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Article

Copper-Modified Zeolites and Silica for Conversion of Methane to Methanol

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Abstract: Powder materials containing copper ions supported on ZSM-5 (Cu-Zeolite Socony Mobil-5) and SSZ-13 (Cu-Standard Oil synthesised zeolite-13), and predominantly CuO nanoparticles on amorphous SiO$_2$ were synthesised, characterised, wash-coated onto ceramic monoliths and, for the first time, compared as catalysts for direct conversion of methane to methanol (DCMM) at ambient pressure (1 atm) using O$_2$, N$_2$O and NO as oxidants. Methanol production was monitored and quantified using Fourier transform infrared spectroscopy. Methanol is formed over all monolith samples, though the formation is considerably higher for the copper-exchanged zeolites. Hence, copper ions are the main active sites for DCMM. The minor amount of methanol produced over the Cu/SiO$_2$ sample, however, suggests that zeolites are not the sole substrate that can host those active copper sites but also silica. Further, we present the first ambient pressure in situ infrared spectroscopic measurements revealing the formation and consumption of surface methoxy species, which are considered to be key intermediates in the DCMM reaction.

Keywords: methane partial oxidation; DCMM; supported copper ions; methoxy reaction intermediate species; in situ infrared spectroscopy; Cu-ZSM-5; Cu-SSZ-13; Cu/SiO$_2$

1. Introduction

Methane is the main component in natural gas, which attracts much attention as an abundant hydrocarbon source. In some regions, methane from renewable sources, biomethane or biogas, is becoming increasingly available as well. Renewable methane is beneficial as a green drop-in fuel or chemical feedstock that can increase industrial sustainability. To make use of methane in practice, however, it is often beneficial to convert it to a liquid compound as to increase the energy density, and facilitate distribution and storage. One strategy is to make methanol through partial oxidation of methane. Methanol is one of the industrial platform chemicals that also has the advantage of being biodegradable [1]. Present industrial methanol production from methane is an energy intensive process carried out in two steps: partial oxidation of methane to syngas (H$_2$ and CO) at elevated temperature followed by catalytic conversion of syngas to methanol at high pressure. The process infrastructure is costly and therefore direct conversion of methane to methanol (DCMM), preferably at low temperature, is an attractive alternative with lower energy loads and potentially cheaper installation costs. This solution, however, faces great challenges as both oxygen and methane are difficult to activate for catalytic partial oxidation, whereas methanol, once formed, may easily undergo further unwanted reactions that ruin the selectivity.
Methane monooxygenases (MMOs) are naturally occurring enzymes that have the ability to selectively oxidise methane to methanol under ambient conditions [2]. The active sites of MMOs are di-iron [3] or di-copper centres [4] in a peptide ligand environment. Inspired by the structure and chemical functionality of MMOs, copper exchanged zeolites are considered to be inorganic analogues to the MMOs with respect to functionality of the copper sites [5–7]. To produce methanol over copper zeolites, however, a quasi-catalytic reaction sequence is commonly employed. In this approach, an oxidative activation of the copper zeolite at high temperature is required before methane can be oxidised at a lower temperature. Subsequently, methanol is released from the catalyst upon extraction using water, ethanol or other solvents. Although this activation-reaction-extraction sequence can be avoided under some certain conditions [8,9], the catalytic activity requires to be significantly improved in order to be industrially relevant for DCMM.

With the aim to design more efficient catalysts based on copper zeolites, much efforts have been put into identifying the active sites for this reaction both experimentally [5–7,10–13] and theoretically [12–16]. Early studies suggest that the so-called α-oxygen in iron complexes (analogue to the di-iron centres in the α subunit of MMO [17]) is the key to methane activation [18]. Similarly, copper dimers have been proposed to be the necessary sites for hosting the reactive oxygens for methane activation [7,11]. Later studies, however, indicate that different types of copper species, i.e., copper monomers [16], copper dimers [6,10,12], copper trimers [13] or small copper clusters [19] in zeolites, can catalyse the partial oxidation of methane to methanol. The variety of active copper species should in principle bring increased flexibility to the catalyst design as an advantage. It is, however, not clear if the requirement for active copper sites can be generalised and applied more broadly for catalyst synthesis, i.e., zeolite-free systems. Therefore, it is of great interest to comparatively investigate materials containing different types of copper species. Moreover, unlike many other metal-zeolite reaction systems, no reaction intermediates, presumably such as surface-bound methyl or methoxy groups [20], have been directly observed for copper-modified small-pore zeolites under DCMM reaction conditions.

In the present work, we investigate materials containing copper ions supported on ZSM-5 (Cu-Zeolite Socony Mobil-5 [21]) and SSZ-13 (Cu-Standard Oil synthesised zeolite-13 [22]), as well as predominantly CuO nanoparticles on amorphous SiO$_2$, for direct oxidation of methane to methanol and use in situ infrared spectroscopy to monitor formation/consumption of surface species that play a role in the methanol formation. Methanol production over Cu-zeolites and Cu/SiO$_2$ is detected over coated monolith samples for the first time. We report that DCMM occurs over copper ions and that these copper species exist on silica but are more abundant in zeolite structures. We present—under ambient pressure—the formation/consumption of mechanistically important methoxy species over Cu-ZSM-5, Cu-SSZ-13 and Cu/SiO$_2$ during DCMM.

2. Results and Discussion

2.1. Methanol Production

Figure 1 presents the amount of produced methanol over the Cu-ZSM-5, Cu-SSZ-13 and Cu/SiO$_2$ sample. As can be seen in the figure, methanol is produced over all samples during the extraction step. Methanol production, however, for Cu-ZSM-5 (regardless of oxidant) and Cu-SSZ-13 (O$_2$ or N$_2$O) is clearly higher than that for Cu/SiO$_2$ or H-ZSM-5 (not shown), which is negligible. Interestingly, the use of different oxidants for the activation step results in similar amounts of formed methanol during extraction for the Cu-ZSM-5 sample whereas for the Cu-SSZ-13 sample, the methanol formation is clearly dependent on the oxidant. For Cu-ZSM-5, DCMM reaction has been correlated (only) with the mono(µ-oxo)dicupric site as characterised by the absorption band at 22,700 cm$^{-1}$ in UV–vis spectrum [6,10]. Thus, it seems from the present results that this site can be activated by different oxidants. On the contrary, multiple absorption features in the UV–vis [9,23] and Raman [24,25] spectra have been reported for O$_2$/N$_2$O activated Cu-SSZ-13, which is indicative of the presence of various
Cu species active for DCMM. Moreover, the observed UV–vis bands after O\textsubscript{2} and N\textsubscript{2}O activation \cite{9} differs, suggesting that each oxidant activates distinct Cu species. This may be the reason for the different amounts of formed methanol observed here when using O\textsubscript{2} or N\textsubscript{2}O.

![Figure 1](image)

**Figure 1.** Methanol production over Cu-ZSM-5, Cu-SSZ-13 and Cu/SiO\textsubscript{2} at 1 atm using O\textsubscript{2}, N\textsubscript{2}O or NO as oxidants.

2.2. Catalyst Characterisation

In Figure 2a, the XANES spectra of Cu-ZSM-5, Cu-SSZ-13 and Cu foil at the Cu K-edge are shown. The spectra of Cu-ZSM-5 and Cu-SSZ-13 overlap with each other. No obvious pre-edge peak for Cu(I) (well defined peak at 8982–8984 eV \cite{26,27}) or pre-edge shoulder for metallic Cu (Figure 2a, black spectrum) can be observed. Both spectra present a sharp absorption at about 8995–8998 eV. This is due to the 1s-to-4p electronic transition of Cu(II) species \cite{26}, indicating that the dominating oxidation state of the copper species is Cu(II) in both copper zeolite samples. The featureless pre-edge, however, signifies the absence of CuO species (weak absorption at about 8976–8979 eV and a shoulder at about 8985–8988 eV \cite{27}), indicating that the Cu-ZSM-5 and Cu-SSZ-13 samples do not contain detectable amounts of large CuO domains. The spectrum of the Cu foil presents an evident pre-edge feature around 8983 eV with resonance features above the edge that are clearly different from the spectra of Cu-ZSM-5 and Cu-SSZ-13. Figure 2b presents the Fourier transforms of the Cu K-edge EXAFS spectra of the Cu-ZSM-5 and the Cu-SSZ-13 sample as well as that of the reference compounds: Cu, Cu\textsubscript{2}O and CuO. Both Cu-ZSM-5 and Cu-SSZ-13 sample exhibit an intensive peak at around 1.5 Å, associated with the neighbouring O atoms. The absence of peaks at the range of 2.5–3 Å, suggesting the lack of neighbouring Cu atoms, indicating that isolated Cu ions are the dominant Cu species in these samples. Moreover, the calculated Cu/Al ratio of the Cu-ZSM-5 and Cu-SSZ-13 sample is 0.38 and 0.14 respectively. At such ion-exchange levels, Cu dispersion is 100% in ZSM-5 \cite{28} and the Cu species in SSZ-13 are dominantly monomers \cite{29}.

In Figure 2c, the XRD patterns of the Cu-ZSM-5, Cu-SSZ-13 and Cu/SiO\textsubscript{2} samples are shown. The XRD patterns of the Cu-ZSM-5 and Cu-SSZ-13 samples exhibit only characteristic peaks of the respective zeolite structure \cite{30} (the XRD patterns of the parent zeolites are presented in the Supplementary Materials Figure S1), while no reflections of crystalline Cu species are visible. This suggests that the Cu species in these samples are smaller than 2–3 nm. Additional CO and NO adsorption experiments shown in the Supplementary Materials Figure S2 confirm the presence of cationic copper species in both the Cu-ZSM-5 and the Cu-SSZ-13 sample. For the diffractogram of the Cu/SiO\textsubscript{2} sample, reflections characteristic of crystalline CuO are evident, indicating the existence of CuO particles. The mean crystallite size of CuO is 28.3 nm calculated with Scherrer’s equation \cite{31} (shape factor 0.89) using the full width at half-maximum (FWHM) of the characteristic peak of CuO (111) (2θ = 38.92°). The CO and NO adsorption spectra shown in Figure S2 (Supplementary Materials), however, indicate the presence of cationic copper species in small amount on the Cu/SiO\textsubscript{2} sample.
The results from XRD and CO/NO adsorption experiments picture the Cu/SiO$_2$ sample dominated with CuO nanoparticles accompanied by small amount of cationic Cu species.

Figure 2. (a) XANES spectra of the Cu-ZSM-5 (red), Cu-SSZ-13 (blue) and Cu foil (black), as reference; (b) magnitude of Fourier transformed EXAFS spectra (k-weight = 2) of Cu-ZSM-5 (red), Cu-SSZ-13 (blue), Cu foil (solid black line), Cu$_2$O (dashed black line, the Farrel Lytle database #cu2o.514) [32] and CuO (dotted black line, the Farrel Lytle database #cuoxop.027) [32]; (c) XRD patterns of the Cu-ZSM-5, Cu-SSZ-13 and Cu/SiO$_2$ samples; the characteristic reflections of the CuO crystalline structure are denoted with asterisks (*); the coloured bars at the bottom representing the reflections of Cu (green, SpringerMaterials sd_1928261), Cu$_2$O (red, SpringerMaterials sd_1928262) and CuO (black, the American Minerologist Crystal Structure Database #0018812).

2.3. In Situ IR Study of Methane Oxidation and Water Extraction

Figure 3 presents the IR spectra during methane oxidation (solid lines) and water extraction (dashed lines) for all three samples. The presented spectra are focused on the C-H and C=O stretching vibration regions. Beside the gas phase methane (3017 cm$^{-1}$) [33], C-H stretching bands originated from adsorbed species are visible between 2800 and 3050 cm$^{-1}$ for all three samples after methane oxidation. For the Cu-ZSM-5 sample, absorption bands of methoxy groups adsorbed on Brønsted acid sites (2987 cm$^{-1}$) [34–37], formate on Cu (2906 cm$^{-1}$) [37] and CO on Cu (2157 cm$^{-1}$) [38] appear after 2 h exposure to methane. The evolution of these bands indicates that methane is oxidised and the oxidation products are stable on the sample surface. The low intensity of the bands, however, suggest low concentration of the adsorbed oxidised species. With longer exposure time to methane, CO accumulates on the copper species while the amount of C-H containing species remains fairly constant. Similar features at the C-H stretching vibrational region in IR spectra has been previously observed over Cu-MOR upon exposure to methane at higher pressure [39]. After exposing the Cu-SSZ-13 and Cu/SiO$_2$ samples to methane for 2 h, a peak at 2968 cm$^{-1}$ arises for both samples while the peak at 2911 cm$^{-1}$ is visible only for Cu-SSZ-13. Though it is expected that these bands are associated with adsorbed species originated from methane, the exact assignments are not apparent. Bands at wavenumbers close to 2968 cm$^{-1}$ ($\nu_3$ mode) and 2911 cm$^{-1}$ ($\nu_1$ mode) have been observed during methane adsorption on silica [40,41] and zeolites [41–43] due to dissociative adsorption of methane. Moreover, methoxy groups adsorbed on Brønsted acid sites (2968 cm$^{-1}$), extra framework Al (2978 cm$^{-1}$) and Si (2957 cm$^{-1}$) may contribute to the band at 2968 cm$^{-1}$ for the Cu-SSZ-13 sample. It is clear that methane can adsorb dissociatively on the Cu-SSZ-13 and Cu/SiO$_2$ samples at 250 °C.
The absence of features in the C=O stretching vibration region, however, suggests that the ability of these samples to catalyse further oxidation of methane at 250 °C is negligible. Interestingly, CO forms during methane oxidation over the Cu sites in the Cu-ZSM-5 sample but not over the Cu-SSZ-13 sample. This can be due to the higher concentration of copper in the Cu-ZSM-5 sample, which is more than twice the amount of copper in the Cu-SSZ-13 sample. Moreover, a previous study has shown that Cu-SSZ-13 exhibits much higher methanol selectivity and lower CO or CO$_2$ selectivity during catalytic methane oxidation compared to Cu-ZSM-5 with similar Cu loading [9]. It has been discovered that zeolites with the majority of the adsorption sites in 8-membered ring (MR) rather than in 6, 10 or 12 MRs (e.g., SSZ-13) can host higher concentrations of Cu species active for methanol formation [24,44]. Therefore, the lack of CO formation in the Cu-SSZ-13 sample can be a combination of low Cu loading that results in copper sites predominantly favouring formation of methanol rather than CO. Furthermore, the Cu species in Cu-SSZ-13 has been shown to be considerably more stable than Cu-ZSM-5 for which copper species may agglomerate to larger Cu-oxo clusters that promote CO formation [45]. After water extraction (dashed lines in Figure 3), though most bands remain for the Cu-ZSM-5 and Cu-SSZ-13 samples, the bands related to methoxy on Brønsted acid sites (2978 cm$^{-1}$), formate (2906 cm$^{-1}$) and CO (2157 cm$^{-1}$) decrease in intensity for Cu-ZSM-5, while the intensity of band at 2968 cm$^{-1}$ decreases for Cu-SSZ-13. It is anticipated that the methoxy species adsorbed on the Cu-ZSM-5 and Cu-SSZ-13 samples react with water and desorb from the sample surface as methanol, leaving other more strongly adsorbed species, presumably methyl. For the Cu/SiO$_2$ sample, however, no obvious decrease in intensity is observed for the band at 2968 cm$^{-1}$, which suggest that a trivial amount of methanol is produced during water extraction. These speculations are further supported by the activity studies discussed above.

![Image of IR spectra](image_url)

**Figure 3.** IR spectra of the Cu-ZSM-5, Cu-SSZ-13 and Cu/SiO$_2$ sample exposed to methane (solid line marked with exposure time) and after water extraction for 10 min (dashed line) at 250 °C. The IR measurements were carried out at 1 atm.

### 2.4. Concluding Discussion

In summary, X-ray-based characterisation and infrared analysis of CO/NO adsorption show that the prepared Cu-ZSM-5 and Cu-SSZ-13 samples contain cationic copper species. On the contrary, the Cu/SiO$_2$ sample is dominated by CuO particle sites and silica sites with the presence of cationic
copper species in small amount. Methanol production is, to our knowledge for the first time, detected over the Cu-ZSM-5, Cu-SSZ-13 and Cu/SiO$_2$ monolith catalysts. The choice of sample form is different from that of the previous literatures which were conducted over powder or pellet samples. The monolith samples allow sufficient flow without detrimental pressure drop as to achieve reasonable time resolution in the FTIR gas phase analysis. The in situ infrared measurements reveal the formation of surface bound methoxy species as a likely important reaction intermediate during methane oxidation as well as the consumption of these methoxy species during water extraction, which is considerably more pronounced for the zeolitic systems. Hence, the higher methanol formation from Cu-ZSM-5 and Cu-SSZ-13 compared with Cu/SiO$_2$ can be attributed to the isolated Cu ions in consistence with previous suggestions [5,10,11,14–16,46]. Notably, here, the minor amount of formed methanol (3.5–6.4 µmol/g Cu) over the Cu/SiO$_2$ sample regardless of oxidant is an interesting observation. Although the Cu/SiO$_2$ sample contains CuO particles as observed by XRD, one can not neglect the presence of copper ions possibly in the form of monomers, dimers or small ensembles. These ions are likely responsible for the formation of methanol in this case. The reason for the low amount of formed methanol may in this case be due to the low abundance of ionic copper species, or that the ionic copper species co-exist with larger CuO particles, which promote total oxidation such that the selectivity towards methanol becomes low. This speculation in turn suggests that the zeolite structure is not the only type of substrate that can host copper species active for DCMM as generally discussed hitherto. One may thus envisage that the choice of support may be more flexible than previously discussed such that catalyst design should primarily target the creation of small ensembles of copper ions, however, not necessarily contained in zeolites. In fact, low methanol production (less than 1 µmol/g Cu) has been previously observed over alumina containing Cu/silica system [7]. A very recent study also described the formation of active Cu species when proper conditions were used [47]. This is encouraging as for example ZSM-5 is a dehydration catalyst that is used to convert methanol to dimethyl ether (DME) in the well known methanol to gasoline (MTG) process [48] and therefore not the ideal substrate when striving for high methanol production. In fact, when much methanol is adsorbed, DME formation is evident already at 175 °C [37], which is in the target temperature range suitable for DCMM. At present, however, the low methanol formation presented here and elsewhere allows for using ZSM-5 without any particular issues concerning DME formation.

3. Experimental Section

3.1. Catalyst Preparation

For this study, Cu-zeolite samples, Cu-ZSM-5 and Cu-SSZ-13, were prepared using aqueous ion-exchange [6]. The ion-exchange was carried out by mixing aqueous solutions of Cu(NO$_3$)$_2$ (0.1 M, 100 mL/g zeolite) with H-ZSM-5 (Si/Al = 13.5, Akzo Nobel, Amsterdam, The Netherlands) or H-SSZ-13 (Si/Al = 10, synthesised according to the method described by Shishkin et al. [49,50]) at room temperature for 24 h. The pH of the solution was kept at around 4.5 by addition of ammonia solution when necessary. After ion-exchange the slurry was filtered and the solid fraction was washed with Milli-Q water (18 MΩ·cm) and then dried at 120 °C in air overnight. Inductively coupled plasma-sector field mass spectrometry (ICP-SFMS) gives a Cu loading of 2.8 wt.% for the Cu-ZSM-5 sample and 1.3 wt.% for the Cu-SSZ-13 sample. The Cu/SiO$_2$ sample was prepared using incipient wetness impregnation where an aqueous solution of Cu(NO$_3$)$_2$·5H$_2$O (Sigma-Aldrich, St. Louis, MO, USA, ACS reagent, 0.29 M, 1.66 mL/g silica) was slowly added to the silica support (Akzo Nobel, Kromasil, 200 Å, 5 µm). The mixture was then instantly frozen by liquid nitrogen and freeze-dried over night before calcined in air at 350 °C for 3 h. The Cu loading was 3.0 wt.% for the Cu/SiO$_2$ sample. Part of the Cu-ZSM-5, Cu-SSZ-13 and Cu/SiO$_2$ powder samples were used for wash-coating cordierite monolith substrates (Corning, New York, NY, USA, 400 cpsi, L = 15 mm, Ø = 13 mm). For each catalyst sample, a slurry was prepared by mixing the powder catalyst sample with a binder (Sasol, Sandton, South Africa, Disperal P2) at a weight ratio of 80:20 in Milli-Q water. The calcined monolith substrates
were coated with thin layers of the wash-coat until the added solid material on each substrate reached 0.2 g. The monolith samples were finally calcined at 600 °C for 3 h.

3.2. Activity Test

Catalytic activity tests of the prepared monolith samples were carried out using a chemical flow reactor system equipped with an FTIR analyser (MKS 2030 FTIR spectrometer) for continuous analysis of the effluent stream. The flow reactor consists of a horizontal quartz tube surrounded with an insulated metal coil for resistive heating. The catalyst temperature is measured by a type K thermocouple and controlled with a PID regulator (Eurotherm, Worthing, UK). The feed gas system consists of separate mass flow controllers (Bronkhorst Hi-Tech, Ruurlo, Netherlands, Low-∆P-Flow) for the different gases and a water vapour generator that catalytically produces ultra-pure water vapour from high-purity H₂ and O₂ gases [51]. The activity test for direct conversion of methane to methanol was carried out through an activation-reaction-extraction sequential approach at 1 atm. In this approach, the samples were first activated at 550 °C with the oxidant (20% vol O₂, 300 vol ppm N₂O or 0.1% vol NO) for one hour before exposure to 2% vol CH₄ at 150 °C for one hour. The products were then extracted with water vapour (4% vol for Cu-SSZ-13 and Cu/SiO₂, and 8% vol for Cu-ZSM-5) at 150 °C. The methanol production was acquired by applying a peak area integration of the methanol concentration as measured by the gas phase FTIR analyser during the water extraction step. During this phase methanol was the main product together with a minor amount of CO₂.

3.3. Characterisation

To correlate the methanol formation to relevant materials properties, X-ray based characterisation was carried out. The local environment of copper was characterised by X-ray absorption spectroscopy (XAS) at beamline I811 at the MAX IV Laboratory, Lund, Sweden. Spectra were recorded at the Cu K-edge (8979 eV) in fluorescence mode. The photon energy was calibrated using a Cu foil measured simultaneously with the sample. The X-ray absorption near edge structure (XANES) spectra were processed using the Athena software [52].

The crystal phases of the samples were determined by X-ray diffraction (XRD) using a Bruker XRD D8 Advance instrument with monochromatic CuKα₁ radiation scanning 2θ from 20 to 60° (step size 0.029°, dwell time 1 s).

The in situ infrared spectroscopic measurements were carried out in diffuse reflectance mode using a VERTEX 70 spectrometer (Bruker) equipped with a liquid nitrogen cooled mercury cadmium telluride detector with the band width 600–12,000 cm⁻¹, a Praying Mantis™ diffuse reflectance accessory and a high-temperature stainless steel reaction chamber (Harrick Scientific Products Inc., New York, NY, USA). All spectra were measured between 900 and 4000 cm⁻¹ with a spectral resolution of 1 cm⁻¹. The instrumental aperture was 3 mm wide with a four times sensitivity gain. About 85 µL sample was loaded into the reaction chamber. Methane oxidation experiments were carried out for all three samples, i.e., Cu-ZSM-5, Cu-SSZ-13 and Cu/SiO₂, at 1 atm. After pre-treatment with 500 vol ppm N₂O at 550 °C for one hour, 2% vol of methane was fed to the sample at 250 °C. Finally, the extraction step was carried out with 0.25 g/h water in Ar at 250 °C. All spectra were recorded in pure Ar. The backgrounds were taken in Ar at 250 °C for each sample after the sample pre-treatment. Baseline subtraction is carried out for all spectra using the Igor Pro software. For the IR study, the set reaction temperature is 250 °C instead of 150 °C, which is used in the flow reactor. The reason for using this set temperature is that the cell design causes temperature gradients in the sample bed, such that the temperature in the volume probed by IR is considerably lower than the set temperature [53]. The set reaction temperature used in the present study results in similar temperatures for the flow-reactor experiments and the IR measurements.
4. Conclusions

For copper-based catalytic materials, the direct conversion of methane to methanol requires ionic copper sites. Such sites are abundant in copper-exchanged zeolites, i.e., Cu-ZSM-5 and Cu-SSZ-13, which show clear methanol formation, but seem to exist also in Cu/SiO$_2$, although to a minor extent reflected by the minor methanol formation. In situ infrared spectroscopic measurements reveal that on these sites, the methanol formation proceeds through the formation/consumption of surface methoxy species, which are considered to be important intermediates in the direct conversion of methane to methanol.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/8/11/545/s1. Figure S1: XRD patterns of the H-ZSM-5 (red) and H-SSZ-13 (blue) samples, Figure S2: IR spectra after (a) CO adsorption and (b) NO adsorption on the Cu-ZSM-5, the Cu-SSZ-13 and the Cu/SiO$_2$ sample, Table S1: BET surface area ($S_{BET}$), micropore volume and chemical composition of the Cu-ZSM-5, Cu-SSZ-13 and Cu/SiO$_2$ sample.

Author Contributions: X.W. carried out all experiments and is main responsible for preparing the paper; N.M.M. assisted in the XAS measurements; J.N. assisted in the XAS measurements; S.C. assisted in the set-up and operation of the XAS beam line; J.G. interpreted the XRD results; M.S. guided and discussed the experiments; P.-A.C. is principle investigator who conceived the idea and supervised the work.

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Conflicts of Interest: The authors declare no conflict of interest.

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