In situ Investigations of Nanostructured Copper-Zincoxide catalysts for Methanol Steam Reforming

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Cu/ZnO catalysts are used for the methanol synthesis, water-gas shift reaction and are also known to be active for the catalytic conversion of methanol with water vapour (steam reforming) to produce hydrogen. Recently, we were able to show that the catalytic activity of binary Cu/ZnO catalysts is correlated to bulk structural defects such as microstrain in the copper nanoparticles [1]. In order to further investigate how such microstructural characteristics can be controlled and determined by the preparation conditions, Cu,Zn- hydroxycarbonate precusrors (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 for 0, 15, 30 and 120 min. in the mother liquid [2].
Bulk structural changes of the active catalyst in methanol steam reforming were studied using in-situ XRD and in-situ XAS combined with on-line mass spectroscopy. It was found that the Cu/ZnO catalyst obtained from the precursors aged for longer times (30 and 120 min) exhibited a much-increased H_2 production rate. The decreasing Cu particle size (130 Å = 0 min ageing to 100 Å = 120 min ageing) and the resulting higher Cu surface area alone cannot explain the increase in activity. However, the H_2 production rate correlates well with the microstrain determined by XRD line profile analysis in the catalytically active copper nanoparticles. In addition, structural changes in the short range order of the active catalysts determined by detailed analysis of the Cu-K edge and Zn-K edge EXAFS were correlated to the increase in catalytic activity.

[1] M.M. Günter, T. Ressler, B. Bems, C. Büschner, T. Genger, O. Hinrichsen, M. Muhler, R. Schlögl, *Catal. Lett.* 71 (1-2) **2001**, 34-37 [2] B. Bems, M. Schur, A. Dassenoy, H. Junkes, D. Heirein, R. Schlögl, *Chem. Eur. J.* (9) **2003**, 2039-2052