



	Experiment title: Structural informations about copper exchanged zeolites in methane activation	Experiment number: CH-3234
Beamline: BM01B	Date of experiment: from: 03.11.2010 to: 08.11.2010	Date of report: 25.02.2011
Shifts: 15	Local contact(s): Wouter van Beek	<i>Received at ESRF:</i>
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Report:

Introduction

The activation and functionalization of methane is one of the great challenges in catalysis. In particular, the direct conversion of natural gas into methanol is considered to be attractive because of its transformation in liquid feedstocks. However, the stability of methane and the high reactivity of the intermediates towards oxidation have limited the success. So far commercial industrial processes for the direct route from methane to methanol do not exist. In laboratory scale the intraporous formation of methanol from methane on copper exchanged zeolites has been successfully proved [1]. To obtain methanol the catalyst is activated in oxygen and afterwards treated with methane and finally with water. However, the converted methanol amount corresponds only to a minority of the total copper amount present in the samples. This indicates that only a specific copper oxide species plays an active role in the catalysis. To stabilize and increase the amount of this proposed active species also copper histamine complexes were exchanged into the zeolite framework.

However, the question arises to what extent the copper histamine complexes influence the structure and properties of the exchanged zeolite. To reach a complete understanding of the catalyst morphology the investigation of the structural transformation from the copper oxide species, which is formed during activation in oxygen, into an assumed methoxy species after methane loading is essential.

Experimental

H-ZSM-5 samples were prepared by exchanging a commercial Na-ZSM-5 sample (Si/Al = 12.5, Süd-Chemie) 3 times with a NH_4NO_3 solution and a subsequent treatment in synthetic air at 500 °C (10 °C min^{-1}) for 5 h. Cu was incorporated by ion exchange with Cu(II)acetate in aqueous solution. To prepare catalysts with different concentrations of Cu, this procedure was repeated different times (1, 3, 7).

The copper histamine exchanged zeolites were prepared by liquid phase ion exchange. A commercial NaY (Zeolyst Int. CBV100, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5/1$) was equilibrated at pH 7 at room temperature for 3 h and afterwards different concentrations of copper histamine were added. The solutions were stirred for 48 h at room temperature and subsequently dried for 48 h at 60 °C.

XAFS experiments were performed at beamline BM01B. 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). The XANES data were collected during activation in oxygen at 200 °C - 400 °C and after flushing with Helium during exposure of the catalysts to methane at 200 °C. To analyze the XANES spectra *XANES dactyloscope* software was used [2]. All recorded XANES spectra were normalized to unity.

Results

The analysis on the XANES data of the copper exchanged zeolites shows that the spectra before and after activation of differently exchanged materials are virtually identical (Fig. 1). That means that there is essentially only one species formed, because a major fraction of additional extra framework Cu species at higher Cu loadings would change the spectra and can hence be excluded. All spectra (before and after activation in oxygen) show only peaks for Cu^{2+} . Heating the samples in oxygen leads to a change in geometry for all samples, but no change of the oxidation state is visible. The catalytic site is subsequent not formed during the ion exchange, but only upon heat-treatment in O_2 .

The XANES spectra of O_2 -treated Cu-ZSM-5 (Fig. 1b) show a reasonably good match with $\text{Cu}(\text{OH})_2$ [3]. Thus, we suggest for the O_2 -treated Cu-ZSM-5 catalysts a four oxygen coordinated planar symmetry as in $\text{Cu}(\text{OH})_2$. This geometry remains also present after reaction with methane. However, after methane loading an additional sharp peak at 8981 eV is formed providing evidence that some Cu^{2+} is reduced to Cu^+ . This Cu^+ fraction decreases with increasing quantity of Cu exchanged, but the catalytic activity increases progressively. This indicates that the minority Cu^+ site at low Cu loading is irrelevant for the productive catalytic reaction and that Cu is not reduced by the reaction from methane to methanol.

In contrary to these results, we observe a completely different behavior of the copper histamine exchanged zeolites (Fig. 2). Before activation of the samples in oxygen Cu^{2+} species are present leading to characteristic peaks at 8977 eV and 8986 eV. Furthermore the spectra show a good agreement with those of 4-coordinated copper(II) complexes with four nitrogen ligands as reported in literature [4]. After activation these two peaks disappear, (see insert of Fig. 2b) and a new peak at 8982 eV appears, which indicates a change in the copper oxidation state from Cu^{2+} to Cu^+ . During methane loading the intensity is increasing and a slight shift was observed, which refers to a coordination change. The spectra after methane loading conforms a 3-coordinated T-shaped copper(I) complex with nitrogen and oxygen/carbon atoms [4].

These results suggest, that in the case of copper histamine exchanged zeolites the formation of Cu^+ is required for the methane activation.

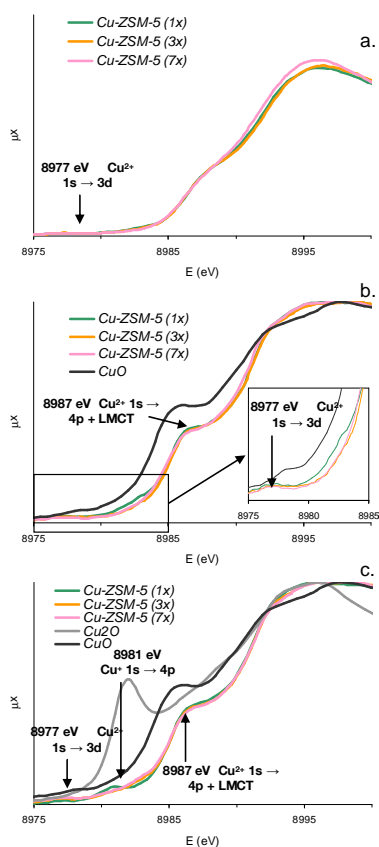


Fig. 1: XANES of different Cu-ZSM-5 **a.** before activation **b.** after activation in O₂ **c.** after methane loading.

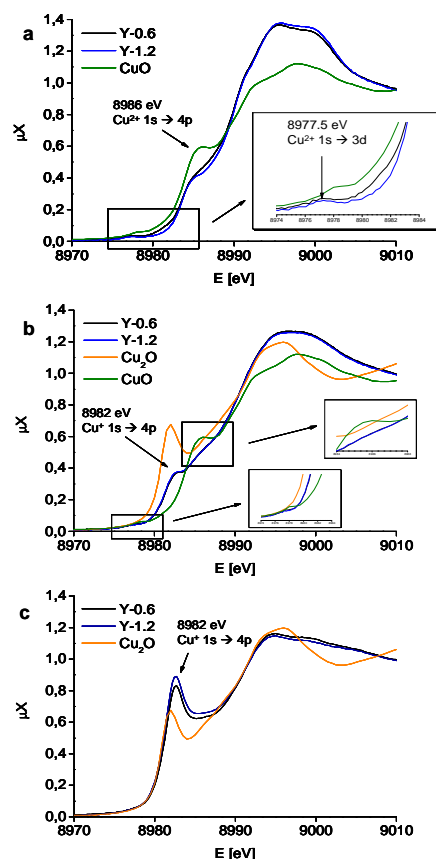


Fig. 2: XANES of two copper histamine samples **a.** before activation **b.** after activation in O₂ **c.** after methane loading.

Conclusion

The results for the Cu-ZSM-5 indicate that Cu²⁺ is not reduced to Cu⁺ during the activation of methane. In the active site Cu remains as Cu²⁺ in the oxidized (oxygen loaded) and the reduced (methane loaded) state. In contrary, the results for the copper histamine exchanged zeolites indicate that Cu⁺ is necessary for methane activation. In the activation step the Cu²⁺ is reduced to Cu⁺ and during methane loading a T-shaped 3-coordinated species seems to be generated. To identify the overall structure of the copper further measurements are necessary.

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