures (Fig. 5).

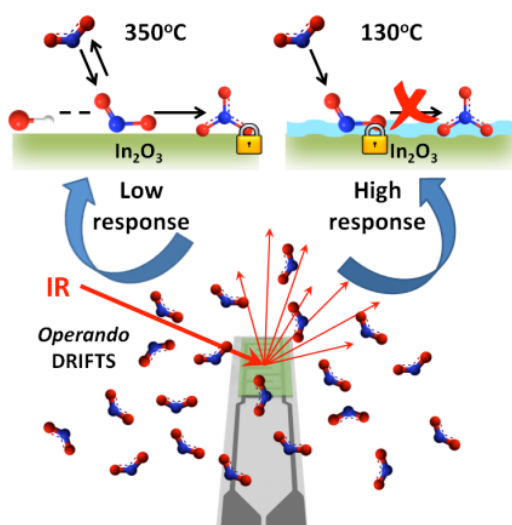


Fig. 5 – Temperature-dependent NO₂-sensing mechanisms elucidated by operando DRIFTS.

Articles

“CO₂ activation over catalytic surfaces”

ChemPhysChem (2017) 18, 3135-3141

A. Álvarez, M. Borges, J.J. Corral-Pérez, J. Giner-Olcina, L. Hu, D. Cornu, R. Huang, D. Stoian, A. Urakawa

“Temperature-Dependent NO₂ Sensing Mechanisms over Indium Oxide”

ACS Sensors (2017) 2, 1272-1277

S. Roso, D. Degler, E. Llobet, N. Barsan, A. Urakawa

“Challenges in the Greener Production of Formates/Formic Acid, Methanol, and DME by Heterogeneously Catalyzed CO₂ Hydrogenation Processes”

Chemical Reviews (2017) 117, 9804–9838

A. Álvarez, A. Bansode, A. Urakawa, A.V. Bavykina, T.A. Wezendonk, M. Makkee, J. Gascón, F. Kaptejin

“CO₂ Catalysis”

ChemSusChem (2017) 10, 1036-1038

A.W. Kleij, M. North, A. Urakawa

“Solution combustion synthesis of highly dispersible and dispersed iridium oxide as anode catalyst in PEM water electrolysis”

Journal of Material Chemistry A (2016) 5, 4774-4778

M.G. Chourashiya, A. Urakawa

“CO₂-to-Methanol Hydrogenation on Zirconia-Supported Copper Nanoparticles: Reaction Intermediates and the Role of the Metal-Support Interface”

Angewandte Chemie International Edition (2017) 9, 2318-2323

K. Larmier, W.-C. Liao, S. Tada, E. Lam, R. Verel, A. Bansode, A. Urakawa, A. Comas-Vives, C. Copéret



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“Catalysis under microscope: Unraveling the mechanism of catalyst de- and re-activation in the continuous dimethyl carbonate synthesis from CO₂ and methanol in the presence of a dehydrating agent”

Catalysis Today (2017) 283, 2-10

D. Stoian, A. Bansode, F. Medina, A. Urakawa