

Methane to acetic acid over Cu-exchanged zeolites: mechanistic insights from a site-specific carbonylation reaction

Supporting Information

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Experimental

Ion Exchange

Commercial zeolites NH₄-MOR (CBV21A, Si/Al = 10) and NH₄-ZSM-5 (CBV2314, Si/Al = 12.5) were purchased from Zeolyst International.

Sodium Exchange

Partially exchanged zeolites were prepared by mixing 1 g of zeolite in 36 mL of 0.05 M, 0.1M, 0.4 M, 0.820 M, or 1.64 M solutions of NaCH₃COO (> 99%, Sigma-Aldrich, *ReagentPlus*, CAS 127-09-3) at 80°C for 12 hours. Zeolites were subsequently filtered while hot and rinsed with 120 mL of deionized H₂O. Zeolites were then dried for 4 h at 110°C in a drying oven. To prepare zeolites in the full sodium form, the above procedure was performed three times at an exchange concentration of 2.44M NaCH₃COO.

Copper Exchange of H-MOR for Na/Al < 0.55 (Cu/Al = 0.20 – 0.25)

To ensure lower amounts of copper in the zeolite, partially exchanged zeolites into the copper form were prepared by mixing 1 g of H-MOR in 60 mL of 0.01M Cu(NO₃)₂•(H₂O)₃ (98%, Sigma-Aldrich, CAS 10031-43-3) at 25°C for 12 h. The suspension was then filtered at room temperature and rinsed with 300 mL of deionized H₂O. This procedure was followed for H-MOR with Na/Al < 0.55.

Copper Exchange of Partially Na exchanged MOR for Na/Al > 0.55 (Cu/Al = 0.20 – 0.25)

As Na/Al increased above 0.55, higher levels of copper were exchanged into MOR from copper nitrate. To ensure that Cu/Al remained between 0.20-0.25, 1 g of Na-MOR with Na/Al > 0.55 was mixed in 60 mL of 0.005M Cu(NO₃)₂•(H₂O)₃ (99%, Sigma-Aldrich) at 25°C for 12 h. The filtering procedure was the same as noted above.

Copper Exchange of H-MOR (Variable Cu/Al)

Exchange of copper into NH₄-MOR at various levels was prepared by suspending the zeolite into a 0.0025, 0.005, and 0.01 M solutions of Cu(NO₃)₂•(H₂O)₃ at room temperature for 12 h. The same filtering procedures were followed as above.

Copper Exchange of Na-MOR (Variable Cu/Al)

Exchange of copper into Na-MOR at various Cu/Al was done as described above. Solutions of 0.0025, 0.00375, 0.005, and 0.01 M Cu(NO₃)₂•(H₂O)₃ solutions were mixed with Na-MOR at room temperature for 12 h. The zeolite was then filtered as described above.

Table S1. Exchange Conditions, Sodium, and Copper Contents of MOR and ZSM-5

<i>Sodium Acetate (M)</i>	<i>Copper Nitrate (M)</i>	<i>Na/Al</i>	<i>Cu/Al</i>
0.05	0	0.31	0
0.1	0	0.45	0
0.4	0	0.58	0
1.64	0	0.80	0
2.44 x3	0	0.97	0
0	0.01	0.033	0.20
0.05	0.01	0.11	0.23
0.1	0.01	0.16	0.22
0.4	0.01	0.21	0.25
0.81	0.005	0.36	0.24
2.44	0.005	0.49	0.23
0	0.0025	0.030	0.10
0	0.005	0.010	0.17
2.44 x3	0.0025	0.79	0.098
2.44 x3	0.00375	0.76	0.15
2.44 x3	0.005	0.64	0.22
2.44 x3	0.01	0.36	0.37
0 ^b	0.01	0	0.47
0 ^c	0.01	0.01	0.44 ^c
2.44 x3 ^c	0.01	0.18	0.47 ^c

a: Copper acetate monohydrate (98%, Sigma-Aldrich, CAS 6046-93-1) was used for this exchange

b: The pH of the copper nitrate solution was adjusted to 6.47 using ammonium hydroxide (5.0 M, Sigma-Aldrich, CAS 1336-21-6)

c: NH₄-ZSM-5 (Zeolyst, Si/Al = 11.5) was the parent zeolite

After exchanges, all zeolite samples were calcined under 100 mL/min of dry air (Airgas) while being heated 1 K/min to 823 K and held for 5 h. Calcination converted the NH₄⁺ counter cations into H⁺, resulting in the Brønsted acid form of Cu-MOR. Copper, sodium, and aluminum contents were determined using inductively coupled plasma atomic emission spectroscopy (ACTIVA-S, Horiba Scientific).

Methane Oxidation and Carbonylation Reactions

Methane oxidation and carbonylation reactions were conducted in a continuous, tubular flow reactor (stainless steel tube, O.D. 12.5 mm, wall thickness = 0.889 mm). The reactor tube was mounted inside of a single-zone furnace (850W / 115V, Applied Test Systems Series 3210). A thermocouple (Omega, model TJ36-CASS-18U) was aligned along the tube center such that

its tip reached the middle of the height of the tube. Zeolite particles (1.5 g, sieved into 500 – 1000 μm particles) were packed between quartz wool frits resting on the thermocouple. The thermocouple was connected to a Digi-Sense model 68900-10 temperature controller. The reactor was equipped with gas tanks for argon, oxygen, methane, and carbon monoxide (all ultra high purity from Airgas). All gas lines were run through molecular sieve 5A (S-trap, Sigma-Aldrich) and calcium hydride traps (95%, Sigma-Aldrich, CAS 7789-78-8) to remove trace amounts of water in the gas streams. Prior to reaction, the zeolite was calcined in 50 mL/min flowing oxygen for 5 h at 823 K and cooled under flowing oxygen to reaction temperature (473 K). Upon reaching reaction temperature, the bed was purged under 50 mL/min of Ar for 1 hr. The gas flow was then changed to the reaction mixture of 10 mL/min methane and 15 mL/min Ar for a 30 min reaction. After methane oxidation, the gas flow was changed to 200 mL/min of CO and the reactor was pressurized to 1000 kPa gauge pressure for 30 min. Afterwards, the reactor was immediately depressurized, purged under Ar and cooled to room temperature.

Methanol and acetic acid extraction was performed by removing the zeolite bed from the tube, weighing, and sealing into a glass vial. The zeolite was then suspended in deuterium oxide (2.5 mL D_2O /g zeolite) and stirred at 550 rpm for 2 h. The suspension was then transferred to conical vials and centrifuged for 10 min at 6,000 rpm. The supernatant was removed and its contents were analyzed using ^1H -NMR (Varian Mercury 300). For quantification of methanol and acetic acid, 1,4-dioxane (> 99%, Aldrich, CAS 123-91-1) was the internal standard (28.5 μL dioxane / mL supernatant).

$^{18}\text{O}_2$ -Labeled Experiments

In the tubular reactor described above, 0.75 g of sieved zeolite (500 – 1000 μm diameter) was packed into a stainless steel tube (O.D. 6.35 mm, wall thickness 0.889 mm) suspended on a quartz wool frit. The zeolite was calcined in flowing oxygen (50 mL/min) at 723 K for 4 h. The gas flow was switched to argon for 1 hr to destroy any formed copper-oxo species. Then the flow was switched to 30 mL/min of $^{18}\text{O}_2$ (97 atom %, Sigma-Aldrich) for 4 min. The argon and $^{18}\text{O}_2$ calcination cycle was repeated two more times. The zeolite bed was cooled under $^{18}\text{O}_2$ to 473 K. The bed was purged under argon and then switched to methane (10 mL/min) for 30 min. After the reaction, the bed was cooled to room temperature. The zeolite was removed from the tube, suspended in 1.25 mL dH_2O , stirred for 2 h, and centrifuged for 10 min at 6,000 rpm. The supernatant was then injected into a GC-MS (Agilent Technologies, model 7890A) equipped with a Paraplot Q column (Agilent Technologies, 50 m x 0.32 mm ID, 10.0 μm). The oven was isothermal at 413 K for 7 min.

To determine if ^{18}O exchange occurs between ^{18}O -methanol and Bronsted acid sites at room temperature, 0.30 g of Cu-H-MOR (Cu/Al = 0.17) was suspended in a solution of 1.00 mL of 20 mM $\text{CH}_3^{18}\text{OH}$ in water and stirred at room temperature for 2 h. The mixture was centrifuged at 6000 rpm for 10 min, and the supernatant was extracted and injected into a GC-MS.

^{13}C Methane Oxidation and Carbonylation

Methane oxidation and carbonylation reactions with ^{13}C labelled reagents were conducted in a similar setup as for the analogous reactions with ^{12}C reagents except the stainless steel tubular reactor had an O.D. of 6.35 mm and wall thickness of 0.889 mm. 0.400 g of zeolite

sample (pelleted and sieved to 250 – 500 μm) were packed between quartz wool frits resting on a thermocouple (Omega, model TJ36-CASS-116U) aligned along the middle of the tube. The zeolite was calcined under oxygen for 5 h at 823 K and then purged under argon for 1 hour upon cooling to 473 K. Methane oxidation was performed by pressurizing the reactor to 103 kPa gauge under static ^{13}C CH₄ (99 atom %, Aldrich, CAS 6532-48-5) for 30 min. If carbonylation was to take place, the tubular reactor was purged twice with 103 kPa gauge of ^{13}C CO (99 atom %, Aldrich, CAS 1641-69-6). The third refill was kept static in the reactor for 6 h. After reactions with the ^{13}C reagents, the reactor was purged with argon and cooled to room temperature.

Adsorption of ^{13}C Methanol and Acetic Acid on Cu-MOR

Adsorption of liquid ^{13}C reagents onto zeolite samples was done with the same reaction setup as described for ^{13}C methane oxidation and carbonylation except a septum within a T-joint was installed upstream of the zeolite bed. Under a carrier flow of argon (50 mL/min) and a zeolite bed held at 423 K, 5 μL of ^{13}C -methanol (99 atom %, Cambridge Isotope, CAS 14742-26-8) or ^{13}C -acetic acid (99 atom %, C2 (methyl group), Cambridge Isotope, CAS 1563-80-0) were injected four times. The zeolite bed was purged for another hour before being cooled to room temperature.

^{13}C -MAS NMR Experiments

For all experiments with ^{13}C reagents, the zeolite samples were cooled to room temperature under argon. The ends of the reactor were sealed from atmosphere, and the zeolite bed was transferred to a glovebox under argon atmosphere. The zeolite bed was then packed into 4 mm (o.d., 80 μL fill volume) ZrO₂ MAS rotors (Revolution NMR, Fort Collins, Co) equipped with a vespel drive tip (sealed using Epoxy) and a top cap containing two rubber o-rings.

Solid-state NMR experiments were performed using a home-built 500 MHz spectrometer (courtesy of Dr. D. Ruben, Francis Bitter Magnet Laboratory – MIT) equipped with a Magnex high field NMR magnet (11.7 T). ^{13}C magic-angle spinning (MAS) NMR experiments were collected using a 4 mm triple-resonance ($^1\text{H}/^{13}\text{C}/^{15}\text{N}$) Chemagnetics (Fort Collins, CO) probe equipped with a Kel-F stator housing. The spinning frequency was between 8 and 10 kHz and regulated with a Bruker MAS controller. Sample temperatures were maintained at 295 K and cooled to account for frictional heating using a stream of cooling gas. ^{13}C single pulse (Bloch) experiments were acquired using a $\pi/2$ of 2.5 μs (^{13}C $\gamma B_1/2\pi = 100$ kHz), and between 16 k and 64 k co-added transients. $^{13}\text{C}[^1\text{H}]$ cross polarization experiments were collected with a contact time of 2 ms and, between 2 k and 16 k co-added transients. The ^{13}C Hartmann-Hahn condition was optimized using a ramp on ^{13}C and 50 kHz $\gamma B_1/2\pi$ on ^1H . Recycle delays were between 1.5 and 30 seconds, depending on the Cu content. All data were acquired using high-power TPPM ^1H decoupling optimized for a ^1H $\gamma B_1/2\pi = 100$ kHz. ^{13}C data were referenced using adamantane (40.49 ppm) as a secondary standard with respect to DSS, 4,4-dimethyl-4-silapentane-1-sulfonic acid (0 ppm). Variable temperature ^1H and ^{13}C experiments at -40, 0 and +40 $^\circ\text{C}$ were acquired using a home-built 700 MHz NMR Spectrometer equipped with a 3.2 mm triple-resonance ($^1\text{H}/^{13}\text{C}/^{15}\text{N}$) Chemagnetics probe. Samples were treated identically, although placed in 3.2 mm o.d. ZrO₂ rotors. ^{13}C acquisition parameters were similar as stated above although data was

acquired at 18 kHz with a 1.5 ms contact time. ^1H MAS NMR data were acquired using a Bloch and Hahn-Echo experiment, 128 co-added transients and a recycle delay of 3 seconds.

UV-vis-NIR spectroscopy

UV-vis spectra were taken with a Cary 5000 UV-Vis-NIR spectrometer (Agilent Technologies) equipped with a Praying Mantis diffuse-reflectance accessory (Harrick Instruments). Background spectra were sodium or acid form of the parent zeolite that were calcined (823 K, 5 h under oxygen) and the spectral range was from $4,800\text{ cm}^{-1}$ to $50,000\text{ cm}^{-1}$. Samples were finely ground in a mortar and pestle and loaded into a Harrick high temperature reaction chamber equipped with quartz windows. The sample was calcined under flowing oxygen (50 mL/min) at 823 K for 5 h, cooled under oxygen, and then purged under Ar. The sample was subsequently heated to 823 K under argon for 3 h. After spectra were taken for both heat treatments, the parent copper zeolite was recalcined under oxygen at 823 K for 5 h, cooled to room temperature, and then exposed to methane flow (50 mL/min) at 473 K for 30 min. Before a spectrum was taken, the sample was cooled to room temperature and purged in argon for 1 hr.

Electron Paramagnetic Resonance (EPR) Spectroscopy

10-11 mg of sieved zeolite samples (500 – 1000 μm) were placed in Thin Wall Precision Quartz EPR tubes (4 mm OD, 250 mm length, Wilmad-Labglass, 707-SQ-250MM). For pre-treatment, the tube was lowered into a single-zoned furnace (GTF 11/50/150B, Carbolite). A thermocouple (Omega, model TJ36-CASS-116U) was placed inside the furnace alongside the EPR tube and connected to a temperature controller (YO-89000-00, 110V, Digi-Sense). Gas flow into the EPR tube was diffusion mediated by continuously flowing gas past the EPR tube through a rapid purge valve (Chemglass). The gas molecules are then able to diffuse into the EPR tube to the zeolite sample. The carrier gas was either oxygen or argon at 200 mL/min. The sample was heated 1 K/min to 823 K, soaked for 5 h, and cooled to room temperature. After reaching room temperature, the sample was purged under flowing argon (275 mL/min) for 2 h. While under argon, the sample was transferred into an argon atmosphere glovebox (UNILab, MBraun) where the EPR tube was sealed with epoxy resin.

X-band (9.5 GHz) EPR experiments were performed using a Bruker ElexSys E580 spectrometer using a rectangular ER 4122 SHQE-W1 cavity operating in TE₁₀₂ mode. Sample temperature control was achieved using an ESR 900 flow cryostat with liquid nitrogen and an ITC 503S temperature controller (Oxford Instruments). Powdered samples were maintained at 90 K during acquisition. Spectra were acquired with a microwave frequency of 9.40 GHz, a modulation amplitude of 0.2 mT and a microwave power of 0.63 mW

Propylamine Adsorption for Quantification of Bronsted Acidity

Propylamine adsorption and subsequent temperature programmed reaction/desorption were performed to quantify the Brønsted acid sites in select Cu-MOR zeolites. After adsorbing propylamine onto Brønsted acid sites and heating the zeolite, the propylamine decomposes into ammonia and propylamine in a one-to-one ratio per Bronsted acid site.¹ Propylamine adsorption reactions were conducted in a quartz U-tube reactor (O.D.6.35 mm, Altamira AI-2210). The U-tube was mounted above a single-zone furnace (GTF 11/50/150B, Carbolite). A thermocouple

(Omega, model TJ36-CASS-116U) was aligned along the tube center such that its tip just touched the top of the catalyst bed. Zeolite particles (10 - 50 mg) were packed between quartz wool frits just below the thermocouple. The reactor was equipped with gas tanks for 1% argon balance helium and dry air (Airgas). All gas lines were run through a molecular sieve 4A trap (Agilent Technologies) to keep the catalyst bed dry. Prior to reaction, the zeolite was calcined in 90 mL/min flowing air for 5 h at 823 K and cooled to room temperature (298 K). The zeolite was purged under 100 mL/min of 1% Ar/He for 30 min. The gas flow was then passed through a saturator containing n-propylamine (98%, Aldrich, CAS 107-10-8) kept at 298 K for 1 hr. The gas flow was switched to bypass the saturator and purge the zeolite bed of any excess propylamine for 30 min. The sample was then heated at 5 K/min to 523 K, held isothermal for 1 hr, and finally ramped at 5 K/min to 873 K. The concentration of propylamine ($m/z = 59$), propylene ($m/z = 41$), ammonia ($m/z = 17$), and argon ($m/z = 20$) were tracked on-line using a quadrupole mass spectrometer (Hiden HPR-20). The concentration of propylene was calibrated within the mass spectrometer immediately after the experiment by pulsing 5 mL samples of 1000 ppm propylene/1% Ar/He using a 6-way gas sampling valve (Vici E60, Valco Instruments). Calculation of $[H^+]$ was performed by setting $[H^+]$ equal to the number of propylamine molecules desorbing from the zeolite. Total $[Al^{3+}]$ was calculated by ICP-AES. It was assumed that all Al in the zeolite was tetrahedrally coordinated in the framework.

Table S2: Propylamine desorption over Cu-MOR samples in Figure 1

Na/Al	Cu/Al	$\mu\text{mol/g}_{\text{cat}}$ propylene	H^+/Al
0.03	0.20	278.5	0.50
0.11	0.23	214.3	0.41
0.16	0.22	193.5	0.27
0.36	0.24	149.2	0.14
0.64	0.22	101.9	0.08

Dissolution of Zeolites in Hydrofluoric Acid

To analyze the organic content on the zeolite surface after methane oxidation and carbonylation reactions, as described above, the 0.8g of zeolite was dissolved in 3.0 mL of 48 wt% hydrofluoric acid and stirred for 2 hr. A 1 mL aliquot of the solution was diluted in 1 mL of deuterium oxide. 0.5 mL of the mixture was transferred to a Teflon liner (5 mm OD, 203.2 mm length, Wilmad Labglass) that was inserted into a standard quartz NMR tube for 1H -NMR analysis. 10 μL of 1,4-dioxane was used as an internal standard. A control experiment showed that both methanol and acetic acid were not destroyed in the hydrofluoric acid solution.

Extraction and Characterization of Methanol and Acetic Acid

Methane oxidation and carbonylation products were extracted from zeolites by suspension in deuterium oxide, stirring for 2 h, and centrifugation at 6,000 rpm for 10 min. To quantify the amount extracted, a 25 μL internal standard of 1,4-dioxane (99%, Sigma-Aldrich, CAS 123-91-1) was injected into the NMR tube.

Referencing the peak for water to be 4.790 ppm^2 , the peaks for methanol and acetic acid were found to be 3.30 and 1.97 ppm respectively (Figure S1 B and C). The peaks from the product extraction from Cu-MOR (Cu/Al = 0.20) closely matched these peaks (3.32 and 2.03 ppm) (Figure S1 A). The small shift in the NMR peaks for both compounds was likely due to trace leaching of cupric ions into solution.

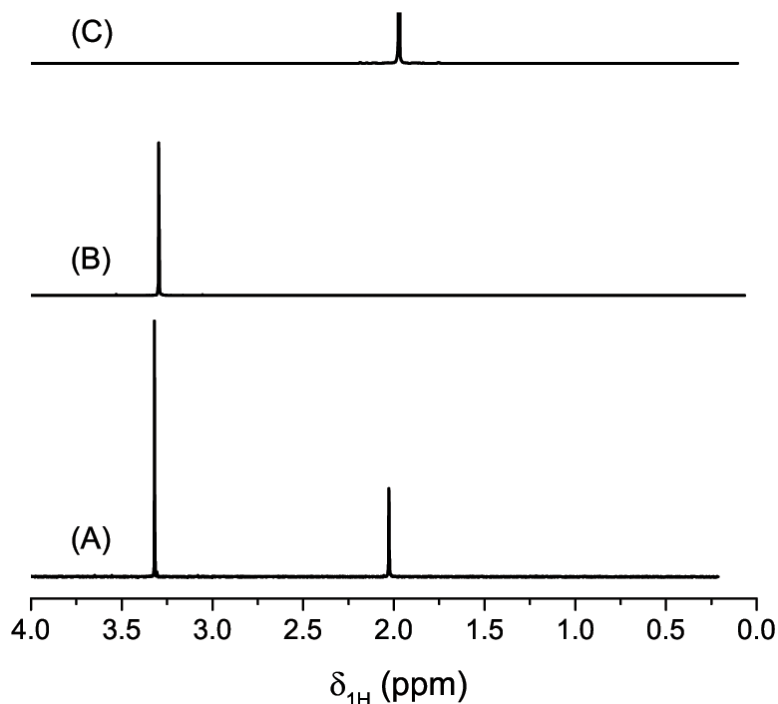


Figure S1. ^1H NMR spectra of the product extract from A) Cu-MOR (Cu/Al = 0.20), B) methanol in deuterium oxide, and C) acetic acid in deuterium oxide

¹⁸O Calcination and Methane Oxidation over Cu-MOR

Table S3: Methanol extraction from zeolites calcined under ¹⁸O₂ and subsequent methane oxidation

Zeolite Precursor	Cu/Al	% CH ₃ ¹⁸ OH Extracted
H-ZSM-5	0.44	4.6
H-MOR	0.17	0.6
Na-MOR	0.22	34.0
Na-MOR	0.36	34.2

Reaction conditions: Activation at 723K under 30 mL/min ¹⁸O₂, Reaction T = 473 K, Reaction time = 0.5 h.

To quantify the percentage of methanol in solution consisting of CH₃¹⁸OH, a calibration curve was made using various mixtures of CH₃¹⁶OH and CH₃¹⁸OH. Volumetric mixtures of 0%, 10%, 25%, 50%, and 100% CH₃¹⁸OH were prepared and injected into a GC-MS. These compositions were then plotted against the ratio of the mass fragments at 33 and 31. A correlation with excellent linearity was recovered (Figure S2).

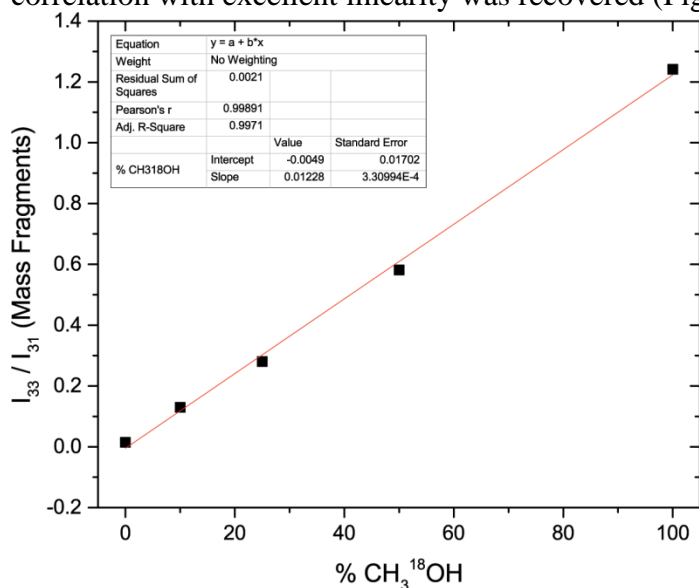


Figure S2: Calibration Curve of the composition of CH₃¹⁸OH in solution as separated by GC-MS

One possible source of CH₃¹⁶OH during extraction could have been the adsorption of CH₃¹⁸OH onto a Bronsted acid site to form a methoxy species that would rehydrate into CH₃¹⁶OH. To determine the extent of ¹⁸O exchange between CH₃¹⁸OH and Bronsted acid sites in Cu-H-MOR (Cu/Al = 0.17), the zeolite was suspended and mixed (600 rpm) in a 20 mM solution of CH₃¹⁸OH in water for 2 h. The resulting suspension was centrifuged at 6000 rpm for 10 min, and the supernatant was extracted and injected into a GC-MS. Compared to the amount of CH₃¹⁸OH in the as-prepared 20 mM CH₃¹⁸OH solution, the percent of extracted CH₃¹⁸OH dropped by only 7.8% after mixture with Cu-H-MOR. Thus, the extent of ¹⁸O scrambling at room temperature was significantly less compared to the 99.4% and 64% scrambling observed in Cu-H-MOR and Cu-Na-MOR, respectively, after reactions. Thus, loss in CH₃¹⁸OH extraction must have occurred from migration of the CH₃¹⁸OH from a copper site to a Brønsted acid site immediately after methane oxidation and before extraction.

Table S4: CH₃¹⁸OH Extraction from Cu-H-MOR Suspended in CH₃¹⁸OH/Water Solution

Treatment	% CH₃¹⁸OH
CH ₃ ¹⁶ OH	0.0
20 mM CH ₃ ¹⁸ OH (as prepared)	100
20 mM CH ₃ ¹⁸ OH (mixed with Cu-H-MOR)	92.2
CH ₄ Oxidation (Cu-H-MOR, Cu/Al = 0.17)	0.6
CH ₄ Oxidation (Cu-Na-MOR, Cu/Al = 0.22)	34

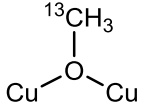
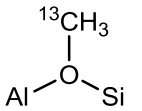
The percentage of CH₃¹⁸OH extracted from Cu-Na-MOR was significantly lower than that observed by Sels and coworkers on Cu-Na-ZSM-5.³ On Cu-Na-ZSM-5, CH₃¹⁸OH extraction was around 75% from the zeolite, while CH₃¹⁸OH extraction from Cu-Na-MOR was at 36% in this study. This was likely attributed to incomplete destruction of the Cu^{II}-O-Cu^{II} active sites³ and isotopic exchange with ¹⁶O over other copper oxides⁴ during calcination under ¹⁸O₂. Varying the number of calcination cycles with ¹⁸O₂ produced higher CH₃¹⁸OH extracted from Cu-Na-MOR. As the number of calcination cycles under ¹⁸O₂ increased, the percentage of CH₃¹⁸OH extracted after methane oxidation doubled. Thus, in the limit of several calcination cycles, the majority of methanol extracted from Cu-Na-MOR would likely be CH₃¹⁸OH.

Table S5: CH₃¹⁸OH Extraction from Cu-Na-MOR zeolites calcined multiple times under ¹⁸O₂

Cu/Al	# ¹⁸O₂ Calcination Cycles	% CH₃¹⁸OH
0.22	2	17.9
0.22	3	36.0
0.36	1	12.5
0.36	3	36.2

Surface Characterization of Surface Products using ^{13}C -MAS NMR

Table S6: ^{13}C Chemical Shifts of Methoxy Species on Cu-MOR

Species	^{13}C Chemical Shift (ppm)	Species #
	61	1
	56-57	2
$^{13}\text{CH}_3\text{OH}$	53	3

$^{13}\text{C}[^1\text{H}]$ CP MAS NMR experiments confirmed the products of the methane oxidation and carbonylation reactions on surface of Cu-MOR. In Cu-H-MOR (Cu/Al = 0.20), three peaks at 53.4, 55.9, and 61.2 ppm formed in the methoxy region upon $^{13}\text{CH}_4$ oxidation (Figure S3). The peak at 53.4 ppm was attributed to chemisorbed methanol. The peak at 55.9 ppm were methoxy species formed on Bronsted acid sites.⁵ Several possibilities existed for the nature of the methoxy species at 61.2 ppm. Various adsorbed dimethyl ether species have resonances from 60 – 65 ppm,⁵ but the formation of dimethyl ether from highly dispersed oxidation active sites was highly unlikely. Thus, the peak at 61.2 ppm likely corresponded to a methoxy species on a copper site. Since Cu^{2+} species are paramagnetic, a resonance of a methoxy species on a Cu^{2+} site could undergo severe broadening and an induced chemical shift to higher or lower frequency – hence making it difficult to observe. However, the binding of the methoxy species after methane oxidation over the mono-(μ -oxo)dicupric site is a methoxy species bridging the $\text{Cu}^{\text{II}}\text{-O-Cu}^{\text{II}}$ site. Since the mono-(μ -oxo)dicupric site is magnetically coupled (spin ad-mixed) and EPR silent, a methoxy species on that site should be observable using MAS NMR. Moderately fast MAS NMR experiments were performed at variable temperature to further probe any paramagnetic shift effects – no additional resonances appeared at lower or higher frequency nor were the resonance observed sensitive to temperature.⁶ Furthermore, control adsorption of $^{13}\text{CH}_3\text{OH}$ onto Cu-H-MOR did not reveal the 61.2 ppm signal but other signals at 60.0 and 64.6 ppm (Figure S7), suggesting that the nature of the this resonance is not molecular dimethyl ether or methanol on Cu^{2+} ions. Thus, the 61.2 ppm signal was tentatively attributed to the bridging methoxy species on the mono-(μ -oxo)dicupric active site. After carbonylation, peaks at 188.5, 24.7, and 21.5 ppm appeared. The peaks at 188.5 and 21.5 were from the formation of acetic acid on the Cu-MOR surface.⁷ Since there was no other resonance other than at 188.5, the carbonyl carbon of acetic acid was not bound to the zeolite framework or a copper site.⁷⁻⁸ Thus, the peak at 24.7 ppm is most likely the methyl group of acetic acid interacting with Bronsted acid sites through hydrogen bonding. After carbonylation under ^{13}CO for 6 h, the peak at 55.9 ppm for methoxy species on Bronsted acid⁵ sites disappeared. Additionally, the ratio of the areas of the 61.2 and 53.4 peaks reduced from 6.67 to 2.55. This reduction in the area of the 61.2 signal could have arisen through the reaction of a carbonylation active copper site or the decomposition of methoxy species over 6 h at 473 K. Regardless, methoxy species formed on Bronsted acid sites and were involved in the carbonylation reaction.

Even at lower Bronsted acid site count and higher copper content, the same peak around 56 ppm decreased after carbonylation. Over Cu-H-MOR (Cu/Al = 0.47), the same peaks at 61.3, 55.5, and 53.4 ppm were observed after reaction with $^{13}\text{CH}_4$ (Figure S4). After exposure to ^{13}CO for 6 h, two new resonances at 21.5, 24.7, and 188.5 ppm appeared, corresponding to acetic acid. Within the methyl region, the peak at 55.5 ppm decreased relative to the 53.4 and 61.3 ppm peaks, as in Cu-H-MOR (Cu/Al = 0.20), showing that the Bronsted acid sites were directly involved in carbonylation.

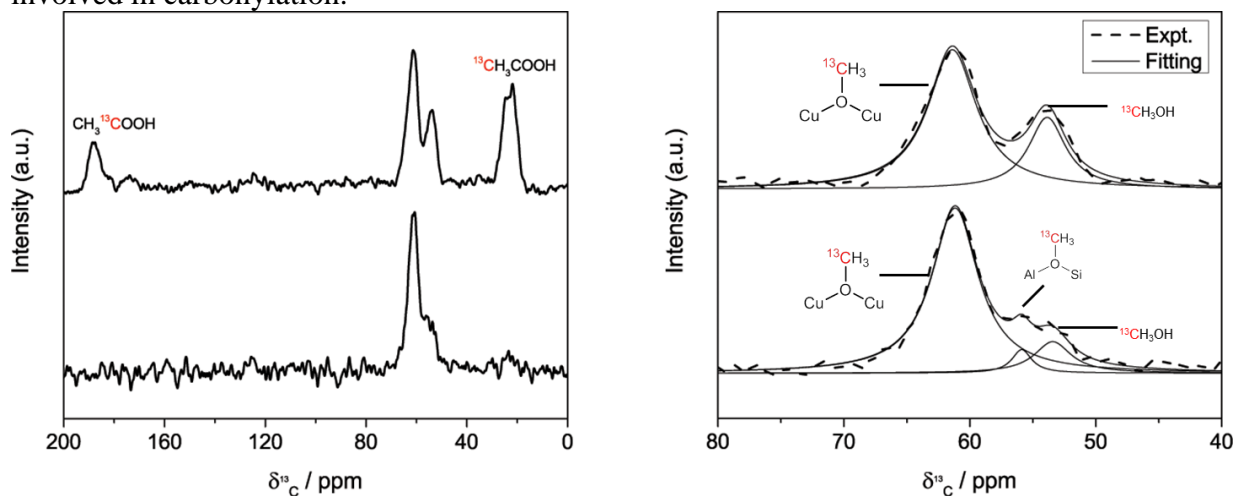


Figure S3. $^{13}\text{C}[^1\text{H}]$ CP MAS NMR spectra of Cu-MOR (H-MOR precursor, Cu/Al = 0.20) after $^{13}\text{CH}_4$ oxidation (bottom spectrum) and after $^{13}\text{CH}_4$ oxidation and ^{13}CO carbonylation (top spectrum). (Left) Full ^{13}C MAS NMR spectra of Cu-H-MOR (Cu/Al = 0.20) after reaction with $^{13}\text{CH}_4$ (bottom) and $^{13}\text{CH}_4 + ^{13}\text{CO}$ (top). (Right) Enlarged spectral region containing methoxy resonances. Simulated (solid) Lorentzian peaks are shown below the experimental (dashed) spectra.

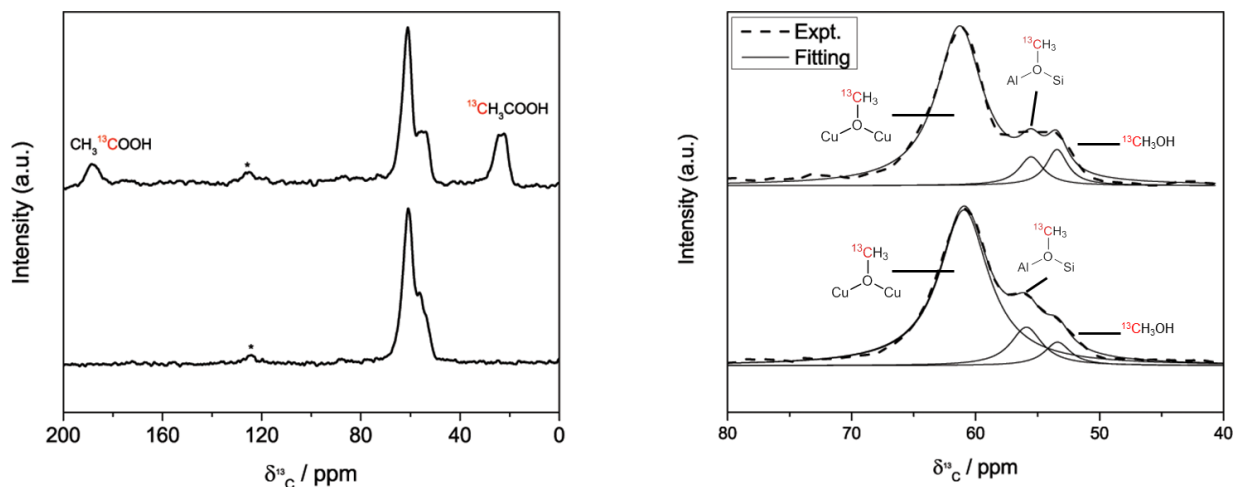


Figure S4. $^{13}\text{C}[^1\text{H}]$ CP MAS NMR spectra of Cu-MOR (H-MOR precursor, Cu/Al = 0.47) exchanged at pH = 6.47 after $^{13}\text{CH}_4$ oxidation (bottom spectrum) and after $^{13}\text{CH}_4$ oxidation and ^{13}CO carbonylation (top spectrum). (Left) Full ^{13}C MAS NMR spectra of Cu-H-MOR (Cu/Al = 0.47) after reaction with $^{13}\text{CH}_4$ (bottom) and $^{13}\text{CH}_4 + ^{13}\text{CO}$ (top). (Right) Enlarged spectral region containing methoxy resonances. Simulated (solid) Lorentzian peaks are shown below the experimental (dashed) spectra.

However, when the carbonylation activity was quenched in Cu-Na-MOR, no methoxy species were observed to form on Bronsted acid sites. Only two resonances formed upon Cu-Na-MOR after $^{13}\text{CH}_4$ oxidation: at 60.9 and 53.6 ppm. After carbonylation with ^{13}CO , the 60.9 ppm

peak reduced in height relative to the 53.6 ppm peak and formed resonances at 22.5 ppm. This peak most likely resulted from surface coke forming from the decomposition of methyl groups over the six hour carbonylation. The peak at 86.7 ppm is methanediol. These assignments were supported by the ^{13}C -NMR spectrum of the products extracted from the Cu-Na-MOR surface (Figure S6). The observed resonances in the liquid extraction were at 82.3 and 49.5 ppm. The 14.2 ppm resonance in the liquid extraction appeared to be an artifact. Regardless, no acetic acid was observed to form on Cu-Na-MOR, showing that Bronsted acidity and surface methoxy species are intermediates for the carbonylation reaction.

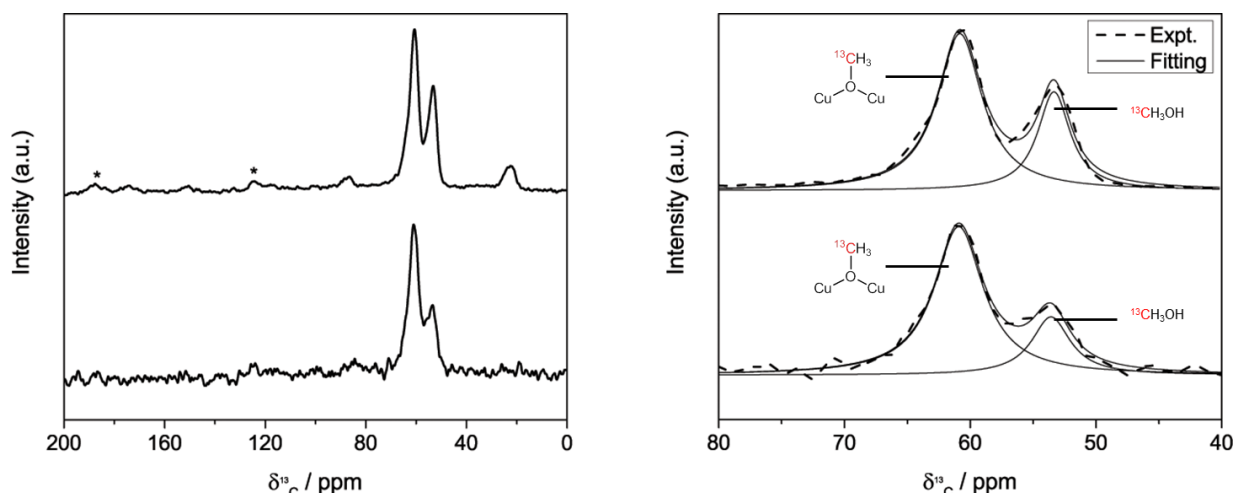


Figure S5. $^{13}\text{C}[^1\text{H}]$ CP MAS NMR spectra of Cu-MOR (Na-MOR precursor, Cu/Al = 0.36) after $^{13}\text{CH}_4$ oxidation (bottom spectrum) and after $^{13}\text{CH}_4$ oxidation and ^{13}CO carbonylation (top spectrum). (Left) Full ^{13}C MAS NMR spectra of Cu-Na-MOR (Cu/Al = 0.36) after reaction with $^{13}\text{CH}_4$ (bottom) and $^{13}\text{CH}_4 + ^{13}\text{CO}$ (top). (Right) Enlarged spectral region containing methoxy resonances. Simulated (solid) Lorentzian peaks are shown below the experimental (dashed) spectrum.

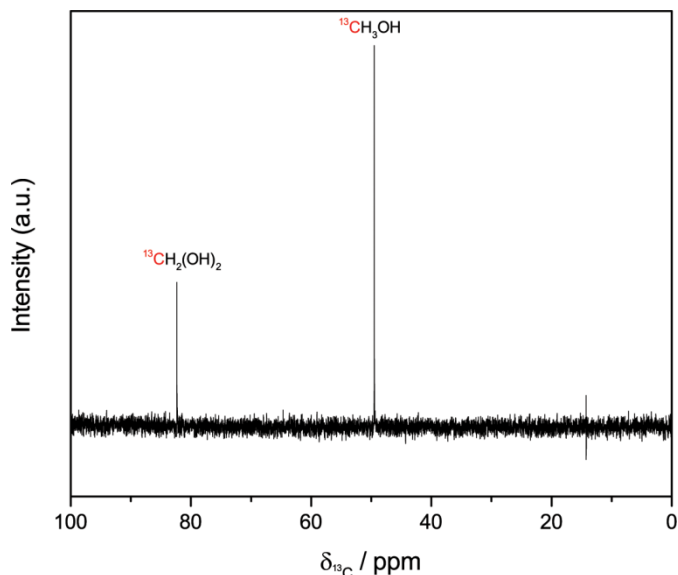


Figure S6. ^1H -NMR of liquid extraction in D_2O of Cu-Na-MOR (Cu/Al = 0.36, Na/Al = 0.37) after reaction with $^{13}\text{CH}_4 + ^{13}\text{CO}$ for 6 h.

Control Adsorptions of ^{13}C Methanol and Acetic Acid on Cu-MOR

Methanol was adsorbed onto Cu-H-MOR ($\text{Cu}/\text{Al} = 0.20$) and produced four peaks (Figure S7) in the methoxy region. The two peaks at the lowest field corresponded to methanol (53 ppm) and surface methoxy species on a Bronsted acid site (56 ppm). The assignment for the surface methoxy species was in agreement with a past assignment⁵ of methoxy species (57 ppm) on H-MOR (CBV20A, $\text{Si}/\text{Al} = 10$, Zeolyst) from the same vendor as the H-MOR used in this study. The two peaks at 60.0 and 64.6 ppm most likely corresponded to either dimethyl ether or methanol adsorbed onto copper ions. The exact nature of these peaks was unknown, however.

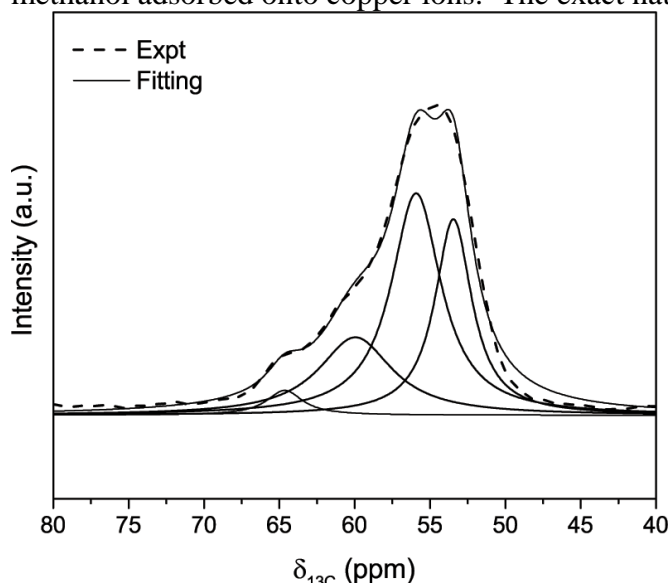


Figure S7. $^{13}\text{C}[^1\text{H}]$ CP MAS NMR spectra ^{13}C -Methanol adsorbed onto Cu-H-MOR ($\text{Cu}/\text{Al} = 0.20$). Simulated (solid) Lorentzian peaks are shown below the experimental (dashed) spectrum.

The methyl group of acetic acid was examined by adsorbing ^{13}C -acetic acid (^{13}C on methyl group only) onto Cu-H-MOR ($\text{Cu}/\text{Al} = 0.20$). Three peaks were found at 24.7, 22.0, and 19.7 ppm. The 22.0 ppm and 19.7 shifts corresponded to the methyl group of acetic acid physisorbed onto the zeolite. The higher field peak at 24.7 ppm was the methyl group of acetic acid when the carbonyl oxygen was either interacting with a copper site or a proximal Bronsted acid site through hydrogen bonding.

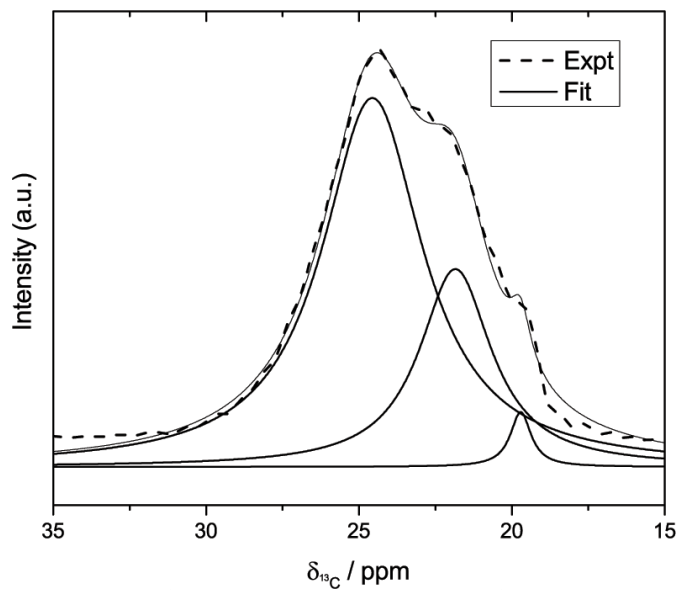


Figure S8. $^{13}\text{C}[^1\text{H}]$ CP MAS NMR spectrum of ^{13}C -Acetic Acid (Methyl group) adsorbed onto Cu-H-MOR (Cu/Al = 0.20). Simulated (solid) Lorentzian peaks are shown below the experimental (dashed) spectrum.

Ultra-violet-Visible Spectroscopy

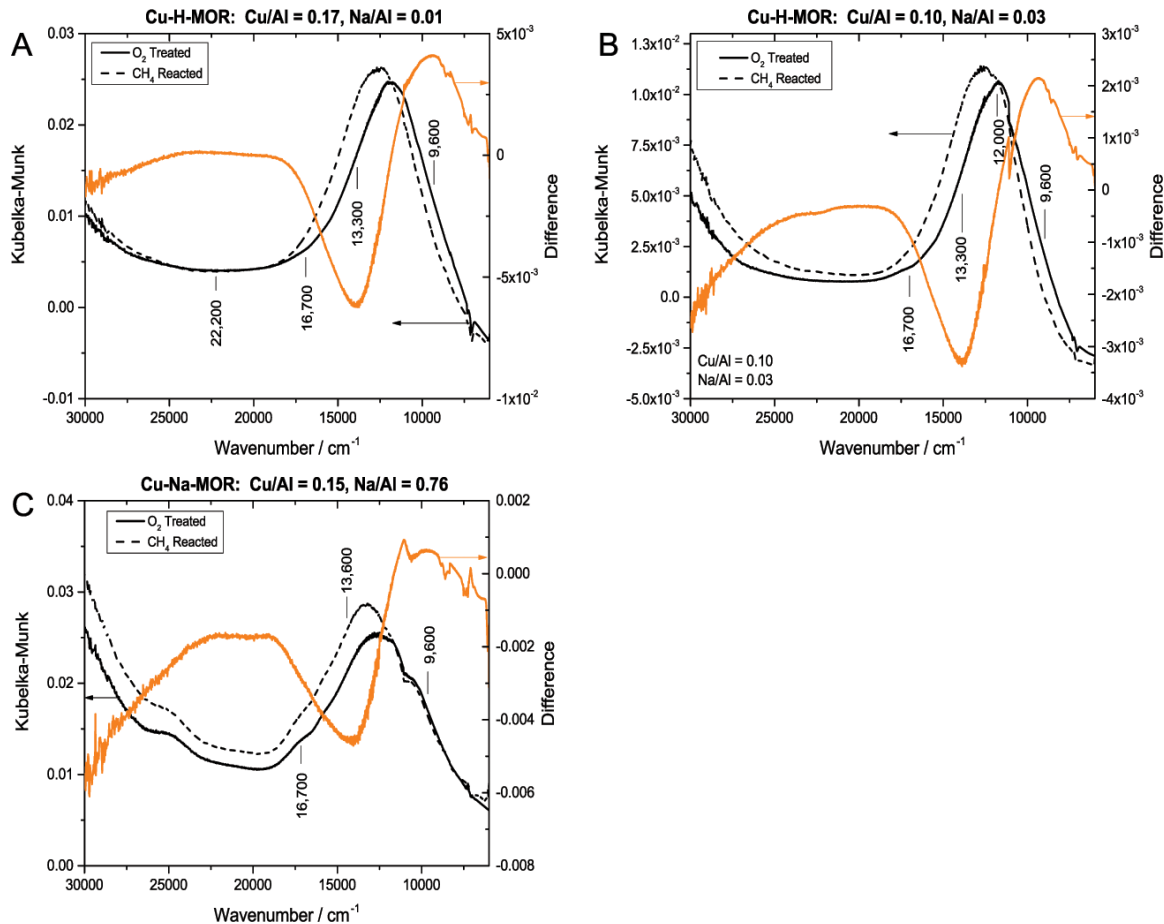


Figure S9. Diffuse Reflectance UV-visible spectra of (A) Cu-H-MOR (Cu/Al = 0.17), (B) Cu-H-MOR (Cu/Al = 0.10), and (C) Cu-Na-mor (Cu/Al = 0.15). Each zeolite was calcined under oxygen (solid) at 823 K for 5 h and reacted under methane (dashed) at 473 K for 2 h. Difference spectrum (calcined – CH_4 reacted) is in orange.

Figure S9 shows the visible region of Cu-MOR samples at low copper content ($\text{Cu/Al} < 0.20$) after calcination and then reaction after methane. In the Cu-H-MOR samples (A and B), the intensity of the $13,300 \text{ cm}^{-1}$ band decreased after reaction with methane as well as a shoulder at $9,600 \text{ cm}^{-1}$. Only a trace of the band at $22,200 \text{ cm}^{-1}$ was visible in sample A. In contrast to Cu-H-MOR, the sodium exchanged Cu-MOR had only a very small shoulder at $9,600 \text{ cm}^{-1}$ (C).

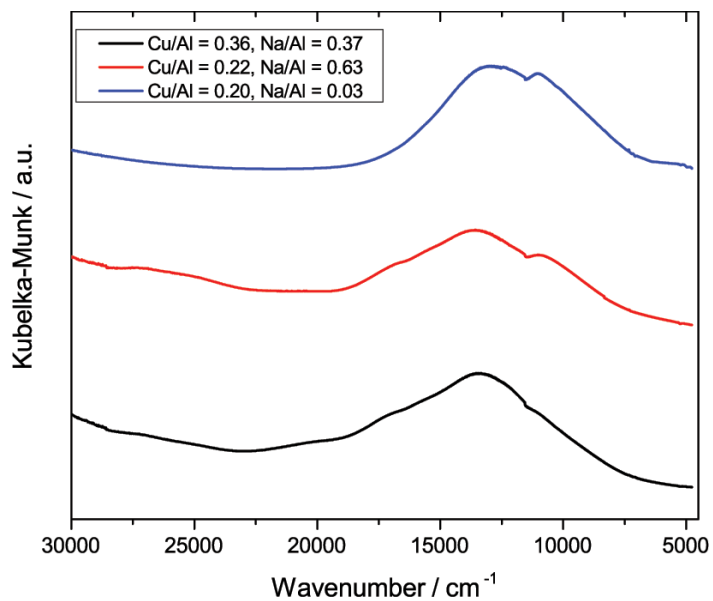


Figure S10: Vis-NIR Spectra of Cu-MOR zeolites calcined under oxygen (823 K) for 5 h

Figure S10 shows the visible and near-infrared regions of Cu-MOR zeolites at various copper content and Bronsted acidity after calcination under oxygen. No bands characteristic of water were observed at $5,200\text{ cm}^{-1}$ and $7,000\text{ cm}^{-1}$, thereby ruling out the possibility of water as the agent for the migration of methoxy species away from the copper centers.

Dissolution of Cu-MOR in Hydrofluoric Acid (HF)

After methane oxidation and carbonylation reactions over Cu-MOR, the total organic content on the zeolite surface was quantified by dissolving the zeolite in hydrofluoric acid. The product distribution from Cu-H-MOR (Cu/Al = 0.17) and Cu-Na-MOR (Cu/Al = 0.22, Na/Al = 0.55) shows that more acetic acid is produced when Bronsted acid sites are present. Additionally, the acetic acid-to-methanol ratio is at least as high as when products are extracted with water compared to the true surface composition.

Table S7: Product Extractions from Cu-MOR from Dissolution in HF vs. Extraction in D₂O

Parent Zeolite	Cu/Al	Na/Al	HF Dissolution ($\mu\text{mol/g}_{\text{cat}}$)		D ₂ O Extraction ($\mu\text{mol/g}_{\text{cat}}$)		Extraction Efficiency (%)
			Methanol	Acetic Acid	Methanol	Acetic Acid	
H-MOR	0.17	0.02	29.2	31.7	14.2	19.8	55
H-MOR ^a	0.17	0.02			26.0	22.6	80
Na-MOR	0.22	0.55	14.6	7.4	10.5	5.0	70

a: This experiment corresponds to Cu-H-MOR (Cu/Al = 0.17) in Figure 5. Extraction efficiency was calculated based on total organic content of the HF dissolution experiment

Dimethyl Ether Carbonylation on H-MOR and H-ZSM-5

Kinetic studies of dimethyl ether carbonylation on H-MOR by Iglesia and coworkers⁹ were conducted in packed-bed reactors under steady-state flow conditions. Since the reactions in this work were conducted in a stop-flow, batchwise manner, control reactions of dimethyl ether carbonylation on H-MOR were conducted to confirm the same dependence of the extent of carbonylation on the Bronsted acid content within the 8-membered rings^{9c,10}.

Dimethyl ether carbonylation reactions were performed in the same packed bed reactor described in the experimental setup for methane oxidation reactions. H-MOR or H-ZSM-5 (1.5 g, 500 – 1000 μm particles) were packed between quartz wool frits. Prior to reaction, the zeolite was calcined in 50 mL/min flowing oxygen (UHP, Airgas) for 5 h at 823 K and cooled under flowing oxygen to reaction temperature (473 K). The gas flow was changed to 50 mL/min of Ar for 1 hr to purge the system. Afterwards, the reaction mixture of 10 mL/min of dimethyl ether and 15 mL/min Ar for a 30 min reaction was brought over the zeolite bed. Upon saturating the surface with methoxy groups, carbonylation was performed with 200 mL/min of carbon monoxide (CO) at 10 bar gauge pressure for 30 min. Afterwards, the reactor was immediately depressurized, purged under Ar and cooled to room temperature. Once at room temperature, the zeolite bed was removed from the tube, weighed, and put into a sealed glass vial. The extraction procedure followed was identical to that described above for methane oxidation.

Carbonylation of dimethyl ether performed in stop flow mode still exhibited the same dependence of acetic acid production on Bronsted acidity. As the sodium content increased in H-MOR, the extracted acetic acid and methyl acetate decreased. Previous infrared spectroscopic studies on the same type of H-MOR zeolite (CBV21A, Zeolyst) calculated the H/Al of Bronsted acid sites in the 8-membered rings to be 0.55^{9c}. For Na/Al above 0.55, the extracted acetic acid and methyl acetate was essentially zero. Thus, the stop flow experiments reinforced that Bronsted acidity in the 8-membered rings was needed for carbonylation to occur, which was analogous to the continuous flow experiments.

The methanol extracted remained roughly constant despite the sodium content of H-MOR. At low Na/Al, the methanol extracted was predominantly from the Bronsted acid sites in the 12-membered rings where carbonylation was not favorable. For Na/Al < 0.55, the number of Bronsted acid sites in the 12-membered rings should remain constant from the sites in the 8MR pockets being preferentially quenched by sodium, so the methanol extracted should be roughly constant. However, for Na/Al of 0.8, the number of Bronsted acid sites must have been reduced such that the methanol extracted will decrease. The increased methanol extracted at high sodium content could have reflected the adsorption of dimethyl ether on sodium cations and its subsequent hydrolysis during extraction.

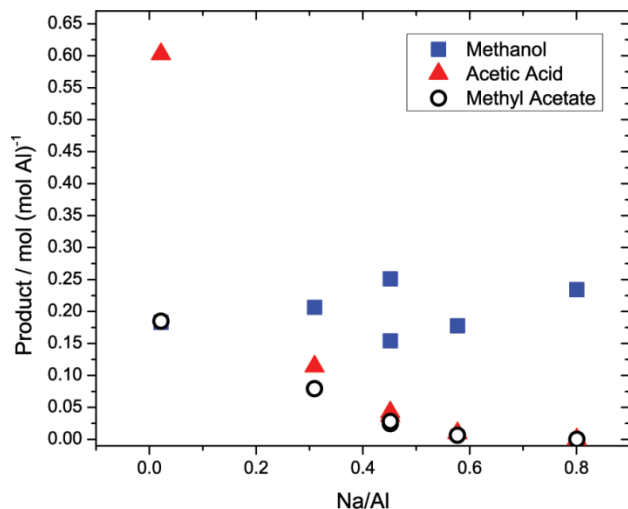


Figure S11. Carbonylation of Dimethyl Ether over H-MOR

Comparing the carbonylation activity of H-ZSM-5 with that of H-MOR, the amount of acetic acid extracted from H-ZSM-5 was 30-fold lower per aluminum site (Figure S12). This illustrated the importance of the Bronsted acid sites in 8-membered rings for carbonylation activity.

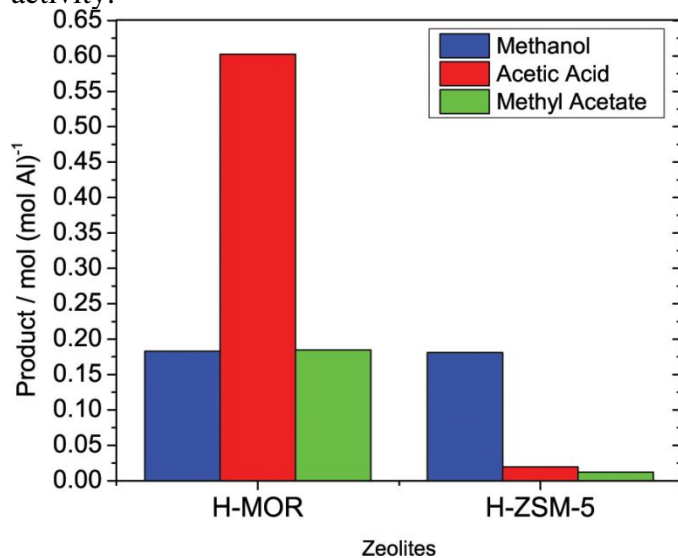


Figure S12. Carbonylation of dimethyl ether over H-MOR (Si/Al = 10) and H-ZSM-5 (Si/Al = 11.5)

X-Band EPR Spectra of Cu-MOR Samples

The full X-band EPR spectra of the Cu-MOR samples is shown in Figure S13. In the perpendicular region, the hyperfine splitting patterns of each Cu^{2+} species were not well resolved due to overlapping features. Only in Cu-Na-MOR with $\text{Cu}/\text{Al} = 0.22$ was a specific g_{xx} resolved as 2.06. The hyperfine splitting was more well defined after calcination in Cu-Na-MOR with $\text{Cu}/\text{Al} = 0.36$, possibly from another Cu^{2+} species becoming EPR silent.

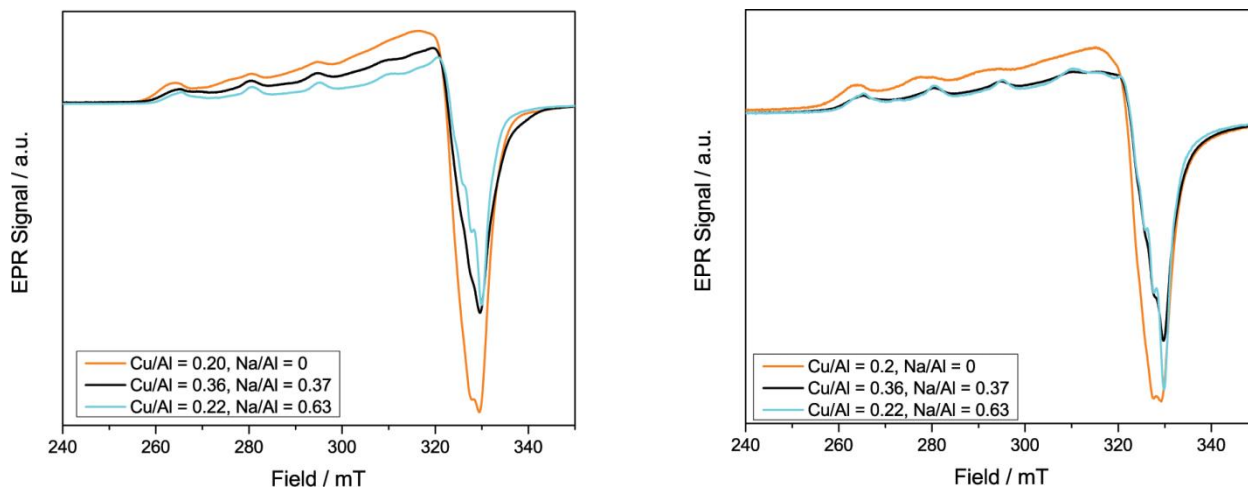


Figure S13. EPR Spectra (9.40 GHz) of (orange) Cu-H-MOR ($\text{Cu}/\text{Al} = 0.20$, $\text{Na}/\text{Al} = 0.03$), (black) Cu-Na-MOR ($\text{Cu}/\text{Al} = 0.36$, $\text{Na}/\text{Al} = 0.37$), and (cyan) Cu-Na-MOR ($\text{Cu}/\text{Al} = 0.22$, $\text{Na}/\text{Al} = 0.63$). (Left) Cu-MOR thermally treated under Ar for 3 h at 823 K and (Right) Cu-MOR calcined under O_2 for 5 h at 823 K and purged under Ar before acquisition.

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