	Experiment title: ***In-situ* characterization of Cu exchanged zeolites for in the direct oxidation of methane to methanol**	**Experiment number**: CH-3675
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Report:

Introduction

The direct oxidation of methane to methanol is one of the dream reactions in chemistry as it could enable a direct path for the highly atom efficient upgrading of natural gas to commodity chemicals such as polymers or resins being indispensable for the everyday life. However, highly efficient catalysts have been lacking and until recently only Cu zeolites appear as leads to catalyze the direct conversion of methane to methanol. Despite various efforts the nature of the catalytic active center in Cu zeolites remained unclear, mainly due to the poor homogeneity of the materials However, the amount of methanol converted corresponds only to a minority of the total number of copper atoms present in the samples. This indicates that only a specific copper oxide species plays an active role in the catalysis.

Experimental

ZSM-5 and MOR commercial samples (Si/Al = 11, Süd-Chemie) were used to prepare Cu-exchanged zeolites. The NH_4-ZSM-5 and NH_4-MOR were treated in synthetic air at 500°C (10 °C min^{-1}) for 8 h to get the protonated form. The prepared H-ZSM-5 and H-MOR materials were subsequently exchanged in aqueous Cu(II)acetate solution.
XAFS experiments were performed at beamline BM26A. The catalysts were pressed into self supporting wafers (ca. 60 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 450°C, during exposure of the catalysts to methane at 220°C and after water-steam treatment. The sample was heated to 450 °C and maintained at this temperature for 1 h under O_2 (*catalyst activation step*). After cooling in O_2 to 220 °C and short flush with He, CH_4 was flown 4 h through the catalyst (*methane loading step*). The temperature was then decreased under He flow to 135 °C and a mixture of water steam/He was passed 2 h through the catalyst (*water steam

treatment step). During this final step the main product, methanol, as well as CO_2 and traces of dimethylether were released into the gasphase. The catalytic cycle consists of three distinct steps with stable intermediates, where changes in the structure and / or oxidation state of the active sites will be followed by XANES and EXAFS. As an additional experiment for Cu-ZSM-5 and Cu-MOR samples (reduction of Cu-zeolites in inert atmosphere at high temperatures) a He treatment at 450°C was performed.
To analyze the XANES and EXAFS spectra, *Athena and Arthemis* software was used.

Results

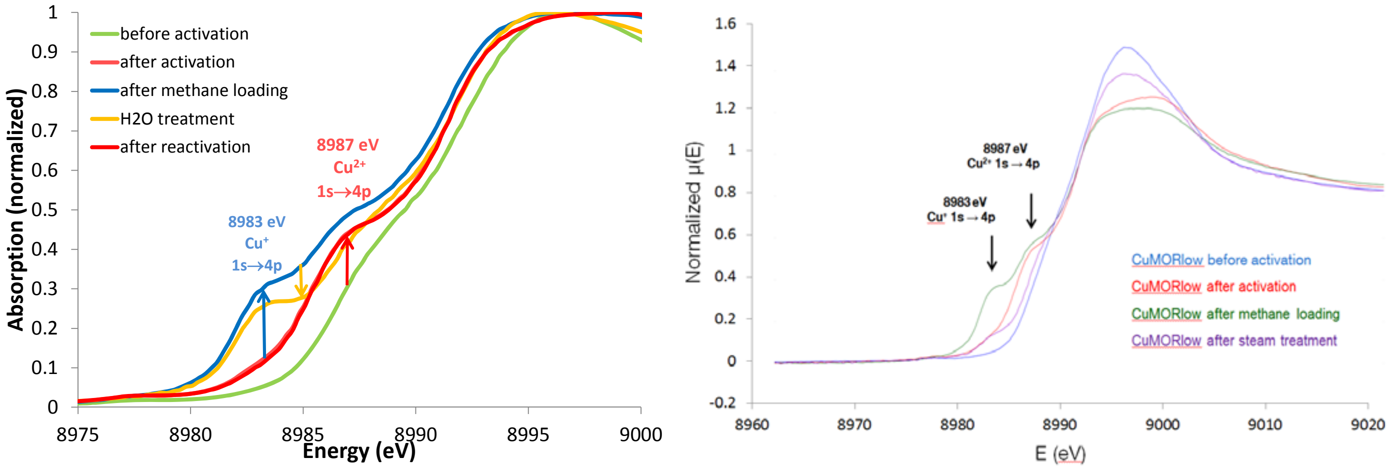

Figure 1: XANES of Cu-ZSM-5 (3 wt.%Cu):left, Cu-MOR (1 wt.% Cu):right (catalytic cycle).

The analysis on the XANES data of Cu-ZSM-5 and Cu-MOR are shown in Figure 1. A weak pre-edge feature at 8977 eV (dipole-forbidden, 1s->3d transition) that is indicative of the Cu^{2+} state was observed. The structure is changing after activation in oxygen (8987 eV Cu^{2+}, 1s->4p transition). The catalytic site is obviously not formed during the ion exchange, but only upon heat-treatment in O_2. After reaction with methane a strong new peak at 8983 eV (Cu^{+}, 1s->4p transition) is present, providing evidence that Cu^{2+} is reduced to Cu^{+} while the new feature at 8987 eV was maintained. The weak pre-edge feature at 8977 eV disappears after loading with methane. In the last step of the catalytic cycle, where water steam is passed through the catalyst bed to obtain methanol in the gas phase, the intensity of the peak at 8983 eV is hardly decreasing for the samples with low Cu concentration (1 wt. % Cu), indicating that a fraction of Cu^{+} is reoxidized to Cu^{2+}. For the Cu-zeolites containing 3 wt. % Cu, a minor decrease in intensity was observed. After closing the catalytic cycle, the catalyst was reactivated in O_2. XANES spectra after the first and second activation step were identical, indicating that the structure of the active site is retained along the catalytic cycle and is not decomposed during the release of methanol to the gas phase. During He treatment at 450°C, a reduction of Cu^{2+} to Cu^{+} was observed. The degree of reduction is much higher than the reduction with methane during the catalytic cycle. For Cu-MOR samples similar results were obtained.

Conclusions

Copper catalysts for the direct low temperature methane oxidation reaction were examined by EXAFS and XANES to investigate the changes in the structure and oxidation state of the active sites. The results showed a change in geometry during O_2-activation. After methane-loading Cu^{2+} is reduced to Cu^{+}. The structure of the active site retained along the catalytic cycle, indicating good catalyst stability. In situ XANES results revealed detailed redox process during closed catalytic cycle.