Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Materials and Methods

Zeolite synthesis

A gel slurry was prepared with a molar composition of (SiO_2 : Al_2O_3 : Na_2O : TMACl : water = 15.2 : 1 : 7.1 : 1.4 : 460). Ludox HS-30 were the silicon source for MAZ-slow and MAZ-fast. The slurry was transferred to a Teflon autoclave and placed in a rotational oven at 373K for 21 days. 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.

Cation exchange

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 .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 omega was confirmed with a lab based PANalytical X'Pert Pro MPD instrument using Cu Kα radiation. Data was recorded from 5 to 70 2θ with a step size of .033° and a scan speed of .028°/s

Scanning electron microscopy

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

Nuclear magnetic resonance

Solid-state ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR) measurements were performed on a Bruker 400 UltraShield spectrometer at a resonance frequency of 104.29 MHz. A 4 mm MAS probe was filled with each sample and spun at 10 kHz. Chemical shifts were referenced to $(NH_4)Al(SO_4)_2\cdot 12H_2O$ for aluminum.

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.

FTIR spectroscopy of adsorbed probe molecules and in-situ FTIR

IR spectra were recorded on a Thermo Nicolet iS50 FTIR spectrometer equipped with DTGS detector at a 4 cm^{-1} optical resolution and 128 scans. Prior to the measurements, the sample (20mg) were pressed in self-supporting discs and activated in the IR transmission cell attached to a vacuum line at 673 K for 4 h. Then, the samples were oxidized in 300 torr of oxygen at 673K for 2h. The oxygen was then removed by subsequent evacuation at 673K for 20 min. A low temperature vacuum cell cooled with liquid nitrogen was used for nitrogen monoxide (NO) adsorption measurements. Calibrated aliquotes of the gases were introduced into the cell and the spectra were collected immediately. Pressure was measured by a Pfeiffer gauge. Difference spectra were obtained by the subtraction of the spectra of the activated samples from the spectra of samples with the adsorbate. The subtraction was performed using the OMNIC 9.1 software package.

Reaction with methane was carried out in situ in the vacuum IR cell. Prior to the measurements, the samples were oxidized in situ as described above. CH_4 pressure was 300 torr, temperature 473K and reaction time 30 min. After the reaction, the sample was evacuated at 473K for 10 min, cooled down and the spectrum was acquired.

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 measurement were conducted in transmission geometry.

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 O_2/moisture trap was used. Gas flows were controlled by mass flow controllers. 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.[S1] A type K insulated thermos couple was inserted into the sample bed for temperature measurements.

Methane to methanol reaction testing

Zeolite samples were sieved to 150-250μm. Approximately 0.5 grams of samples were loaded into stainless steel autoclave (Premex Reactor Ag). Samples were activated at 723K under pure O_2 flow for 1 hour with approximately 25mL/min. The temperature was reduced to 473K and then purged for 15 minutes in pure helium. Pure methane was then introduced at 1 bar or 6 bar into the reactor and kept at 473K for 30 minutes. The reactor was then cooled to room temperature.

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 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. Only one cycle of extraction was conducted on each sample.

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. To form the reduced standard, each sample was heated to 723K under pure CH_4 flow. Figure 3S shows the reduced XANES spectra for MAZ-slow and MAZ-fast.

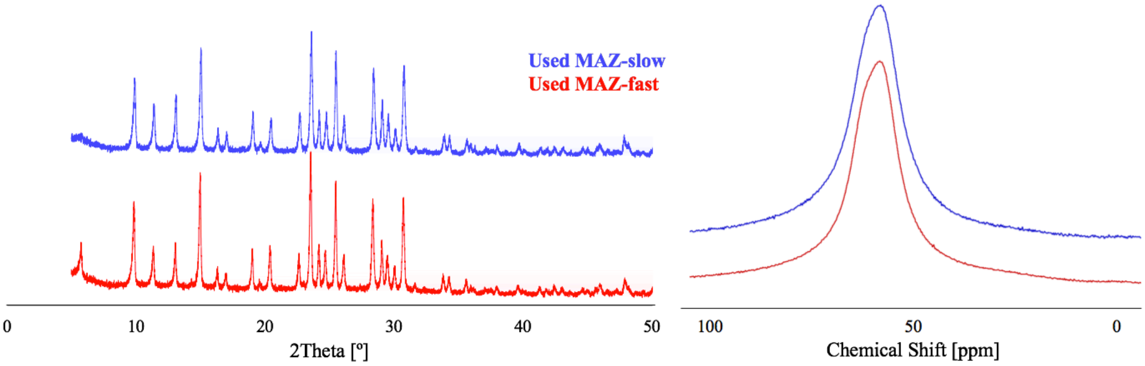


Figure 1S: (Left) XRD pattern of MAZ-fast and MAZ-slow after reaction(1 bar methane)/methanol extraction. (Right) ^{27}Al MAS NMR spectra of MAZ-slow and MAZ-fast after reaction and methanol extraction. No extra framework aluminum (~ 0 pp) detected and the distribution in the two t-sites are similar. There is some distortion of the aluminum signals from the paramagnetic effects of Cu(II).

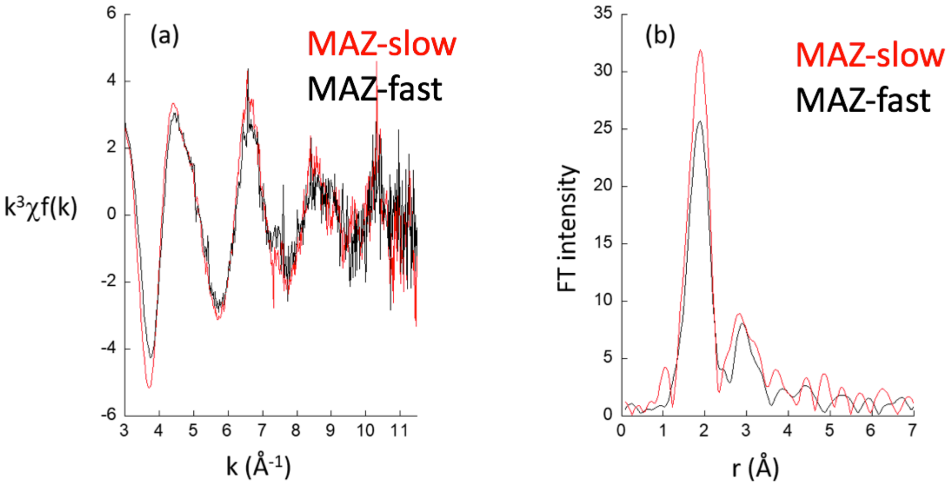


Figure 2S: (Left) Cu K-edge EXAFS spectra of activated MAZ-slow and MAZ-fast. (Right) Fourier transforms (k-space 3-11 (Å^{-1}) of activated MAZ-slow and MAZ-fast.

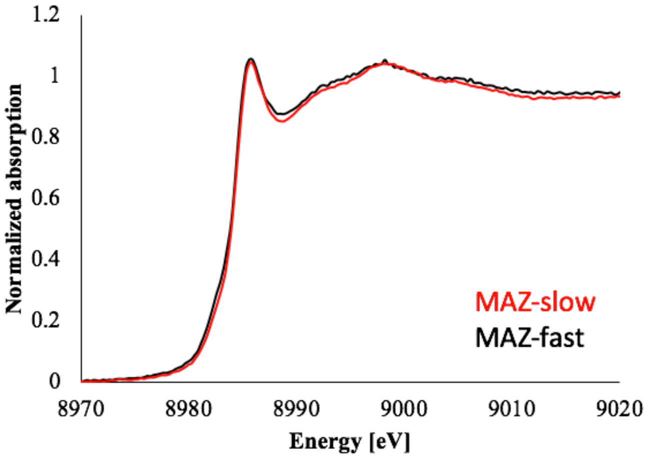


Figure 3S: Cu K-edge XANES spectra of reduced MAZ-slow and MAZ-fast. Each sample was reduced by flowing CH_4 at 723K. The spectra comprise the internal standards for Cu(I) for each sample to be used in the subsequent quantification of Cu(I) using LCA analysis.

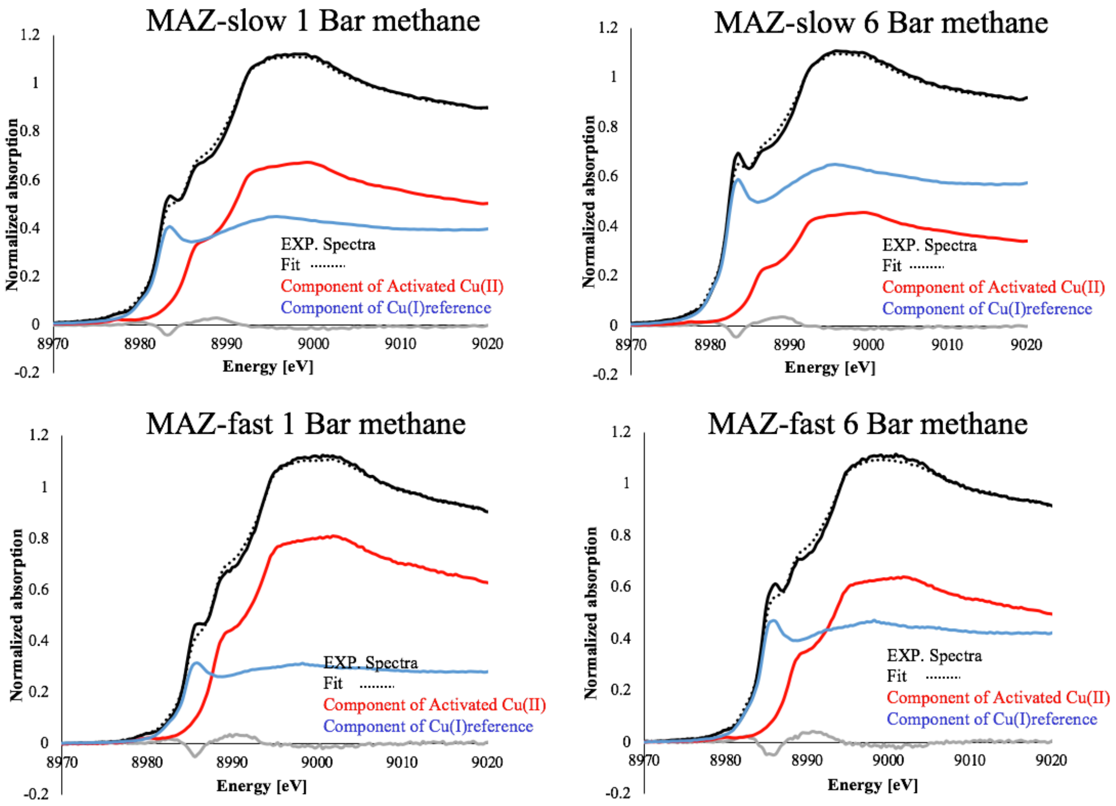
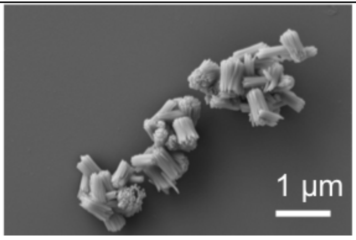
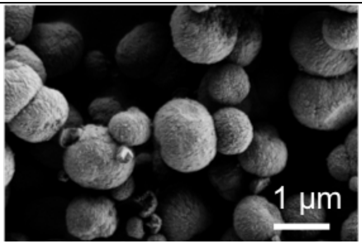
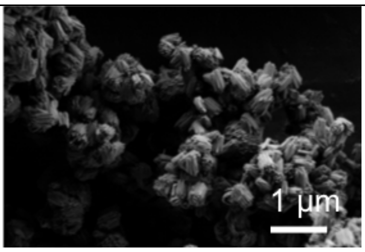
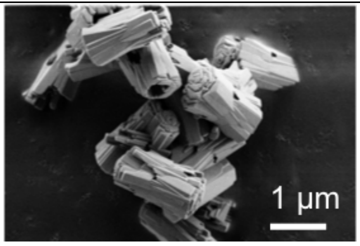
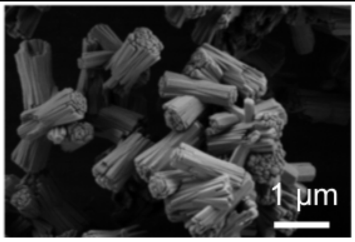
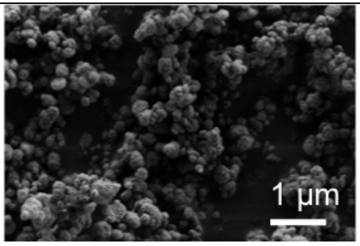


Figure 4S: The XANES spectra of reacted MAZ-slow and MAZ-fast with the resulting linear combination fit. The activated Cu(II) and the Cu(I) reference component are also included.

Table 1S: SEM micrographs of additional synthesis of MAZ

Sample	SEM image
Varying the structure directing agent	
MAZ_TMAbr	
MAZ_TMAOH	
Varying silicon source (slow rotation)	
MAZ_AS_Slow	
MAZ_SM_Slow	
Varying rotation speed (fast)	
MAZ_SM_Fast	
MAZ_AS_Fast	

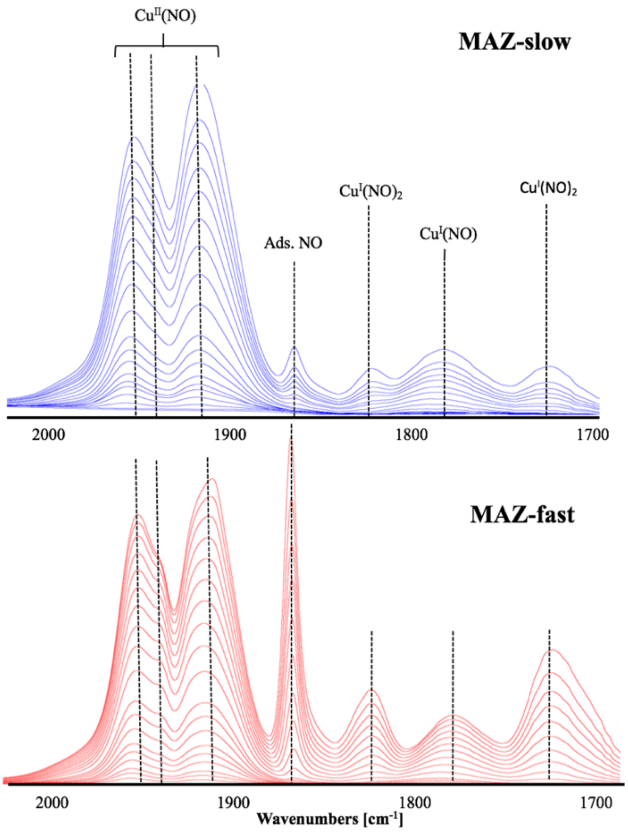


Figure 5S: FTIR spectra of nitrogen monoxide adsorbed over Cu-MAZ-fast and Cu-MAZ-slow.

Bands in the 2000-1900 cm^{-1}are attributed to the NO interacting with the copper (II). Both samples show similar peaks centered around 1955, 1943, and 1914 cm^{-1} and indicate the activated Cu(II) are similar. The Cu(I) species are attributed to autoreduction, because the sample is placed under vacuum at 673K after activation to remove the oxygen. The intensity of the peak 1870 cm^{-1}varied between samples. This peak is attributed to NO interacting with the zeolite's surface, and the difference is a product of the different morphologies.[S2]

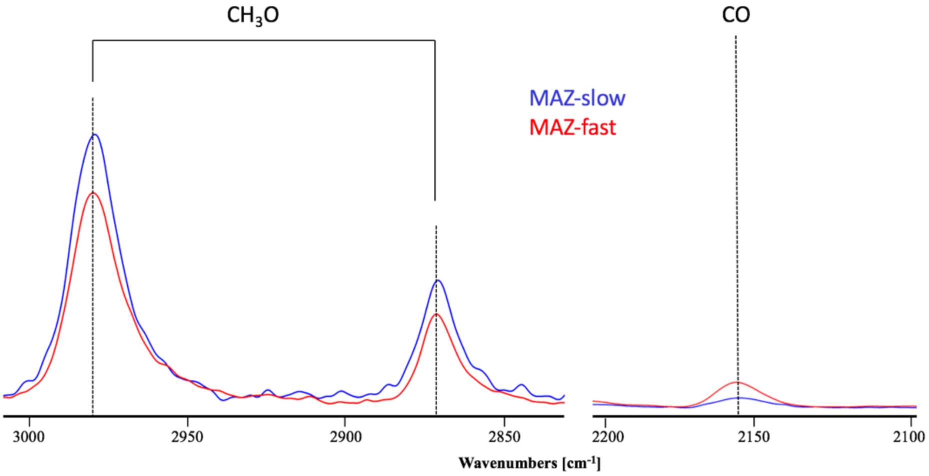


Figure 6S: FTIR spectra of methoxy and carbon monoxide species formed during reaction with methane at 473K for MAZ-fast and MAZ-slow.

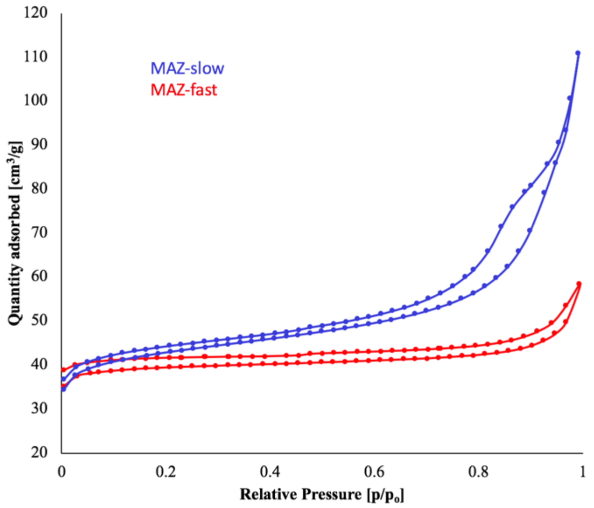


Figure 7S: N2 gas adsorption and/desorption isotherms for calcined MAZ-slow and MAZ-fast. MAZ-fast has a shape of a typical microporous zeolite. Meanwhile MAZ-slow features a hysteresis loop either resulting from the arrangement of rods with each other or mesopores. Both samples were pretreated overnight under vacuum at 573K.

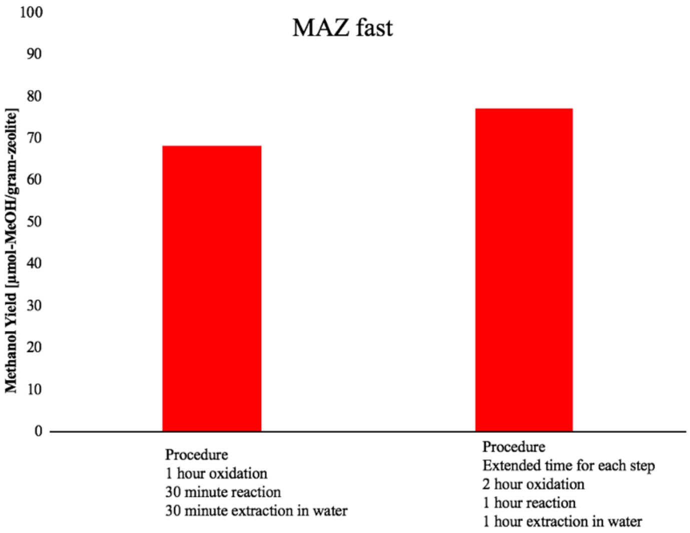


Figure 8S: Methanol yields for MAZ-fast when the steps during the activation, reaction, and extraction are conducted at longer times. There is a small increase (10 µmol/gram zeolite) in methanol yield; however, the methanol yields are still well below the yield for MAZ-slow (150.9 µmol/gram zeolite)

S1 P. J. Chupas, K. W. Chapman, C. Kurtz, J. C. Hanson, P. L. Lee, C. P. Grey, *J. Appl. Cryst.*, 2008, 41, 822-824

S2 V. L. Sushkevich, D. Palagin, J. A. van Bokhoven, *Angew. Chemie-Int. Ed.*, 2018, 57, 8906-8910.