Petrochemistry and Refining in a Changing Raw Materials Landscape
DGMK Conference October 9 – 11, 2017 in Dresden, Germany

Generation of Solar Fuels Based on H_2O and CO_2 Using Copper Catalysts

S. Kreft, S. Wohlrab, H. Junge, M. Beller
Leibniz Institute for Catalysis at the University of Rostock, Rostock, Germany

Abstract

Sustainable energy supply and economical use of resources are one of the central challenges and require most important developments of the 21st Century. In this respect, hydrogen technology takes a special significance because of its storage and conversion to electrical energy as well as its generation from suitable starting materials (especially water). As a result of the depletion of fossil fuels reserves there is an accumulation of carbon dioxide in the atmosphere. Although this problem cannot be simply resolved by consumption of CO_2 in chemical processes, there is a growing interest to convert this inexpensive and non-toxic C1 building block into useful derivatives. Concerning these two economically relevant topics, the photocatalytic reduction of water to hydrogen as well as the photocatalytic conversion of CO_2 constitutes a straightforward way using abundant sources. Due to lower costs, non-toxicity and their abundancy, the replacement of noble metal catalysts by cheap 3d metals is of special interest. In this respect, we investigated the ability of copper compounds for H_2O and CO_2 reduction processes.
Concerning to hydrogen generation, we developed systems containing copper(I) and copper (II) compounds as homogeneous water reduced reduction catalysts (WRC), $[Ir(ppy)_2(bpy)]PF_6$ as a photosensitizer (PS) in a THF/H_2O mixture and triethylamine as the sacrificial electron donor (SR). CuI as the WRC was found to be the most active compound. Aberration-corrected HAADF-STEM measurements revealed a part transformation of the copper precursor into Cu containing nanoparticles. Further, with respect to nanoparticles formation, we synthesized heterogeneous copper catalysts, which were stabilized on mesoporous silica and prepared by various synthesis methods. These materials were investigated in the same reaction setup for water reduction. Firstly, supported copper catalysts were more active than the non-supported ones. Furthermore, a new Cu(II)-material, $Cu_2Cl(OH)_3/SiO_2$, for the hydrogen generation from water showed the highest activity. The materials were investigated, inter alia, by transmission electron microscopy, x-ray absorption- and electron paramagnetic resonance spectroscopy.
In the field of carbon dioxide utilization, a system containing a highly porous Cu/TiO_2 aerogel in an aqueous media without using an additional electron source was investigated for the photocatalytic CO_2 reduction. Studies resulted in the formation of CO, which is an important educt for the chemical industry, and H_2. Furthermore, recycling experiments with this catalyst led to an increased selectivity towards CO (100 %). Therefore, this system allows a sustainable, environmental, non-toxic and cheap alternative for reducing CO_2 with only using a non-noble metal catalyst in an aqueous media under light irradiation.