

# Supporting Information

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

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### BET surface area analysis of the Cu-ZSM-5, Cu-SSZ-13 and Cu/SiO<sub>2</sub> sample

The specific surface area and pore size distribution of the samples were determined by nitrogen sorption at -196 °C using a Micromeritics ASAP 2010 instrument. Prior to analysis, the sample was degassed in N<sub>2</sub> at 220 °C for 20 h. Respective surface areas were then determined according to the standard Brunauer-Emmett-Teller (BET) method using  $P/P_0 = 0.05-0.21$ . The results are presented in Table 1.

Table S1: BET surface area ( $S_{\text{BET}}$ ), micropore volume and chemical composition of the Cu-ZSM-5, Cu-SSZ-13 and Cu/SiO<sub>2</sub> sample.

Sample	Cu loading (wt %)	$S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	micropore volume (cm <sup>3</sup> g <sup>-1</sup> )
Cu-ZSM-5	2.8	327	0.118
Cu-SSZ-13	1.3	632	0.233
Cu/SiO <sub>2</sub>	3.0	186	0.010

## XRD patterns of the parent H-ZSM-5 and H-SSZ-13 samples

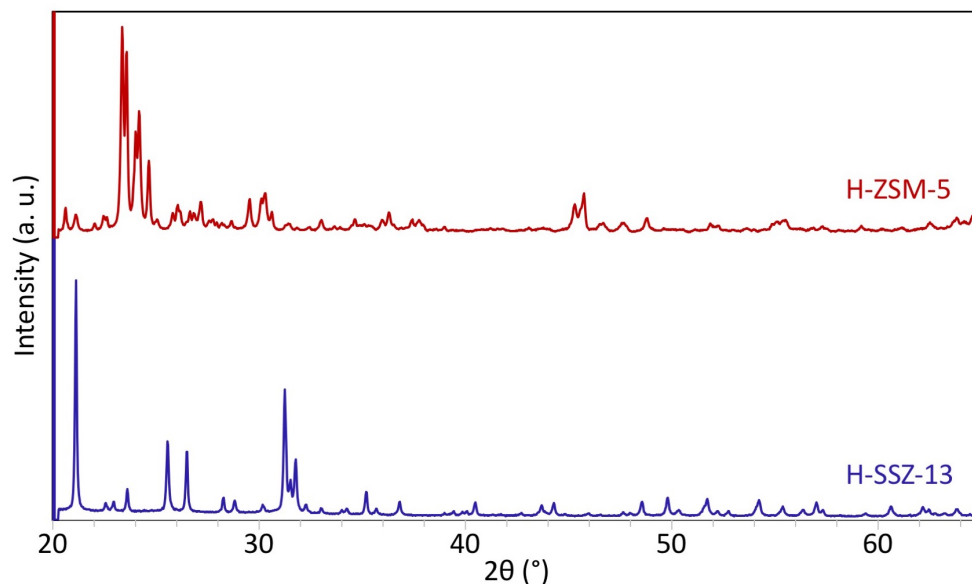


Figure S1: XRD patterns of the H-ZSM-5 (red) and H-SSZ-13 (blue) samples.

## CO and NO adsorption over the Cu-ZSM-5, Cu-SSZ-13 and Cu/SiO<sub>2</sub> sample

CO and NO adsorption experiments were carried out on all three samples, *i.e.* Cu-ZSM-5, Cu-SSZ-13 and Cu/SiO<sub>2</sub>. After pre-treatment of the samples with O<sub>2</sub> at 550 °C for one hour, 300 ppm of CO or NO was fed to the samples at 30 °C. The CO exposure time was 1 min for the Cu-ZSM-5 and the Cu/SiO<sub>2</sub> sample, 1.5 min for the Cu-SSZ-13 sample, and the NO exposure time was 2 min all the samples. The samples were flushed in Ar for 10 min before the spectra were recorded. The backgrounds were taken in Ar at 30 °C for each sample after the pre-treatment. The recorded spectra is shown in Figure S2 and the band assignments are listed in Table S2

As shown in Figure S2a, the absorption bands stemming from CO adsorbed on Cu<sup>+</sup> (2157 cm<sup>-1</sup> for the Cu-ZSM-5 and the Cu-SSZ-13 samples, 2137 cm<sup>-1</sup> for the Cu/SiO<sub>2</sub> sample) appear after CO exposure on all three samples. In Figure S2b, NO adsorbed on Cu<sup>2+</sup> (1911 cm<sup>-1</sup> for the Cu-ZSM-5 and the Cu-SSZ-13 samples, 1889 cm<sup>-1</sup> for the Cu/SiO<sub>2</sub> sample) and on Cu<sup>+</sup> (1811 cm<sup>-1</sup> for the Cu-ZSM-5 sample) are evident after NO exposure. All these

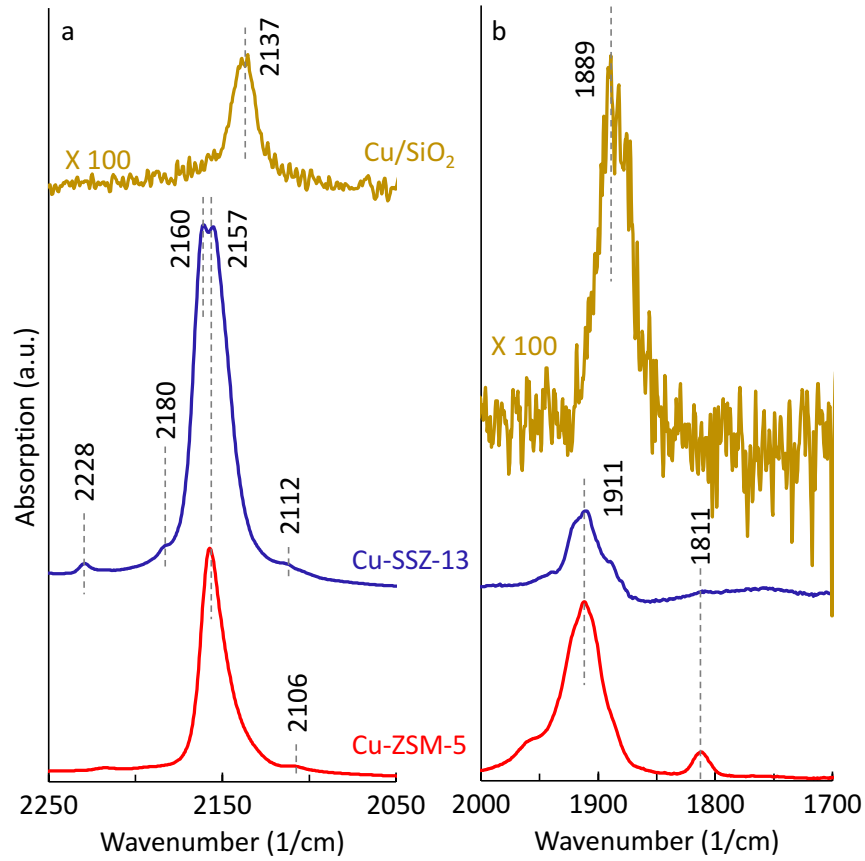


Figure S2: IR spectra after (a) CO adsorption and (b) NO adsorption on the Cu-ZSM-5, the Cu-SSZ-13 and the Cu/SiO<sub>2</sub> sample.

Table S2: Assignments of vibrational bands observed by IR spectroscopy after CO and NO adsorption for the Cu-ZSM-5, Cu-SSZ-13 and Cu/SiO<sub>2</sub> samples.

wavenumber (cm <sup>-1</sup> )	assignment	reference
<b>CO adsorption</b>		
2228	$Cu^{2+} - CO$	1
2180	$Cu^{+} - (CO)_2$	1
2160, 2157, 2137	$Cu^{+} - CO$	1-4
2112, 2106	$Cu^0 - CO$	5
<b>NO adsorption</b>		
1911, 1889	$Cu^{2+} - NO$	1,4,6
1811	$Cu^{+} - NO$	1,6

absorption bands suggest the existence of cationic Cu species. The low intensity of the absorption bands of the Cu/SiO<sub>2</sub> sample, however, indicates the presence of merely small amount of cationic Cu species in the sample.

## References

- (1) Szanyi, J.; Kwak, J. H.; Zhu, H.; Peden, C. H. F. *Phys. Chem. Chem. Phys.* **2013**, *15*, 2368–2380.
- (2) Kwak, J. H.; Varga, T.; Peden, C. H. F.; Gao, F.; Hanson, J. C.; Szanyi, J. *J. Catal.* **2014**, *314*, 83–93.
- (3) Zhang, Y.; Drake, I.; Briggs, D.; Bell, A. *J. Catal.* **2006**, *244*, 219–229.
- (4) Hadjiivanov, K.; Knozinger, H. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1132–1137.
- (5) Mrquez-Alvarez, C.; McDougall, G.; Guerrero-Ruiz, A.; Rodriguez-Ramos, I. *Appl. Surf. Sci.* **1994**, *78*, 477 – 484.
- (6) Zhang, R.; McEwen, J.-S.; Kollar, M.; Gao, F.; Wang, Y.; Szanyi, J.; Peden, C. H. F. *ACS Catal.* **2014**, *4*, 4093–4105.