

Water is the oxygen source for methanol produced in partial oxidation of methane in a flow reactor over Cu-SSZ-13

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SUPPORTING INFORMATION

Experimental

Materials. N,N,N-trimethyl-1-adamantylammonium hydroxide (TMAdaOH, 25wt%, SACHEM) Ludox® HS-40 colloidal silica (40wt% suspension in water, Sigma Aldrich), aluminum hydroxide (reagent grade, Sigma Aldrich), and sodium hydroxide pellets (ACS grade, VWR) were used as received in the zeolite synthesis. Ammonium nitrate was obtained from Acros Organics (99%) and used for ammonium ion exchange. Copper (II) sulfate pentahydrate (99%, Alfa Aesar) was used for copper ion exchange. CaCl₂ (≥97, Fluka) was used to prepare aqueous solutions with various concentrations to control H₂O vapor pressure. Methane (≥99.99%, O₂ ≤ 5 ppm (v/v), Airgas), helium (≥99.999%, O₂ ≤ 1 ppm (v/v), Airgas), hydrogen (≥99.999%, Airgas), 400 ppm CO₂ (balance N₂, Airgas), dimethyl ether (≥99.99%, Sigma-Aldrich) and air (Airgas) gas cylinders were used as received. Water-¹⁸O (≥98 atom % ¹⁸O, Sigma-Aldrich) and deuterium oxide (D, 99.9%, Cambridge Isotope Laboratories) were used as received in methane activation reactions.

Zeolite synthesis. The synthesis gel molar composition was 1 SiO₂/ 0.133 Al₂O₃/ 0.25 TMAdaOH/ 0.25 Na₂O/ 44 H₂O. As an example, 8.865 g of TMAdaOH was dissolved in 8.090 g of deionized water (18 MΩ) and stirred for 15 minutes. 0.109 g of aluminum hydroxide and 1.284 g of 5M NaOH aqueous solution were added to the solution. The mixture was stirred for another 15 minutes before adding 3.15 g of colloidal silica. The final mixture was stirred at room temperature for 2 h, then transferred to a Teflon-lined stainless-steel autoclave and placed in an oven for 6 days at 160 °C in a rack rotating at approximately 60 rpm. The solids were recovered by vacuum filtration, washed with copious amount of deionized water, and dried at room temperature overnight. The as-made sample was calcined in air at 550 °C for 8 h to ensure complete combustion of any remaining organic structure directing agents.

Ion exchange. After calcination, all samples were converted to the NH_4 -form by ion exchanging them with 250 ml of 0.1 M aqueous solution of NH_4NO_3 at 80 °C for 8 h. The solids were recovered by vacuum filtration, washed with deionized water, and dried at room temperature overnight.

Copper exchanged SSZ-13 samples were prepared by liquid ion exchanging of 1g of NH_4 -SSZ-13 with 500 mL of 1 M CuSO_4 at 80 °C for 1 h.[22] The product was recovered by vacuum filtration and washed with excess deionized water. The wet solids were placed in the oven at 80 °C overnight until dry.

Analytical

X-ray diffraction (XRD) measurements were performed with a Rigaku MiniFlex 600 diffractometer with $\text{Cu K}\alpha$ radiation over a range of 4–50° 2 θ . Nitrogen adsorption experiments were performed on a Micromeritics ASAP 2020 at 77 K using approximately 50 mg of a sample. Energy-dispersive X-ray spectroscopy (EDAX) chemical analyses were obtained on a Hitachi 3400 electron microscope. Chemical analyses were performed by Galbraith Laboratories. CH_4 (Aalborg Instruments), He (Aalborg Instruments), air (Aalborg Instruments), and 1% O_2 (Bronkhorst) flow was controlled with independent mass flow controllers. Water vapor was introduced into the stream using a humidifier (Perma Pure MH-Series) and isotopically labelled water vapors were introduced using a saturator. CH_4 , CH_3OH and dimethyl ether concentrations in the reaction mixture were monitored by a gas chromatograph (Agilent Technologies, model 7890N) equipped with a HP-Plot-Q column (Agilent, 30m, 0.32 mm, 19091P-Q04) and flame ionization detector. The permanent gas products were monitored using a Carboxen 1006 PLOT column (Sigma-Aldrich, 30 m, 0.32 mm ID, 24241-U) and a thermal conductivity detector. The IR measurements of methane oxidation with isotopically labelled ^{18}O -water were performed on a Nicolet iS50R FTIR spectrometer equipped with an MCT/B detector and a 2.4 m heated gas cell

(Pike Technologies). A spectral resolution of 4 cm^{-1} was used to collect spectra, which are reported in transmittance (%). Each reported spectrum is an average of 300 scans. The heated gas cell was connected to the outlet of the reactor. The gas products leaving the reactor flowed through the cell under atmospheric pressure at $150\text{ }^{\circ}\text{C}$.

Catalytic testing

The partial oxidation of methane to methanol over Cu-SSZ-13 was tested in a continuous, tubular flow reactor. 400 mg of a catalyst with a nominal size of 500-850 μm was loaded in a $\frac{1}{4}$ " OD stainless steel tube, which was then placed inside an electric furnace. The total flow rate was held at 40 sccm to achieve the weight hourly space velocity (WHSV) of $6000\text{ ml h}^{-1}\text{ g}_{\text{cat}}^{-1}$. The catalyst was treated before the reaction under flowing air for 2 h at $550\text{ }^{\circ}\text{C}$. Then it was cooled to the desired reaction temperature under air. Upon reaching the reaction temperature, the catalyst was purged with He for 30 min. Then CH_4 was introduced for 40 min followed by CH_4 (49.5 kPa), H_2O (2.3 kPa), O_2 (0.025 kPa) and balance He. All measurements were done at 1 bar. 2.0 g of Cu-SSZ-13 with particle size of 500-850 μm was loaded a $\frac{1}{4}$ " ID a quartz tube to achieve the WHSV of $1200\text{ ml h}^{-1}\text{ g}_{\text{cat}}^{-1}$.

Considerations of O_2 impurity effect on the continuous partial oxidation of methane

The upper bound of the concentration of dissolved oxygen in water at room temperature is calculated using Henry's law. It is 0.00027 M. The partial pressure of water vapor in the stream is 2.3 kPa or 22705 ppm. Thus, the maximum O_2 concentration coming from water bath would be 0.11 ppm. These calculations strongly suggest potential oxygen impurities in the water bath are not the explanation for the results obtained.

Ultra-high purity methane and helium have less than 5 ppm and 1 ppm molecular oxygen impurities (v/v). Hence, the maximum possible molecular oxygen impurity in the stream would be 3 ppm (v/v). The upper bound of the CH_3OH production rate from O_2 impurity would be 1.61

$\mu\text{mol}_{\text{CH}_3\text{OH}}/\text{g}_{\text{cat}}\cdot\text{h}$. The oxygen balance calculation shows that molecular oxygen coming from methane and helium gases is low and incompatible with the observable methanol production rate. Further, if there was significant O_2 contamination this should have come to light in the FTIR results for the experiments performed with H_2^{18}O .

The ^{18}O abundance in nature is 0.2%. The $^{18}\text{O}_2$ concentration in the reactor would be 0.01 ppm, which is not enough to account for the methanol production rate.

Results

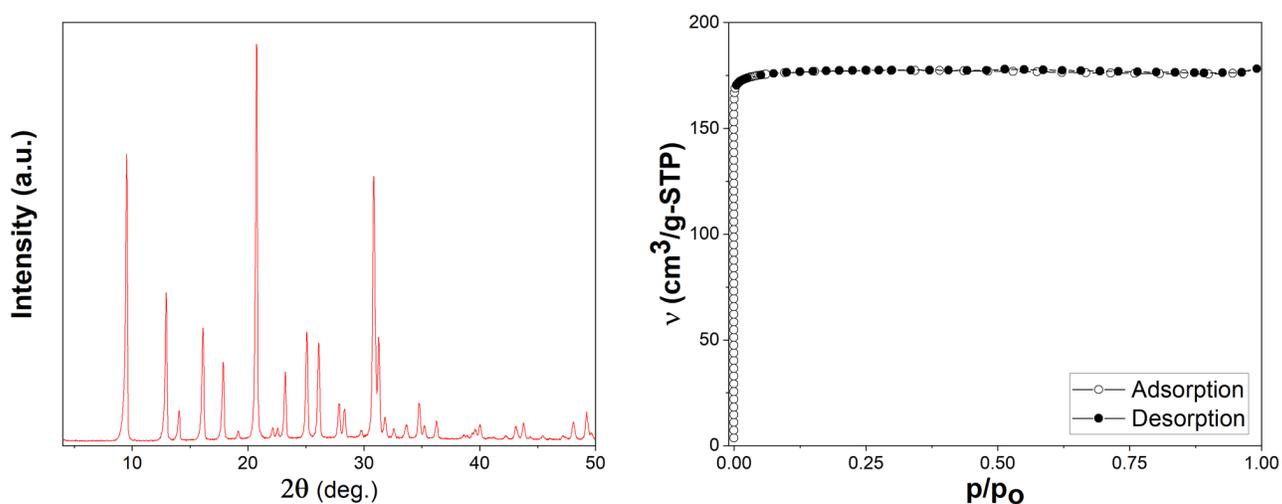


Figure S1. The PXRD pattern (left) and N_2 adsorption isotherm (right) of as-made SSZ-13. The micropore volume of SSZ-13 is $0.27 \text{ cm}^3/\text{g}$ consistent with CHA structure.

Table S1. Elemental composition results of Cu-SSZ-13 sample

Sample	Si/Al (ICP/EDX)	Cu/Al (ICP/EDX)
Cu-SSZ-13	$9.73/9.98 \pm 0.17$	$0.33/0.34 \pm 0.04$

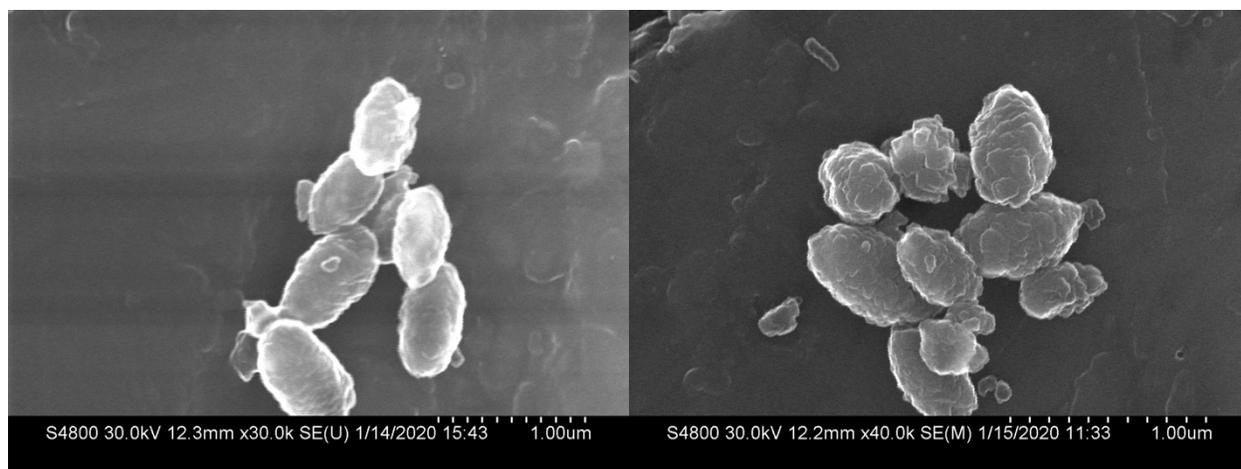


Figure S2. SEM images of as-made SSZ-13 (left) and Cu-SSZ-13 (right).

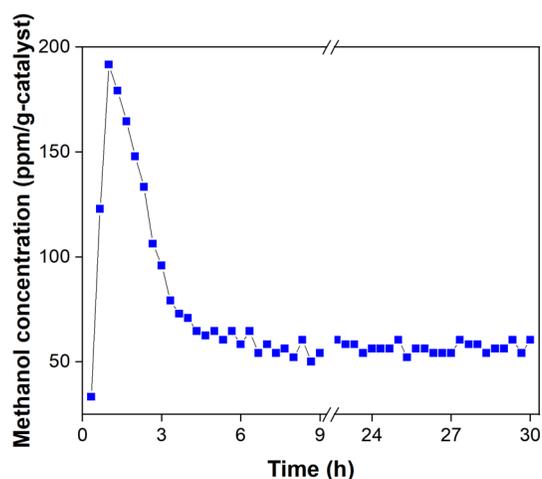


Figure S3. Methanol concentration versus time for methanol production over Cu-SSZ-13 in the presence of D₂O. Catalyst was pretreated at 550 °C for 2 h under flowing air, cooled to 225 °C under air and purged with He for 30 min. Initial dry oxidation of CH₄ at 6000 mL h⁻¹ g_{cat}⁻¹ for 40 min. Reaction conditions for methane activation in absence of molecular oxygen: T = 225 °C, WHSV = 6000 mL h⁻¹ g_{cat}⁻¹, P_{CH₄} = 49.5 kPa, P_{H₂O} = 2.3 kPa and balance He.

Gas mixture	Specific activity ^a	Site time yield ^b
CH ₄ /H ₂ O/He	5.30 ± 0.37	10.9 ± 0.8
CH ₄ /D ₂ O/He	6.12 ± 0.37	12.6 ± 0.8
CH ₄ /H ₂ ¹⁸ O/He	6.16 ± 0.40	12.7 ± 0.4

Table S2. Values of the specific activity and site time yield for the data shown in Figure 3. ^a μmol_{CH₃OH}/g_{cat}-h. ^b mol_{CH₃OH}/mol_{Cu}-h × 10⁻³

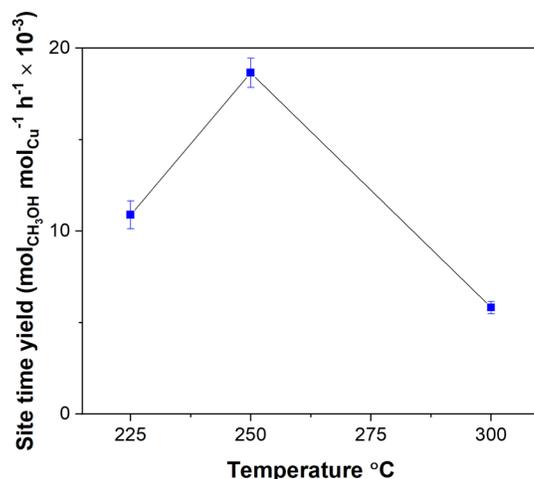


Figure S4. STY versus temperature for methanol production over Cu-SSZ-13 in the absence of O₂. Catalyst was pretreated at 550 °C for 2 h under flowing air, cooled to 225 °C under air and purged with He for 30 min. Initial dry oxidation of CH₄ at 6000 mL h⁻¹ g_{cat}⁻¹ for 40 min. Reaction conditions for methane activation in absence of molecular oxygen: T = 225 - 300 °C, WHSV = 6000 mL h⁻¹ g_{cat}⁻¹, P_{CH₄} = 49.5 kPa, P_{H₂O} = 2.3 kPa and balance He.

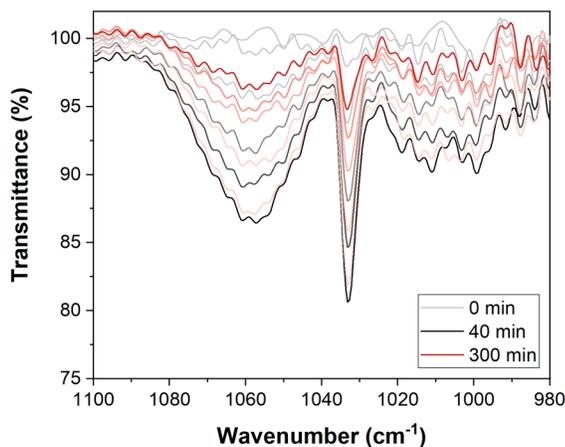


Figure S5. Time resolved IR spectra for the C-O stretching region. Catalyst was pretreated at 550 °C for 2 h under flowing air, cooled to 225 °C under air and purged with He for 30 min. Initial dry oxidation of CH₄ at 6000 mL h⁻¹ g_{cat}⁻¹ for 40 min. Reaction conditions for methane activation in absence of molecular oxygen: T = 225 °C, WHSV = 6000 mL h⁻¹ g_{cat}⁻¹, P_{CH₄} = 49.5 kPa, P_{H₂O} = 2.3 kPa and balance He.

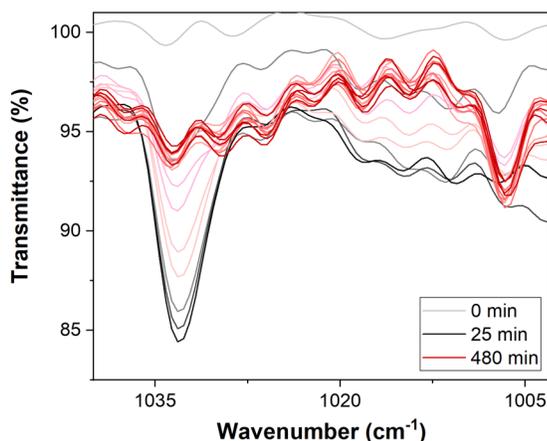


Figure S6. Time resolved IR spectra for the C-O stretching region. Catalyst was pretreated at 550 °C for 2 h under flowing air, cooled to 250 °C under air and purged with He for 30 min. Initial dry oxidation of CH₄ at 6000 mL h⁻¹ g_{cat}⁻¹ for 40 min. Reaction conditions for methane activation in presence of molecular oxygen: T = 250 °C, WHSV = 4800 mL h⁻¹ g_{cat}⁻¹, P_{CH₄} = 49.5 kPa, P_{H₂O} = 2.3 kPa, P_{O₂} = 0.025 kPa (250 ppm) and balance He.

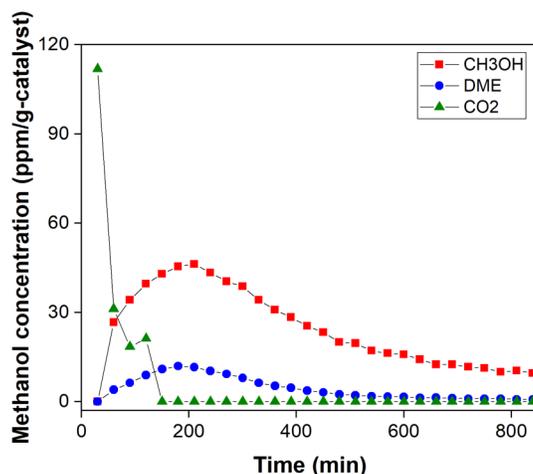


Figure S7. Methanol concentration versus time for methanol production over Cu-SSZ-13 in the presence of H₂O. Catalyst was pretreated at 550 °C for 2 h under flowing air, cooled to 250 °C under air and purged with He for 30 min. Initial dry oxidation of CH₄ at 1200 mL h⁻¹ g_{cat}⁻¹ for 40 min. Reaction conditions for methane activation in absence of molecular oxygen: T = 250 °C, WHSV = 1200 mL h⁻¹ g_{cat}⁻¹, P_{CH₄} = 49.5 kPa, P_{H₂O} = 2.3 kPa and balance He.

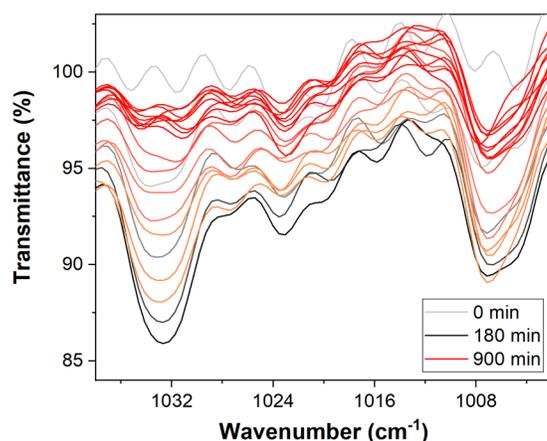


Figure S8. Time resolved IR spectra for the C-O stretching region. Catalyst was pretreated at 550 °C for 2 h under flowing air, cooled to 250 °C under air and purged with He for 30 min. Initial dry oxidation of CH₄ at 1200 mL h⁻¹ g_{cat}⁻¹ for 40 min. Reaction conditions for methane activation in absence of molecular oxygen: T = 250 °C, WHSV = 1200 mL h⁻¹ g_{cat}⁻¹, P_{CH₄} = 49.5 kPa, P_{H₂¹⁸O} = 2.3 kPa and balance He.

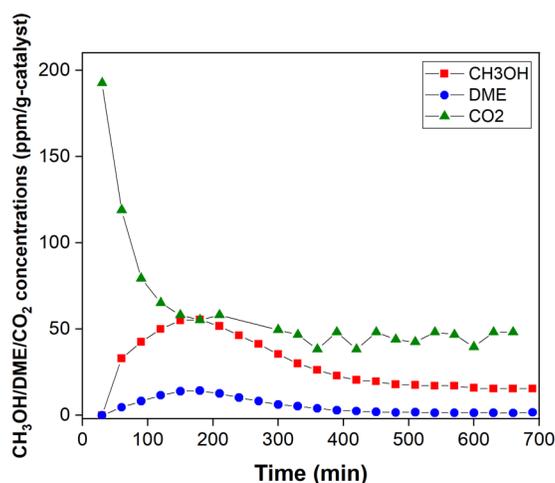


Figure S9. Methanol concentration versus time for methanol production over Cu-SSZ-13 in the presence of H₂O. Catalyst was pretreated at 550 °C for 2 h under flowing air, cooled to 250 °C under air and purged with He for 30 min. Initial dry oxidation of CH₄ at 1200 mL h⁻¹ g_{cat}⁻¹ for 40 min. Reaction conditions for methane activation in presence of molecular oxygen: T = 250 °C, WHSV = 1200 mL h⁻¹ g_{cat}⁻¹, P_{CH₄} = 49.5 kPa, P_{H₂O} = 2.3 kPa, P_{O₂} = 0.025 kPa (250 ppm) and balance He.

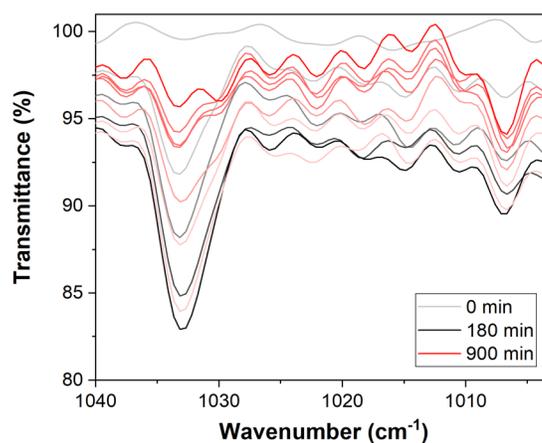


Figure S10. Time resolved IR spectra for the C-O stretching region. Catalyst was pretreated at 550 °C for 2 h under flowing air, cooled to 250 °C under air and purged with He for 30 min. Initial dry oxidation of CH₄ at 1200 mL h⁻¹ g_{cat}⁻¹ for 40 min. Reaction conditions for methane activation in presence of molecular oxygen: T = 250 °C, WHSV = 1200 mL h⁻¹ g_{cat}⁻¹, P_{CH₄} = 49.5 kPa, P_{H₂¹⁸O} = 2.3 kPa, P_{O₂} = 0.025 kPa (250 ppm) and balance He.

	r _{total} (μmol _{CH₃OH} /g _{cat} -h)	r _{CH₃OH} (μmol _{CH₃OH} /g _{cat} -h)
CH ₄ /H ₂ O	1.13±0.07	1.13±0.07
CH ₄ /H ₂ O/O ₂	6.82±0.46	1.65±0.04

Table S3. The specific activity results for the data shown in Figure S6 and S8.