Cite this: Chem. Commun., 2012, 48, 404-406

## COMMUNICATION

## Catalytic conversion of methane to methanol over Cu-mordenite<sup>†</sup>

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Received 20th September 2011, Accepted 27th October 2011 DOI: 10.1039/c1cc15840f

Methane can be converted to methanol over copper-exchanged mordenite at 200 °C. Methanol could be recovered at the end of the reactor. This multi-step reaction opens the possibility for methane to methanol conversion in a closed catalytic cyclic reaction system.

Although much sought after, the use of methane as a chemical feedstock is still greatly limited.<sup>1</sup> The high C–H bond strength of methane and its perfect symmetry make it an extremely challenging molecule for chemical attack.<sup>2</sup> Oxidation reaction routes are generally futile since the oxidation products of methane are more reactive than methane itself. This pushes the overall chemical system to total oxidation, unless methanol or its precursor is stabilized. Partial oxidation has been achieved by a homogeneous Pt–bipyrimidine-catalyzed process by the formation of methyl bisulfate that can be hydrolyzed to methanol. The reaction proceeds with excellent yields of methane partial oxidation products.<sup>3,4</sup> However, such outstanding activity and selectivity trades off with the use of harsh acidic conditions and the inability to separate and recover the catalyst and product.

A known mild and controlled oxidation is performed by an enzymatic system, methane monooxygenase (MMO), which converts methane to methanol under the ambient living conditions of the host methanotroph. The active species consists of diiron sites for the soluble MMO and dicopper sites for the particulate MMO.<sup>5</sup> These binuclear centers create a bridged oxidizing species sufficiently strong to attack the C-H bond of methane. The microporous structure of pentasil zeolites, such as ZSM-5, stabilized the binuclear centers analogous to those present in MMOs. Fe-ZSM-5 converted methane to methanol at room temperature.<sup>6,7</sup> A Cu-FeZSM-5 system was also described to convert methane to methanol with N2O above 230 °C.8 High temperature autoreduction of  $Fe^{3+}$  to  $Fe^{2+}$  under strong chemical stabilization in the zeolite matrix generates sites which cannot be reoxidized by O2 but only by N2O. These sites are capable of selective hydrocarbon oxidation.9 Zeolites ZSM-5 and mordenite (MOR) stabilize binuclear Cu centers, which convert methane to methanol at 130-200 °C without α-oxygen from N2O but only using O<sub>2</sub> as an oxidant.<sup>10</sup> The UV-vis absorption band at 22 200 or at 22 700 cm<sup>-1</sup> was assigned as the spectroscopic signature of the active copper site in Cu–MOR and Cu–ZSM-5, respectively.<sup>10,11</sup> The same UV-Vis signature at 22 700 cm<sup>-1</sup> was related to the catalytic decomposition of nitric oxide and was proposed to be similar in structure to a bis( $\mu$ -oxo) dicopper species by Cu K-edge X-ray absorption spectroscopy (XAS).<sup>12,13</sup> The identity of the active site leaves room for discussion, since the percentage of total metal sites present that is involved in the methane to methanol conversion is low. More recent resonant Raman measurements coupled to normal coordinate and density functional theory calculations suggested the structure of the active site to be a bent mono( $\mu$ -oxo) dicopper center.<sup>14,15</sup>

Despite uncertainties about the structure of the active site, metal–zeolite assisted methane conversion was the first step in bridging a structure-specific and biochemically-controlled enzymatic system to a heterogeneous catalytic system. The main drawback, however, is that in all previous reported systems, methanol was obtained only through extraction, and never directly.<sup>6,10,11,16</sup> During these previous studies, some intermediate formed after reacting methane at temperatures higher than 130 °C with a preoxidized catalyst did not desorb to produce methanol. Extraction at room temperature, using a wet solvent, enabled the detection of methanol.<sup>16</sup> Our goal was to produce s methanol without having to perform the solvent extraction step, and such that methanol can be detected at the end of the reactor.

Cu–MOR was synthesized by ion exchange (S1 and S2, ESI†). It was calcined in O<sub>2</sub> at 450 °C and then reacted with methane at 200 °C. Fig. 1 shows the UV-Vis spectra collected of Cu–MOR after calcination and after interaction with methane. The formation of an absorption band at 22 700 cm<sup>-1</sup> after calcination and the disappearance of this band after reaction with methane were observed. This suggests that the synthesized Cu–MOR stabilized the dicopper active site previously reported to activate methane.<sup>11</sup>

To obtain complementary information about the structure of Cu species, Cu K edge XAS measurements were performed at the SuperXAS beamline of the Swiss Light Source, Villigen, Switzerland. The X-ray absorption near edge structure (XANES) region probes the empty p density of states, and hence carries the chemical fingerprints of oxidation state, coordination geometry and ligand electronegativity. Fig. 2 shows the XANES spectra of Cu–MOR after activation in oxygen and reaction with methane. The presence of a weak

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 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available. See DOI: 10.1039/c1cc15840f



Fig. 1 Room temperature UV-Vis spectra of Cu–MOR taken after calcination in  $O_2$  at 450 °C (—) and subsequent CH<sub>4</sub> interaction at 200 °C (---).



Fig. 2 Cu K edge XANES spectra of Cu–MOR taken of the as-prepared catalyst in He at room temperature (---), during calcination in  $O_2$  at 350 °C (---), and during CH<sub>4</sub> interaction at 200 °C (--).

pre-edge feature at 8977.5 eV and high intensity of the rising edge feature at 8987 eV mark the  $Cu^{2+}$  character of the Cu sites after calcination.<sup>17</sup> Interaction with methane formed a feature at 8983 eV, which is attributed to cuprous ions.<sup>17</sup> The accompanying feature at 8986 eV has been assigned to the presence of a 4-coordinate  $Cu^+$  or a very covalent  $Cu^{2+}$  complex.<sup>17</sup> Given the overall shape of the spectrum, reduction of part of the Cu sites took place. These XAS data indicate that a large fraction of Cu changes structure during the reaction steps, which includes the proposed redox activity of the copper sites during methane conversion.<sup>15</sup>

The amount of methanol that could be extracted from our Cu-exchanged MOR, determined by taking out the material after methane interaction and stirring in water at room temperature with subsequent gas chromatographic (GC) analysis, was 13 µmol MeOH per g Cu–MOR. This is comparable to the previously reported value of 11 µmol  $g^{-1}$  using a 1 : 1 water/ acetonitrile extraction medium,<sup>10</sup> and in agreement with the changing carbon content in the sample (see S5, ESI†).

An indirect method to quantify the amount of reacted methane is to heat the catalyst bed in inert gas and detect



Fig. 3 Mass spectrometer-detected signal of m/z = 44 attributed to CO<sub>2</sub> during heating in He at 5 °C min<sup>-1</sup> of Cu–MOR directly after CH<sub>4</sub> interaction at 200 °C.

the resulting  $CO_2$  by mass spectrometry. The  $CO_2$  mass spectrometer trace after methane interaction at 200 °C and heating in helium (Fig. 3) indicated a broad desorption profile of m/z = 44, which is attributed to CO<sub>2</sub>, in agreement with earlier findings.<sup>10</sup> On the other hand, if after methane interaction and without changing temperature, a wet stream of helium was allowed to flow through the catalyst material, methanol was observed in the gas phase as shown by the mass spectrometer data (Fig. 4). The m/z = 31 signal, which is attributed to methanol, showed a sharp increase with the onset of the m/z = 18 signal, which is attributed to water. By leading the reactor effluent through a cold trap and using GC detection, methanol was observed. Subsequent heating in helium after methanol had been desorbed did not show CO<sub>2</sub> desorption but merely residual water (Fig. 4). This means that the intermediate was removed and the only detected species in the gas phase was methanol. S6 (ESI<sup>+</sup>) illustrates that methanol was obtained in a second reaction cycle in equal amounts. This illustrates the ability of Cu-MOR to be regenerated and enables collecting methanol in a batch-wise manner from a single reactor.



**Fig. 4** Mass spectrometer-detected signals of H<sub>2</sub>O (m/z = 18), CO<sub>2</sub> (m/z = 44) and MeOH (m/z = 31) during the treatment of wet He at 200 °C after methane interaction, and the subsequent heating in dry He at 5 °C min<sup>-1</sup>.

The Cu-MOR catalyst both activates methane and subsequently strongly stabilizes the formed intermediate. We illustrate a means to react this intermediate with water, which resulted in methanol desorption. The inability to desorb the intermediate through heating in inert gas, instead yielding CO<sub>2</sub>, means that the intermediate is strongly bound and can react with oxygen to form  $CO_2$ . We propose that the role of steam is either the reaction of the intermediate to methanol or the displacement of methanol by competitive adsorption. It has been previously proposed that the solvent used during extraction not only simply dissolves the product formed on Cu-ZSM-5 but also provides protons to the reaction intermediate, most likely a methoxy species on the catalyst surface.<sup>16</sup> Polar and protic solvents such as ethanol and water/acetonitrile yielded higher amounts of methanol than hexane and acetonitrile during extraction at room temperature. On Fe-ZSM-5, extraction with dry solvents such as acetonitrile and tetrahydrofuran vielded virtually no methanol while the addition of increasing amounts of water until 10 vol% correspondingly increased the yield of extracted methanol.<sup>7</sup> Methanol was proposed to form due to the hydrolysis of methoxy groups.<sup>7,18</sup> DFT calculations showed that this hydrolysis is relatively facile from an energy perspective.<sup>19</sup> Another possibility is that the product is already present as surface-adsorbed methanol held by hydrogen bonds to Cu<sup>20</sup> or to the zeolite lattice oxygens wherein the introduction of water distorts the H-bonds,<sup>21</sup> and may facilitate desorption. Either way, we demonstrated a practical feasibility of water-assisted desorption of methanol on-stream that could close a reaction cycle. After methanol desorption, successive steps of switching to dry inert gas and heating in oxygen to 450 °C apparently removed excess water and provided for active oxygenated sites, respectively, for the next cycle of methane to methanol conversion. Thermal treatment has been reported to induce dehydration and autoreduction of Cu sites,<sup>22</sup> a requisite for activating molecular  $O_2$ .<sup>15</sup> The cycling experiment (S6, ESI<sup> $\dagger$ </sup>) showed the capability of regenerating Cu-MOR for converting methane to methanol in a cyclic batch-wise operation.

In summary, we have shown a multi-step process to produce methanol from methane on a preoxidized Cu–MOR catalyst *via* activation and subsequent hydration. This opens the possibility of operating the system in a catalytic cycle.

The authors thank Dr Frank Krumeich for the TEM measurements, Silvia Koechli for ICP, Peter Fleckenstein for the trapping and quantification work. Beamtime support of

Christian Koenig, David Stibal, Marco Servalli, Stephan Rummelts, and Chen Lin is appreciated.

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