In-situ charge transport characterization of catalysts using the microwave Hall effect technique

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Introduction

The reduction of CO₂ emissions is one of the most challenging endeavors of our society today. From a chemical point of view the greenhouse gas could be an attractive C1 building block for valuable chemicals. One important intermediate for chemical industry is methanol, which is produced over a Cu/ZnO/Al₂O₃ catalyst from a CO/CO₂/H₂ mixture. The challenge for the future is to decrease the necessary CO content to a minimum. However, there is still no general agreement about the active sites and the working mode of the Cu/ZnO catalyst [1]. In order to have a better mechanistic understanding for this and other heterogeneously catalyzed hydrogenation reactions, the investigation of charge transfer at the Cu-ZnO interface at industrially relevant conditions could shed more light on the working mode. The influence of charge carriers participating in these redox processes on the catalytic performance can be studied by electrical conductivity and Hall mobility measurements. Therefore, the microwave cavity perturbation technique (MCPT), which was pioneered by Slater [2], was applied to measure the electrical conductivity and Hall mobility. In comparison to conventional conductivity methods, MCPT is a contact-free technique avoiding contact resistance and electrode-related problems, thus being perfect for studies of catalysts under reaction conditions. An in situ MCPT setup was successfully developed to observe conductivity changes in catalysts for different reaction mixtures [3]. Furthermore, we are applying the in situ microwave Hall effect (MHE), also based on the perturbation technique [4], for measuring the Hall mobility of catalysts in reactive atmospheres and at elevated temperatures.

Materials and Methods

A bimodal cylindrical cavity system is needed to observe the Hall mobility of charge carriers at microwave frequencies. In this context we started to develop an in-situ MHE system, which contains a silver plated cylindrical bimodal TE112 cavity [4]. The upper part in Figure 1a) shows schematically the position of the sample inside the reactor tube in the cavity. Moreover, a network analyzer is used to generate the microwaves and to measure the transmission of the microwave power through the cavity. Without external magnetic field, charge carriers in the catalyst oscillate at microwave frequencies in one direction of the cavity. A transmission is not observed since the electric microwave field (driving mode) cannot interact with the perpendicular mode of the bimodal cavity. If an external magnetic field (B) perpendicular to the microwave field is switched on a second electric field due to the Lorentz force (F=eq (E+ v x B)) is induced in the perpendicular direction. This field causes the excitation of the perpendicular mode (MHE mode) in the bimodal cavity observable as increase in the transmission signal (ratio of incoming and outgoing power). The absolute value of the transmission as function of B gives information on the type (electrons or holes), the concentration and the Hall mobility of the majority charge carriers. The carrier type is identified by the sign of the slope of the transmission vs. magnetic field curve (holes = positive slope, electrons = negative slope), the mobility is deduced from the absolute value of the slope, and the concentration from the ratio between conductivity and mobility.

Results and Discussion

In order to calibrate the method, charge carrier mobilities were measured for several single crystals. Different types of dopants (electrons and holes) show inverse trends in the MHE mode (Figure 1b), verifying that the method can be used to discriminate between n- and p-type semiconductors. Catalytically relevant ZnO single crystal and powder samples were also investigated and could be identified as n-type semiconductor (Figure 1c). The mobility of these different semiconductors is in the same range as the literature data proving that we are able to measure absolute mobilities of catalysts in a quartz tube reactor. The reactor will be connected to a gas delivery manifold and a gas analysis system in order to simultaneously analyze the charge carrier mobility and the catalytic performance with the aim to identify electronic structure-function relationships of active Cu/ZnO catalysts in the hydrogenation of CO₂.

Significance

Our investigation of electrical conductivities and mobilities of different semiconducting catalysts will contribute to the understanding of heterogeneously catalyzed redox reactions. Thus the methodology provides a new physical descriptor for catalyst activity and selectivity in order to rationally design better catalysts.

Figure 1. a) Bimodal cavity (TE112) of the in situ MHE setup. b) MHE of Ge single crystals (p-type and n-type). c) MHE of ZnO powder (n-type).

References
3. M. Eichelbaum et al., PCCP, 14, 1302 (2012)