Catalytic Processes under Fluctuating Conditions for Renewable Energy Storage

Report on the DFG Priority Programme “SPP 2080” Annual Status Colloquium held in Leipzig, February 17-18, 2020.

The 2-day Status Colloquium of the DFG Priority Programme SPP 2080 "Catalysts and reactors under dynamic conditions for energy storage and conversion" was held on February 17-18, 2020 at the Faculty of Chemistry and Mineralogy of the University of Leipzig. The goal of this event was to present and discuss the newest results in the projects of this programme, one year after the launch of the Programme in 2018. The Colloquium gathered 75 participants, principal investigators, postdoctoral and doctoral researchers, students as well as guest lecturers. The research is presently conducted in more than 30 groups that are working together in 12 consortia with strong interconnection.

Apart from the many highlights in the presentations (oral and poster) of the twelve consortia, the event was enriched by two excellent plenary talks from invited speakers. On the first day, by Prof. Atsushi Urakawa from Delft University of Technology talked about “Playing with kinetics and thermodynamics for CO_2 conversion”, where he convinced the audience about methods to take advantage of Le Chatelier’s principle to efficiently convert CO_2 into methanol and other fuel molecules. On the next day, Prof. Karen Chang from Technical University of Denmark covered a different side of the CO_2 topic, namely “Theoretical Investigations of Electrochemical CO_2 reduction”, where she eluded on new developments for concepts of improving the theoretical description of electrochemical processes at the solid-liquid interface.

Participants of the SPP 2020 Annual Status Colloquium in Leipzig, February 17-18, 2020. Credit: M. Gebauer.

All consortia presented their latest results in stimulating talks, followed by lively and productive discussions. The talks were organized in topic-specific sections, namely electrocatalysis, methanol synthesis, methane and hydrocarbon formation under dynamic reaction conditions.

In the hydrocarbon synthesis session, Aleks Arinchtein representing the Kondratenko/Bentrup/Krähnert consortium showed detailed electron microscopy and Raman spectroscopy characterization of iron oxide/carbide Fischer-Tropsch catalysts for CO_2 conversion into higher hydrocarbons in the fresh state and post-catalysis, revealing the formation of multiple phases with different catalytic activity, having implementations for operation under dynamic conditions. The speakers of the Seidel-Morgenstern/Petkovska/Kienle consortium presented a model-based study to maximize the methanol output by applying forced periodic reactor operation using the nonlinear frequency-response approach.

New approaches to methanol synthesis from CO and CO_2 were presented by Malte Behrens representing the Behrens/Grunwaldt/Studt consortium, who showed the controlled synthesis of Cu/Zn standard catalysts with Al and Ga promoters for methanol synthesis, *operando* X-ray absoption spectroscopy under dynamic operations, supported by DFT-calculations on interaction of Cu with Zn or ZnO. The Gläser/Jentys/Deutschmann consortium showed results on hydrogenation of CO_2 to methanol under dynamic reaction conditions, introducing a novel concept for carbon capture and utilization.

In the next session, four talks were dedicated to the conversion of CO_2 into methane. The Bäumer/Mädler/Thöming consortium presented results on long-term stable cobalt-based catalysts for the dynamically operated Sabatier reaction. Wolfgang Kleist representing the Kleist/Bauer/Zobel consortium presented the approach MOFCO_2DYN-X^2: New CO_2 methanation catalysts from MOF precursors – Structures and mechanisms under dynamic conditions by combination of (synchrotron-based) hard X-ray techniques. The Sundmacher/Sheppard/Gläser consortium presented results of multiscale analysis and rational design of dynamically operated integrated catalyst-reactor systems for methanation of CO_2. The Freund/Klumpp consortium showed work on temporally and spatially resolved *operando* analysis in a microstructured reactor, for gaining a kinetic description of CO_2 methanation while taking catalyst decativation and dynamic conditions into account.

Critical topics of electrocatalytic methods, hereunder water electrolysis and electrocatalytic CO_2 reduction, were also covered by four talks. The speakers of the Krewer/Grunwaldt/Cherevko consortium presented catalyst synthesis by flame-spray pyrolysis, testing via cyclic voltammetry, *operando* X-ray absorption spectroscopy and kinetic modelling of IrO_2/RuO_2-based oxygen-evolution reaction catalysts for water electrolysis. Christoph Scheurer representing the Eichel/Reuter/Schlögl consortium presented their results on “Transient High-temperature Oxygen Evolution Reaction”. The Jacob/Over consortium presented a DFT-backed simulation of stabilizing the mixed oxide (Ir,Ru,Ti)O_2 and explained the interesting phenomenon of pitting corrosion of a IrO_2-coated RuO_2 catalyst for electrocatalytic hydrogen production. Arno Bergman representing the Magnussen/Roldan Cuenya consortium presented the design and in-depth synchrotron-X-ray studies on nano-structured Ag/Cu_2O cube catalysts for CO_2 electroreduction.

In addition, almost every PhD / postdoctoral researcher presented the detailed results on scientific posters. In order to encourage high quality, motivation and networking the SPP2080 programme awarded 5 poster prizes to most voted posters during the conference dinner, where more scientific exchange took place. The first prize for the best poster, a travel grant of up to 1000 EUR to any SPP 2080-relevant conference/event, was awarded to Daniel Escalera (Helmholtz Institute Erlangen-Nürnberg for Renewable Energy) for his contribution "Electrochemical stability testing of IrRu-based water splitting catalysts with downstream analytics". The following poster prizes, a book "Catalysis" (Eds. Beller, Renken and van Santen) and a limited SPP 2080 memorabilia, were awarded to Dilara Issayeva (University of Leipzig) for her contribution "Sorption of CO_2 on Pd-loaded Amine-functionalized Silica under Continuous Flow Conditions", to Christoph Sinn (University of Bremen) for his work "Towards MRI of CO_2 Methanation", to Antonia Herzog (Fritz-Haber Institute Berlin) for her contribution "Design and operando insight of Ag NP-decorated Cu_2O nanocubes for CO_2 electroreduction" and to Jakub Pazdera (TU München) for his work "A novel CO_2 utilization concept - mechanistic investigation by in-situ IR".

Dr. D. Escalera receiving the 1000 EUR travel award for "Best Poster" during the SPP2080 Status Meeting dinner, handed by Prof. Dr. J.-D. Grunwaldt and Prof. Dr. R. Gläser. Credit: E. Saraçi.

Overall, the meeting was a lively scientific discussion, networking inside and outside of the consortia and a fruitful exchange of career-related ideas. Besides the research, the programme provides financial support for especially female scientists and young scientists with families in building their careers in academic and R&D environments, as well as perspective group leaders in establishing own groups and applying for own funding.

Background, Goals and Structure of the DFG Priority Programme "SPP 2080"

In the age of renewable energy sources, new concepts of energy conversion and storage are required. In contrast to battery technology, catalytic processes are not limited to electric power, but focus on transforming low-energy molecules into reactive high-energy molecules. Basic pillars of chemical energy storage identified today are electrolysis of water to hydrogen and oxygen, as well as hydrogenation of CO_2 to fuels and chemicals - methane, methanol, hydrocarbons, ethers and higher alcohols. All these processes require heterogeneous catalysts.

Germany's renewable power sources are dominated by solar power in the south and wind in the north. Unlike conventional energy sources (coal, nuclear, hydroelectric, geothermal) with controllable output, solar and wind power supply depends strongly on time of day and year as well as weather. Corresponding power output may change on the time scale from minutes to hours to days, which is outside of our control. For the catalytic processes mentioned above, this means that fluctuations occur in the power that drives water electrolysis, leading to a fluctuating hydrogen supply which is used in all the subsequent reactions. Hence, power and hydrogen drop-outs are the additional parameter that must be taken into account when designing catalytic systems for renewable energy storage.

Traditionally, catalysts for energy storage processes are operated at stationary conditions under a constant input of reactive feedstock and energy, and can undergo long-term changes such as

deactivation, which are generally well-studied. In contrast, the driving of these processes under fluctuating or dynamic conditions is a research and engineering field that is largely unexplored.

The 3-year German Research Foundation-funded Priority Programme "SPP 2080" launched in 2018 has at its core the study of the effect of dynamic conditions on well-known catalytic systems, such as iridium-ruthenium electrolysis catalysts, nickel-based CO_2-methanation or copper-zinc catalysts for methanol synthesis. The focus within the Programme is to re-visit the elementary reactions, catalytic cycles and molecular transport in the light of dynamic operation, as well as study the effect on transport in reactors and between particles, catalyst restructuring and segregation, sintering and recrystallization as well as solid-state diffusion.

In order to treat the given problem from all facets, the Programme involves 32 research groups from German Universities, grouped into 12 consortia according to the processes that are being studied. The interdisciplinary consortia consist of chemists, chemical engineers, physicist and mathematicians. The main five disciplines necessary for treating each problem are: (i) *operando* characterization, that is, interrogation of the structure of the catalyst under operation conditions in contrast to 'before and after', (ii) computational chemistry based on density-functional theory calculations, allowing an accurate prediction of the most energetically favorable chemical structure or intermediate, (iii) kinetic and multiscale modelling of catalysts and reactions, (iv) tailored synthesis of model catalysts for specifically obtaining information on active/inactive sites and (v) novel reactor engineering and concepts.

Many of the research efforts involved have been running in advance of the launch of the Programme, and have been subsequently coordinated to collaborate on these common topics of interest. The topics are lead by principal investigators and are the center of many Ph.D. theses and postdoc research projects currently in progress across Germany.

More information of the "SPP 2080" Programme is available online at www.spp2080.org.

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