CECAM Workshop Scientific Report

Workshop: Future challenges in CO2-reduction

Organizers: Michel Dupuis (Pacific Northwest Natl. Lab. Richland, USA)
Jan Rossmeisl (Technical University of Denmark, Copenhagen)
Wey Yang Teoh (City University of Hong Kong)
Thomas Frauenheim (U-Bremen, Germany)

Location: University of Bremen, Germany,
08.-12. October 2012

I. Summary – Scope of the workshop

The workshop "Future challenges in CO2-reduction" was held at the University of Bremen, Germany from October 8th to 12th 2012. In total, 64 participants from France, Germany, Italy, The Netherlands, Spain, USA, UK, Denmark, Italy, China, Japan, South Korea, India, Brazil, Iceland, Sweden, Switzerland attended the workshop.

The programme consisted of 25 invited lectures, one poster session presenting 25 posters and many events (reception / conference dinner) to allow for informal exchange. The lectures were scheduled to last 40 min, including 5-10 min discussion time. In addition to this extended time for discussion, the chairpersons were instructed to introduce the subject of the session and to actively participate in the discussion. This "Gordon-conference-style" was essential to guarantee a vivid discussion. The organizers ensured that well-established scientists acted as invited speakers and chairpersons.

Concerning the poster session, we accepted only 25 posters to allow for an intense exchange of ideas at each single poster. Here, we encouraged in particular the young scientists to ask questions. Five Posters has been selected for oral presentation, 12 minutes each, including discussion. The participation of PhD students was supported by partly covering local accommodation costs.

Due to the compact organization and accommodation in one hotel only all participants had to stay together for the whole time of the conference, which additionally enforced the scientific discussion which was mandatory since scientists from various separated fields, i.e. advanced quantum chemistry, DFT and beyond, thermal catalysis, photo- and electro-catalysis, organo-metallic complexes, metal and oxide surfaces, , Scanning Probe Techniques, spectroscopy, etc. were attending the meeting to merge ideas and formulate a common goal for future directions, method developments and collaboration between experiment and theory.

Financial support from the European Science Foundation (ESF), Psi-k Charity, DFG, the Fond der Chemischen Industrie and the German CECAM node multiscale modelling from first principles, cecam-mm1p.de at the University Bremen is gratefully acknowledged.

II. Scientific content and discussion

Main outcome of key presentations

The program included contributions dealing with heterogeneous catalytic transformations of CO2, homogeneous transformations using inorganic molecular catalysts, and also CO2 transformation by means organic reductants. Also included in the program were general presentations about characterization techniques as well as theory and modeling techniques.

Aiming for a small focused workshop with about 60-70 participants the workshop helped to stimulate exchange, awareness of challenges, approaches and achievements in the respective fields, as well as ideas to unite current formulations to promote the modeling of electrocatalysis, photocatalysis, and thermal catalysis for the activation and reduction of CO2. This is especially beneficial to the sizable cluster of PhD students and postdoctoral researchers to firstly be inspired, and later adopt such multi- and interdisciplinary approach in the field of CO2 reduction.

Identification of the major problems in our current understanding of CO2-reduction have been successfully addressed. To this end we brought together theoretical and experimental communities that are seeking predictive power and general understanding of mechanistic processes.

Report on selected discussions

We were organizing invited overview talks by highly recognized experts from the following fields:

A. Electrochemical reduction (Homogeneous and heterogeneous catalytic conditions)

Kubiak (UC San Diego), Batista (Yale), *Appel* (Pacific Northwest), and *Concepcion* (North Carolina) reported on the design of molecular catalysts for both the methanol and CO route, highlighting the role of bifunctionality in the catalysts to bind CO2 to the active site and then activate CO2, either through O cleavage or interaction with a proton or a cation. A detailed computational analysis by *Camaioni* (Pacific Northwest) underscored the nature and critical role and interactions of protons in activation of CO2 toward methanol. In heterogeneous situation, *Peterson* (Brown) demonstrated the power of the recently proposed protocol for modeling electrochemical processes, whereby all intermediates arising from concurrent addition of protons and electrons in the presence of a superimposed potential, are computationally identified, thus permitting to identify descriptors that exhibit volcano behavior. *Rauchfuss* (U Illinois) illustrated the connection and similarities between molecular electrocatalysts and natural enzymes through the design of a hydrogenase-like active site linked to an electron donor fragment, incorporating the chemical functionalities discussed by Kubiak, Appel, and Conception. Finally *Conception* highlighted also progress in water oxidation catalysis for proton generation that complements CO2 reduction in solar-to-fuel conversion.

B. Photo-induced reactions (Homogeneous and heterogeneous catalytic conditions)

- Fujita (Brookhaven Nat. Lab., USA)
- Jan Schouten (U Leiden, NL)

- Leung (Sandia NL, USA)
- Muckerman (Brookhaven Nat. Lab., USA)
- Morikawa (Toyota, Japan)
- Tripkovic (Tech U Lyngby, Denmark)

C. Thermal catalytic decomposition/reduction

- Shaikhutdinov (Fritz Haber Institute, Berlin, Germany)
- Teoh (City U, Hong Kong, S.A.R.)
- Grunwaldt (Karlsruhe Institute of Technology, Germany)
- Scheffe (Swiss Federal Institute of Technology, ETH Zurich, Switzerland)

The electrochemical reduction of CO2 by pyridinium ion reported and developed by the group of Bocarsly (Princeton U) remains intriguing and was the subject of several presentations of computational research by *Batista* (Yale), *Lim* (Colorado), and *Keith* (Princeton). Batista suggested that hydridic hydrogens on the Pt electrode play a key role in the CO2 reduction. The electrode surface is also proposed to play a role in the investigation of Keith et al. who established that pyridinyls radicals are not active participants in the reduction.

The studies of key mechanisms in thermal catalytic reduction of CO2 to syngas, methanol, formic acids, etc. is an emerging topic. As shown by Teoh (City University of Hong Kong, SAR), Grunwaldt (KIT, Germany) and Shaikhutdinov (FHI, Germany) the engineering of metal oxide surfaces plays critical roles in controlling the intermediate species and in turn determine the overall reactivity. While the goal has been to lower the reaction temperatures, that is, to lower energy requirement, Scheffe (ETH, Switzerland) shows the applications of high thermal reactions in solar-thermal reactors. To achieve this, the challenge has been to preserve the surface properties shown by Teoh at high temperatures.

D. Capture

The challenging problem of CO2 capture was discussed by *Wang* (Beijing U Chem Tech, China). Wang showed how multi-scale modeling, combining atomistic scale quantum mechanics and mesoscale molecular mechanics and dynamics provided the basis for computer-aided design of mesoporous materials for capture of CO2 with significantly enhanced performance.

E. Characterization

Characterizing the behavior of catalysts operando is critical to understanding mechanism, specificity, and stability of catalytic processes. In situ microscopy and spectroscopy are techniques that allow to “watch” catalysts in action. *Grunwaldt* (Karlsruhe Inst Tech) highlighted findings from X-ray based techniques applied to CO2 reduction, and other chemistries. Teoh (CityU, Hong Kong) further presented important insights on heterogeneous chemistries through in situ IR techniques.

F. Theory and Modeling

The impact of theory and computations for interpreting and predicting critical intermediates, mechanisms, and energy profile was highlighted in most presentations, covering heterogeneous and homogeneous processes. Calculations not only provide critical insights on structure and dynamics that are often difficult to derived from experimental observations (*Mei*, Pacific Northwest; *Keith*, Princeton), but they also have reached a high level of quantitative accuracy that can be readily used for prediction. *Batista* (Yale U), *Peterson* (Brown U), *Camaioni* (Pacific Northwest), *Muckerman* (Brookhaven), *Nova* (Barcelona), and *Dupuis* (Pacific Northwest) were among the presenters that highlighted this role of computations.

III. Assessment of the results and impact on future direction of the field

To what extend the objectives have been achieved I somehow tried to suumarize

The foremost objective of the workshop was to bring together hitherto rather separate communities. Aiming for a small focused workshop with about 60-70 participants the workshop helped to stimulate exchange, awareness of challenges, approaches and achievements in the respective fields, as well as ideas to unite current formulations to promote the modeling of electrocatalysis, photocatalysis, and thermal catalysis for the activation and reduction of CO2. We have achieved these objectives by inviting an equal number of leading experts from theoretical and experimental contributions. These have been supplemented by keynote talks by a respective number of eminent experimental colleagues that set the stage and define the targets. The speakers have been specifically chosen to cover a broad range of approaches and topics within the fields to provide the participants with a good overview of the present state-of-the-art. The format consisted of seven half-days in 4 days 40 minutes talks including ample time for discussion after each talk (30 plus 10). For the latter we adopted the style of Gordon conferences and specifically invited renowned colleagues as discussion leaders. To ensure full and active participation of also the young emerging researchers attending the meeting a poster session has been organized on the first evening.

More specifically we were aiming to address the following objectives:

Identification of the major problems in our current understanding of CO2-reduction. To this end we brought together theoretical and experimental communities that are seeking predictive power and general understanding of mechanistic processes. We were organizing invited overview talks by highly recognized experts from the following fields:

A. Electrochemical reduction (Homogeneous and heterogeneous catalysis)

B. Photo-induced reactions (Homogeneous and heterogeneous catalysis)

C. Thermal catalytic decomposition/reduction

December 19th 2012

The Organizers