Investigation of copper particles supported on SBA-15 as methanol steam reforming catalysts

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Introduction
Cu/ZnO/Al₂O₃ catalysts are frequently used for H₂ production by methanol steam reforming (MSR). For subsequent fuel cell application CO formation by methanol decomposition and reversed water gas shift reaction \(^{[1]}\) needs to be avoided. Hence, developing improved catalysts requires a good understanding of the correlations between structure and catalytic performance. Therefore, suitable model systems are developed. Investigating Cu/ZnO and Cu/ZnO/Al₂O₃ catalysts revealed a relationship between increasing catalyst activity and microstrain in Cu particles of the active catalysts.\(^{[2, 3]}\)

Because in these model systems chemical and structural complexity are varied simultaneously, Cu particles supported on nanostructured silica (SBA-15) was chosen as additional model system. Different sizes of disordered well-dispersed Cu particles have been deposited on the silica support. Investigations of the Cu particles focus on correlations between evolution of catalytic activity and microstructure during varying reaction conditions.

Experimental
Silica SBA-15 was impregnated via incipient wetness with an ammonia Cu citrate solution. Subsequent decomposition of the precursor resulted in CuO particles supported on SBA-15, which were reduced to Cu particles under H₂ atmosphere at 250 °C. In situ studies were conducted by XRD and QEXAFS at the Cu K edge at HASYLAB, Hamburg. Furthermore, in situ measurements were carried out under MSR conditions (2 % MeOH and 2 % H₂O balanced by He at 250 °C). Stability of particles was tested up to 360 °C under MSR conditions. Moreover, 5 % O₂ were added temporarily to the MSR feed and oxidation and re-reduction were followed by in situ XAS at the Cu K edge.

Results
After reduction of the copper oxide precursor in hydrogen, Cu particles of various sizes depending on the Cu loading were observed. Time-resolved QEXAFS showed the
formation of intermediate Cu$_2$O during reduction of CuO to Cu metal (Figure 1). Under MSR conditions the dispersed Cu particles supported on silica SBA-15 exhibited good catalytic activity and high thermal stability up to 360 °C within 21 h. Only slight sintering effects were observed by XRD. Methanol decomposition contributed significantly at temperatures above 330 °C. Furthermore, in situ XRD/MS and QEXAFS/MS measurements indicated higher catalytic activity after temporary addition of O$_2$ under methanol reforming conditions. Adding O$_2$ to MSR feed yielded rapid formation of CuO/Cu$_2$O, which was subsequently re-reduced to Cu under MSR conditions. Apparently, the effect of oxidation on the Cu particle size was more pronounced than the effect of thermal treatment. In spite of the increasing Cu particle size after this “redox” cycle, the corresponding microstructure appeared to be more active than that of the original copper phase.

Figure 1: Temperature resolved QEXAFS during reduction (left) and fourier transformed $\chi(k)*k^3$ of the reduced Cu particles at room temperatur (right) of 1 wt% Cu supported on silica SBA-15.

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References: