Electronic Supporting Information for the manuscript entitled:

Catalytic conversion of methane to methanol over Cu-mordenite

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S1. Preparation of Cu-MOR:

The Cu-MOR catalyst was prepared by aqueous ion exchange of Na-MOR and Cu-acetate at room temperature. 35 g of Na-MOR (Si/Al = 11, ZeoChem) was stirred into a 0.01 M solution of $Cu(CH_3CO_2)_2.H_2O$ in deionised water (pH~5.8, V=2.73 L). After 24 hours, the suspension was vacuum filtered. The ion exchange/filtration procedure was repeated three times, each time with a fresh 0.01 M solution of $Cu(CH_3CO_2)_2.H_2O$. After the last filtration, the powder was washed with deionised water (1.5 L) and dried at 110ºC for 10 hours. The dried powder was pressed into pellets at 2 tons for 10 seconds, lightly ground, and sieved to 250-500μm size fraction. The material was calcined in situ before every reaction run.

S2. Characterization of Cu-MOR:

N_2 physisorption (BET) measurements were performed on a Micromeritics ASAP 2010 instrument. Around 100 mg of material was evacuated at 250ºC to less than 0.02 mbar prior to measurement to remove volatiles from the zeolite pores. The BET surface area was 386 m^2/g.

X-ray diffraction (XRD) measurements were done on a Bruker AXS diffractometer in Bragg-Brentano geometry with CuKα radiation. The samples were evenly pressed on the sample holder that rotated during measurement. Diffractograms were collected at a step size of 0.01 in 2θ. The diffractogram only showed peaks belonging to mordenite, suggesting the absence of Cu or copper oxide crystalline particles greater than 3 nm.

Transmission electron microscopy (TEM) measurements were made in bright and dark field contrasts using a Tecnai F30ST microscope. The material was thinly spread on a carbon foil supported on a copper grid. TEM showed the integrity of the zeolite channels and the absence of large Cu particles.

For Cu elemental analysis, Cu-MOR was dissolved in 5 mL of aqua regia (1:3 fresh mixture of concentrated HNO_3 and HCl) and 1 mL of HF followed by microwave heating at 160ºC for 20 minutes. The solution was quantitatively transferred to a sample vial and diluted to 40 mL with deionized water. The resulting solution was subsequently analyzed by ICP for Cu content, which was 4.3 wt%. This gave a calculated Cu/Al value of 0.38.

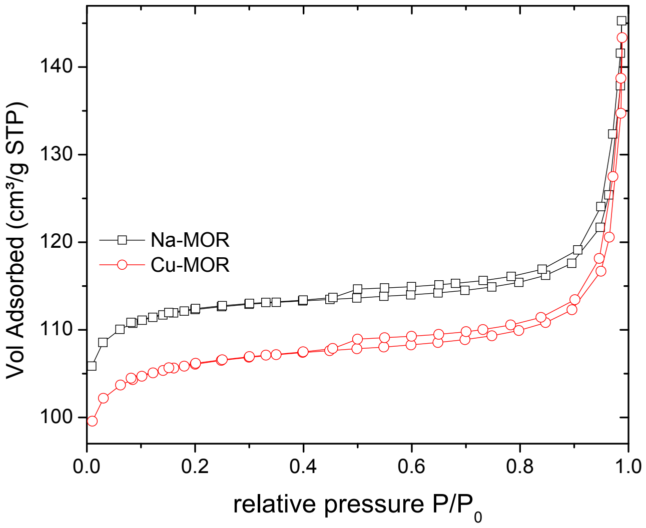

Fig. S2.1. N_2 physisorption isotherms before and after Cu ion exchange. BET surface areas were 410 m^2/g and 386 m^2/g respectively. The overall shapes of the isotherms are similar.

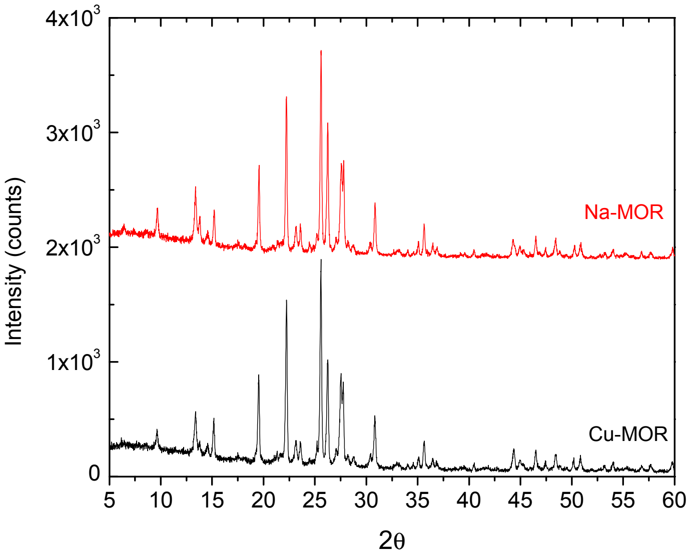

Fig. S2.2. XRD patterns of Na-MOR and ion-exchanged Cu-MOR. After ion-exchange and drying, no new peaks attributed to crystalline copper or copper oxide aggregates (<3nm) are present.

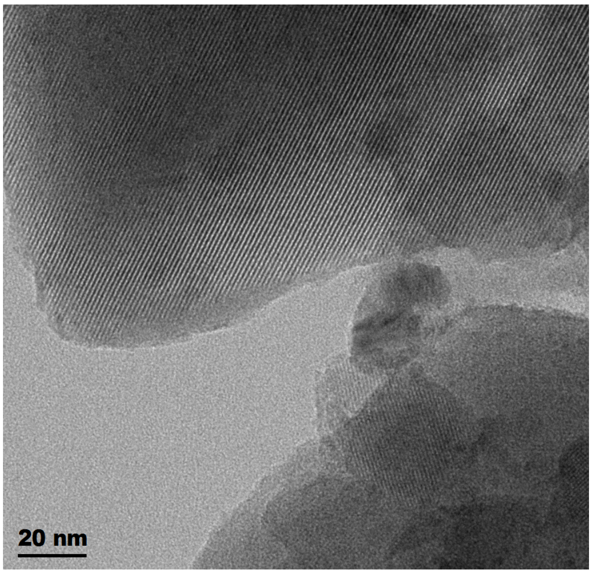

Fig. S2.3. TEM image of Cu-MOR after ion-exchange and drying. The intact zeolitic channels are visible.

S3. Catalytic Experiments

The catalyst (~0.7 g) was loaded in a quartz reactor (ID=8mm, OD=12mm) and mounted in an oven. Mass flow controlled feed gas goes through a gas mixing scheme shown in Fig. S3.1. The wet helium stream goes through a water bubbler at room temperature. A 4-port valve (V7) allows flow stabilization of the stream before the reactor with the desired gas flow before feeding to the reactor. All the gas lines are heated at 110ºC to prevent any condensation. The outlet of the reactor is able to switch between a quadrupole mass spectrometer (Pfeiffer) line and a cold trap line. The stream going into the cold trap line is collected by a 2 mL volumetric flask that is immersed in isopropanol cooled with liquid nitrogen. Olive lines connect the volumetric flask to incoming and outgoing streams.

Cu-MOR was heated at 1/min to 450ºC in a stream of 50 mL/min pure O_2 and calcined at this temperature for 4 hours. After cooling to 50ºC in the same flow of O_2 the excess gas phase O_2 was flushed with a 50 mL/min flow of He for 5 minutes. A 30 mL/min stream of 5% CH_4/He was introduced, and the material was heated at 10º/min until 200ºC. The methane stream was held for 20 minutes until which the stream was switched to 30 mL/min of wet (water-saturated flow at room temperature) helium for desorption and collection of the product in a 2 mL volumetric flask at -78ºC (iPrOH/LN_2) overnight.

The collected product was allowed to warm to room temperature, dosed with 2 μL of acetonitrile as internal standard and diluted with water until the 2 mL mark, and then analysed by GC.

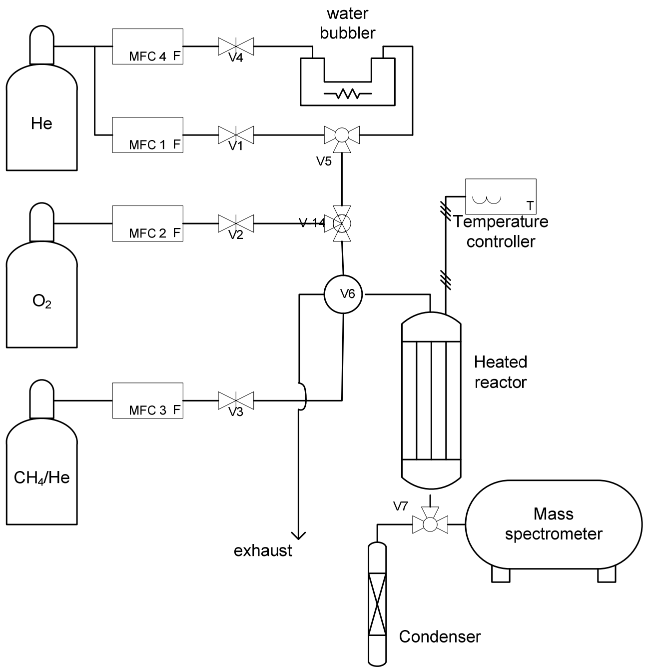

Fig. S3.1. Gas mixing scheme and reactor set-up for catalytic experiments.

S4. Extraction, trapping, and GC measurements

The total amount of methanol formed was quantified by extraction in water. After calcination and methane interaction at 200ºC, the methane flow was switched off, and the catalyst bed was cooled to room temperature. The reacted material was taken mixed with 3 mL of water in a screw-capped centrifuge vial, and stirred for 2 hours. Afterwards, the vial was placed in an ultrasonic bath for 30 minutes. The mixture was centrifuged and filtered. The resulting clear solution was transferred to a 2 mL volumetric flask and added with 2 μL acetonitrile as internal standard and subsequently analyzed with an Agilent 6890 GC (Restek column, 3m, ID=0.25mm) with FID detector. The oven was held for 10 minutes at 40ºC and subsequently heated by 20º/min to 200ºC.

The methanol that can be desorbed from the catalyst bed was trapped in a 2 mL cold volumetric flask as described in S3 and analyzed with GC.

S5. Carbon Analysis

The Cu-MOR samples, subjected to different stages of the reaction run, were analyzed for carbon with a LECO CHN-900 machine. Duplicates of around 2 mg of the material were used. The combustion product of the material (as CO_2) was quantitatively analyzed by infrared spectroscopy. The results were compared with acetylaniline as standard.

Table S5.1. Carbon analysis results of Cu-MOR from different stages in the reaction program.

Cu-MOR sample	Description	C content (%)	
		Trial 1	Trial 2
1. as-prepared	aqueous ion exchanged with copper acetate and dried at 110ºC	0.16	0.17
2. calcined	after Cu-exchange, dried at 110ºC, calcined at 450ºC for 4 hours in O_2, and cooled in O_2 to room temperature	0.07	0.08
3. CH_4-reacted	Calcined Cu-MOR reacted with 5% CH_4/He at 200ºC for 20 minutes, and cooled to room temperature	0.10	0.11
4. H_2O-flushed	Calcined Cu-MOR reacted with 5% CH_4/He at 200ºC for 20 minutes and reacted with a wet He stream for 6 hours to desorb MeOH.	0.07	0.07

The carbon content of the as-prepared Cu-MOR decreased from 0.16% to 0.07% with calcination. The carbon content gain of 0.03% during methane interaction was lost with several hours of interaction with the wet helium stream at 200ºC. This was shown to correspond to the observed MeOH signals in the mass spectrometer trace. A carbon content loss of 0.03±0.01% corresponds to 33 – 16 µmol of MeOH, which almost coincides with the 13 µmol of MeOH obtained during extraction with water at room temperature by GC analysis.

S6. Regenerability of Cu-MOR

The ability of the Cu-MOR material to be regenerated was demonstrated by performing two consecutive cycles of methanol production and desorption. Fig. S6.1 shows the schematics of the procedure employed.

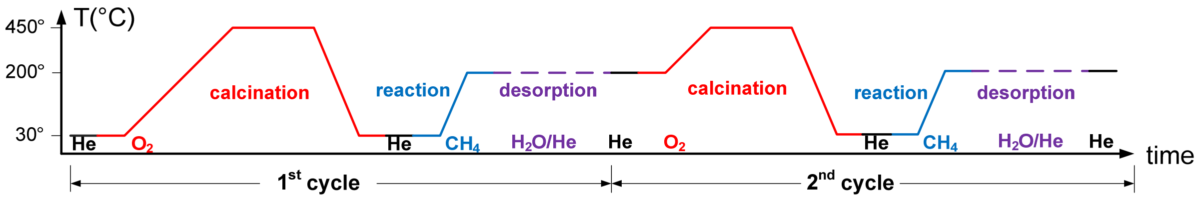

Fig. S6.1 Schematic diagram of the cycling process employed for Cu-MOR

For the 1st cycle, Cu-MOR was treated according to the procedure described in S3 with the product stream monitored by mass spectrometer. After 7 hours treatment with 30 mL/min of wet helium for methanol desorption, the feed was switched to dry helium for 1 hour at 200°C to remove excess water. The flow was switched to a stream of 50 mL/min O_2 for 1 hour at 200°C, and then the catalyst was heated by 1°/min to 450°C and calcined for 4 hours. The material was cooled to room temperature and the 2nd cycle of reaction with methane and treatment with wet helium at 200°C for methanol desorption was performed.

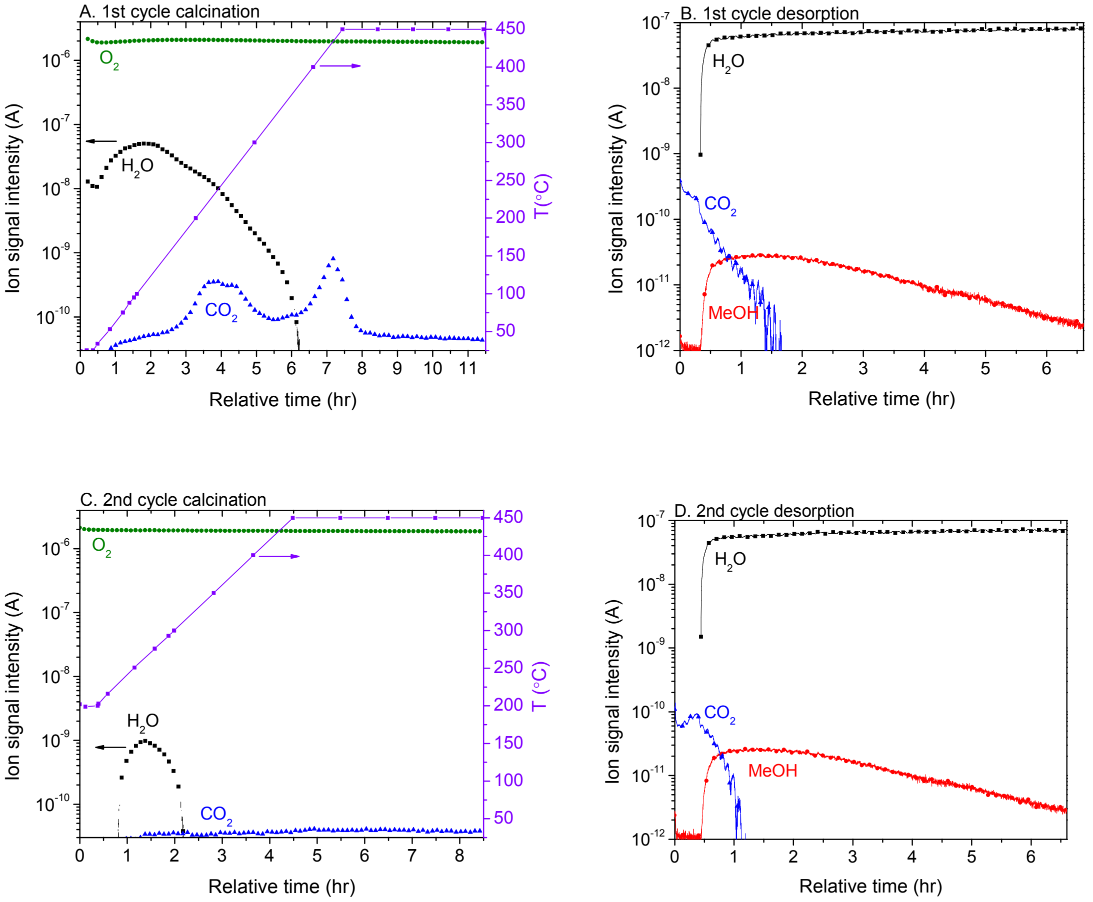

Fig. S6.2 Mass spectrometer-detected signals of O_2 (*m/z*=32), H_2O (*m/z*=18), CO_2 (*m/z*=44) and MeOH (*m/z*=31) during the 1st cycle of (A) calcination in O_2, (B) desorption by treatment of wet He at 200ºC after methane interaction, and 2nd cycle of similar (C) calcination and (D) desorption.

Calcination of Cu-MOR in the 1st cycle produced CO_2 (Fig. S6.2A), which is attributed to the combustion of organic substances that could have come from the copper acetate precursor used for the ion exchange. After calcination at 450°C, the Cu-MOR material is virtually free of carbon-containing residues. Reaction of the calcined material with methane at 200°C and subsequent treatment with wet helium allowed the observation of methanol in the product stream (Fig.S6.2B). The 2nd calcination (Fig. S6.2C) showed virtually no CO_2 desorbed during the heating to 450°C in oxygen, which means that the adsorbed material from the reaction with methane in the 1st cycle was removed during the treatment in wet helium, in the form of CO_2 and MeOH. Reaction with methane followed by desorption with wet helium in the 2nd cycle

(Fig. S6.2D) showed MeOH, similar to that in the 1st cycle. This demonstrates that Cu-MOR was successfully reactivated and is regenerable for cyclic/catalytic methanol production.

S7. UV-Vis measurements

Cu-MOR (30 mg, 250-500 μm) was loaded to a quartz reactor (OD=3mm, t=0.1mm), and positioned by quartz wool on both sides. It was heated by an external air blower. The temperature inside the catalyst bed was calibrated by an internal thermocouple. The quartz reactor was connected to the same gas feed equipment used as in S3.The material was always cooled to room temperature during spectra acquisition.The UV probe (reflection/backscattering, QR400-7-SR-125F, OD=3.18mm), connected by optical fiber to the spectrometer, was positioned at the center of the bed at 1mm from the surface for good signal to noise ratio. The entire set-up was covered by a black box to minimize stray light. UV-Vis spectra were recorded by a Maya 2000 Pro (Ocean Optics, Spectra Suite 2000) spectrometer at a scan rate of 200 ms per spectrum from 9000 cm^{-1} to 45000 cm^{-1}. 1000 scans were averaged to produce the spectra in Fig.3. A spectrum of Na-MOR was used as reference. Polynome baseline correction was performed on OPUS.

S8. XAS experiments

Cu K-edge experiments were performed at the SuperXAS beamline of the Swiss Light Source of the Paul Scherrer Institute, Villigen, Switzerland. Transmission EXAFS scans were performed with a Si-111 double crystal monochromator with the beam size approximately 100 μm horizontal by 115 μm vertical. An appropriate amount of sample to produce an absorption edge jump between 1 and 2 was mounted on a transmission reactor for in situ XAS measurements. Controlled gas flows were channeled to the reactor through the gas mixing scheme in S3 and the product gas was monitored by a mass spectrometer. A copper foil spectrum was collected for energy calibration (E_0=8979 eV). Standard data reduction and processing steps were performed by XDAP.

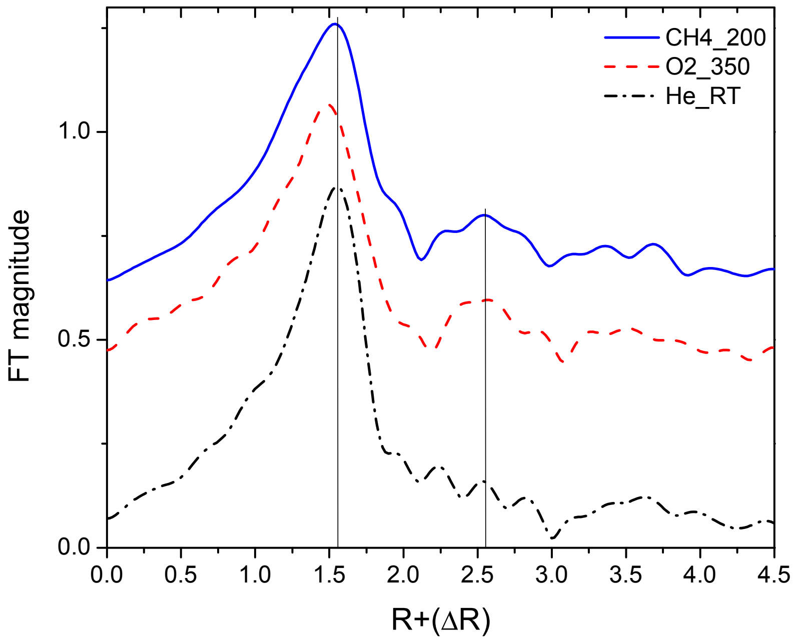

Fig. S8.1. Fourier transform of EXAFS spectra of Cu-MOR taken of the as-prepared catalyst in He at room temperature (— • —), during calcination in O_2 at 350ºC (— —), and during CH_4 interaction at 200ºC (—). The first coordination shell around 1.6 Å belongs to Cu-O scattering while the second coordination shell around 2.6 Å formed after calcination, which could be fitted as a Cu-Cu contribution.