

Conversion of Methane to Methanol on Copper-Containing Small-Pore Zeolites and Zeotypes

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Supporting Information

S.1 Experimental Section

S.1.1 Materials

Materials received from commercial vendors were: Na-mordenite (Tricat, Si/Al = 5), H-ZSM-5 (Zeolyst, CBV 2314, Si/Al = 11.5), and H-SAPO-34 (ACS Materials). Materials synthesized in-house were: SSZ-13, SSZ-16, and SSZ-39. The in-house syntheses were carried out following the procedures in Refs. 1-3 with minor modifications, such as Si/Al ratio or silicon sources, and using commercially available chemicals. Materials used as silicon and aluminum sources were: sodium silicate solution (Sigma Aldrich, 26.5 wt% SiO₂), Na-Y (Zeolyst, CBV 100, Si/Al = 2.47), tetraethyl orthosilicate (Sigma, >98%), and aluminum triethoxide (Aldrich, 97%). Other materials were: trimethyladamantylammonium hydroxide (Sachem, 25 wt%), 1,1,3,5-tetramethylpiperidinium hydroxide (Sachem, 20 wt%), copper (II) acetate (Aldrich, 98%), copper (I) chloride (Sigma-Aldrich, 97%), ammonium nitrate (Sigma-Aldrich, ≥98%), sodium nitrate (Sigma-Aldrich, ≥99%), barium sulfate (Sigma, ≥97.5%), and deionized water. Gases were: O₂ (Keen, Grade 4.7), N₂ (Keen, Grade 5), helium (Keen, Grade 5), methane (Matheson, 99.99%), and propane (Matheson, 99.999%).

S.1.2 Ion-Exchange Procedures

S.1.2.1 Conversion of Materials to Na-form or H-form

Ammonium exchange of materials either synthesized in-house or purchased in the Na-form was performed three times for 2 h at a temperature of 80 °C with a solution of 1 M NH₄NO₃, the volume of which was 40 ml per gram of material. The materials were collected by vacuum filtration between each ion-exchange. After the final exchange, calcination was performed in an open air Thermolyne furnace by heating the material at a rate of 3 °C min⁻¹ to 550 °C and holding at that temperature for 2 h. The same procedure was used to obtain materials in the Na-form, except a 1 M NaNO₃ solution was used instead of NH₄NO₃. Materials that contained sodium from the original synthesis were exchanged two times instead of three times. The Na-materials were calcined before exchange with copper (II) acetate.

S.1.2.2 Copper (II) Ion-Exchange

Copper (II) ion-exchange was performed by placing materials in the Na-form in an aqueous solution of copper (II) acetate. The volume of the ion-exchange solution was 200 ml and was held constant, while the moles of copper and mass of zeolite were varied. The moles of copper added to each solution was equivalent to that required for full exchange of the material (i.e. Cu/Al for aluminosilicates or Cu/Si for silicoaluminophosphates equal to 0.5). The exchange was performed by stirring the aqueous mixture of the materials overnight (14–18 h) at room temperature, and the solid material was recovered by vacuum filtration. The ion-exchange was repeated until a Cu/Al ratio greater than 0.25 was achieved for aluminosilicates. After the final exchange, the samples were vacuum filtered and washed with deionized water using 1.0–1.5 L of deionized water per gram of material. The amount of copper loaded on the material was determined by measuring the disappearance of copper acetate from the ion-exchange solutions with UV–Vis spectroscopy. The copper content of the material determined by UV–vis spectroscopy and the nominal aluminum content of the material were used to generate the Cu/Al ratio for materials exchanged with copper (II) acetate. The amount of materials and copper acetate used in the exchanges is provided in Table S1, as well as the final Cu/Al ratios.

Table S1 Quantity of materials used in copper (II) ion-exchanges and the resulting Cu/Al ratios

Zeolite (Framework)	Nominal Si/Al or Al+P/Si	Si/Al or Al+P/Si by EDX	Mass of zeolite or zeotype / g	Mass of copper (II) acetate / g	Number of times exchanged	Final Cu/Al
Mordenite (MOR)	5	6.5 ± 0.5	2.00	0.476	1	0.34 ± 0.06
SAPO-34 (CHA)	6 ^a	5.7 ± 0.4	1.00	0.106	4 ^b	0.17 ± 0.06
SSZ-13 (CHA)	6	5.4 ± 0.2	0.632	0.136	2	0.35 ± 0.07
SSZ-13 (CHA)	12	9.9 ± 0.7	0.631	0.074	2	0.35 ± 0.06
SSZ-16 (AFX)	6.5	5.9 ± 0.3	0.901	0.183	2	0.34 ± 0.07
SSZ-16 (AFX)	10	8.9 ± 0.8	0.555	0.077	2	0.45 ± 0.08
SSZ-39 (AEI)	10	9.8 ± 0.5	0.331	0.046	2	0.26 ± 0.06
ZSM-5 (MFI)	11.5	11.0 ± 1.0	2.00	0.235	1	0.34 ± 0.06

^a Based on ICP in Ref. 4 and highlighted on the suppliers website

^b Calcined between exchanges 2 and 3, and 3 and 4, in a Thermolyne furnace. The calcinations were performed to allow migration of copper ions to the interior of the SAPO-34 crystal as suggested in Ref. 5.

^c Measured by EDX

S.1.2.3 Copper (I) Ion-Exchange

Ion-exchange with copper (I) chloride was performed in situ prior to methane conversion. The apparatus used was the same as described in Section S1.3.1. Copper (I) chloride powder was loaded in the quartz tube above 0.300 ± 0.005 g of the H-form zeolite or zeotype powder. The

two solids were physically separated by quartz wool. The copper (I) chloride loading was more than required for full exchange of the material (Cu/Al for aluminosilicates or Cu/Si for silicoaluminophosphates was equal to 1.5). The reactor was heated at $2\text{ }^{\circ}\text{C min}^{-1}$ to a temperature of $650\text{ }^{\circ}\text{C}$ with N_2 flowing at 50 sccm and held for 10 h. The reactor was then cooled to $450\text{ }^{\circ}\text{C}$, the gas flow was stopped, and vacuum treatment was applied for 6 hours at 0.2 atm. After vacuum treatment, 50 sccm of O_2 was introduced and the protocol for methane conversion described in Section 1.3.1 was carried out. The complete ion-exchange and methane conversion procedure is outlined in Figure S2.

S.1.3 Equipment

S.1.3.1 Apparatus Used For Methane Conversion

Gas flows were controlled by mass flow controllers (Brooks Instrument). The zeolite or zeotype material was loaded in a quartz tube (ID = 7 mm) and was supported by quartz wool. A ceramic radiant full cylinder heater (Omega, CRFC-26/120-A) was used to heat the quartz tube. The furnace temperature was controlled using a thermocouple placed around the center of the quartz tube and an Omega CN/74000 temperature controller. The effluent stream was directed to a gas chromatograph (Agilent 7890A) which was used for quantification of methanol. A Supel-Q PLOT column (Supelco, 30 m x 0.32 mm) was used for separation, and a flame ionization detector was used for quantification. The temperature of the GC oven was held constant at $80\text{ }^{\circ}\text{C}$ and injections were taken every 3 min. The effluent stream was also monitored with a mass spectrometer (Pfeiffer OmniStar GSD 320).

S.1.3.2 Apparatus Used to Collect UV–vis Spectra

A UV–vis spectrometer (JASCO, V-5500) equipped with an integrating sphere (JASCO ISV-469) was used to collect diffuse reflectance UV–vis spectra. About 120 mg of material was placed in a U-shaped quartz tube, which was connected to gas lines, for each experiment. Before spectra were collected, the U-shaped tube was secured at the opening of the integrating sphere. The apparatus thus allowed for the material to be treated under gas flow at room temperature while continuously collecting spectra, whereas spectra could not be collected while heat was

applied. To treat the material at high temperature, the tube was separated from the integrating sphere and wrapped with heating tape and insulation. The temperature was controlled using a K-type thermocouple placed around the outside of the tube at the sample location and a temperature controller (Watlow, Series 965). Gas flows were controlled by needle valves, and flow rates were measured with a digital gas flowmeter (Agilent, ADM 1000).

S.1.3.3 X-ray Powder Diffraction

X-ray diffractograms were collected using a Philips X'Pert powder diffractometer with a Cu K α source ($\lambda = 1.5418 \text{ \AA}$) over the range of $2\theta = 5.0\text{--}50.0$ with a step size of 0.02° and scan rate of 2 s per step.

S.1.3.4 Scanning Electron Microscopy

The elemental composition of Cu-exchanged materials was determined by Energy Dispersive X-ray Spectroscopy (EDX) on a JEOL JSM 7400F electron microscope operating with an accelerating voltage of 15 keV and a current of 10 μA . Each spectrum was collected for 100 seconds from a $50 \mu\text{m} \times 50 \mu\text{m}$ region containing zeolite crystals. Final values are the average of five spectra collected on five different regions.

S.1.4 Experimental Procedures

S.1.4.1 Procedure For Conversion of Methane to Methanol

The procedure used for conversion of methane to methanol consisted of three steps, *i*) oxidative pretreatment of the material, *ii*) admission of methane, and *iii*) removal of methane from the gas stream and admission of water vapor. Pretreatment of materials ion-exchanged with copper (II) acetate was performed by heating at $2 \text{ }^\circ\text{C min}^{-1}$ to a temperature of $450 \text{ }^\circ\text{C}$ in O_2 flowing at 50 sccm and holding for 10 h. The furnace was then cooled to $60 \text{ }^\circ\text{C}$, and the gas flow was changed to a mixture of 4 sccm of methane and 50 sccm of N_2 . The temperature was held at $60 \text{ }^\circ\text{C}$ for 20 min and then increased by $5 \text{ }^\circ\text{C min}^{-1}$ to $200 \text{ }^\circ\text{C}$ and held for another 20 min. Methane was then removed from the gas stream and N_2 was diverted through a water-containing saturator. The mass of Cu-material used in each experiment was $0.300 \pm 0.005 \text{ g}$. The exact procedures for

materials either exchanged with copper (II) acetate or copper (I) chloride are outlined in Figures S1 and S2, respectively.

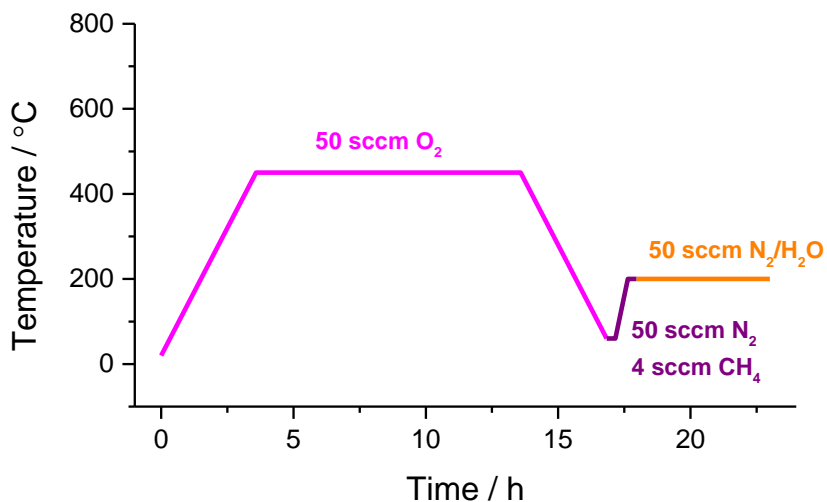


Figure S1. Temperature profile and gas flow rates used for conversion of methane to methanol on materials ion-exchanged with copper (II) acetate.

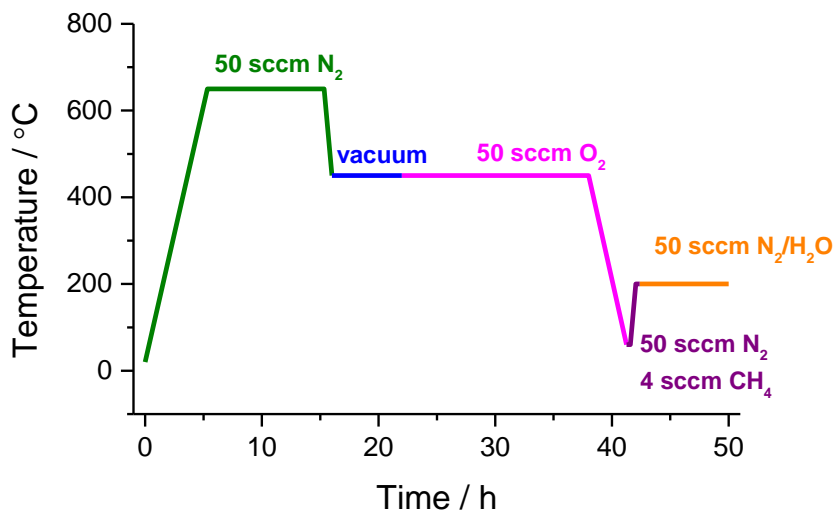


Figure S2. Temperature profile and gas flow rates used for ion-exchange of H-form materials with copper (I) chloride and subsequent conversion of methane to methanol.

S.1.4.2 Procedures for Collection of UV–vis Spectra

Spectra were collected using the apparatus described in Section S.1.3.2. Barium sulfate in a quartz U-tube was used to collect a background spectrum before each experiment. Before gas or heat treatment of the microporous materials, a spectrum was taken of the hydrated material held in the quartz U-tube. Then, the U-tube was wrapped in heating tape and heated at a rate of 5 °C min⁻¹ to 450 °C in either O₂ or helium flowing at 20 sccm. After being held at 450 °C for 2 h, the material was cooled to room temperature, still under gas flow, and a spectrum was collected. O₂ was used as the pretreatment gas for materials that were subsequently exposed to water or propane. When water was added to the gas stream, O₂ was diverted through a single-legged saturator containing water at room temperature. Helium was used as the pretreatment gas for Cu-SSZ-16 that was subsequently exposed to O₂. After pretreatment, the Cu-SSZ-16 was cooled to room temperature under helium flow. After 10 min at room temperature, the gas flow was switched to O₂ flowing at 20 sccm. Before admission of water or propane, several spectra were taken over the course of 30 min. When propane was added to the gas stream, O₂ flow was concurrently stopped and the new gas stream consisted only of propane flowing at 20 sccm.

S.2 Additional Figures

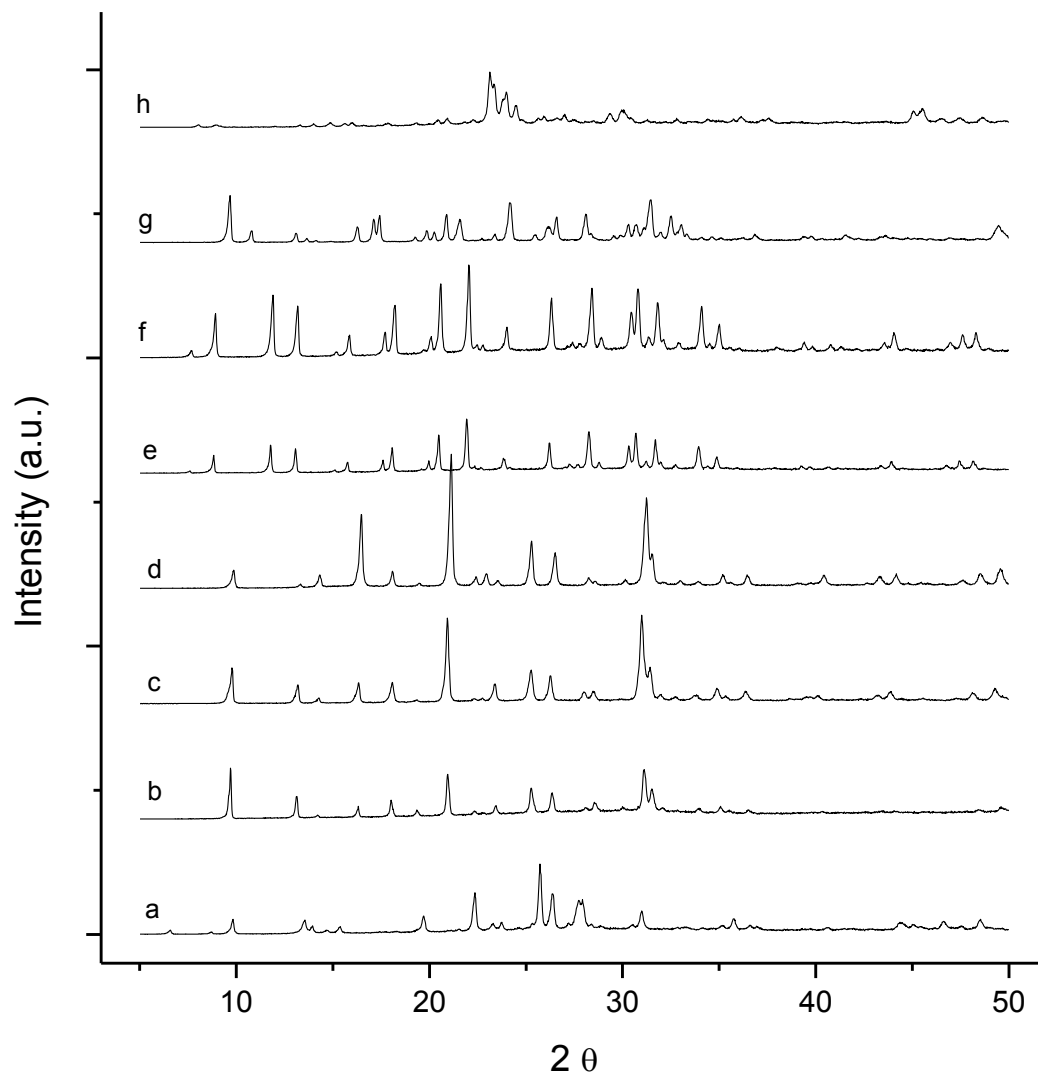


Figure S3. XRD patterns of a) Na-mordenite, b) H-SAPO-34, c) as-synthesized SSZ-13, Si/Al = 6, d) as-synthesized SSZ-13, Si/Al = 12, e) as-synthesized SSZ-16, Si/Al = 6 f) as-synthesized SSZ-16, Si/Al = 10, g) as-synthesized SSZ-39, Si/Al = 10 and h) Na-ZSM-5.

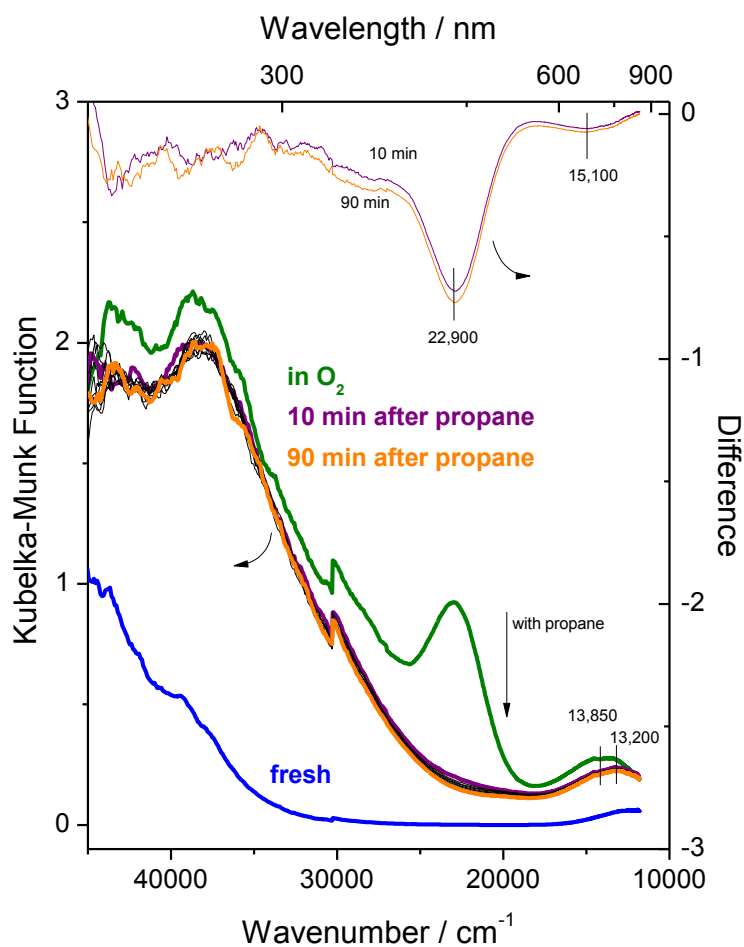


Figure S4. Diffuse reflectance UV-vis spectra of Cu-ZSM-5 (prepared with copper (II) acetate) before and during interaction with propane. The spectrum of the hydrated material is denoted in the figure as “fresh”. The material was treated in O₂ flowing at 20 sccm for 2 h at a temperature of 450 °C and then cooled to room temperature (green line). After a period in flowing O₂ during which the spectra did not change, the gas flow was switched to 20 sccm of propane and spectra were collected over a period of time indicated in the figure. Difference curves (right axis) are of the spectrum in O₂ minus the spectrum collected at a specified time on stream. The artifact at 30,000 cm⁻¹ is caused by a lamp change in the spectrometer.

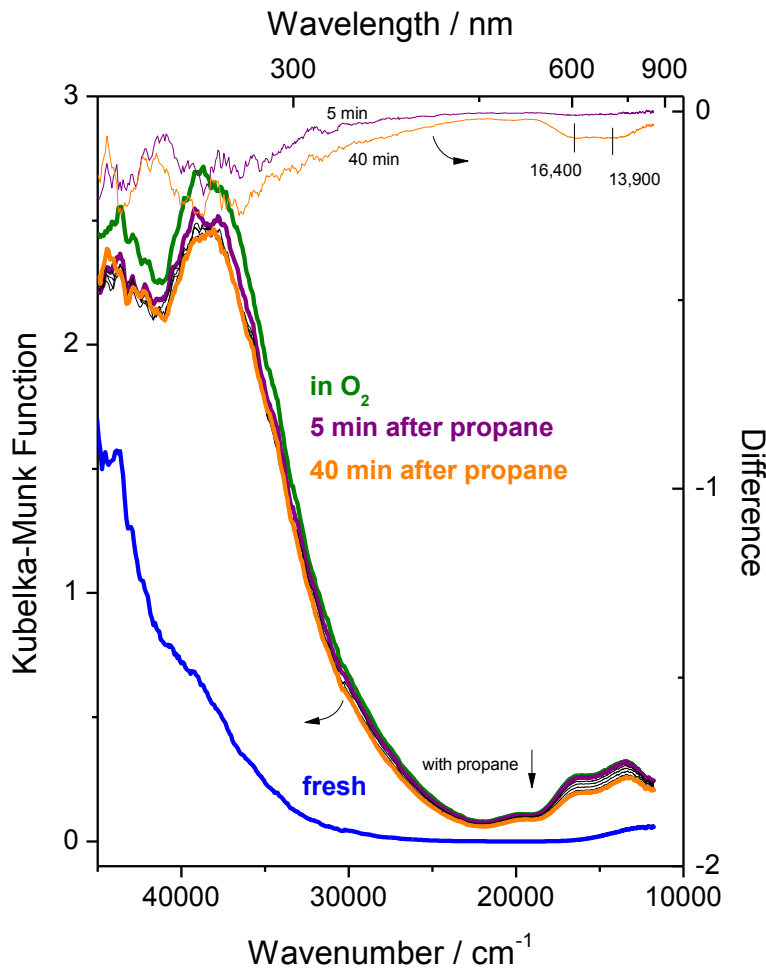


Figure S5. Diffuse reflectance UV-vis spectra of Cu-SSZ-13 (Si/Al = 6, prepared with copper (II) acetate) before and during interaction with propane. The spectrum of the hydrated material is denoted in the figure as “fresh”. The material was treated in O₂ flowing at 20 sccm for 2 h at a temperature of 450 °C and then cooled to room temperature (green line). After a period in flowing O₂ during which the spectra did not change, the gas flow was switched to 20 sccm of propane and spectra were collected over a period of time indicated in the figure. Difference curves (right axis) are of the spectrum in O₂ minus the spectrum collected at a specified time on stream.

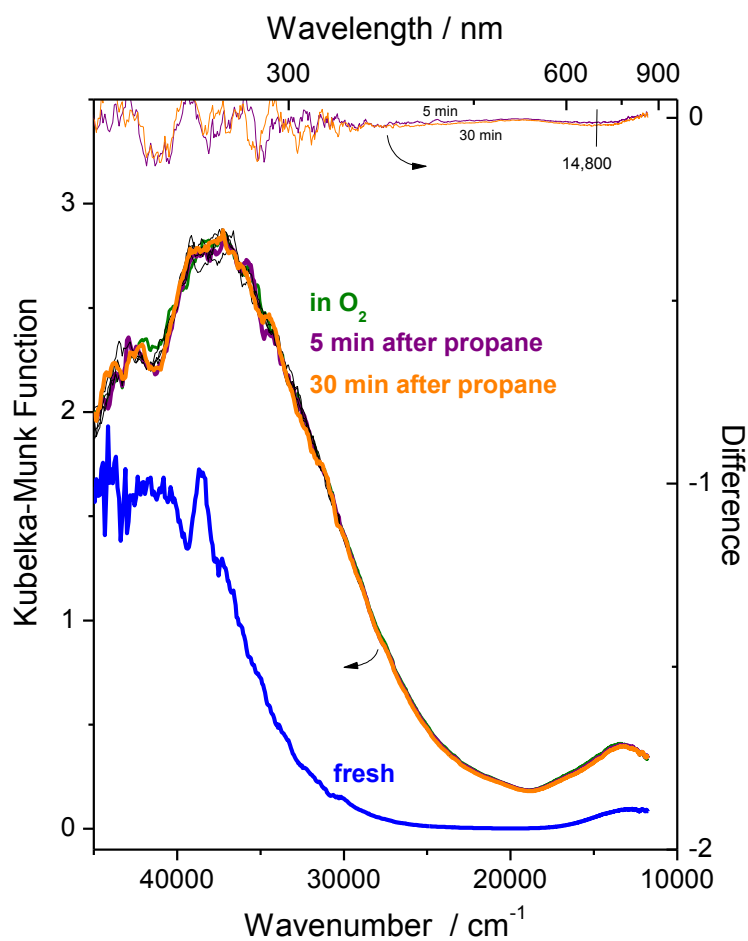


Figure S6. Diffuse reflectance UV-vis spectra of Cu-mordenite (prepared with copper (II) acetate) before and during interaction with propane. The spectrum of the hydrated material is denoted in the figure as “fresh”. The material was treated in O₂ flowing at 20 sccm for 2 h at a temperature of 450 °C and then cooled to room temperature (green line). After a period in flowing O₂ during which the spectra did not change, the gas flow was switched to 20 sccm of propane and spectra were collected over a period of time indicated in the figure. Difference curves (right axis) are of the spectrum in O₂ minus the spectrum collected at a specified time on stream.

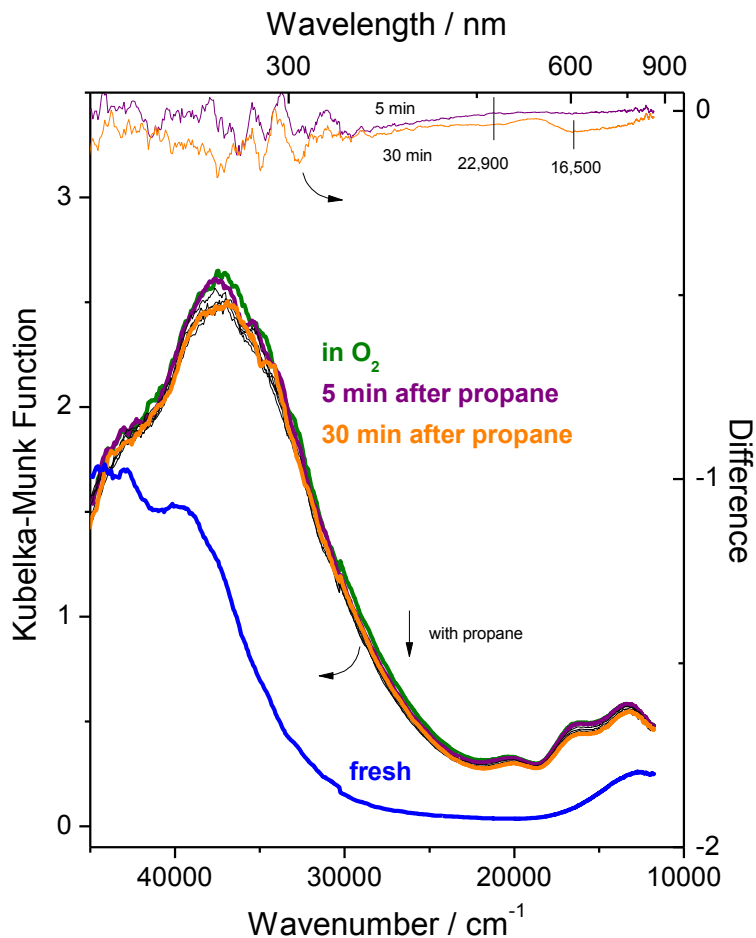


Figure S7. Diffuse reflectance UV-vis spectra of Cu-SSZ-16 (Si/Al = 6.5, prepared with copper (II) acetate) before and during interaction with propane. The spectrum of the hydrated material is denoted in the figure as “fresh”. The material was treated in O₂ flowing at 20 sccm for 2 h at a temperature of 450 °C and then cooled to room temperature (green line). After a period in flowing O₂ during which the spectra did not change, the gas flow was switched to 20 sccm of propane and spectra were collected over a period of time indicated in the figure. Difference curves (right axis) are of the spectrum in O₂ minus the spectrum collected at a specified time on stream.

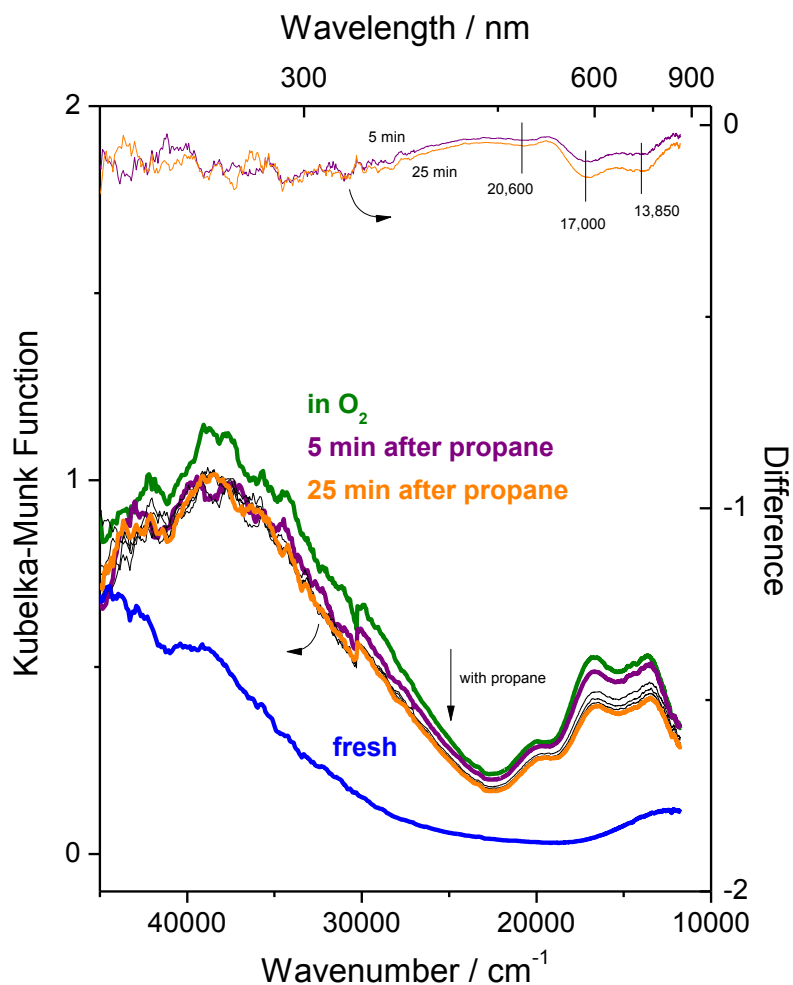


Figure S8. Diffuse reflectance UV-vis spectra of Cu-SSZ-39 (prepared with copper (II) acetate) before and during interaction with propane. The spectrum of the hydrated material is denoted in the figure as “fresh”. The material was treated in O₂ flowing at 20 sccm for 2 h at a temperature of 450 °C and then cooled to room temperature (green line). After a period in flowing O₂ during which the spectra did not change, the gas flow was switched to 20 sccm of propane and spectra were collected over a period of time indicated in the figure. Difference curves (right axis) are of the spectrum in O₂ minus the spectrum collected at a specified time on stream. The artifact at 30,000 cm⁻¹ is caused by a lamp change in the spectrometer.

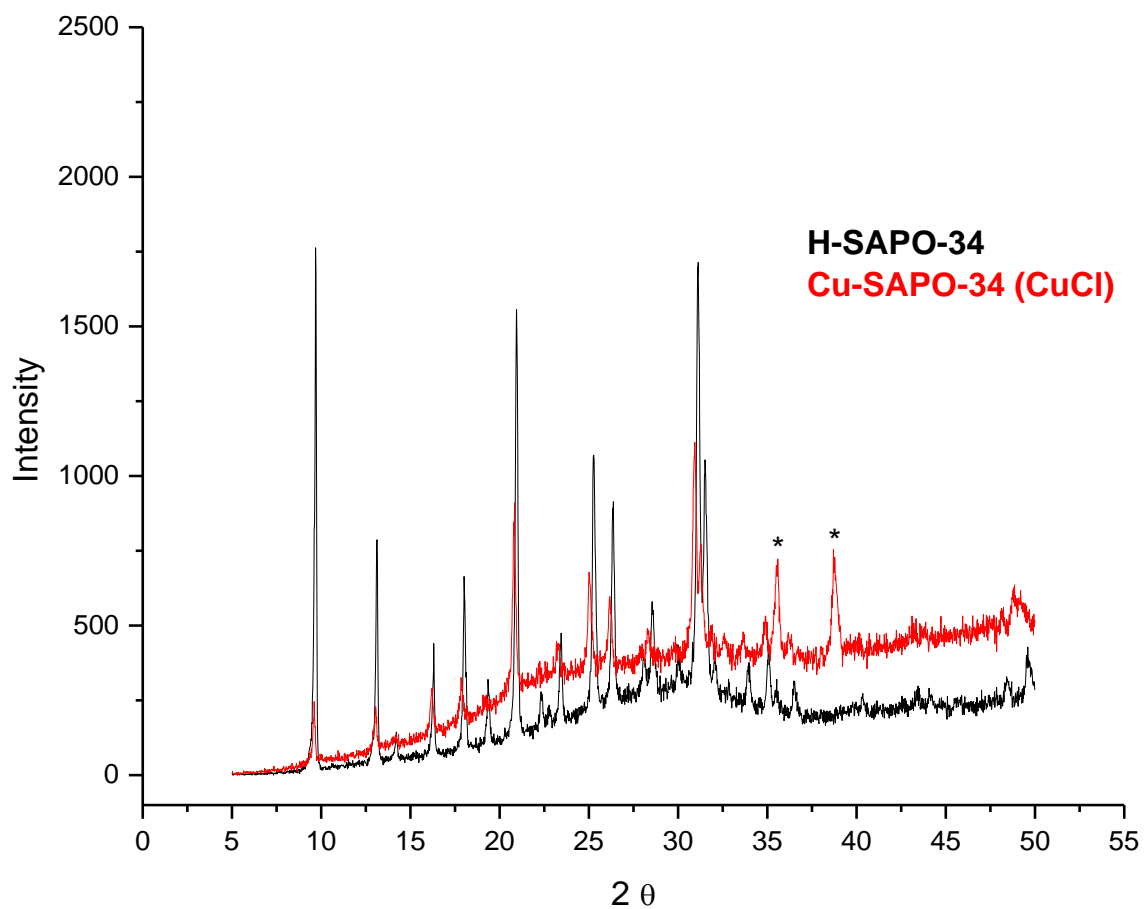


Figure S9. XRD patterns of, a) fresh H-SAPO-34 and b) Cu-SAPO-34 loaded with copper (I) chloride after use in methane conversion. Asterisks (*) indicate reflections assigned to the (111) and (-111) reflections of CuO.

Table S2 Elemental compositions and amount of methanol produced by other (not top-performing) Cu-zeolites and zeotypes

Zeolite	Si/Al or Al+P/Si	Cu/Al	Cl/Al	Methanol ($\mu\text{mol g}^{-1}$)	Methanol/Cu (mol/mol)
Mordenite	5	0.5 ± 0.1	0.3 ± 0.1	34	0.03
SAPO-34 ^a	5	0.17 ± 0.06	-	< 1	< 0.001
SSZ-13	6	0.6 ± 0.3	0.4 ± 0.1	5	0.003
SSZ-13	12	0.8 ± 0.3	0.3 ± 0.1	10	0.008
SSZ-16	6.5	0.7 ± 0.4	0.3 ± 0.1	12	0.01
SSZ-16	10	1.1 ± 0.2	0.5 ± 0.1	15	0.008
SSZ-16 ^a	10	0.45	-	2	0.002
SSZ-39	10	1.1 ± 0.3	0.5 ± 0.1	17	0.01
ZSM-5	11.5	0.9 ± 0.1	0.4 ± 0.1	9	0.009

^a Materials were exchanged with copper (I) chloride except for SAPO-34 and SSZ-16 (Si/Al = 10), which were exchanged with copper (II) acetate

Table S3. $d \leftarrow d$ transitions of copper (II) ions in Cu-exchanged zeolites and zeotypes

Zeolite (Framework type)	$d \leftarrow d$ Transitions / cm^{-1}
SAPO-34 (CHA)	12,500, 15,800
ZSM-5 (MFI)	14,000
Mordenite (MOR)	13,500
SSZ-16 (AFX)	13,400, 16,200, 20,300
SSZ-13 (CHA)	13,500, 16,200, 19,700
SSZ-39 (AEI)	13,700, 16,750, 20,100

References

- [1] T.D. Pham, Q. Liu, R.F. Lobo, *Langmuir* 2013, **29**, 832.
- [2] R.H. Archer, S.I. Zones, M.E. Davis, *Microporous Mesoporous Mater.* 2010, **130**, 255.
- [3] P. Wagner, Y. Nakagawa, G.S. Lee, M.E. Davis, S. Elomari, R.C. Medrud, S.I. Zones *J. Am. Chem. Soc.* 2000, **122**, 263.
- [4] D. Wang, L. Zhang, J. Li, K. Kamasamudram, W.S. Epling, *Catal. Today* 2014, **231**, 64.
- [5] P.N.R. Vennestrøm, A. Katerinopoulou, R.R. Tiruvalam, A. Kustov, P.G. Moses, P. Concepcion, A. Corma, *ACS Catal.* 2013, **3**, 2158.