In-situ Investigations of Cu/ZnO Catalysts in Methanol Steam Reforming as a Function of the Ageing Conditions in Catalyst Preparation

B.L. Kniep, F. Girgsdies, R. Jentoft, M. Schur, T. Ressler

Department of Inorganic Chemistry, Fritz-Haber-Institut of the MPG, Faradayweg 4-6, 14195 Berlin, Germany

Cu/ZnO catalysts are used for methanol synthesis and are also known to be active for methanol steam reforming. We investigated microstructrual characteristics of the active catalyst and their influence for the catalytic activity in methanol steam reforming. Cu-Zn hydroxycarbonate precursors (ratio Cu/Zn = 70/30 mol %) were prepared by coprecipitation from metal nitrate and sodium carbonate solutions at constant PH (PH = 7). The precipitates were aged in their pristine solutions at times of 0, 15, 30 and 120 min.

It was found that Cu/ZnO catalysts obtained from precipitates that were aged for longer times (30 min and 120 min) exhibited a much-increased H_2 production rate. Bulk structural changes of the four CuO/ZnO precursors during activation in hydrogen or methanol/water gas mixture were studied using time resolved in-situ XAS measurements at the Cu-K edge. Reduction kinetics and phase transitions were compared to TG/DSC and in-situ XRD results. With increasing ageing time the onset of reduction decreases, accompanied by a decrease in Cu particle size from 130 Å to 100 Å. The activated catalyst was investigated under working conditions during methanol steam reforming by a detailed analysis of the Cu K edge and Zn K edge EXAFS. Upon addition of oxygen to the feed gas followed by reduction, structural changes of the catalyst in the medium range order were observed that are correlated to an increase in catalytic activity.