



Copper-exchanged omega (MAZ) zeolite: copper-concentration dependent active sites and its unprecedented methane to methanol conversion

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Abstract: The direct conversion of methane to methanol may provide a way to utilize methane that is otherwise wasted. Here we have explored one of the most promising copper zeolite materials to date, copper-exchanged omega (**MAZ**) zeolite. With highly crystalline and uniform zeolite omega, we can produce 150 umol-methanol/gramzeolite under 1 bar methane and as high as 200 umol-methanol/gramzeolite under 30 bar methane, the highest yield ever reported. Furthermore, zeolite omega's ability to convert methane to methanol has a distinct copper-concentration dependent behavior. At lower copper loadings, Cu-**MAZ** is inactive, and once a minimum copper loading is reached, Cu-**MAZ** converts methane to methanol more selective than the widely studied Cu-mordenite. With the unprecedented high conversion and selectivity, Cu-**MAZ** provides insight into the active copper phase and its mechanism which was quantified as two electrons per molecule of methanol produced.

During petroleum extraction, methane often accompanies the crude oil as it is carried to the surface. Utilizing this methane is not always economically feasible due to the low price of methane and the high costs of contaminant removal and transportation.^[1] Depending on local regulations, this methane is exhausted as waste or converted to carbon dioxide by flaring.^[2] Ultimately this results in a waste of fossil fuels with an estimated 143 billion m³⁻ /year.[3] To avoid this waste, converting this methane to more valuable molecules like methanol could be a win-win situation for economics and the environment.^[4] Directly converting methane to methanol has its share of scientific challenges that have given it a reputation as the "dream reaction."[5-7] The methane must be stabilized in a partially oxidized state rather than undergo much more favorable complete oxidation to carbon dioxide.^[7,8] Copper exchanged zeolites can do just that when a stepwise looping procedure is applied.^[9–17] The most widely studied copper zeolites are ZSM-5 and mordenite, and the overall methanol yield has improved over the last 15 years as we have gained better understanding of the procedure, extraction and favorable zeolite characteristics.^[9-23] However, the yield is still below any industrially viable levels, and there is no consensus on the active site or mechanism responsible for the methane to methanol conversion.^[9,10,13,15,18,21,23-27] This has led researchers to explore

[a] Amy Knorpp, Dr. Mark Newton, Prof. Dr. Jeroen A. van Bokhoven Institute for Chemical and Bioengineering ETH Zurich Vladimir-Prelog-Weg 1, 8093 Zurich (Switzerland) E-mail: jeroen.vanbokhoven@chem.ethz.ch
[b] Dr. Ana B. Pinar, Dr. Vitaly Sushkevich, Prof. Dr. Jeroen A. van Bokhoven Laboratory for Catalysis and Sustainable Chemistry Paul Scherrer Institute 5232 Villigen (Switzerland) E-mail: ana.pinar@psi.ch other zeolites and non-zeolite materials in an attempt to achieve higher yields of methanol or uniform active sites.^[14,17,28,29] In one such survey of zeolite types, zeolite omega (**MAZ**)^[30] was shown to be comparable to mordenite (**MOR**) in the conversion of methane to methanol.^[28] However, zeolite omega was not pure and contained a common co-phase sodalite (**SOD**). By synthesizing a pure, highly crystalline and uniform zeolite omega, we report here an unprecedented conversion of methane to methanol for copper zeolites which allows for better understanding of the active sites and its mechanism.

A series of Cu-omega (Cu-MAZ) samples were prepared through cation exchange with varying amounts of copper ranging from 1.5 wt.% to 4.7 wt.% The details on the sample synthesis and its characterization are given in the Supporting Information. Each sample was tested for methane to methanol conversion under the conventional stepwise procedure^[9,10,13-15,17,18,21] (activation at 723K in oxygen and reaction at 473K with methane at 1 bar) as well as under a high-pressure procedure using methane at 30 bar and at 473K during the methane reaction step.^[20] For comparison, a commercial mordenite (Zeoflair 800, Zeochem AG, Si/Al = 10) was also tested. Copper-exchanged mordenite (Cu-MOR) is known to begin converting methane to methanol at low copper concentrations, $^{\left[15\right] }$ and we observed a similar trend (Figure 1). However, a different trend is observed for Cu-MAZ. There is a minimum copper concentration required before any methane is converted to methanol. This is reminiscent of the copper-dependent behavior of Cu-ZSM-5^[9,10] where at low copper concentrations no methanol is formed, and inactive copper resides in the 6-membered rings of ZSM-5.[31] As copper concentration increases in Cu-ZSM-5, the active site was determined spectroscopically as a Cu dimer (i.e. CuOCu).^[18] However, for ZSM-5 only a small fraction (5-10%) of the additional copper is active with the majority remaining inactive, thus resulting





in low methanol yields (10-20 µmol-MEOH/g-zeolite) at higher copper contents.^[9,10] Cu-**MOR** shows no minimum Cu threshold activity behavior, but Cu-**MOR** has been shown to contain mixed co-existing inactive and/or multiple active copper sites.^[24] Generating single sites within zeolites has been one way to make a step forward in identifying the active site, as seen for the identification of trimers in mordenite.^[15]

By contrast to ZSM-5, in **MAZ** nearly all additional copper is active after the minimum copper requirement is reached. As the copper concentration is increased, the methanol yield increases at a higher rate than for mordenite with a methanol yield as high as 150 μ mol-MeOH/g-zeolite for 1 bar of methane. Methanol yield can further be increased to 200 μ mol-MeOH/g-zeolite by reacting with methane at 30 bar.

For the lowest copper concentration (1.5 wt%. Cu), methanol was not produced during the reaction at 1 bar. By extrapolating the x-intercept in Figure 1 for the active samples, we can quantify the inactive copper and the minimum concentration of copper needed in zeolite omega for methane to methanol conversion (297 µmol-Cu/g-zeolite for 1 bar). By increasing the methane pressure to 30 bar, the methanol yield increases across all copper concentrations and shifts the x-intercept by 71 µmol-Cu/g-zeolite to 226 µmol-Cu/g-zeolite. We speculate that the pressure is activating previously inactive sites, as was seen in mordenite.^[20] By noting the slope (Figure 1), the amount of coppers participating per methanol for the 1 bar procedure is 2.8 mol-Cu/mol-MeOH and for the 30 bar procedure it is 2.6 mol-Cu/mol-MeOH, suggesting that at least two copper atoms are required for methanol formation, and proposed sites with three or more participating coppers can be excluded for this system.

By in-situ Fourier-transform infrared spectroscopy (FTIR), Cu-MAZ shows superior selectivity to Cu-MOR, and this explains in part the better performance of Cu-MAZ over Cu-MOR. Across all copper loadings of Cu-MAZ, no by-products were observed, but for Cu-MOR both carbon monoxide (Figure 2) and formate (Figure S7) were detected. The framework structure of omega provides a favorable environment to stabilize the methoxy species rather than over-oxidation. The asymmetric and symmetric vibrations of the C-H methyl group for these methoxy species were observed in the FTIR and follow a similar concentration-



Figure 2: In-situ FTIR spectra of surface species formed during the reaction with methane at 473K for 30 minutes. (Left) Methoxy is the surface intermediate species for methanol. (Right) Carbon monoxide is formed due to unselective conversion of methane to methanol in Cu-**MOR**.

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Figure 3: In-situ Cu K-edge XANES spectra of Cu-**MAZ** with varying copper loadings at the end of reaction with methane at 473K. The activated form is after treatment in oxygen at 723K for 1 hour, and the reduced state was formed by heating to 723K in methane.

dependent behavior as observed in reactor studies (Figure 1). For the lowest loaded zeolite omega, no methoxy species were detected, and this further confirms the reactivity studies that show that this sample is inactive. As the copper content increases, the methoxy species become more prominent as expected from the reaction studies and surpasses mordenite (Figure S7).

To better understand the role of copper in the reaction, we examined this series of Cu-**MAZ** samples by in-situ XAS at the DUBBLE and SNBL beamlines at the European Syncrotron Radiation Facility. Changes in the Cu K-edge XANES spectra were monitored throughout the activation and reaction steps. This technique allows for in-situ probing of the oxidation states and is sensitive to local electronic and geometric structure of the copper.^[32,33] Similar to what has been observed in other Cu-zeolites^[12,13,15,17], during activation the maximum absorption decreases while a shoulder at 8986 eV becomes pronounced due to the dehydration and the lowering of the first coordination shell (Figure S5).

The XANES spectra were similar for all loadings of copper for the activation phase (Figure S5). However, the samples varied greatly for the conversion of Cu(II) to Cu(I) during the reaction step (Figure 3). The lowest loaded/inactive sample only showed a small amount of Cu(II) converted to Cu(I). As the copper content increased, the conversion of Cu(II) to Cu(I) increases.

An accurate correlation and quantification of the reduction of Cu(II) to Cu(I) due to methanol formation can be complicated by the formation of by-products like carbon monoxide, which will also convert Cu(II) to Cu(I). However, given the distinct regions of active and inactive copper in Cu-**MAZ**, the correlation between Cu(I) and methanol is apparent, and the high selectivity of zeolite omega means that quantification of the mechanism will be more accurate than for any other previous Cu-zeolite.^[34] By comparing Cu(I) to the methanol production, we are able to quantify the electrons involved in the conversion of methane to methanol on Cu-omega at each loading (Figure 4) as well as for additional synthesized Cu-**MAZ** samples (Table S2). With this method, about two electrons are participating in the conversion of each methane to methanol, pointing toward a two-electron redox mechanism.

In Figure 4, we summarize two methods to quantify the copper and electrons involved for the conversion of methane to



Figure 4: (Right Axis) Ratio of μ mol of Cu(I) formed during reaction by the μ mol of methanol formed. (Left Axis) Ratio of calculated μ mol active copper to μ mol of methanol when 1 bar and 30 bar methane was used.

methanol in Cu-**MAZ**. The first method is quantifying the moles of Cu(II) converted to Cu(I) as determined by XANES per mole methanol. The second method is quantifying the moles of active copper per mole methanol. To quantify the active copper, we subtract the inactive copper as determined by the x-intercept from the total copper concentration. For both methods, the values primarily fall in between 2-3 with one method representing the electron and the other methods participating coppers. From this set of Cu-MAZ samples, mol-MeOH/mol-activeCu ratios as high as 0.48 were found when the extraction was repeated until no methanol was detected (Figure S8).

A wide range of active sites have been proposed with varying mechanism as well as a large range of different number of coppers involved.^[9,10,13,15,18,23-27] Here we do not wish to add to the confusion by proposing one active site for Cu-**MAZ**, this study, however, allows constraints to be put onto the proposed active site based on experimental evidence. The mechanism must involve a Cu(II) to Cu(I) coupling with two electrons, and the number of coppers involved is very close to two.

In conclusion, Cu-**MAZ** provides a superior environment for the selective conversion of methane to methanol that results in higher selectivity and high methanol yields than have previously been reported. Furthermore, its copper-dependent behavior and remarkable selectivity allows progress in our fundamental scientific understanding on how this copper zeolite (Cu-**MAZ**) converts methane to methanol which must involve two electrons and coppers.

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One of the most promising copper zeolite materials to date is explored for the direct conversion of methane to methanol, copper-exchanged omega (MAZ) zeolite. At lower copper loadings, Cu-MAZ is inactive, and once a minimum copper loading is reached, Cu-MAZ converts methane to methanol with remarkable selectivity and an unprecedented methanol yield which allowed for the determination of the mechanism as a two-electron process.



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Copper-exchanged omega (MAZ): copper-concentration dependent active sites for methane to methanol conversion