Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information
Methane Adsorption and Methanol Desorption for Copper Modified Boron Silicate

Xueting Wang,[ab] Alexander Shishkin,[ab] Felix Hemmingsson,[ab] Magnus Skoglundh,[ab] Francisco Javier Martinez-Casado,[c] Lorenz Bock,[a] Alexander Idström,[a] Lars Nordstierna,[a] Hanna Härelind[ab] and Per-Anders Carlsson[ab*]

[a] *Department of Chemistry and Chemical Engineering, Chalmers University of Technology, 412 96 Gothenburg, Sweden.*

[b] *Competence Centre for Catalysis, Chalmers University of Technology, 412 96 Gothenburg, Sweden.*

[c] *MAX IV Laboratory, Lund University, 221 00 Lund, Sweden.*

[*] *per-anders.carlsson@chalmers.se*

XRD analysis of the H-SSZ-13, BS and Cu-BS samples

Figure S2 presents the XRD patterns of the H-SSZ-13 and Cu-BS samples. Both patterns exhibit characteristic reflections for the chabazite structure. No obvious reflections from Cu species can be observed from the Cu-BS sample indicating well dispersed Cu species.

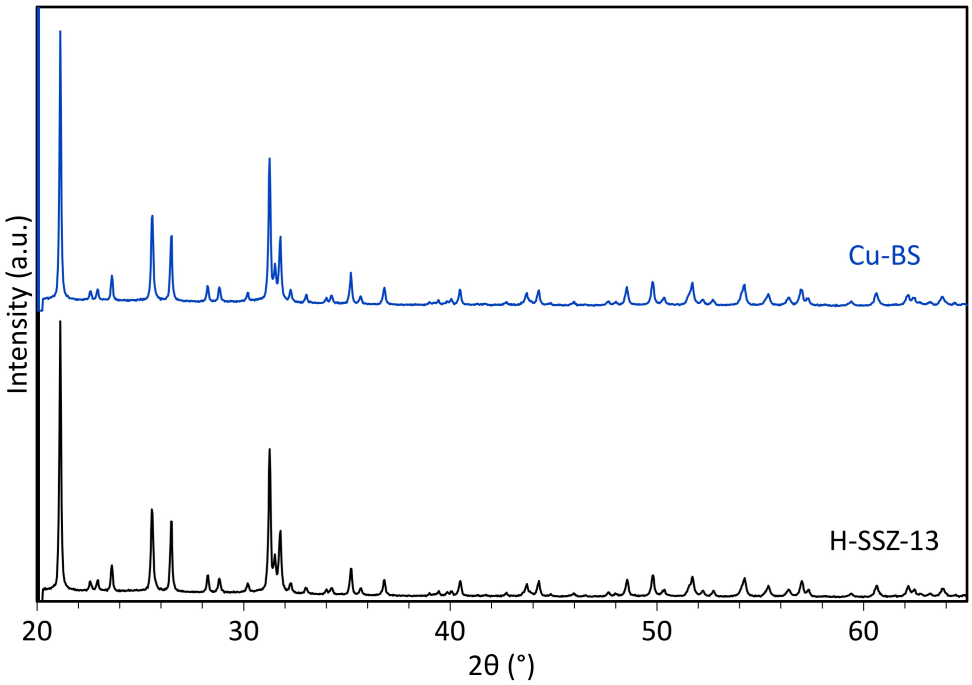

Figure S1: X-ray diffractograms for the H-SSZ-13 (black) and Cu-BS (blue) samples.

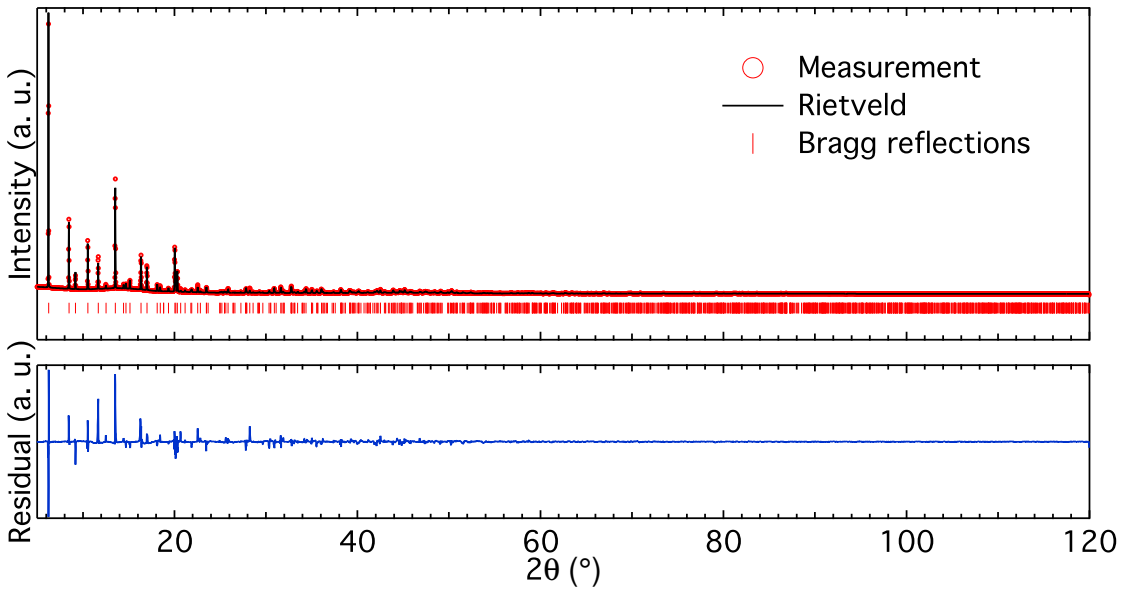

Figure S2: High-resolution X-ray diffractogram (upper panel) and Rietveld refinement (lower panel) for the BS sample.

DSC-MS measurements of the BS, Cu-BS, H-SSZ-13 and Cu-SSZ-13 samples

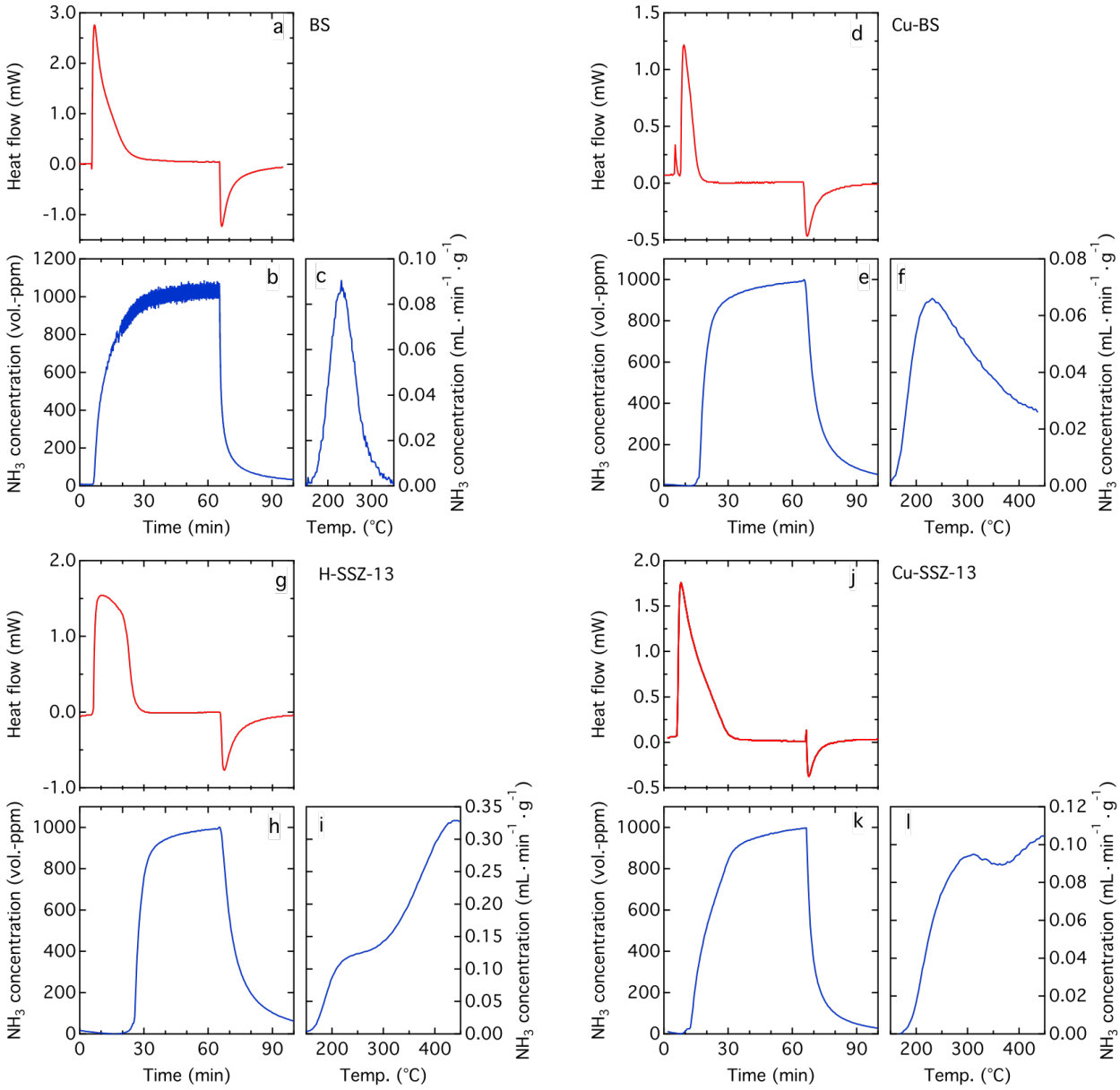

Figure S3: Thermogram (a, d, g, j) and ammonia mass spectrometer signal during NH_3 adsorption (b, e, h, k), and NH_3 desorption profile during linear heating (c, f, i, l) of the BS, Cu-BS, H-SSZ-13 and Cu-SSZ-13 sample.

Infrared analysis for CO/NO adsorption on the Cu-BS sample

CO and NO adsorption experiments were carried out on the Cu-BS sample using a VERTEX70 spectrometer (Bruker) equipped with a liquid nitrogen cooled mercury cadmium telluride detector with the band width 600-12000 cm^{-1}, a Praying Mantis^{TM} diffuse reflectance accessory and a high-temperature stainless steel reaction chamber (Harrick Scientific Products Inc.). The spectra were measured between 900 and 4000 cm^{-1} with a spectral resolution of 1 cm^{-1}. About 85 μl sample was loaded into the reaction chamber. After pre-treatment of the samples with O_2 at 550 °C for one hour, 300 ppm of CO or NO was fed to the samples at 30 °C. The spectra were taken in Ar after CO/NO adsorption for 1 min. The backgrounds were taken in Ar at 30 °C after the pre-treatment. The recorded spectra is shown in Figure S4.

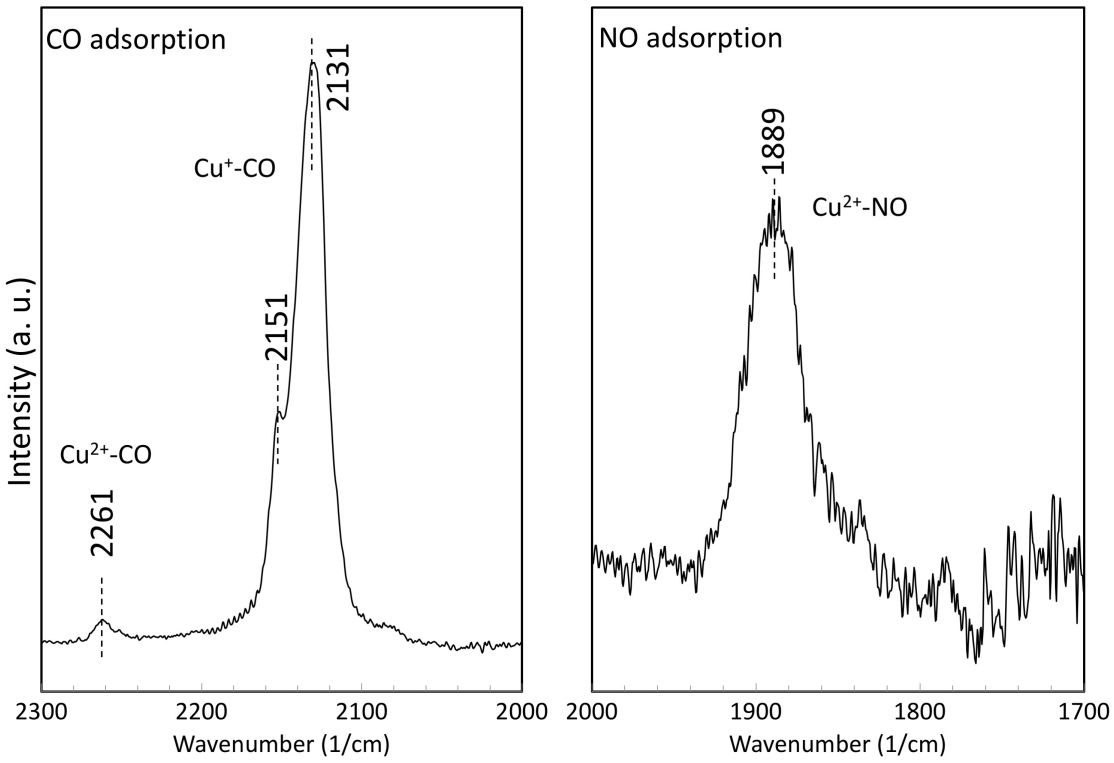

Figure S4: Infrared spectra recorded after CO adsorption (left) and NO adsorption (right) on the Cu-BS sample.

The absorption band at 2151 and 2131 cm^{-1} for the CO chemisorption spectrum (Figure S4 left panel) can be assigned to CO adsorbed on Cu^{+}.[1–3] The band at 2151 cm^{-1} is similar to that from the strong CO adsorption on Cu^{+} observed on Cu-ZSM-5,[4] while the slightly red-shifted band 2131 cm^{-1} may be originated from CO coadsorbed with OH groups[2] on Cu^{+} or CO on Cu nanoparticles.[1] The band at 2261 cm^{-1} is associated with CO adsorbed on Cu^{2+}.[5] The spectrum recorded after NO adsorption (Figure S4 right panel) exhibit one band at 1889 cm^{-1}. This band is assigned to NO adsorbed on Cu^{2+}.[5,6] The CO and NO chemisorption experiments suggest that Cu ions were successfully exchanged into the B-SSZ-13 structure.

Full infrared spectra for the methane exposure experiments

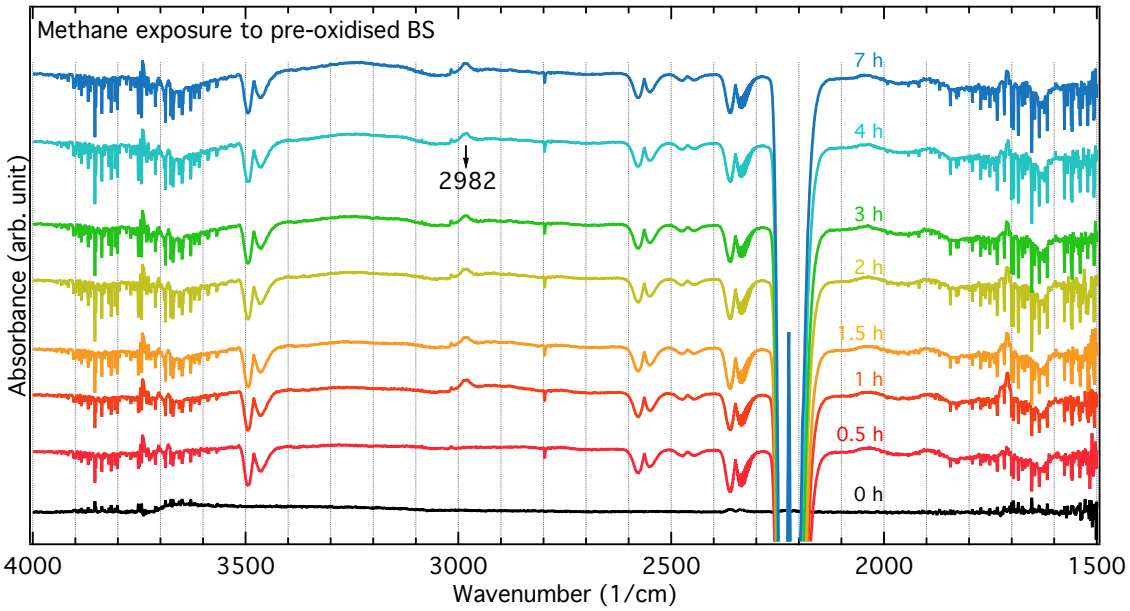

Figure S5: Infrared spectra for pre-oxidised BS exposed to methane at 250 °C during 0 to 7 h. The spectrum at 0 h was taken in presence of 500 ppm of N_2O whereas the remaining spectra were recorded in Ar.

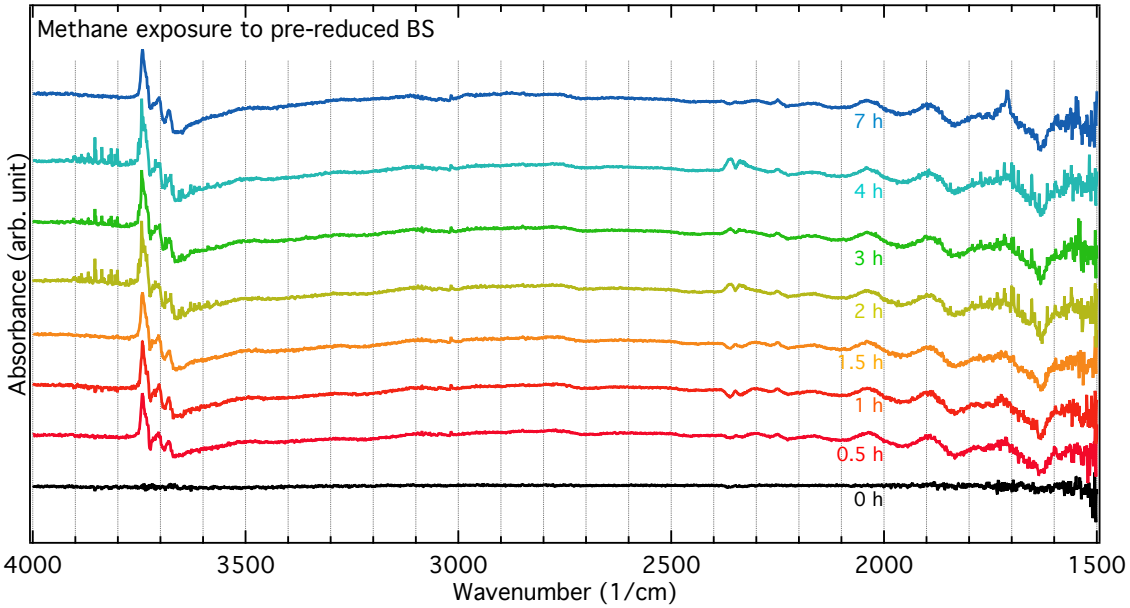

Figure S6: Infrared spectra for pre-reduced BS exposed to methane at 250 °C during 0 to 7 h. All spectra were recorded in Ar.

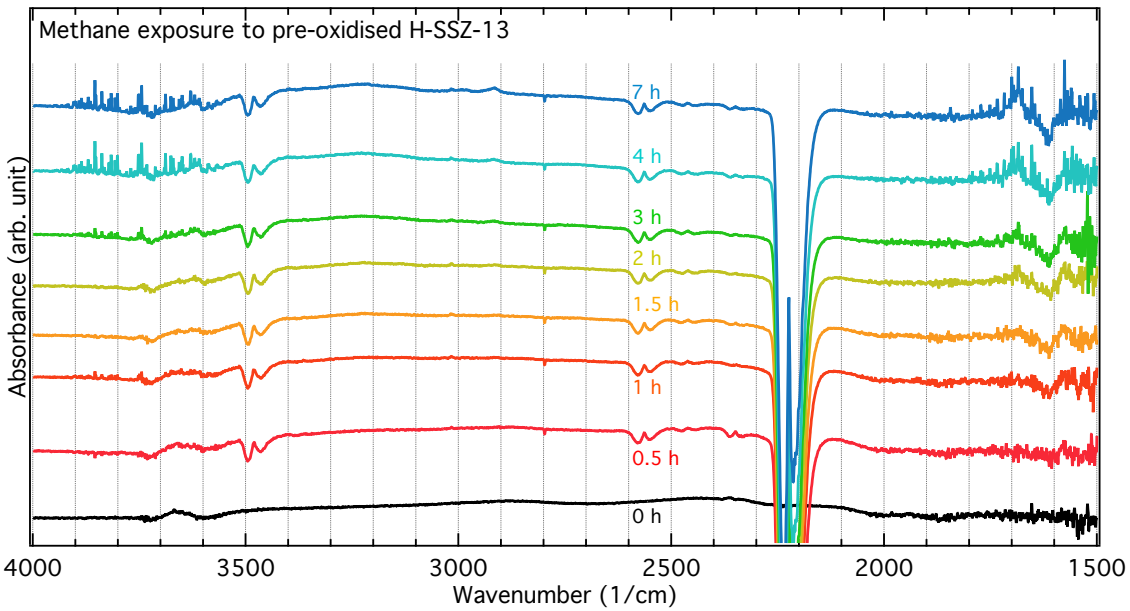

Figure S7: Infrared spectra for pre-oxidised H-SSZ-13 exposed to methane at 250 °C during 0 to 7 h. The spectrum at 0 h was taken in presence of 500 ppm of N_2O whereas the remaining spectra were recorded in Ar.

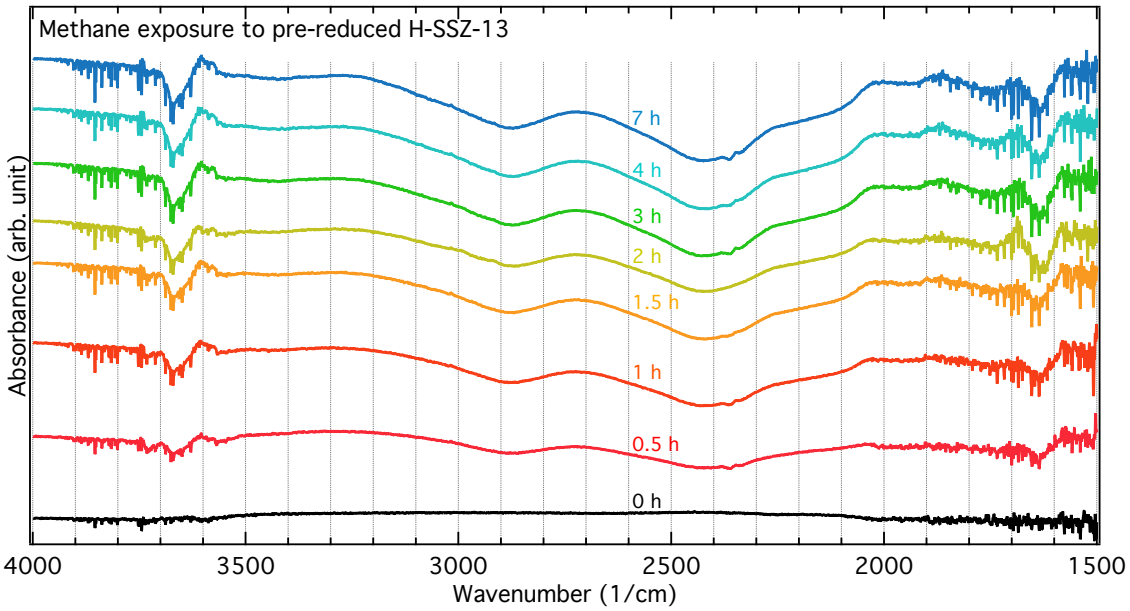

Figure S8: Infrared spectra for pre-reduced H-SSZ-13 exposed to methane at 250 °C during 0 to 7 h. All spectra were recorded in Ar.

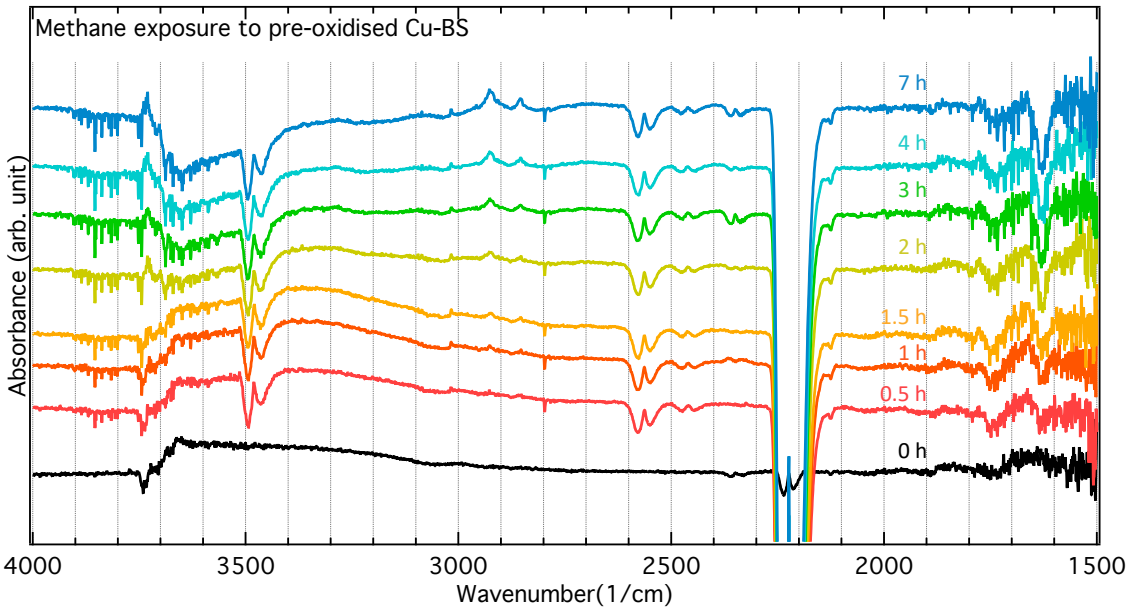

Figure S9: Infrared spectra for pre-oxidised Cu-BS exposed to methane at 250 °C during 0 to 7 h. The spectrum at 0 h was taken in presence of 500 ppm of N_2O whereas the remaining spectra were recorded in Ar.

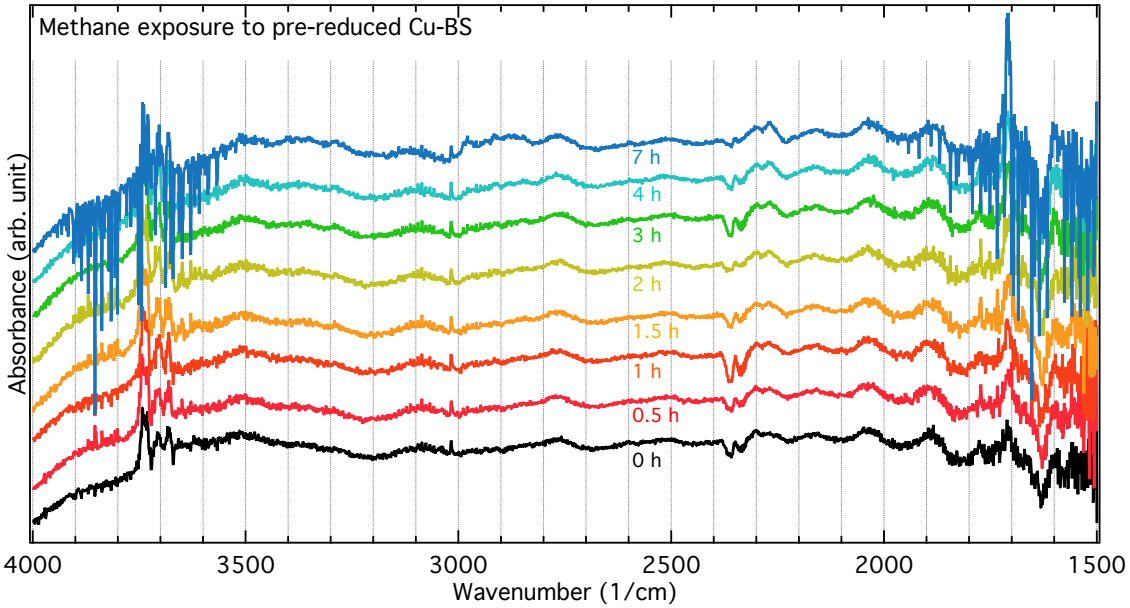

Figure S10: Infrared spectra for pre-reduced Cu-BS exposed to methane at 250 °C during 0 to 7 h. All spectra were recorded in Ar.

Full infrared spectra for the methanol desorption experiments

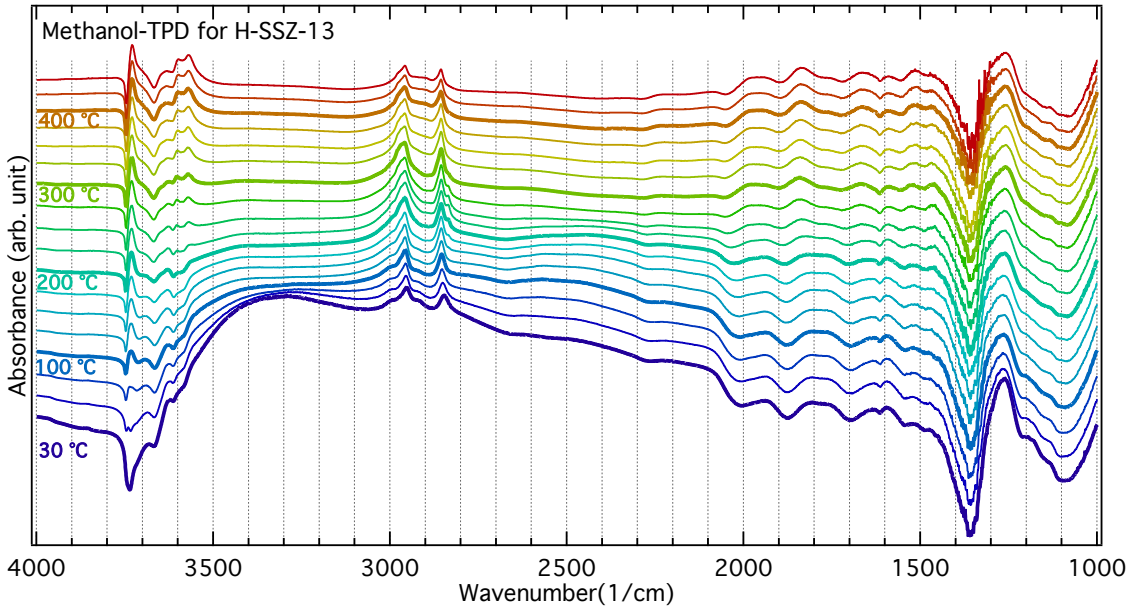

Figure S11: Infrared spectra collected during temperature programmed desorption of methanol from the H-SSZ-13 sample ramping the temperature from 30 to 450 °C.

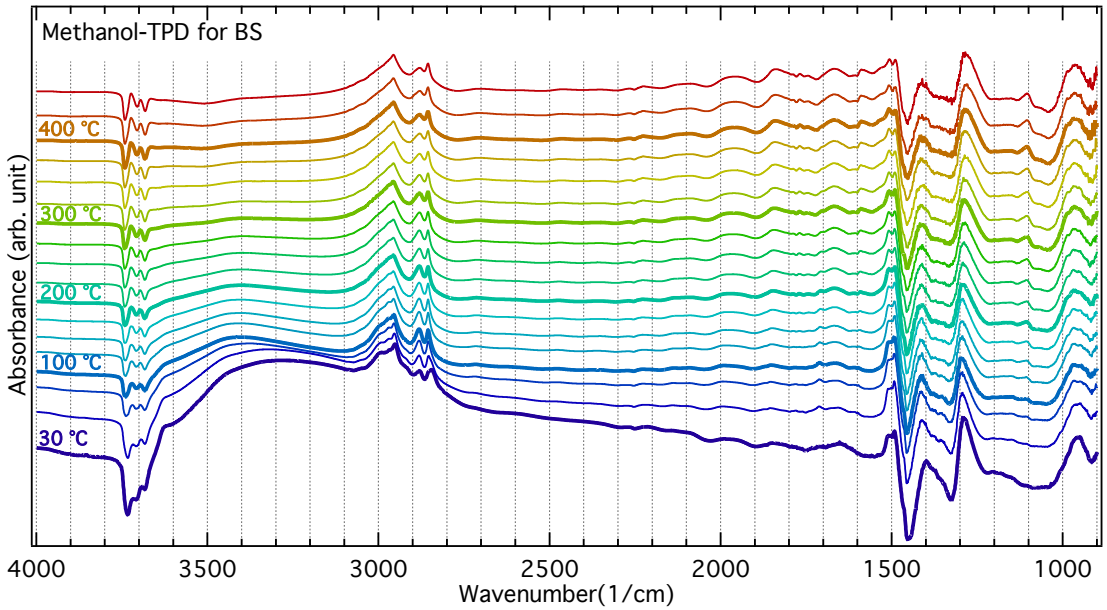

Figure S12: Infrared spectra collected during temperature programmed desorption of methanol from the BS sample ramping the temperature from 30 to 450 °C.

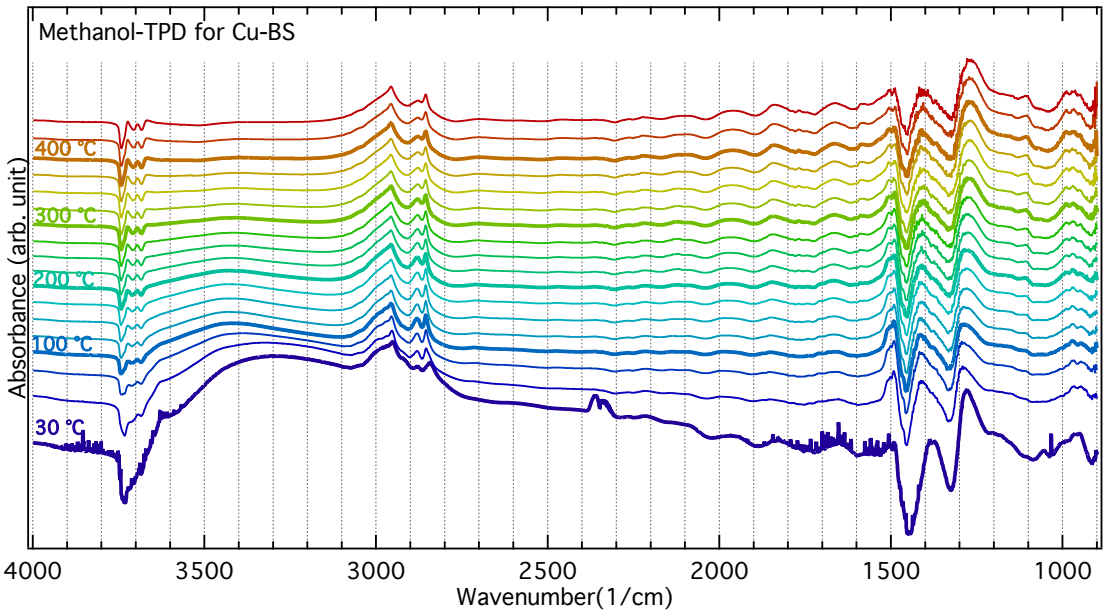

Figure S13: Infrared spectra collected during temperature programmed desorption of methanol from the Cu-BS sample ramping the temperature from 30 to 450 °C.

References

(1) Hadjiivanov, K.; Knozinger, H. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1132–1137.

(2) Concepcion, P.; Boronat, M.; Millan, R.; Moliner, M.; Corma, A. *Top. Catal.* **2017**, *60*, 1653–1663.

(3) Kwak, J. H.; Zhu, H.; Lee, J. H.; Peden, C. H. F.; Szanyi, J. *Chem. Commun.* **2012**, *48*, 4758–4760.

(4) Hadjiivanov, K. I.; Kantcheva, M. M.; Klissurski, D. G. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4595–4600.

(5) Szanyi, J.; Kwak, J. H.; Zhu, H.; Peden, C. H. F. *Phys. Chem. Chem. Phys.* **2013**, *15*, 2368–2380.

(6) Zhang, R.; McEwen, J.-S.; Kollar, M.; Gao, F.; Wang, Y.; Szanyi, J.; Peden, C. H. F. *ACS Catal.* **2014**, *4*, 4093–4105.