

Abschlussbericht

zum Thema

Selective synthesis of active Cu-oxo clusters in zeolites for methane activation at low temperatures

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1. Introduction

The increasing availability of natural gas as well as its worldwide dispersion asks for new processes to convert methane into easily condensable chemicals. Partial oxidation of methane into methanol at mild temperatures ($< 400\text{ }^{\circ}\text{C}$) is a process of great potential but catalytically challenging. Methane monooxygenases (MMO) enzymes can convert methane into methanol at ambient temperature. A biomimetic inorganic counterpart has been found in transition metal ion exchanged zeolites. Particularly, Cu-oxo clusters hosted in zeolite micropores have been found active in methane oxidation with O_2 at mild temperatures [1,2]. To date, dicopper $[\text{Cu}_2\text{O}]^{2+}$ [1] and tricopper $[\text{Cu}_3\text{O}_3]^{2+}$ species [2], both having μ -oxo bridges between Cu ions, have been identified as active sites.

Contrary to enzymes, methane oxidation on Cu-zeolite catalysts needs to be performed in a staged fashion: the oxidative activation of the catalyst requires high temperatures ($400\text{--}500\text{ }^{\circ}\text{C}$) and is separated from reaction of CH_4 on the surface. To overcome this limitation, it is necessary to understand the chemical steps that lead to the formation and regeneration of the active Cu-oxo clusters.

2. Results

2.1. Study of the ion exchange procedure on different zeolite frameworks

The conditions for aqueous Cu-exchange were previously adjusted to achieve a single site trimeric Cu species in MOR [3]. Different Cu loadings and Si/Al ratio of zeolites were studied (Table 1), while pH of the Cu solution was adjusted to 5.7 to avoid the formation of inactive CuO clusters. Zeolites containing 8-MR pores but with 3 different topologies, FER, DDR and CHA, were selected to investigate the effect of the pore structure in the formation of active Cu-oxo clusters.

Table 1. Properties and activity of Cu-DDR and Cu-CHA catalysts.

Topology	Si/Al (-)	Cu concentration ($\mu\text{mol/g}$)	Total yield of CH_4 oxidation ($\mu\text{mol/g}$)	$\text{CH}_3\text{OH} + \text{DME}$ selectivity (%)	Cu efficiency (-)
FER	9.0	151	22	35	0.15
		300	118	75	0.39
		510	72	70	0.14
DDR	30	44.6	0.9	93	0.020
		64.1	1.4	79	0.021
CHA	6.0	149	2.3	93	0.015
		298	19	75	0.064
	10	153	14	76	0.093
		293	52	73	0.18

The activity of the synthesized catalysts was tested in the 3-stage reaction of methane to methanol (activation in pure O_2 at $500\text{ }^{\circ}\text{C}$ for 1 h, CH_4 loading in 90% $\text{CH}_4/10\%$ He at $200\text{ }^{\circ}\text{C}$ for 4 hours and steam-assisted product desorption at $135\text{ }^{\circ}\text{C}$ in 50% $\text{H}_2\text{O}/50\%$ He mixture) and results are shown in Table 1 and Figure 1. Under these reaction conditions, all active Cu sites are assumed to undergo one catalytic turnover. Therefore, quantitative analysis of the products provide the number of active sites in the catalysts. The activity of catalysts can be evaluated by their Cu efficiency, defined as $(\text{mol of } \text{CH}_4 \text{ converted})/(\text{mol of Cu})$.

Only low Cu concentrations are exchanged in DDR, probably due to its low Al content. Nevertheless, it should be noted that most of the exchanged Cu is forming inactive species, in view of the very low Cu efficiency of Cu-DDR catalysts (0.02). Cu-CHA catalysts, in spite of

allowing a higher concentration of exchanged Cu, also showed Cu efficiency values far from the expected value for tricopper or dicopper species (0.33 and 0.5, respectively).

On the other hand, by the same ion exchange protocol it was possible to introduce up to 500 $\mu\text{mol/g}$ of Cu in FER. Interestingly, at medium loadings (300 $\mu\text{mol/g}$ Cu) the activity and selectivity reached a maximum (Figure 1), with a remarkable Cu efficiency or 0.4. This is the highest methane oxidation activity per Cu reported until date in any Cu-zeolite, as far as we know. The value suggest coexistence of both di- and tri-copper clusters and the virtual absence of spectators, but further spectroscopic studies will be necessary to obtain the structural description of active Cu species formed in FER.

Active Cu species are known to be stabilized by 8-MR [2, 4]. However, the results obtained here indicates that the connectivity of these rings is also relevant for the formation and/or accessibility of active sites for methane oxidation. While 8-MR pores are accessed by 10-MR and 12-MR channels in FER and MOR respectively, in DDR and CHA they are only accessed via 8- and 6-MR openings. Thus, we hypothesize that the active multinuclear Cu species are difficult to form in spatially constrained structures such as DDR and CHA. Thus, Cu ion exchange in these small pore zeolites leads to a majority of Cu monomers, regarded as inactive in methane oxidation. The configuration of Al sites in the zeolite may also play an important role in the stabilization of Cu active clusters and needs to be examined in further studies.

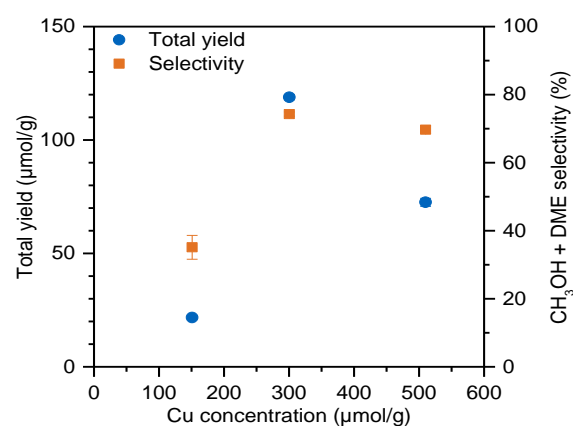


Figure 1. Total yield of CH_4 oxidation and $\text{CH}_3\text{OH} + \text{DME}$ selectivity of Cu-FER catalysts with various Cu concentrations.

2.2. Monitoring the formation of copper-oxo clusters and their evolution upon reaction with methane

Oxidation of Cu-MOR at different temperatures, after thermal treatment in He at 500 $^\circ\text{C}$, has yield similar activities in methane oxidation [5]. This points to a facile formation of the active species in O_2 , once the cluster precursor is thermally formed in inert at 500 $^\circ\text{C}$. In order to investigate the formation of both precursor and oxygen-activated Cu clusters, in-situ spectroscopies were used. The study was limited to a well defined Cu-MOR catalyst (Si/Al = 11, 440 $\mu\text{mol/g}$ Cu), that has been shown to contain $[\text{Cu}_3\text{O}_3]^{2+}$ single sites [2].

First, in situ Cu K-edge X-ray absorption near edge structure (XANES) was carried out during oxidative thermal treatment of the catalyst and a thermal treatment in He followed by contact in O_2 at lower temperatures. Catalysts differently treated were then brought to reaction temperature (200 $^\circ\text{C}$) in O_2 while monitoring in situ XAS, in order to observe the features of the active species prior reaction with methane. Unfortunately, cooling down the catalysts in dry feeds in the XAS in-situ cell led to spectra with characteristic features of rehydrated catalysts in all cases (spectra not shown here). This indicates that the material is highly water-sensitive and small traces in the gas lines can reverse the changes observed during thermal treatment at high temperatures. Due to this problem it was not possible to monitor the formation of the dry active Cu-oxo cluster with XAS.

Similar experiments were monitored with in situ UV-Vis spectroscopy in our labs at TUM. CuMOR was first thermally treated in N_2 at 500 $^\circ\text{C}$ and subsequently activated at 50 $^\circ\text{C}$ and

450 °C in O₂. UV-vis absorption spectra are shown in Figure 2. Under both oxidation treatments it is possible to see the development of the absorption band at ca. 30000 cm⁻¹. This band has been assigned to [Cu₃O₃]²⁺ species [2].

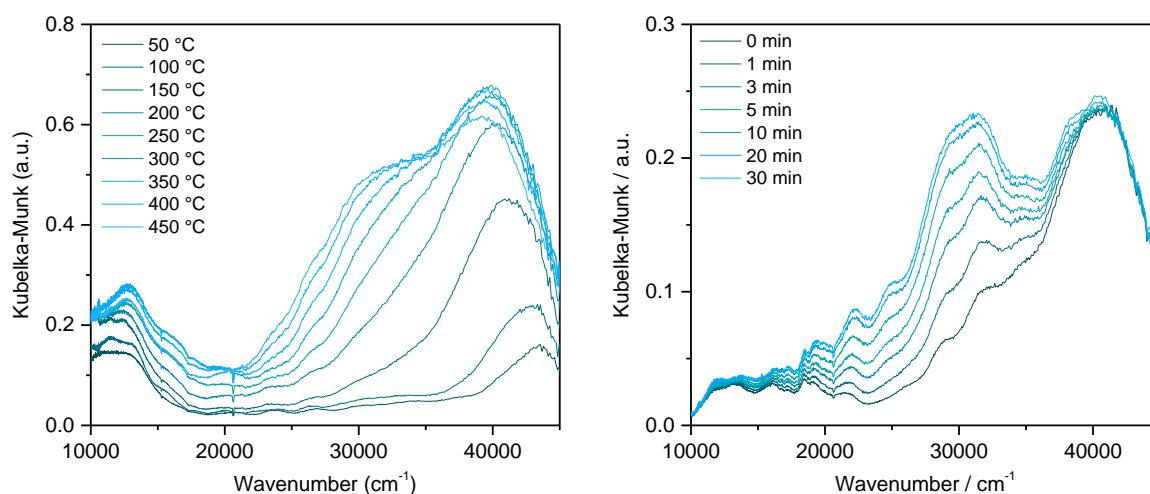


Figure 2. In-situ UV-Vis spectra of Cu-MOR catalyst during thermal activation in O₂ (left) and low-temperature oxidation at 50 °C after thermal activation in N₂ (right)

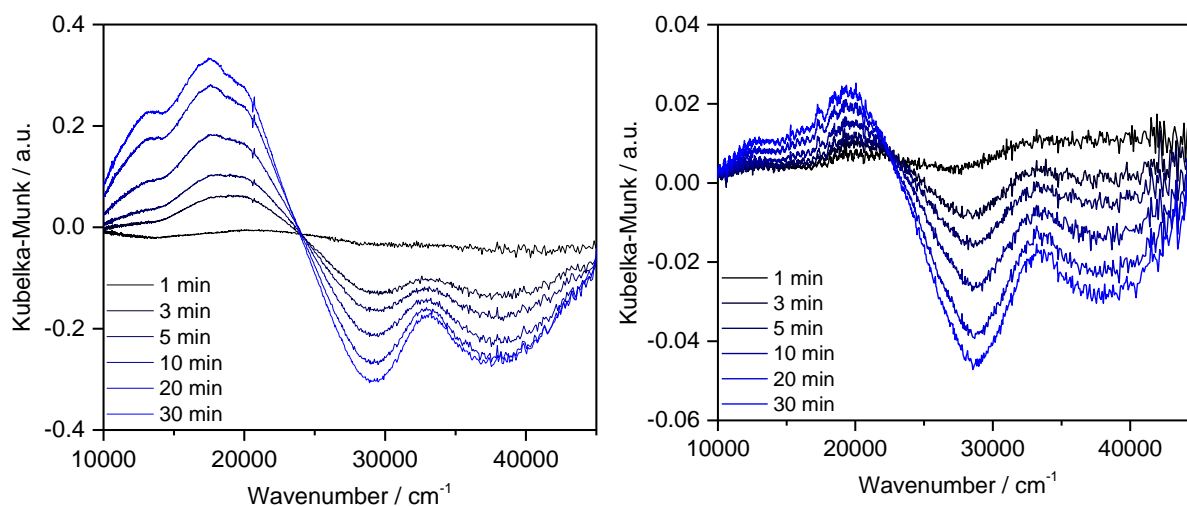


Figure 3. In-situ difference UV-Vis spectra during CH₄ loading at 200 °C on a Cu-MOR catalyst activated in O₂ at 450 °C (left) and in inert (N₂) at 450 °C and subsequently oxidized in O₂ at 200 °C (right).

In situ XANES of the CuMOR catalyst during methane reaction showed that a fraction of Cu²⁺ is reduced to Cu⁺ upon activation of CH₄ on the catalyst. In-situ UV-Vis spectroscopy was performed to monitor reaction of methane on a CuMOR catalyst activated in O₂ at 450 °C and a CuMOR catalyst activated O₂ at 200 °C (after thermal treatment in inert). Figure 3 shows the differential UV-vis spectra for both experiments. Absorption bands at 29000 cm⁻¹ and 37000 cm⁻¹, assigned to [Cu₃O₃]²⁺ and Cu²⁺ ← O ligand-to-metal charge transfer respectively, disappeared upon reaction with methane in both samples. The appearance of bands at 10000-20000 cm⁻¹ are tentatively assigned to Cu⁺ luminescence. Although the technique does not allow quantification of Cu species, the spectra in Figure 3 show that the decrease in absorption bands associated with methane reaction is similar in extent and relative intensities in both samples. This suggests that the nature of the Cu species that reacted with methane are the same independently of the temperature at which CuMOR was contacted with O₂.

The results obtained here indicate that oxidation of Cu precursor occurs readily at temperatures as low as 50-200 °C. This is in good agreement with catalytic tests that showed that the maximum activity of CuMOR (ca. 130 $\mu\text{mol/g}$ of CH_4 converted) can be also achieved when the sample is thermally activated in inert and then contacted O_2 at 50 °C.

3. Conclusions

Study of Cu species in different zeolite structures suggests that only zeolite frameworks with spacious connectivity of the 8-MR features can allow for the formation of multinuclear Cu-oxo species, active in methane oxidation. As a highlight, the Cu efficiency achieved in FER zeolite was the highest so far reported and therefore further studies are planned on this system.

In situ spectroscopy studies allow concluding that active Cu-oxo species formed after oxidation are similar independently of the temperature applied. Therefore, the thermal treatment required for the (re)activation of Cu-zeolites is related to the formation of the cluster precursor, which can be then easily oxidized at low temperatures in presence of O_2 .

4. References

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