

Thesis abstract

Renewable energy is available in excess. The major challenges are the efficient conversion and the daily -and seasonal storage to match the demand for electricity, heat and fuel. Synthetic fuels from Carbon Dioxide and Hydrogen, as starting materials, have the potential to become one of the major pillars in the energy supply since they exhibit the same favorable properties as fossil fuels. Anyhow, the synthetic counterpart to the fossil fuels possess two major advantages: Firstly, it can be synthesized from two abundant resources, CO₂ (from air) and H₂ (from H₂O) and therefore the energy supply -and storage is not subject to restrictions of the geopolitical situation. Secondly, the net CO₂ emission from synthetic fuels can be zero, hence the human impact on the natural climate cycles is reduced.

The aim of this thesis is to contribute to the development of analysis methods that enable an improved investigation of the CO₂ hydrogenation reaction such as quantitative mass spectrometry and infrared thermography. Furthermore, the contribution is in the characterization of the activity of basic catalyst building elements such as Fe, Co, Ni, Cu and Ru.

To achieve these aims, we have developed and build a gas-controlling and analysis system to carry out the experiments in a wide range of conditions. In the frame of setting up the instruments and working on the analysis scripts, a rapid and quantitative gas analysis method by means of mass spectrometry was developed.

In a second step, the CO₂ hydrogenation reaction over Fe, Co, Ni and Cu in their pristine form was investigated with a particular focus on the catalytic activity and the activation energies. An Al₂O₃ supported Ru catalyst was used as reference catalyst. We showed that the reaction goes through a similar rate limiting step on Co, Ni and Ru/Al₂O₃, while the reaction rates are significantly different. Pristine Co showed minor activity in the formation of C₂+ hydrocarbons. Fe was mostly active in the Carbon Monoxide formation. Cu exhibited no catalytic activity without a supporting metal-oxide phase.

Based on these findings, we carried out an in-depth kinetical analysis of the catalytic CO₂ hydrogenation over pristine Ni, Co and Ru/Al₂O₃ was carried out. A reaction model describing the CO₂ hydrogenation over a broad temperature range, taking kinetically, diffusional and thermodynamic limitations into account, was developed. Diffusional limitation occurs at temperatures where the reaction kinetics is already rapid and diffusion of educts - and products to -and from the catalyst and its pores becomes rate limiting before the thermodynamic limitations are approached. The turnover rate of the CO₂ conversion depends critically on the partial pressure of CO₂ in the educts gas stream: With a high CO₂ partial pressure, the catalyst surface saturates and the reaction order approaches zero.

Out of the unsupported pristine metals Fe shows the lowest activation energy, but also the lowest activity while Co showed the highest activity and the highest activation energy for the overall CO₂ conversion. Therefore, we have synthesized bimetallic nanosized pristine Fe-Co catalysts to investigate the influence of alloying Fe to Co and how this influences the activation energies of the formation of methane and C₂-C₅ hydrocarbons. We found clear trends towards higher activation energies with increasing Fe content- attributed to the stronger binding energy of CO₂ to Fe.

Furthermore, a new experiment for thermography was built with the aim to visualization the exothermic reaction dynamics. The dedicated reaction cell with an IR transparent window is coupled with the mass spectrometer. With the rapid gas sampling, the gas composition can directly be linked to the evolution of the thermal signal, contributing to the deeper understanding of the reaction start-up. We found and could prove that a CO₂ covered surface has a strong inhibiting effect on the reaction startup while an H₂ covered surface leads to a linear acceleration of the reaction front in the form of a thermal runaway.

Keywords

Catalytic CO₂ hydrogenation, pristine metal catalysts, reaction thermodynamics, reaction kinetics, visualizing catalysis, infrared thermography, synthetic fuels