Supporting Information

Catalytic Conversion of Methane to Methanol on Cu-SSZ-13 using N_2O as Oxidant

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S.1. Experimental Details

S.1.1. Catalyst preparation

SSZ-13 (Si/Al = 12) was synthesized using a protocol reported elsewhere.¹ The synthesis gel containing 0.681 g aluminum triethoxide (Alfa Aesar, 100%), 2.264 g de-ionized water and 24.864 g *N*,*N*,*N*-trimethyl-1-adamantanamonium hydroxide solution (Sachem Inc., TMAdaOH, 25 wt%) was stirred at 40 °C for 30 minutes to dissolve all of aluminum ethoxide and after cooling to 25 °C, 12.504 g of tetraethyl orthosilicate (Aldrich, 98 wt%) was added to the solution (to obtain a final gel composition of 1 SiO₂: 0.035 Al₂O₃: 0.5 TMAdaOH: 20 H₂O) and stirred for 1 h. The clear solution was then transferred to a 43 mL Teflon-lined autoclave (Parr) and heated at 150 °C statically for 6 days (under autogenous pressure). Hydrothermally produced crystals were centrifuged with 4000 rpm for 6 minutes, washed three times with de-ionized water (200 mL per gram of zeolite) and dried at 80 °C for 3 h (in air, Fisher Scientific Isotemp Lab Oven). The as-made product was calcined in a 22 mm ID quartz tube with a 20 mm quartz frit (Chemglass, medium) with 80 cm³ min⁻¹ air (Keen Gas, total hydrocarbon < 0.1 ppm) flow in a Thermo Scientific Lindberg Blue M furnace. Temperature was maintained at 120 °C (with 5 °C min⁻¹ heating rate) for 2 h to dehydrate the zeolite and at 580 °C (with 5 °C min⁻¹ heating rate) for 2 h to dehydrate the zeolite and at 580 °C (with 5 °C min⁻¹ heating rate) for 6 h to calcine the structure directing agent. The resulting zeolite is H-SSZ-13/12.



Scheme S1. Schematic view of SSZ-13 (CHA). Red represents oxygen atoms and yellow represents Si or Al atoms.

Na-mordenite (Si/Al = 5) was purchased from Tricat (TZM 1011). 5 g of Na-mordenite was ion exchanged in 500 mL of 0.2 M NH₄NO₃ (Sigma-Aldrich, >99%) aqueous solution at 80 °C for 3 h with rigorous stirring. This ion exchange process was repeated three times to ensure complete ion exchange to NH₄-form. After each exchange, the zeolite was vacuum filtered, washed with de-ionized water (200 mL for 1 g zeolite) and dried at 80 °C for 3 h.

NH₄-ZSM-5 (Si/Al = 11.5) was purchased from Zeolyst (CBV 2314). NH₄-form of ZSM-5 and mordenite were dehydrated at 120 °C (with 5 °C min⁻¹ heating rate) for 2 h and calcined at 560 °C (with 5 °C min⁻¹ heating rate) for 8 h with 80 cm³ min⁻¹ air flow to obtain H⁺-form of the zeolites before performing Cu(II) exchange. Copper (II) ion-exchange was performed by exchanging H- or Na-form of the zeolites in copper (II) acetate (Aldrich, 98% purity) aqueous solution at 25 °C for 12 h. The amount of copper (II) acetate in the solutions varied depending on the mass of the zeolite and targeted Cu/Al ratio (Table S1). Cu-SSZ-13 has been exchanged twice with calculated moles of Cu(II) in the solution to give Cu(II)/Al = 0.5 and 0.25, for the first and second exchange respectively. Cu-ZSM-5 was exchanged only once with starting Cu(II)/Al ration of 1 in the solution. H-Cumordenite was exchanged three times with given starting Cu(II) amounts in the solutions (Table S1). Na-Cu-mordenite sample was exchanged from the Na-form. Na-mordenite (Si/Al = 5, Tricat TZM 1011) was exchanged twice with Na⁺ in 1 M NaNO₃ solution at 80 °C for 2 h before the Cu(II) exchange. After stirring the zeolites in Cu(II) acetate solutions for 12 h, the zeolites were separated by vacuum filtration and a sample from the filtrate was kept for UV–vis spectroscopy. The zeolites were then calcined at 550 °C (using a heating rate of 5 °C min⁻¹) for 4 h to remove any residual acetate.

Zeolite (Si/Al)	Volume of solution / mL	Mass of zeolite / g	Cu/Al in the solution (for each exchange)	Mass of copper (II) acetate / g	Number of times exchanged	Resulting Cu/Al from UV–vis
H-SSZ-13 (12)	500	15.00	0.5/0.25	1.78	2	0.41
H-SSZ-13 (12)	50	0.9	0.2	0.06	1	0.13
H-ZSM-5 (11.5)	250	3.1	1	0.76	1	0.44
H-mordenite (5)	250	3	1/1/0.5	1.54	3	0.30
Na-mordenite (5)	200	4.5	0.5/0.5	0.60	2	0.33

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

S.1.2 Analytical Methods

The samples were analyzed by X-ray diffraction using a Bruker D8 powder diffractometer with a Cu K α source ($\lambda = 1.5418$ Å) over the range of $2\theta = 5.0-50.0^{\circ}$ with a step size of 0.02° and scan rate of 2 s per step.

The elemental composition of samples was determined by measuring the initial and remaining Cu(II) acetate concentration in the exchange solution using UV–vis spectroscopy (JASCO, V-5500) over a range between 200 nm and 900 nm. The concentration of Cu(II) acetate remaining in the solution was calculated using a calibration curve (Eq. S1):

$$Concentration (M) = \frac{Absorbance + 0.0384}{26.759}$$

which was obtained from the collected absorption intensities for the d \leftarrow d transition of Cu(II) ion at 776 nm for prepared Cu(II) acetate solutions with concentrations between 0.001 M and 0.02 M. The elemental composition was also checked using X-ray fluorescence obtained by a Rigaku

(S1)

WDXRF at 50 kV and using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) technique in Galbraith Laboratories, Knoxville, Tennessee.

The elemental analysis of the Cu(II) exchanged samples are given in Table S2. Similar Cu/Al ratios on Cu exchanged samples resulted in approximately double Cu concentration on Cu-mordenite (0.83 mmol Cu g^{-1}) when compared to Cu-SSZ-13 and Cu-ZSM-5. Cu(II)-exchanged samples show high crystallinity with no additional phases (Figure S1).

	Nominal	Cu/Al	Si/Al	Cu/Al from	Cu/Al from	Cu
Zeolite	Si/Al	from	from	XRF	ICP	concentration
		UV-vis	XRF			/ mmol Cu g ⁻¹
H-Cu-SSZ-13	12	0.40			0.4	0.50
H-Cu-SSZ-13	12	0.13			0.18	0.22
H-Cu-ZSM-5	11.5	0.44	10.3	0.38		0.54
H-Cu-mordenite	5	0.30	6.3	0.07	0.08	0.17
Na-Cu-mordenite	5	0.33	5.3	0.33		0.83

 Table S2:
 Elemental analysis of copper(II)acetate exchanged samples



Figure S1: Powder XRD pattern of Cu-SSZ-13 (Si/Al = 12), Cu-ZSM-5 (Si/Al = 11.5), Cumordenite (Si/Al = 5), Cu K α , λ = 1.5418 Å

S.1.3. Methane Conversion Experiments

S.1.3.1. Equipment

The hydrated samples (0.300 ±0.005 g and particle size between $250 - 425\mu$ m) were tested for CH₃OH formation using a reactor system described elsewhere (ID = 7 mm).² The catalyst bed length was approximately 1 cm. CH₃OH was analyzed using a gas chromatograph (GC) (Agilent 7890A) with a flame ionization detector and a HP-PLOT Q column (Agilent19091P-Q04, 30 m x 0.32 mm x 0.02 mm). CO and CO₂ were analyzed using a thermal conductivity detector of Agilent 7890A with a HayeSep Q column (Agilent G3591-81121, 12 ft 1/8" 2 mm). The temperature of the oven was set to 140 °C (inlet port was set to 200 °C and the detector temperatures were set to 250 °C) and valve injections of 1 mL volume were taken every 10 minutes with a split ratio of 15:1. The effluent stream was also monitored on-line with a mass spectrometer (Pfeiffer OmniStar GSD 320). Quantification of produced CO for reactions involving O₂ was performed using the calibration of m/z = 28 signal for CO since the CO and O₂ peaks overlapped in TCD chromatograms. Due to the overlapping of the CO and N₂ peaks in TCD chromatograms, we estimate a 10% deviation in the CO production rates.

For the cyclic process experiments, a different GC (Agilent 6890) with a flame ionization detector and Supel-Q PLOT column (Supelco, 30 m x 0.32 mm) was used for CH₃OH quantification. The temperature of the GC oven was held constant at 80 °C and valve injections of 1 mL were taken every 3 minutes.

S.1.3.2. Calibrations

CH₃OH and HCHO calibration peak areas were obtained on a gas chromatograph (GC) (Agilent 7890A) with flame ionization detector and a HP-PLOT Q column (Agilent19091P-Q04, 30 m x 0.32 mm x 0.02 mm) at 140 °C keeping the method the same. CH₃OH/toluene (or HCHO/toluene) solutions of 525 to 2100 ppm CH₃OH (or 54 to 438 ppm HCHO) were prepared by adding 2, 4, and 8 μ l of CH₃OH (or 0.5, 1, 2 and 4 μ l 38% HCHO solution, Sigma Aldrich) in 10 mL of toluene. Then, 1 μ l of the solution was injected manually at the injection port of the GC with a splitting ratio of 15:1. The calibration curve for the CH₃OH response factor (in ppm area⁻¹ units) was obtained from least square fitting of the data in Figure S2.

Table S3:	The concentration of CH ₃ OHand HCHO in 10 mL toluene solutions and
	corresponding peak areas obtained at 1.87 min residence time (1.815 min for
	HCHO) using HP-PLOT Q column

CH ₃ OH concentration /	Peak area	HCHO concentration	Peak area
525.3	127.3	54.8	7.4
1050.7	298.9	109.6	13.7
2101.3	568.1	219.2	37.3
		438.5	80.1



Figure S2: The concentration of CH₃OH and HCHO in prepared toluene solutions versus observed CH₃OH and HCHO peak areas at 1.87 min (1.815 min for HCHO) residence time on HP-PLOT Q column at 140 °C

CO calibration peak areas were obtained on a gas chromatograph (GC) (Agilent 7890A) with a thermal conductivity detector and a HayeSep Q column (Agilent G3591-81121, 12 ft 1/8" 2 mm) at 140 °C keeping the method the same. The response factor for the CO peak (with

residence time = 2.243 min) was obtained using a single point calibration. An average area of 3370.5 was obtained for 24 cm³ min⁻¹ 5.15% CO (Matheson, 99.999%) flow in He. The corresponding response factor was 15.3 ppm area⁻¹.

 CO_2 calibration peak areas were obtained on a gas chromatograph (GC) (Agilent 7890A) with a thermal conductivity detector and a HayeSep Q column (Agilent G3591-81121, 12 ft 1/8" 2 mm) at 140 °C keeping the method the same. The response factor for the CO_2 peak (with residence time = 3.564 min) is obtained using three different concentrations of CO_2 in He (Table S3). The calibration curve can be seen in Figure S3.

Table S4:	The concentration of CO_2 and	l corresponding peal	k areas obtained	l at 3.564 min
	residence time using HayeSep	OQ column		

CO ₂ Concentration	Peak area
/ ppm	
50000	2948.1
24600	1487.3
12705	747.4



Figure S3: The concentration of CO₂ in He versus observed CO₂ peak areas at 3.564 min residence time on HayeSep Q column at 140 °C

CO (m/z = 28) ion currents on a mass spectrometer (Pfeiffer OmniStar GSD 320) were calibrated using 18.8 cm³ min⁻¹ 2.4% and 3.7% CO (Matheson, 99.999%) flow in He. The response factor was found to be 24368.98 mol min⁻¹ ion current⁻¹ for 120 cm³ min⁻¹ flow (Figure S4). The difference in m/z = 28 ion current during reaction was used to calculate CO production rate in mol min⁻¹ using this response factor.



Figure S4: The molar flow rate of CO assuming 120 cm³ min⁻¹ mixture (CO and He) flow versus Ion Current (m/z = 28) of Pfeiffer OmniStar GSD 320 mass spectrometer.

S.1.3.3. 3-Step Cyclic Procedure

Hydrated H-Cu-SSZ-13 (Cu/Al = 0.4) (0.300 ± 0.005 g and particle size between 250 – 425µm) was first activated in 50 cm³ min⁻¹ O₂ (Keen Gas, 99.997% purity) flow or 5 cm³ min⁻¹ N₂O (Keen Gas, medical purity) and 50 cm³ min⁻¹ He flow at 200, 300 or 450 °C for 2 h using a heating rate of 5 °C min⁻¹. After cooling the sample to 200 °C (cooling rate of 5 °C min⁻¹) under continuing treatment gas flow, the flow was switched to 35 cm³ min⁻¹ CH₄ (Matheson, 99.99%), while the temperature was kept at 200 °C for 1 h. After 1 h, the flow was switched to 50 cm³ min⁻¹ He flow, which was diverted through a water-containing saturator kept at 25 °C, while keeping the temperature of the sample at 200 °C. Extracted CH₃OH was then analyzed with a GC as explained above. The standard deviations reported in Table 1 were obtained by repeating above mentioned experiments twice.

S.1.3.4. Catalytic Procedure

Hydrated Cu- zeolites (0.300 \pm 0.005 g and particle size between 250– 425µm) were saturated at 20 °C by 120 cm³ min⁻¹ CH₄/N₂O/He/H₂O flow with designated compositions for 15 min. The feed mixture containing CH₄/N₂O/He was diverted through a water-containing saturator kept at 25 °C unless stated otherwise. Temperature of the samples was increased to reaction temperatures with a heating rate of 5 °C min⁻¹. The system was kept at the reaction temperature for 3 h as samples were analyzed each 10 minutes using GC.

For investigating the effect of H_2O , the water-containing saturator was placed in a water bath thermostat (LAUDA Alpha RA 8) where temperature of the bath was controlled at 60 °C (to obtain a H_2O pressure of 19.9 kPa).

The experiments to investigate the effect of partial pressures on the CH_4 oxidation rates were conducting by changing the partial pressure of the intended gas (CH_4 or N_2O) and the inert (He) in order to keep the flow rate constant (120 cm³ min⁻¹). CH_4 oxidation rate was calculated by adding all the product formation rates together since CH_4 had a significantly larger partial pressure than the products.

The selectivity for CH₃OH, CO or CO₂ was calculated using:

Selectivity of $i(\%) = \frac{i \text{ formation rate } (\mu \text{mol i } g^{-1}h^{-1})}{Total \text{ product formation rate}}$ where total product formation rate is calculated by:

Total product formation rate
=
$$\mu mol CH_3 OH g^{-1}h^{-1} + \mu mol HCHO g^{-1}h^{-1} + \mu mol CO g^{-1}h^{-1} + \mu mol CO_2 g^{-1}h^{-1}$$

CH₄ conversion was calculated by dividing the molar flow rate of carbon products to the initial molar flow rate of CH₄:

Conversion of
$$CH_4(\%) = \frac{\sum_{i=1}^{n} F_i}{F_{CH4,0}}$$

where F_i is the molar flow rate of the product i (since all products have 1 C atom, we did not multiply the molar flow rates with number of carbon atoms), and $F_{CH4,0}$ is the initial molar flow rate of CH₄ (0.095 mol CH₄ h⁻¹ for 30.4 kPa CH₄).

Turnover frequency was calculated by dividing the sum of the specific activities (mol i g⁻¹ h⁻¹) to the Cu concentration (mol Cu g⁻¹, given in Table S2).

The complete results are given in Table S6. The standard deviations in Table S6 and Table S7 were calculated using the GC sample results taken each 10 minutes in a single experiment. Even though the hydration level of the samples resulted in changes in specific activity, CH_4 oxidation results were found to be reproducible even after calcining the spent catalysis at 550 °C for 2 h using pure O₂ (heating rate of 5 °C min⁻¹) and consecutively hydrating at 25 °C:

Table S5:	Catalytic data for reproducibility of CH_4 oxidation on H-Cu-SSZ-13 (Si/Al = 1)	12,
	Cu/Al = 0.4) at 270 °C*	

Reaction No	CH₃OH rate / µmol CH ₃ OH g ⁻¹ h ⁻¹	CO rate / µmol CO g ⁻¹ h ⁻	CO₂ rate / μmol CO ₂ g ⁻¹ h ⁻¹	CH ₃ OH Selectivity/ %	CH ₄ Conversion / %
1	28±1	124±12	22±3	15.8	0.055
2	26±1	129±20	14±6	15.1	0.053
3	31±2	109±11	26±3	18.8	0.052

* 0.300 ± 0.005 g catalyst weight; feed 30% CH₄, 30% N₂O, 3% H₂O balance helium (30.4 kPa CH₄, 30.4 kPa N₂O, 3.2 kPa H₂O, 37.3 kPa He); flow rate: 120 cm³ min⁻¹, WHSV = 19,650 g_{feed} g_{cat}⁻¹ h⁻¹

S.1.4. Diffuse Reflectance UV-vis Spectroscopy

S.1.4.1. Equipment

Diffuse reflectance UV–vis spectra were collected using a UV–vis spectrometer (JASCO, V-5500) equipped with an integrating sphere (JASCO ISV-469) as explained elsewhere.² The hydrated samples (approximately 100 mg) were placed inside a quartz glass U-tube (inside diameter of 4 mm) with quartz square tube addition (1 cm length) where the sample was aligned using quartz wool to obtain a flat reflection surface. The quartz tube was then wrapped with a heating tape and insulation with a K-type thermocouple inserted in between the quartz tube and heating tape next to the sample. A temperature controller (Watlow, Series 965) was used to control the temperature. The quartz tube was connected to gas flow lines for pretreatment of the samples. Spectra were taken at 25 °C, following the cooling of the sample, with continuing gas flow. The flow rates were controlled using Brooks 5850e Series mass flow controllers and 0154E control box.

S.1.4.2. Procedures

Baseline for the UV–vis spectra was obtained using barium sulfate (Sigma) packed inside the same quartz tube. UV–vis spectra were collected following O₂ or N₂O/He pretreatments at 270 °C. The hydrated samples (exposed to air) were heated to 270 °C with a heating rate of 5 °C min⁻¹ and kept at that temperature for 2 h under 20 cm³ min⁻¹ O₂ or 20 cm³ min⁻¹ 30% N₂O (balance He) flow. The samples were then cooled to 25 °C under continuing flow and a spectrum was taken at 25 °C.

S.2. Mass Spectrum of N_2O Decomposition on Cu-SSZ-13 as a Function of Temperature



Figure S5: Mass spectrometer ion current versus time upon 10% N₂O treatment of H-Cu-SSZ-13 (Cu/Al = 0.4) with a heating rate of 5 °C min⁻¹. Note the sudden decrease in N₂O concentration and relative increase in O₂ and N₂ concentrations for temperatures higher than 350 °C indicating catalytic decomposition of N₂O into N₂ and O₂.

S.3. Steady State CH₃OH Formation on Cu-SSZ-13



Figure S6: Steady state concentration of CH₃OH in the exit stream at 270 °C. Feed: 30% CH₄, 30% N₂O, 3% H₂O balance helium; flow rate 120 cm³ min⁻¹, WHSV = 19,650 g_{feed} g_{cat}^{-1} h⁻¹

Sample	Reaction Temperature / °C	Catalyst weight (hydrated) / mg	Cu Conc. / mmol	CH ₃ OH rate / μmol CH ₃ OH	HCHO rate / µmol HCHO	CO rate / µmol CO g ⁻¹ h ⁻¹	CO ₂ rate / µmol CO ₂ g ⁻	CH ₃ OH Selectivity ^[d] / %	HCHO Selectivity/ %	CO Selectivity /%	CO ₂ Selectivity / %	TOF ^[e] / h ⁻¹	CH ₄ Conversion / %
				g ⁻¹ h ⁻¹	g-1 h-1		' h''						
H-Cu-SSZ-13	250	298	0.50	12±1		34±9	4±2.22	24		68	8	0.10	0.016
H-Cu-SSZ-13	260	299	0.50	19±1		42±12	8±3.8	27		61	12	0.14	0.022
H-Cu-SSZ-13	265	300	0.50	21±5	0.5 ± 0.1	66±13	15±5.3	20.7	0.5	64.1	14.7	0.21	0.032
H-Cu-SSZ-13	270	299	0.50	28±1	0.8 ± 0.1	124±12	22±3	15.8	0.4	71.2	12.6	0.35	0.055
H-Cu-SSZ-13	275	300	0.50	34±1	1.1 ± 0.1	208±12	54±4	11.4	0.4	70	18.2	0.60	0.094
H-Cu-SSZ-13	300	301	0.50	55±1	2.1±0.1	1794±52	527±20	2.3	0.1	75.4	22.2	4.80	0.75
H-Cu-SSZ-13	300 ^[b]	300	0.50	49±3	0.5 ± 0.1	262±35	83±14	12.5	0.1	66.7	20.7	0.79	0.12
H-Cu-SSZ-13	270 ^[c]	299	0.50	12±3		49	370±27	3		11	86	0.87	0.13
H-Cu-SSZ-13	300 ^[c]	301	0.50	9±1		55	311±17	2		15	83	0.76	0.12
H-Cu-SSZ-13	270	254	0.22	33±1	0.9±0.1	41±8	8±2	39.7	1.1	49.7	9.5	0.36	0.022
H-Cu- mordenite	270	301	0.17	10±3		28±4	3±2	24		70	7	0.26	0.013
Na-Cu- mordenite	270	300	0.83	2±0.1		152±46	46±14	1.1		75.8	23.1	0.24	0.063
H-Cu-ZSM-5	270	300	0.54	6±1		1632±310	503±96	0.3		76.2	23.5	3.80	0.67

Table S6: Catalytic data for CH₄ oxidation (data complementary to Table 2)^a

[a] Standard reaction conditions: feed 30% CH₄, 30% N₂O, 3% H₂O balance helium (30.4 kPa CH₄, 30.4 kPa N₂O, 3.2 kPa H₂O, 37.3 kPa He); flow rate: 120 cm³ min⁻¹, WHSV = 19,650 g_{feed} g_{cat⁻¹} h⁻¹ [b] Same conditions with [a] except 20% H₂O instead of 3% H₂O [c] Same conditions with [a], 30% O₂ instead of 30% N₂O [d] CH₃OH selectivity calculated as moles (CH₃OH)/ moles (produced) *100 [e] Moles of total oxidation products moles of Cu⁻¹ h⁻¹

H-SSZ-13 was also tested for CH₃OH formation at standard reaction conditions: 270 °C, feed 30% CH₄, 30% N₂O, 3% H₂O balance helium (30.4 kPa CH₄, 30.4 kPa N₂O, 3.2 kPa H₂O, 37.3 kPa He). The CH₃OH formation rate of 2 µmol g_{cat}^{-1} h⁻¹ was significantly smaller than that obtained on Cu-SSZ-13 at the same conditions (28 µmol CH₃OH g_{cat}^{-1} h⁻¹).

S.4. CH₄ and N₂O Reaction Order

Table S7: Effect of CH₄ and N₂O partial pressure on CH₄ conversion (TOF: mol CH₄ converted mol Cu⁻¹ h⁻¹) and CH₃OH production rates at 270 °C on Cu-SSZ-13 (Cu concentration: 0.50 mmol Cu g⁻¹, 20.3 –50.7 kPa CH₄, 30.4 kPa N₂O, 3.2 kPa H₂O, balance He for the first part, 30.4 kPa CH₄, 3 – 30.4 kPa N₂O, 3.2 kPa H₂O, balance He for the second part)

CH₄ Partial Pressure / kPa	CH ₃ OH rate / μmol CH ₃ OH g ⁻¹ h ⁻¹	HCHO rate / μmol HCHO g ⁻¹ h ⁻¹	CO rate / µmol CO g ⁻¹ h ⁻¹	CO2 rate / µmol CO2 g ⁻¹ h ⁻¹	CH3OH Selectivity/ %	HCHO Selectivity/ %	CO Selectivity / %	CO ₂ Selectivity / %	TOF / h ⁻¹	CH4 Conversion / %
20.3	17+1		125±3	34±4	9.4		71	19.6	0.353	0.076
30.4	28±1	0.8 ± 0.1	124±12	22±3	15.8	0.4	71.2	12.5	0.35	0.055
40.5	34+1	1.2 ± 0.1	109±11	22.4±5	20.3	0.8	65.5	13.4	0.335	0.039
50.7	57+1	3.2±0.2	537±18	62±7	9	0.5	81.1	9.4	1.32	0.120
N2O Partial Pressure / kPa	CH ₃ OH rate / μmol CH ₃ OH g ⁻¹ h ⁻¹	HCHO rate / μmol HCHO g ⁻¹ h ⁻¹	CO rate / µmol CO g ⁻¹ h ⁻¹	CO2 rate / µmol CO2 g ⁻¹ h ⁻¹	CH3OH Selectivity/ %	HCHO Selectivity/ %	CO Selectivity /%	CO ₂ Selectivity / %	TOF / h ⁻¹	CH ₄ Conversion / %
3.0	27±1		50±10	26±4	26.2		48.2	25.6	0.208	0.033
10.1	27±0.5		87±14	29±5	18.7		60.7	20.6	0.288	0.044
20.3	32±1		128±10	35±5	16.6		65.4	18	0.393	0.063
30.4	28±1	0.8±0.1	124±12	22±3	15.8	0.4	71.2	12.5	0.35	0.055

The constant TOF with increasing CH₃OH rates and decreasing CO and CO₂ rates for the pressure range of 20.2 kPa to 40.5 kPa suggests limited formation of active sites. At 50.7 kPa, however, we observe significant increase in CO and CO₂ formation rates, which could indicate a change in CH₄ conversion mechanism (probably due to insufficient H₂O pressure), which could involve an additional CH₄ oxidation route directly into CO and CO₂.

Decreasing CH_3OH selectivity and increased CH_4 conversion with increasing N_2O pressure indicates a larger rate order of N_2O on CH_3OH decomposition than on CH_3OH formation.



Figure S7: log-log plot of CH₄ oxidation rate (TOF: mol produced mol Cu⁻¹ h⁻¹) versus partial pressure of CH₄ (between 20.3 kPa and 40.5 kPa) at 270 °C on Cu-SSZ-13 (feed gas composition: 20–40% CH₄, 30% N₂O, 3% H₂O, balance He; flow rate: 120 cm³ min⁻¹)



Figure S8: log-log plot of CH₃OH formation rate (specific activity) versus partial pressure of CH₄ (between 20.3 kPa and 40.5 kPa) at 270 °C on Cu-SSZ-13 (feed gas composition: 20– 40% CH₄, 30% N₂O, 3% H₂O, balance He; flow rate: 120 cm³ min⁻¹)



Figure S9: log-log plot of CH₄ oxidation rate (TOF: mol produced mol Cu⁻¹ h⁻¹) versus partial pressure of N₂O (between 3 kPa and 30.4 kPa) at 270 °C on Cu-SSZ-13 (feed gas composition: 30% CH₄, 3– 30% N₂O, 3% H₂O, balance He; flow rate: 120 cm³ min⁻¹)

S.5. DR UV-vis spectra



Figure S10: Diffuse reflectance UV-vis spectra of Cu-SSZ-13 (Si/Al = 12, Cu/Al = 0.4) after O₂ or 30% N₂O/He treatment at 270 °C. The spectrum of hydrated Cu-SSZ-13 is provided for comparison.



Figure S11: Diffuse reflectance UV-vis spectra of Cu-SSZ-13 (Si/Al = 12, Cu/Al = 0.4), H-Cumordenite (Si/Al = 5) and Cu-ZSM-5 (Si/Al = 11.5) following 30% N₂O/He treatment at 270 °C. Before each spectrum was collected, the sample was cooled to room temperature with continuing N₂O/He flow. The feature at 28,500 cm⁻¹ is caused by a lamp switch in the spectrometer.

S.6. Activation Energy Calculation

Activation energy for CH₄ oxidation was calculated to be 142 kJ mol⁻¹ using Arrhenius plots of the CH₄ oxidation rate (μ mol _{CH4 converted} g_{zeolite}⁻¹ h⁻¹) at the temperature range of 250 – 270 °C (Figure S12). The feed gas mixture for these experiments was: 30% CH₄: 30% N₂O: 3% H₂O balance He



Figure S12: Arrhenius plot of CH₄ oxidation rate (μ mol _{CH4 converted} g_{zeolite}⁻¹ h⁻¹) of Cu-SSZ-13 (Si/Al = 12, Cu/Al = 0.4) at the temperature range of 250 –270 °C.

References:

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