

Materials and Methods

Zeolite synthesis

*MAZ-A*³²

A gel slurry was prepared with a molar composition of (SiO₂ : Al₂O₃ : Na₂O : TMACl : water = 15.2 : 1 : 7.1 : 1.4 : 460). Silicon source was Ludox AS-30. The slurry was transferred to a Teflon autoclave and placed in a rotational oven at 373K for 21 days.

*MAZ-B*³²

A gel slurry was prepared with a molar composition of (SiO₂ : Al₂O₃ : Na₂O : TMACl : water = 15.2 : 1 : 7.1 : 1.4 : 460). Silicon source was Ludox HS-30. The slurry was transferred to a Teflon autoclave and placed in a rotational oven at 373K for 21 days.

*GIS*⁵¹

A gel slurry was prepared with a molar composition of (SiO₂ : Al₂O₃ : Na₂O : water = 10 : 1 : 20 : 173). The slurry was transferred to a Teflon autoclave and placed in a rotational oven at 373K for 7 days.

*MER*⁵¹

A gel slurry was prepared with a molar composition of (SiO₂ : Al₂O₃ : K₂O : water = 10 : 1 : 20 : 1010). The slurry was transferred to a Teflon autoclave and placed in a rotational oven at 453K for 7 days.

*CHA*⁵²

A gel slurry was prepared with a molar composition of (SiO₂ : Al₂O₃ : K₂O : water = 12 : 1 : 5 : 405). Zeolyst CBV-712 was used as silicon and aluminum source. The slurry was transferred to a Teflon autoclave and placed in a rotational oven at 373K for 4 days.

*FER*⁵²

A gel slurry was prepared with a molar composition of (SiO₂ : Al₂O₃ : Na₂O : C₂DN : water = 15.2 : 1 : 1.85 : 19.7 : 592). Ethylenediamine was used as structure directing agent. The slurry was transferred to a Teflon autoclave and placed in a rotational oven at 373K for 14 days.

*LTA*⁵¹

A gel slurry was prepared with a molar composition of (SiO₂ : Al₂O₃ : Na₂O : water = 1.9 : 1 : 3.2 : 128). The slurry was transferred to a Teflon autoclave and placed in a rotational oven at 373K for 1 days.

OFF

A gel slurry was prepared with a molar composition of (SiO₂ : Al₂O₃ : K₂O : TMACl : water = 15.2 : 1 : 3.5 : 1.4 : 460). The slurry was transferred to a Teflon autoclave and placed in a rotational oven at 373K for 21 days.

For all synthesized zeolite, the contents of the autoclave were filtered, rinsed with ethanol and water, and then dried at 333K. The dried powder was then calcined at 823K for 8 hours with a ramp rate of 1°C/min.

MOR6.5 and MOR10

MOR6.5 is the commercially available under the product name CBV 10A from Zeolyst. MOR10 is the commercially available under the product name ZeoFlair 800 from ZeoChem.

Cation exchange

The same cation-exchange procedure was applied to all samples. The zeolite was stirred in 2M solution of ammonium nitrate for 24hr at room temperature. The sample was filtered, rinsed, and

dried. The zeolite was then cation-exchanged with 0.0025M of aqueous copper nitrate solution with 1 gram of material to 100ml of aqueous solution. Each sample was exchanged three times. Between each exchange, a new solution was prepared, and the sample filtered.

Powder X-ray diffraction

The purity of the synthesized zeolites was confirmed with a lab based PANalytical X'Pert Pro MPD instrument using Cu K α radiation. Data was recorded from 5 to 70 2 θ with a step size of .033 $^\circ$ and a scan speed of .028 $^\circ$ /s

Scanning electron microscopy

SEM images of the calcined sample were obtained with a Zeiss Gemini 1530 instrument that was operated at 5 kV.

Gas physisorption

Zeolite samples were pretreated by heating under vacuum to 250 $^\circ$ C overnight. The samples evaluated by nitrogen physisorption on Micromeritics Tristar II 3020 instrument

Elemental Analysis

Copper (Cu), aluminum (Al), and silicon (Si) content was determined using SpectraAA 220FS atomic absorption spectrometer. 10 mg of dried zeolite was digested in 2 ml of concentrated hydrofluoric acid and 3 ml of concentrated nitric acid overnight and then diluted to 50ml with deionized water. Copper, aluminum, and silicon calibration curves were prepared from standard solutions.

In-situ XAS Spectroscopy

XAS measurements were performed at both the Swiss Norwegian beamline (BM 31) and the Dutch-Belgian beamline (BM26A) at the European synchrotron radiation source. Data was collected using a Si (111) monochromator system and ionization chambers. All measurements were conducted in transmission geometry with a plug-flow mini reactor.

Prior to interacting with the sample, the gases were passed through purification columns. A moisture trap was used for the oxygen gas, and for the inert (Ar or He) and methane, a O₂/moisture trap was used. Gas flows were controlled by mass flow controllers (20ml/min), and the pressure was controlled by needle valve. Approximately 20 mg of Cu-MAZ was placed in a 2.0 mm diameter, thin-walled (0.01 mm) borosilicate capillary reactor. The reactor system was a modified version of a reactor described in Chupas et al.⁵³ A type K insulated thermos couple was inserted into the sample bed for temperature measurements. The isothermality of such cell has been validated through further investigated with the larger 2mm capillaries.⁵⁴

FTIR spectroscopy

IR spectra were collected by a Thermo Nicolet iS50 FTIR spectrometer with DTGS detector at a 4 cm⁻¹ optical resolution. 128 scans were collected per measurement. The sample (20 mg) was pressed into disc. For activation, the sample was first heated to 473K at a rate of 10K/min and then oxidized with 20ml/min oxygen at 473K for 1 hour. For reaction, 20ml/min of CH₄ was introduced into the cell and the cell was pressurized to 15 bar, and this pressure was controlled by a Bronkhorst EL-Press back-pressure regulator. The pressure was held constant for 30 minutes. Prior to measurement, methane pressure was released and purged with helium. Spectra difference were taken by subtracting the reacted sample from the activated sample using OMNIC 9.1 software package.

Methane to methanol reaction testing

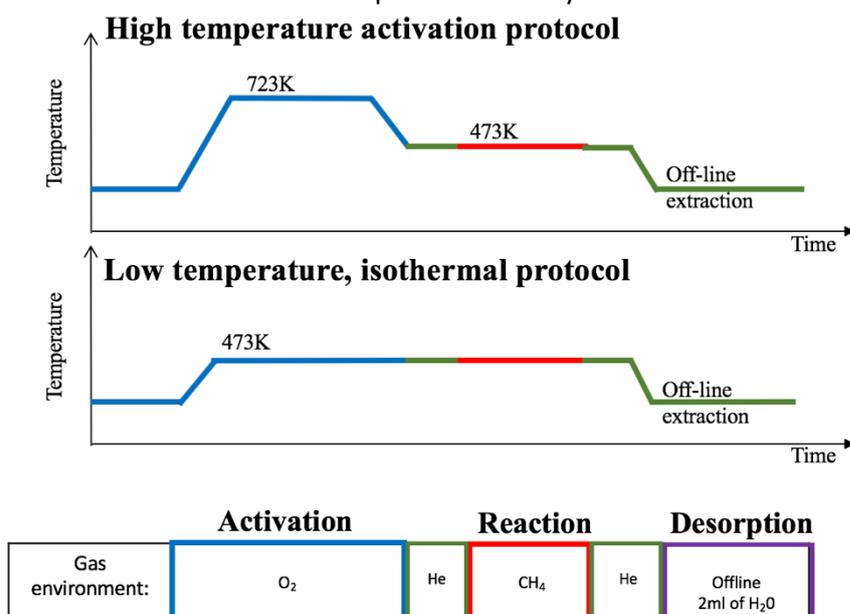
Zeolite samples were sieved to 150-250 μ m. Approximately 0.3 grams of samples were loaded into 60 -mL stainless steel autoclave (Premex Reactor Ag) batch reactor. The reactor equipped

thermocouples inside the reactor and in the jacket. Pressure was adjusted by two valves that control the incoming and outgoing gas.

Samples were heated at a ramp of 10°C/min in oxygen to 723K or 473K with a flow of 25mL/min. At the desired activation temperature, the sample was held for 1 hour at a slight overpressure (ca. 1.5 bar). For the high temperature activation procedure, the temperature was reduced to 473K in O₂ prior to purging. The reactor was purged for 15 minutes in pure helium with a flow of 25mL/min and increase of the reactor medium was observed (~5°C). Once temperature stabilized to 473K, pure methane was then introduced. For low pressure experiments, the flow was adjusted to 25ml/min with a slight over pressure (ca. 1.5 bar). For high pressure experiments, the pressure was adjusted between the incoming and outgoing valve to achieve the desired pressure, and then held under this pressure for 30 minutes at 473K. Pressure was released and the reactor was then cooled to room temperature under helium. Methanol quantification was conducted off-line.

Methanol Quantification

Methanol was extracted off-line by adding 2mL of MilliQ water to yield an aqueous suspension that was stirred for 30 minutes. The sample was then filtered, and analysis was performed on the filtered liquid with a gas chromatograph (Agilent 6890GC equipped with an FID detector). Butanol was added as an external standard after filtration but prior to GC analysis.

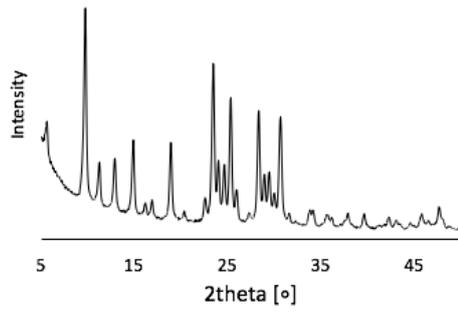


Schematic 1: Temperature and gas profile of the stepwise conversion of methane to methanol for the high temperature activation protocol and the low-temperature isothermal protocol.

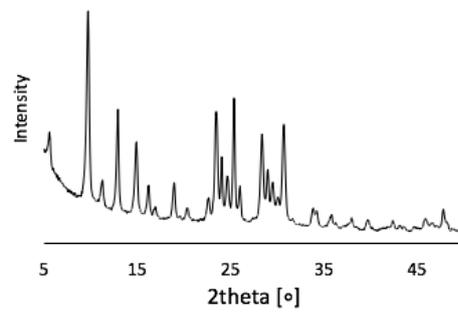
Copper (I) to methanol ratio

The Cu(I) molar amount was calculated for each sample by linear combination fitting by using their activated form and reduced form as standards (450°C in CH₄). Cu(I) formed per methanol was averaged over two separate in-situ Cu K-edge XAS experiments conducted at different beamlines (ESRF BM 31/SNBL and BM 25/DUBBLE).

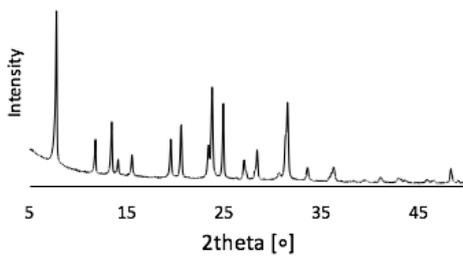
MAZ A



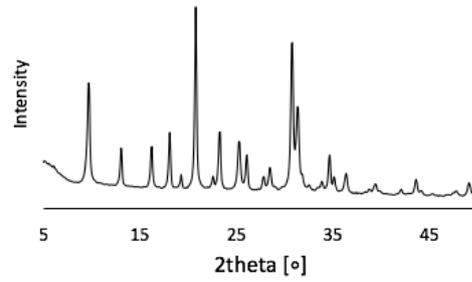
MAZ B



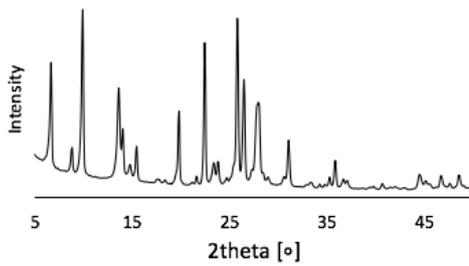
OFF



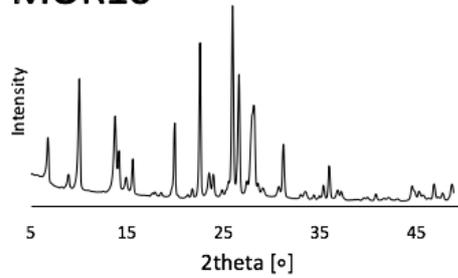
CHA



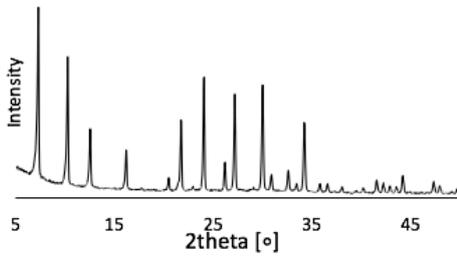
MOR6.5



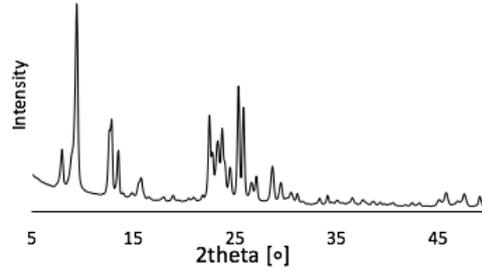
MOR10



LTA



FER



GIS

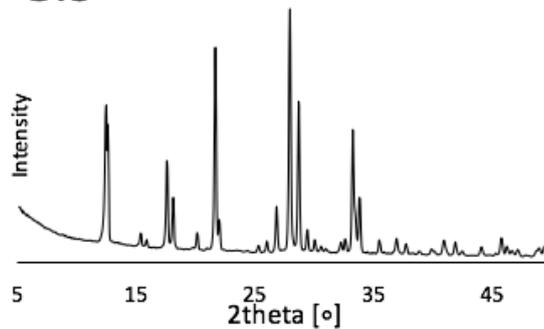


Figure S1: XRD Pattern of synthesized or purchased parent zeolite.

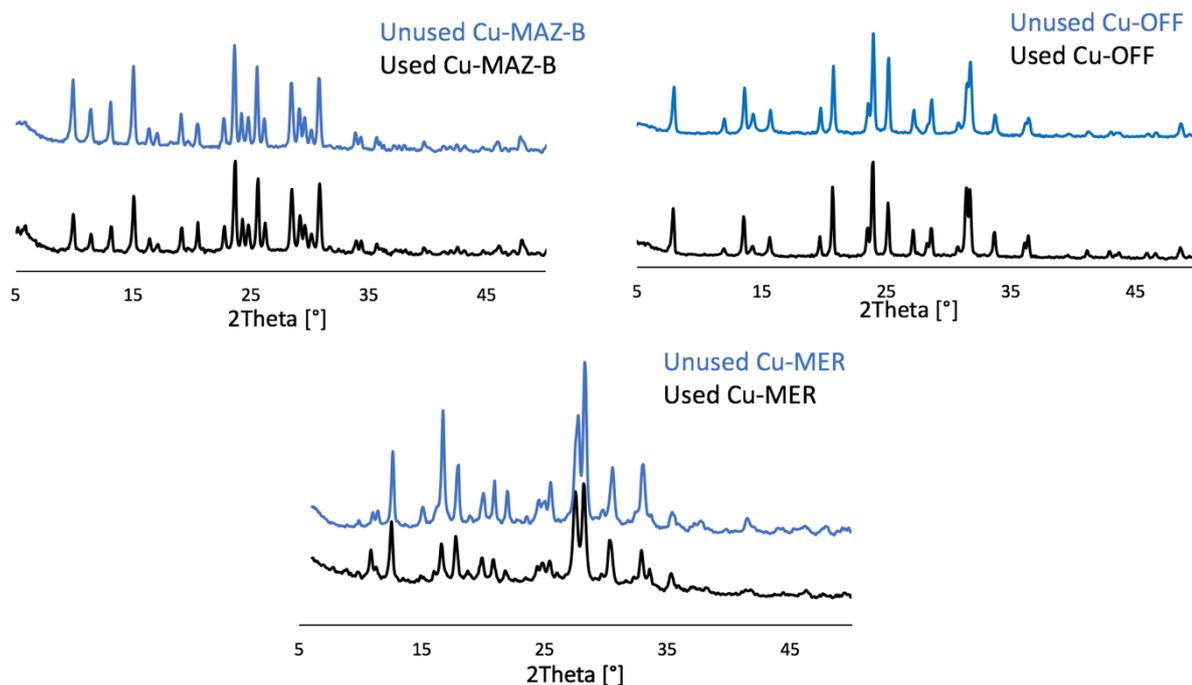


Figure S2: XRD Pattern of MER, OFF, and MAZ-B before and after isothermal reaction conditions (6 bar methane). The zeolite maintained its framework.

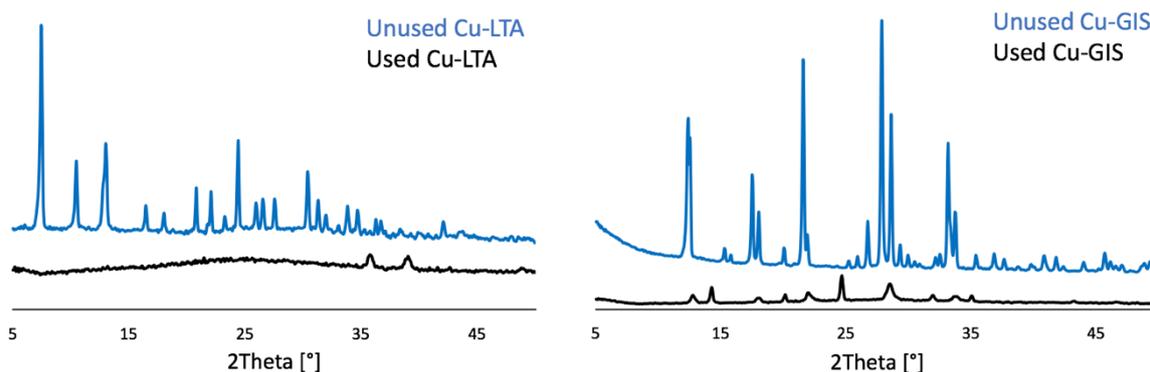


Figure S3: XRD pattern of Cu-LTA and Cu-GIS before and after isothermal conversion of methane (6 bar methane). Under isothermal conditions, the zeolite framework for LTA was not maintained. For GIS, the majority of the crystalline structure was altered with only a minority of the GIS framework maintained.

CHA,^{13,29} FER,^{16,17} MOR,^{11,12,14,15,16} and MAZ^{16,32} are known to maintain their zeolite framework during the stepwise conversion of methane to methanol; however, MER, GIS, OFF, and LTA have not been previously tested for this conversion. Figure S3 shows that MER, OFF, and the high performing MAZ maintains their framework for the isothermal conversion. However despite the low temperature, LTA completely loses its structure, and GIS loses a majority of the GIS structure with only trace amounts of GIS remaining. This explains the low performance of GIS and LTA. On the other hand, MER maintains its structure but no methanol was observed despite its high density of 8-membered rings, a feature hypothesized as beneficial for the conversion of methane to methanol. It has been

shown that different framework may be active at different reaction conditions,²⁸ possibly for MER these standard reaction conditions may not be optimal.

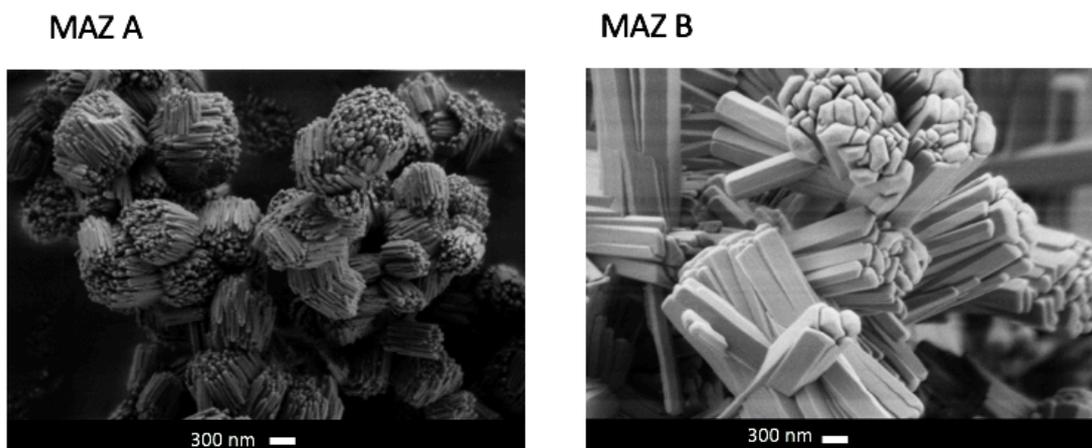


Figure S4: SEM micrographs of MAZ A and MAZ B showing the different morphologies that form due to different synthesis conditions.

Sample name	BET surface area number (m ² /g)	T-plot micropore volume (cm ³ /g)
GIS*	31	0.02
MER*	3.5	-
CHA	20.4	0.04
LTA*	7.0	-
FER	339	0.19
OFF	460	0.20
MOR6.5	366	0.16
MOR10	410	0.18
MAZ A*	137	0.06
MAZ- B*	136	0.04

* N₂ is unable to access the zeolite structure due to the small more opening of frameworks. The BET surface area number and micropore volume will be underestimated for this method.

Table 1S: BET surface area numbers and t-plot micropore volume from N₂ physisorption.

Many of the selected zeolite have 8-membered ring pore structures. Physisorption of N₂ gas typically underestimates the BET surface area number and micropore volume.

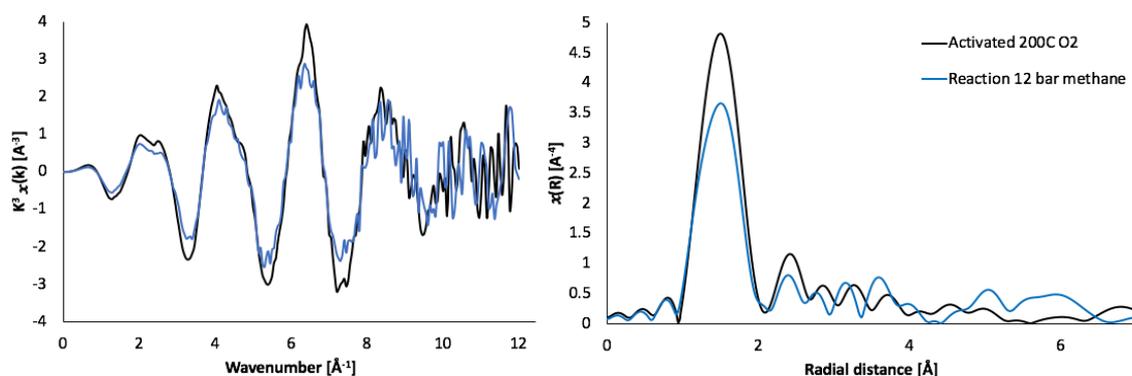


Figure S5: (Left) Cu K-edge EXAFS of activated MAZ-B at 200°C and then reacted at 12 bar methane. (Right) Fourier transforms (k-space 3-12 Å^{-1}) of activated and reacted (12 bar methane).

A sample of MAZ-B was monitored by in-situ XAS throughout the activation and reaction at elevated pressures. Figure S5 shows the EXAFS and its Fourier transform for the activated state and post-reaction (12 bar methane). There is an observable difference in the first shell coordination at 1.9 Å , which is expected as a portion of the copper (II) reduces to copper (I). The nuclearity of the copper remains similar before and after reaction. Any difference in the nuclearity would result in a peak at approximately 3.5 Å . The copper appears to have low nuclearity throughout the activation and reaction.

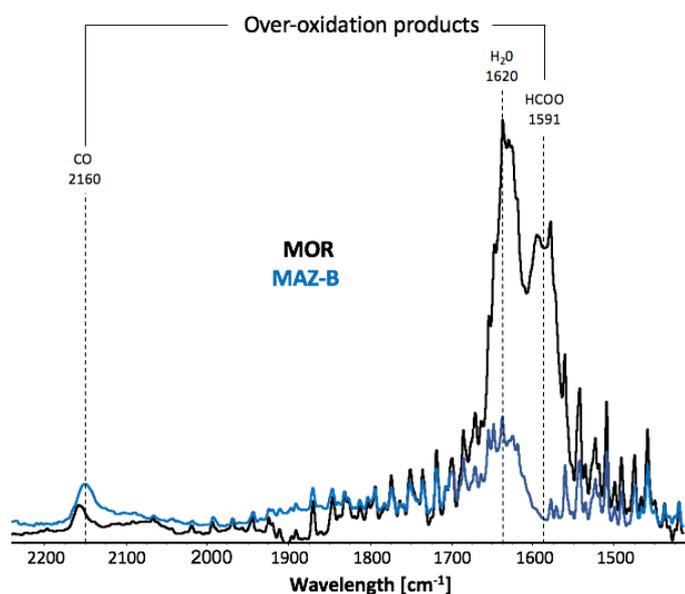


Figure S6: In-situ FTIR of over-oxidation product on MAZ-B and MOR6.5 after reaction with methane at high pressure (15 bar) for isothermal conversion of methane to methanol.

To understand why MAZ-B performs better than other zeolites, in-situ FTIR was conducted under low-temperature isothermal conditions and an elevated methane pressure of 15 bar for MAZ-B and MOR6.5. For MOR6.5, two over-oxidation products were observed: carbon monoxide (2160 cm^{-1}) and formate (1591 cm^{-1}). However for MAZ-B, only carbon monoxide was detected at 2160 cm^{-1} . MAZ-B is able to better protect the methanol from over-oxidation, leading to its superior performance in methane to methanol conversion. Due to the water retained in the zeolite under

isothermal conditions, interference in the 3000-2500 cm^{-1} range makes observation of methoxy species difficult.

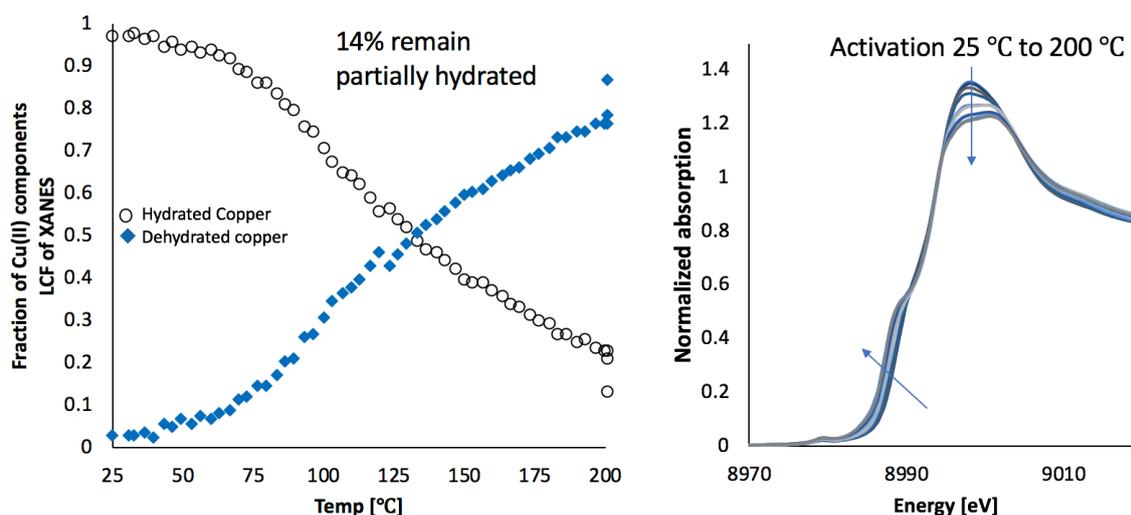


Figure S7: (Left) Linear combination fitting of dehydrated and hydrated copper in MAZ-B during activation for the isothermal procedure. Approximately 14% of the copper remained hydrated. (Right) In-situ Cu k-edge XANES as the Cu-MAZ-B samples was heated in a flow of oxygen to 200°C.

By monitoring the in-situ Cu k-edge XANES throughout the activation process, the extent of hydration was calculated by linear combination fitting. The standard for hydrated copper was the sample at 25°C prior to activation, and the dehydrated standard was a MAZ-B sample that had been heated to 450°C under the high activation temperature procedure. The active site for the conversion under isothermal conditions must be water stable, unlike the many proposed sites for the conventional high activation temperature procedure where no water remains in the zeolite.

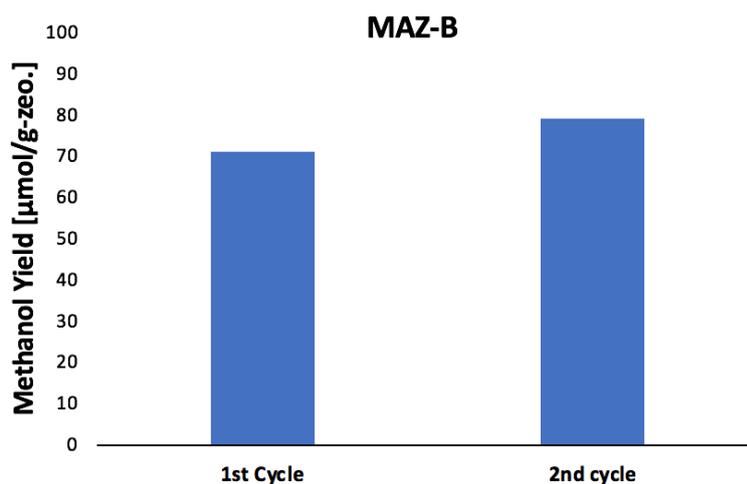


Figure S8: Methanol yield for two cycles for MAZ-B.

A new batch of MAZ-B was synthesized and tested for cycling. After the first cycle and offline extraction of methanol, the sample was dried overnight at 100°C prior to 2nd cycle testing. The

methanol yield increased slightly from cycle 1 (71 μ mol/g) to cycle 2 (79 μ mol/g). The sample did appeared slightly more gray during the 2nd cycles extraction with water.

- S1 S. Mintova, *Verified Syntheses of zeolitic materials*, Elsevier, Amsterdam, 3rd edn., 2016.
- S2 M. D. Oleksiak, A. Ghorbanpour, M. T. Conato, B. P. McGrail, L. C. Grabow, R. K. Motkuri and J. D. Rimer, *Chem. – A Eur. J.*, 2016, **22**, 15961.
- S3 P. J. Chupas, K. W. Chapman, C. Kurtz, J. C. Hanson, P. L. Lee, C. P. Grey, *J. Appl. Cryst.*, (2008), 41, 822-824
- S4 M. A. Newton, S. Checchia, A. J. Knorpp, D. Stoian, W. van Beek, H. Emerich, A. Longo, J. A. van Bokhoven, *Catal. Sci. Technol.*, 2019, 9, 3081-3089