**Supported dimeric copper(I) complexes in methane activation**

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**Introduction**

The direct conversion of natural gas into methanol, which can be directly used as liquid fuel, is one of the great challenges in catalysis. However, the stability of methane and the high reactivity of the intermediates towards oxidation have limited the success of developing a process and an active catalyst for the direct route from methane to methanol. To overcome this problem a three-step method was developed, which allows the direct conversion of methane over copper exchanged zeolites [1] and other oxide supports [2]. The amount of methanol converted indicates that only a minority of copper present in the sample contributes to the methanol formation, which leads to the speculation that only specific copper oxide species are the active sites.

Enzymes such as methane monoxygenase convert methane into methanol under ambient conditions [3]. As the active center in these materials typically contain dicopper cores, we decided to explore dimeric copper complexes grafted on oxide supports as potential catalysts. The materials were already characterized by IR and NMR spectroscopy at the TU München to ensure the success of the grafting procedure.

For a complete understanding of the relation between catalyst morphology and activity the investigation of the structural transformation from the copper oxide species, formed during activation in oxygen, into Cu-methoxy species after exposure the methane is essential.

**Experimental**

The supported copper samples were prepared by incipient wetness impregnation, whereby different amounts of copper were chosen. Afterwards the samples were calcined in synthetic air (100 ml/min) at 120 °C for 12 h (heating rate 1 K/min). The preparation of the grafted complex was performed under inert atmosphere. The precursor was dissolved in two different dry solvents (either cyclohexane or toluene) and afterwards stirred over night with the alumina support. Finally, the samples were washed and dried under vacuum.

XAS experiments were performed at beamline X. The catalysts were pressed into self supporting wafers (ca. 50 mg) and placed into an in-situ XAS cell that can be cooled to liquid nitrogen temperature using a recycle dewar and heated to 450 °C using a sealed heating wire. The X-ray absorption spectra were collected at the Cu K edge (8979 eV during activation in oxygen at 200 °C - 400 °C and after flushing with Helium during exposure of the catalysts to methane at 200 °C. The dactyloscope software was used to analyze the XANES [4].
Results

The XANES (during activation and methane loading) of the supported copper samples are identical regardless of the concentration of copper used. In Fig. 1 the XANES of the sample with the highest amount of copper is shown. In the spectra before and after activation in oxygen only peaks for Cu$^{2+}$ were observed. During heating in an oxygen flow a small change in geometry was observed but no change in the oxidation state is visible. Also during methane loading no distinct changes were observed.

In contrary to these results, we observe a completely different behavior of the copper complex grafted on alumina (Fig. 2, Fig. 3). The sample prepared in toluene (Fig. 2) reveals even before activation in oxygen only Cu$^{2+}$ species. During methane loading a peak at 8982 eV appeared, which indicates a change in the copper oxidation state from Cu$^{2+}$ to Cu$^{+}$. In the sample prepared with cyclohexane (Fig. 3) Cu$^{+}$ was the only species present before activation, indicated by the peak at 8982 eV, while during activation this peak disappears and Cu$^{2+}$ is formed. Furthermore we observed an intensity increase of the 1s $\rightarrow$ 4p absorption during activation and a decrease during methane loading. In addition, the peak at 8982 eV is forming again during the exposure to methane, indicating an oxidation state change.

References