Methane to Methanol Conversion **Hot Paper**

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Isothermal Cyclic Conversion of Methane into Methanol over Copper-Exchanged Zeolite at Low Temperature

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Abstract: *Direct partial oxidation of methane into methanol is a cornerstone of catalysis. The stepped conversion of methane into methanol currently involves activation at high temperature and reaction with methane at decreased temperature, which limits applicability of the technique. The first implementation of copper-containing zeolites in the production of methanol directly from methane is reported, using molecular oxygen under isothermal conditions at 200°C. Copper-exchanged zeolite is activated with oxygen, reacts with methane, and is subsequently extracted with steam in a repeated cyclic process. Methanol yield increases with methane pressure, enabling reactivity with less reactive oxidized copper species. It is possible to produce methanol over catalysts that were inactive in prior state of the art systems. Characterization of the activated catalyst at low temperature revealed that the active sites are small clusters of copper, and not necessarily di- or tricopper sites, indicating that catalysts can be designed with greater flexibility than formerly proposed.*

Direct production of methanol from methane and oxygen is a long standing challenge, which has not yet been solved satisfactorily because of the higher reactivity of primary oxidation products compared to methane.[1] More expensive oxidants, such as oleum,[2] nitric oxide (NO),[3] or hydrogen peroxide[4] may be used. Inspired by nature,[5] methane has been converted by a stepwise activation method, reaction with methane, and extraction with water (Figure 1 A), using iron-,[6] copper-[3,7], and cobalt-exchanged zeolites.[8] In the case of copper-exchanged zeolites, reactivity has been ascribed to μ-oxo dicopper sites[7b,d,g,9], and more recently to a tricopper site,[7i] which required high temperatures (greater than 280°C) for its formation.[7b,10] The reaction must be carried out at lower temperature (up to about 200°C), because methane is otherwise combusted.[7a,d] The tedious heating and cooling procedure performed throughout cycles limit applicability of the technique and prolong cycling time, consequently isothermal conversion is highly desirable. Herein we show a high yielding, low temperature, isothermal cyclic procedure for the oxidation of methane into methanol using molecular oxygen. In contrast with prior studies, we found that copper-exchanged zeolites activated at low temperature (200°C for example) are capable of converting methane into methanol if elevated pressures of methane are employed during the reaction. A stable yield was achieved over several cycles. In situ extended X-ray absorption fine structure (EXAFS) identified the active species as dehydrated copper oxide clusters.[10] No spectroscopic signature assigned to a μ-oxo dicopper site was observed, which proves the presence of an unprecedented reaction mechanism. Our results indicate that materials found to be inactive using high temperature activation, become active under isothermal conditions at elevated methane pressures. The isothermal and regenerable nature of the process is a major breakthrough in the development of an applicable technology for the transformation of methane into methanol. Based on this study, new classes of catalysts may be developed and a practicable solution for one of chemistry's unsolved challenges found.

The effect of pressure on methanol yield was established by screening pressures up to 6 bar of oxygen and up to 37 bar of methane (Figure 1 B–D) using copper-exchanged mordenite (Cu-MOR; Si/Al = 6, 4.7 wt% Cu). Activation at 1 bar of oxygen and 450°C, followed by reaction at 50 mbar of methane (5% in helium) at 200°C, yielded 14.4 $\mu mol\,g^{-1}$ of methanol, which was comparable to reported values.[7d] Activation in a flow of oxygen at 6 bar brought about a decrease in yield to 7.5 $\mu mol\,g^{-1}$. Activation of Cu-MOR at 1 bar of oxygen, using 1, 6, or 36 bar of methane pressure, yielded 45.3, 84.1, or 103.3 $\mu mol\,g^{-1}$ of methanol, respectively. These results show that larger amounts of methanol can be extracted when Cu-MOR is in contact with methane at higher pressures following high temperature (450°C) activation. A 6 bar gas mixture of both oxygen and methane yielded 68.4 $\mu mol\,g^{-1}$ of methanol, indicating that the oxygen activation step has a weak effect on the reaction performance. In contrast, higher methane pressure increased the yield.

Based on the high yield of methanol after high temperature activation, Cu-MOR activation and methane reaction were carried out isothermally at 200°C. At 1 bar of oxygen over a 13 h activation period, and after exposure to 50 mbar (5%) of methane in helium, the methanol yield was very low (0.3 $\mu mol\,g^{-1}$), and comparable to the yield of methanol obtained over Cu-ZSM-5 after activation with NO at 150°C.[3] Similar to the high temperature system, methanol yield increased to 21.2 $\mu mol\,g^{-1}$ when 6 bar of methane was used during the reaction. Methanol was the only product detected

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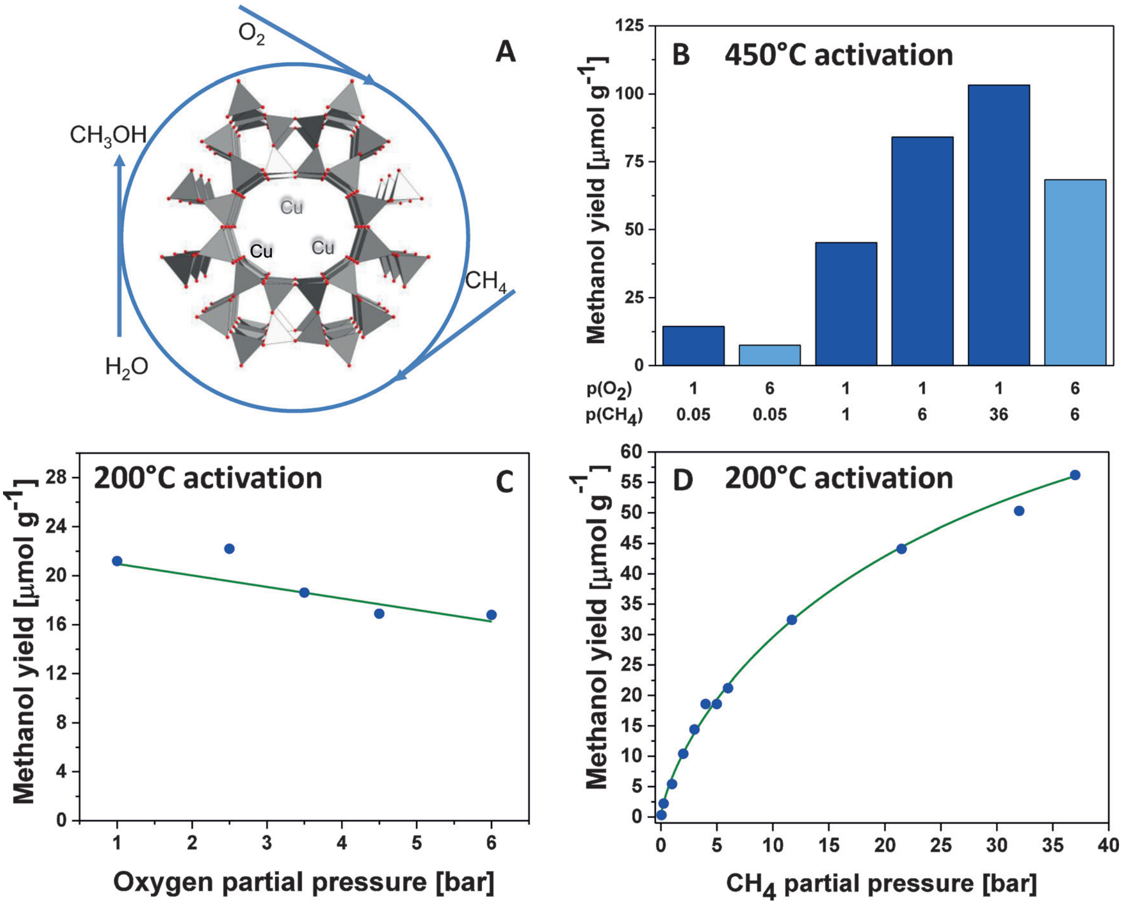

Figure 1. Catalytic cycle and the effect of oxygen and methane pressure on the yield of methanol. A) Catalytic cycle: activation of the catalyst, reaction with methane, and methanol extraction. Presented experiments typically include activation in oxygen flow, purging with helium, reaction with methane (30 min), and extraction with liquid water at room temperature. B) Methanol yields after activation at 450 °C and off-line extraction at different pressures of oxygen and methane. Yields were higher at higher methane pressures, whereas higher oxygen pressures lead to a slightly decreased methanol yield. Pressure is stated in bar (absolute). C) The dependence of activation on oxygen pressure and its effect on methanol yield; methanol yield decreases as oxygen pressure increases. D) Dependence of methanol yield on methane pressure after 13 h activation at 1 bar of oxygen and off-line extraction. The yield of methanol increased to 56.2 µmol g^{-1} at a methane pressure of 37 bar.

by GC-FID after extraction. A blank experiment under identical reaction conditions, using non-copper-exchanged MOR, yielded very little methanol (2.2 µmol g^{-1}), proving that copper is the active species (Supporting Information, Table S1, entry 1). The methanol yield was very low (0.8 µmol g^{-1}; Supporting Information, Table S1, entry 2) when there was no gas flow during activation, suggesting that dehydration is essential for activity. At elevated methane pressure (6 bar), methanol yield decreased slightly from 21.2 to 16.8 µmol g^{-1} upon increase of the oxygen pressure from 1 to 6 bar (Figure 1 C), once again confirming the weak effect of oxygen pressure on the yield of methanol during activation. The slight decrease in methanol yield might be caused by less efficient removal of volatiles. A longer activation period with 1 bar of oxygen led to an increase in the methanol yield. Upon reaction with 6 bar of methane immediately after reaching the reaction temperature under a flow of oxygen, the methanol yield was 10.4 µmol g^{-1} (Supporting Information, Figure S1). When activation was carried out for 4 h, the yield increased to 19.0 µmol g^{-1}, and then more slowly to 25.5 µmol g^{-1} after 42 h of activation.

An increase in methane pressure resulted in higher methanol yields (Figure 1 D), whereas low yields (0.3 µmol g^{-1}) were obtained at low partial pressure. At 37 bar of methane, the yield increased gradually to 56.2 µmol g^{-1}. Thus, a higher methane pressure is advantageous for the reaction with copper oxide after low temperature activation. Figure 1 D illustrates that the maximum has not yet been reached. The reaction was also carried out isothermally after 13 h of activation at 1 bar of oxygen and 6 bar of methane at different temperatures. The yield of methanol at 175 °C was 11.7 µmol g^{-1} (Supporting Information, Table S1, entry 3), slightly less than the yield at 200 °C. This may be due to insufficient activation or variable activity at different reaction temperatures.[7b] Little or no production of CO$_2$ is revealed by mass spectrometric detection during methane interaction at 175 °C, suggesting that the lower yield is not because of over-oxidation (Supporting Information, Figure S2). The yield of methanol was 18.6 µmol g^{-1} at 225 °C (Supporting Information, Table S1, entry 4), virtually the same as that at 200 °C. At 200 °C, the isothermal reaction gave the highest yield overall.

UV/Vis measurements were performed to gain insight into the state of copper within the zeolite under isothermal conditions at 200 °C (Supporting Information, Figure S3). The active site of Cu-ZSM-5 after high temperature activation was recently described as a mono-μ-oxo dicopper site, revealed by a band in the UV/Vis spectrum at 22 700 cm^{-1}.[7a,e,9a] The same feature was found in Cu-MOR.[7b,d] After activation at 200 °C there was no band in the spectrum in the region of 20 000 cm^{-1}, proving the absence of this site. Furthermore, a broad band appeared at 13 500 cm^{-1} and perhaps a shoulder at 16 750 cm^{-1}, which can be assigned to Cu^{2+} species at two aluminum sites and one aluminum site,[7h,9b] respectively. The finding that a μ-oxo dicopper site was not present at 200 °C, indicates that a different copper species is responsible for activity under isothermal conditions. These sites are apparently less reactive than the μ-oxo dicopper core and require higher methane pressure to achieve reduction of copper oxide, consistent with a larger methanol yield at higher methane pressure. Other copper structures in molecular catalysts[11] and solids[7b,h] are reported to yield methanol from methane. TEM measurements of the sample activated at 200 °C show finely dispersed particles (Figure 2 A), some of which are smaller than 1 nm (Supporting Information, Figure S4), that are probably generated during activation (Supporting Information, Figure S5 and S6). Only reflections of the MOR framework are visible in the PXRD pattern, confirming the absence of larger (≥ 3 nm) crystalline copper particles (Supporting Information, Figure S7). Heating of Cu-ZSM-5 to 200 °C induces a loss of bulk water in the hydration sphere of copper.[10] In situ XAS measurements showed that heating above 250 °C results in rather small changes in the local geometric coordination sphere of copper and there is only a little autoreduction of Cu^{2+} into Cu^{+} at 200 °C.[10] The μ-oxo dicopper core is formed after autoreduction of copper oxide and subsequent reaction with oxygen.[10] In low amounts this species may be responsible for the small amount of methanol formed at the lowest methane pressure after high temperature activation. The μ-oxo dicopper core is known to completely react after treatment with 50 mbar of methane.[7b] This observation further suggests that the μ-oxo dicopper core is not formed under isothermal conditions, as additional methanol is produced at higher methane pressures. Condensation of attached hydroxy ligands takes place at significantly higher temperatures of 300–350 °C.[10] EXAFS revealed that the average coordination number of oxygen is high (ca. 3.2) at 200 °C, and the presence of distant copper neighbors suggests a significant fraction of copper oxide clusters and particles, where an average coordination number of four is expected for the closest oxygen neighbors.[10] Generally, after activation at 200 °C Cu-MOR is characterized by dehydrated Cu^{2+}-species, which are present irrespective of the gas environment.[10] X-ray photoelectron spectroscopy (XPS) measurements indicated that a significant fraction of Cu^{2+} was reduced during interaction with 6 bar of methane at 200 °C after 13 h activation at 200 °C (see Supporting Information).

Substituting oxygen with helium during the first cycle of activation resulted in an identical yield (20.0 μmol g^{-1}; Supporting Information, Table S1, Entry 5). These findings suggest that the active sites are small, dehydrated copper oxide clusters. These clusters are less reactive than the μ-oxo dicopper site, and their reduction is only enabled by high methane pressure. The comparable yield obtained after helium activation shows that no oxidation of autoreduced copper species is required and that the oxidation power stems from initially available Cu^{2+}. Cu-MOR with lower copper loading (that is, 0.64 and 3.0 wt %) gave methanol yields of 7.9 and 33.1 μmol g^{-1}, respectively (Supporting Information, Table S1, Entries 6 and 7). The amount of methanol formed per copper atom decreases from 0.078 to 0.071 and 0.029, at copper loadings of 0.64, 3.0, and 4.7 wt %, respectively. Smaller, highly dispersed copper clusters are expected to

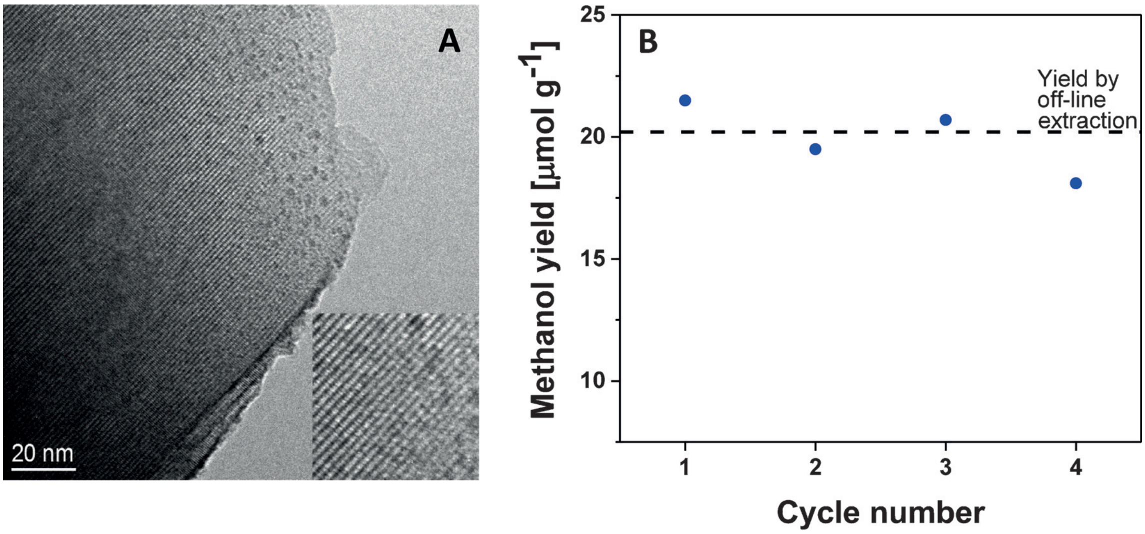

Figure 2. Cycling of the isothermal process at 200 °C. A) TEM image of Cu-MOR activated at 200 °C, showing the intact pore structure of the zeolite and small copper oxide particles. B) Methanol yields after consecutive cycles. In each cycle the yield (about 20 μmol g^{-1}) was stable. A cycle consisted of activation for 8 h at 1 bar of oxygen, reaction with methane at 6 bar, and extraction with steam. The liquid was collected by condensation of the reactor effluent.

form with lower catalyst loadings. Thus, the presence of small copper clusters enhances the activity of the catalyst.

To prove the principle of activating additional sites at elevated methane pressures, and to show applicability in other systems, an investigation of Cu-ZSM-5 (Si/Al = 15, 2.8 wt % Cu) was carried out under isothermal conditions at 200 °C. After activation in oxygen at 200 °C, no spectroscopic signature ascribed to the μ-oxo species was observed (Supporting Information, Figure S8);[7b] the catalyst was inactive at a 10 mbar methane partial pressure (1 % in argon).[3] After activation in oxygen for 13 h and reaction under 32 bar of methane, 17.7 μmol g^{-1} of methanol (Supporting Information, Table S1, entry 8) was obtained, slightly higher than values reported involving high temperature activation.[7a,h] This finding confirms that there are different types of copper species involved in the conversion of methane into methanol at elevated pressure. Cu-Y (Si/Al = 2.7–3.0, 7.6 wt % Cu), which yields less than 1 μmol g^{-1} of methanol after activation at 450 °C with 1 bar of oxygen followed by reaction under 50 mbar of methane (5 % methane in nitrogen),[7b] produced 10.5 μmol g^{-1} (Supporting Information, Table S1, entry 9) of methanol under isothermal conditions at 200 °C and 32 bar of methane. This initial screening suggests that not only copper and zeolites, but also many other catalysts, might be active in selective conversion of methane into methanol.

Repeated cycles were carried out with Cu-MOR to demonstrate applicability of the newly developed procedure described herein. The reaction consisted of activation for 8 h with 1 bar of oxygen and subsequent reaction under 6 bar of methane at 200 °C, followed by on-line extraction of the produced methanol with water at the same temperature (Figure 2 B). A stable methanol yield of about 20 μmol g^{-1} was achieved in each cycle, in close agreement with the yield (20.8 μmol g^{-1}) obtained by liquid extraction, demonstrating the efficiency of the on-line extraction method and the feasibility of a continuous cyclic process. This experiment also showed that the catalyst is stable and reusable. Powder XRD patterns (Supporting Information, Figure S7) and nitrogen physisorption isotherms (Supporting Information, Figure S9 and Table S2) hardly changed, showing that the zeolite framework is stable in this reaction. TEM images reveal finely dispersed particles after activation and subsequent reaction cycles. There was no significant change after successive cycles compared to the activated catalyst (Supporting Information, Figure S6).

In summary, these results constitute a major step towards simplification of the methane to methanol conversion process, opening up new opportunities for catalyst optimization and academic and engineering avenues for one of the most challenging reactions in chemistry and catalysis.

Experimental Section

Copper-exchanged zeolites were prepared by three-fold ion-exchange of the sodium-zeolite using copper acetate hydrate (0.01 M, 78 mL/g$_{\text{Na-zeolite}}$). Reactions were carried out in stainless steel autoclaves: an oxygen flow (70 mL min^{-1}) was employed during activation, followed by purging with helium, subsequent reaction with methane, and concluding with extraction (either with liquid water or on-line with steam) and analysis of the corresponding condensate using GC-FID with acetonitrile as an external standard.

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