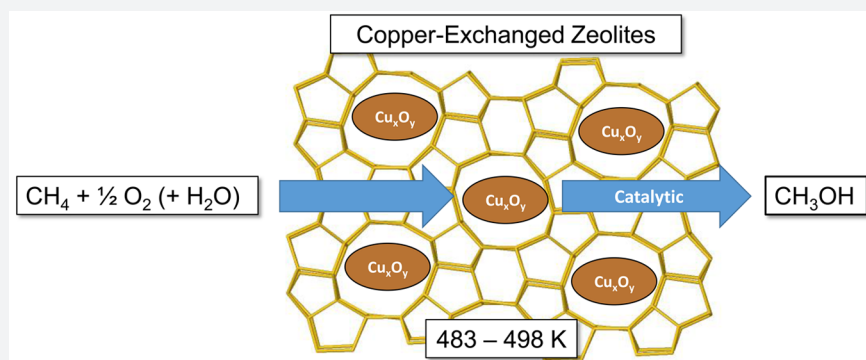


# Catalytic Oxidation of Methane into Methanol over Copper-Exchanged Zeolites with Oxygen at Low Temperature

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**S** Supporting Information



**ABSTRACT:** The direct catalytic conversion of methane to liquid oxygenated compounds, such as methanol or dimethyl ether, at low temperature using molecular oxygen is a grand challenge in C–H activation that has never been met with synthetic, heterogeneous catalysts. We report the first demonstration of direct, catalytic oxidation of methane into methanol with molecular oxygen over copper-exchanged zeolites at low reaction temperatures (483–498 K). Reaction kinetics studies show sustained catalytic activity and high selectivity for a variety of commercially available zeolite topologies under mild conditions (e.g., 483 K and atmospheric pressure). Transient and steady state measurements with isotopically labeled molecules confirm catalytic turnover. The catalytic rates and apparent activation energies are affected by the zeolite topology, with caged-based zeolites (e.g., Cu-SSZ-13) showing the highest rates. Although the reaction rates are low, the discovery of catalytic sites in copper-exchanged zeolites will accelerate the development of strategies to directly oxidize methane into methanol under mild conditions.

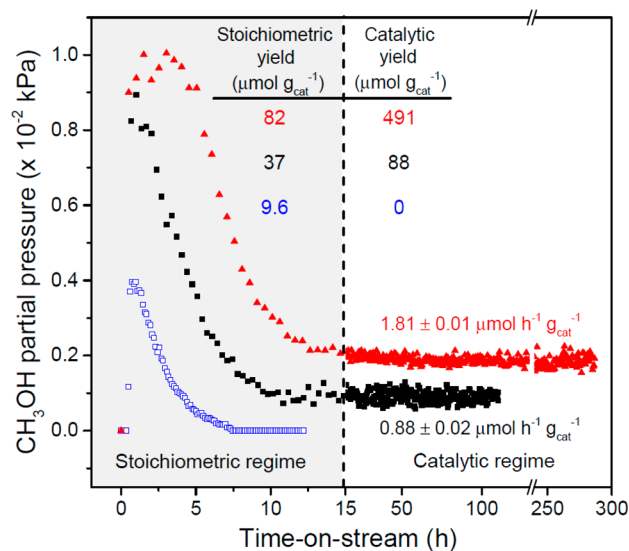
To date, no man-made catalyst can convert methane ( $\text{CH}_4$ ) and oxygen ( $\text{O}_2$ ) directly into methanol ( $\text{CH}_3\text{OH}$ ) at low temperature. For more than 100 years, the selective oxidation of this simple alkane has remained unsolved. This transformation, however, is essential to exploit our highly abundant natural gas reserves, particularly those located in distributed fields or stranded wells that cannot be accessed with large, capital-intensive reforming facilities. Although oxidative C–H bond activation of  $\text{CH}_4$  is thermodynamically and kinetically accessible at low temperatures, the large bond dissociation energy ( $435 \text{ kJ mol}^{-1}$ ) of this molecule hinders C–H cleavage reactions via homolytic or heterolytic pathways. Consequently, few catalysts are capable of preventing overoxidation to carbon dioxide ( $\text{CO}_2$ ). Several alternative strategies for activating methane have been reported, including multistep oxyfunctionalization with Periana catalysts,<sup>1,2</sup> borylation,<sup>3</sup> and electrophilic carbene insertion,<sup>4,5</sup> but all have fallen short of producing methanol directly and do not use oxygen as the oxidizing agent. In contrast, methane monooxygenase enzymes are capable of oxidizing  $\text{CH}_4$  selectively into  $\text{CH}_3\text{OH}$  using  $\text{O}_2$  at room temperature.<sup>6–8</sup> While such biocatalysts are difficult to scale-up, the nature of their active sites provides inspiration for the development of synthetic oxidation catalysts. In this respect,

iron<sup>9,10</sup> and copper<sup>11–13</sup> exchanged zeolites have emerged as a promising class of materials capable of selectively oxidizing  $\text{CH}_4$  into surface-bound methoxy species by hosting active sites akin to those found in  $\text{CH}_4$  monooxygenases. Despite their potential, these materials have only been shown to oxidize  $\text{CH}_4$  to  $\text{CH}_3\text{OH}$  stepwise and stoichiometrically with molecular oxygen ( $\text{O}_2$ )<sup>11,14,15</sup> or catalytically with hydrogen peroxide,<sup>16</sup> making the process prohibitively expensive. Here, we report the first instance of catalytic gas phase oxidation of  $\text{CH}_4$  into  $\text{CH}_3\text{OH}$  with  $\text{O}_2$  under mild conditions. Copper-exchanged zeolite catalysts of various topologies maintain sustained activity and high  $\text{CH}_3\text{OH}$  selectivity at 483 K, while transient kinetic experiments with isotopically labeled molecules confirm catalytic turnover. The discovery of catalytically active sites for  $\text{CH}_3\text{OH}$  production in zeolites will be the foundation to develop new strategies for low temperature catalytic methane oxidation.

The stoichiometric oxidation of  $\text{CH}_4$  to  $\text{CH}_3\text{OH}$  over copper-exchanged zeolites is believed to occur over mono-( $\mu$ -

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oxo) dicupric cores<sup>13,17</sup> or  $[\text{Cu}_3\text{O}_3]^{2+}$  trimeric sites<sup>18,19</sup> generated by flowing anhydrous  $\text{O}_2$  over the zeolite at temperatures above 723 K. These highly reactive electrophilic metal–oxygen species are adept at attacking the strong C–H bonds of  $\text{CH}_4$ , generating surface-bound methoxy groups at temperatures below 473 K.<sup>12</sup> Methoxy groups are typically extracted as  $\text{CH}_3\text{OH}$  by reacting with  $\text{H}_2\text{O}$ , which deactivates the copper sites and necessitates high temperature reactivation under anhydrous  $\text{O}_2$  to perform the next oxidation cycle.<sup>13,15</sup> In the present study, stoichiometric and catalytic  $\text{CH}_3\text{OH}$  production regimes are observed during the gas phase oxidation of  $\text{CH}_4$  over copper-exchanged zeolites with the MFI topology in the sodium (Cu–Na–ZSM-5) or proton (Cu–H–ZSM-5) forms at 483 K and atmospheric pressure (Figure 1). Similar to

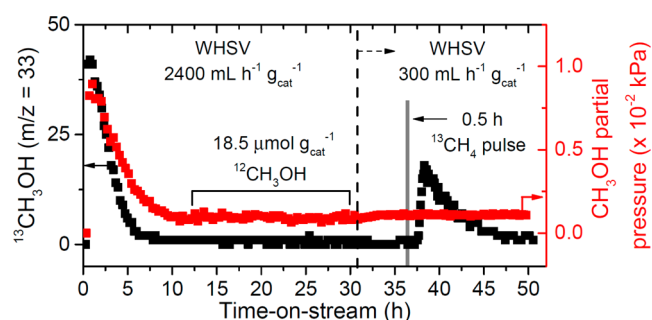


**Figure 1.**  $\text{CH}_4$  oxidation over Cu–ZSM-5. Catalyst pretreatment: 5 h at 823 K under flowing  $\text{O}_2$ , cooled to 483 K under  $\text{O}_2$  flow and then purged under He for 0.5 h. Initial dry  $\text{CH}_4$  oxidation: 0.5 h under  $2400 \text{ mL h}^{-1} \text{ g}_{\text{cat}}^{-1}$  of  $\text{CH}_4$  at 483 K.  $\text{CH}_3\text{OH}$  partial pressure (kPa) with  $\text{He}/\text{H}_2\text{O}/\text{O}_2$  over (blue open squares) Cu–Na–ZSM-5 (Cu/Al = 0.37, Na/Al = 0.26):  $T = 483 \text{ K}$ ,  $\text{WHSV} = 2400 \text{ mL h}^{-1} \text{ g}_{\text{cat}}^{-1}$ ,  $P_{\text{He}} = 98.1 \text{ kPa}$ ,  $P_{\text{H}_2\text{O}} = 3.2 \text{ kPa}$ ,  $P_{\text{O}_2} = 0.0025 \text{ kPa}$  (25 ppm).  $\text{CH}_3\text{OH}$  partial pressure (kPa) with  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ , and  $\text{O}_2$  over (■) Cu–Na–ZSM-5 and (red solid triangles) Cu–H–ZSM-5 (Cu/Al = 0.31):  $T = 483 \text{ K}$ ,  $\text{WHSV} = 2400 \text{ mL h}^{-1} \text{ g}_{\text{cat}}^{-1}$ ,  $P_{\text{CH}_4} = 98.1 \text{ kPa}$ ,  $P_{\text{H}_2\text{O}} = 3.2 \text{ kPa}$ ,  $P_{\text{O}_2} = 0.0025 \text{ kPa}$  (25 ppm).

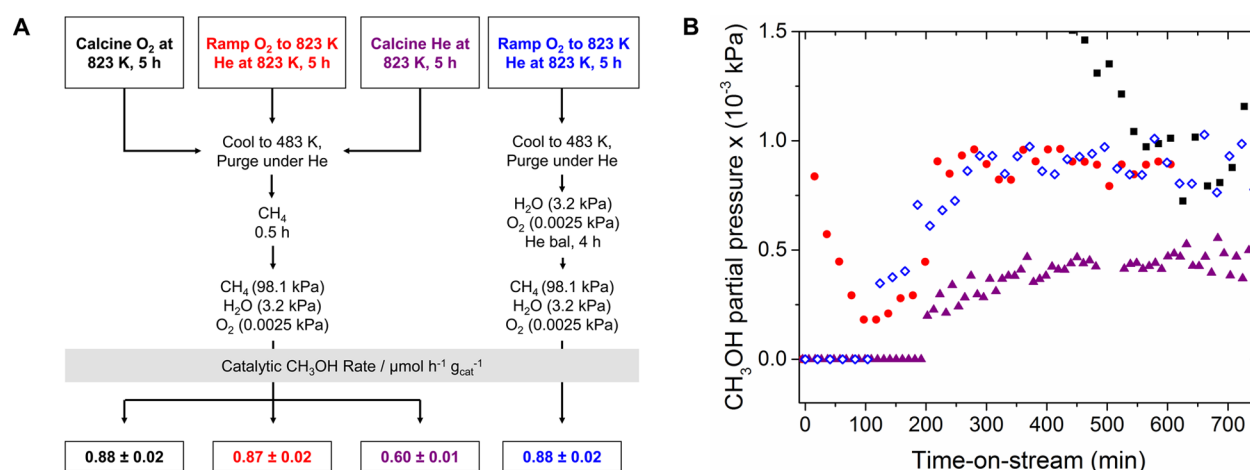
previous studies, the catalysts were activated under flowing  $\text{O}_2$  at 823 K, cooled to reaction temperature, purged with helium (He) for 1 h, and contacted with a pure  $\text{CH}_4$  stream for 0.5 h.<sup>11,13,14</sup> However, unlike previous studies using only  $\text{H}_2\text{O}$  for extraction, we hydrolyzed surface-bound methoxy species by flowing a gas mixture comprised of 3.2 kPa of  $\text{H}_2\text{O}$ , 0.0025 kPa of  $\text{O}_2$  and balance  $\text{CH}_4$ . Under these conditions, Cu–Na–ZSM-5 (Cu/Al = 0.37, Na/Al = 0.26) and Cu–H–ZSM-5 (Cu/Al = 0.31) evolved  $37 \mu\text{mol g}_{\text{cat}}^{-1}$  and  $82 \mu\text{mol g}_{\text{cat}}^{-1}$  of stoichiometric  $\text{CH}_3\text{OH}$ , respectively. These values are more than two times higher than those obtained with Cu–Na–ZSM-5 using only He,  $\text{O}_2$ , and  $\text{H}_2\text{O}$  as the extracting gas ( $9.6 \mu\text{mol g}_{\text{cat}}^{-1}$ ) or those reported by Lobo et al. ( $16 \mu\text{mol g}_{\text{cat}}^{-1}$ )<sup>20</sup> using 3.2 kPa  $\text{H}_2\text{O}$  in  $\text{N}_2$  at 473 K and Schoonheydt et al. ( $8 \mu\text{mol g}_{\text{cat}}^{-1}$ )<sup>11,14</sup> using a 50% v/v acetonitrile aqueous solution for 1 h at 298 K to extract the oxidized products.

Remarkably, sustained  $\text{CH}_4$  oxidation activity was observed when continuing to feed the  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ , and  $\text{O}_2$  gas mixture after all stoichiometric  $\text{CH}_3\text{OH}$  was extracted (Figure 1). Steady state  $\text{CH}_3\text{OH}$  production rates of  $0.88 \pm 0.02 \mu\text{mol h}^{-1} \text{ g}_{\text{cat}}^{-1}$  and  $1.81 \pm 0.01 \mu\text{mol h}^{-1} \text{ g}_{\text{cat}}^{-1}$  were measured for Cu–Na–ZSM-5 and Cu–H–ZSM-5, respectively. Over Cu–Na–ZSM-5,  $\text{CH}_3\text{OH}$  was the main product generated (as determined by  $^1\text{H}$  nuclear magnetic resonance, Figure S1) with a selectivity of  $70.6 \pm 0.4\%$ , while  $\text{CO}_2$  was the only byproduct generated at a rate of  $0.38 \pm 0.02 \mu\text{mol h}^{-1} \text{ g}_{\text{cat}}^{-1}$  (Figure S2).  $\text{CO}_2$  selectivity did not increase when higher conversions were simulated by introducing  $\text{CH}_3\text{OH}$  as a reagent at identical conditions (Supporting Information, Section S2, Figures S3–S4), although most of  $\text{CH}_3\text{OH}$  was dehydrated into dimethyl ether in the presence of acid sites at these conditions (>60% yield). Notably, the steady state  $\text{CH}_3\text{OH}$  production rates persisted without apparent deactivation, generating a total of  $88 \mu\text{mol g}_{\text{cat}}^{-1}$  over 108 h with Cu–Na–ZSM-5—a value roughly five times higher than that reported for the stoichiometric oxidation over Cu–Na–ZSM-5.<sup>20</sup> Similarly, Cu–H–ZSM-5 generated a total of  $491 \mu\text{mol g}_{\text{cat}}^{-1}$  over 288 h—a value ca. 1.4 times larger than the total copper content of the zeolite (Figure S5). The excess  $\text{CH}_3\text{OH}$  produced per copper atom in Cu–H–ZSM-5 coupled with the lack of sustained  $\text{CH}_3\text{OH}$  production in the absence of  $\text{CH}_4$  in the extracting gas mixture over Cu–Na–ZSM-5 (Figure 1, open symbols) are strong evidence that  $\text{CH}_4$  is oxidized catalytically over  $\text{H}_2\text{O}$ -tolerant copper sites.

Catalytic turnover was verified with transient experiments using isotopically labeled molecules coupled with online mass spectrometry (MS).  $^{13}\text{C}$  methoxy species were deposited on the zeolite by flowing  $^{13}\text{CH}_4$  (16.8 kPa  $^{13}\text{CH}_4$  [99 atom %  $^{13}\text{C}$ , Sigma-Aldrich] with balance He) over an activated Cu–Na–ZSM-5 sample for 0.5 h at 483 K and then flowing a regular  $^{12}\text{CH}_4/\text{H}_2\text{O}/\text{O}_2$  gas mixture to extract the methoxy species (detailed procedure found in Figure S6A). As shown in Figure 2, enriched  $^{13}\text{CH}_3\text{OH}$  ( $m/z = 33$ ) was detected in the stoichiometric regime, but unlabeled  $^{12}\text{CH}_3\text{OH}$  was observed in the steady state regime, thus suggesting that new, unlabeled  $^{12}\text{C}$  methoxy species are formed after the initial  $^{13}\text{C}$  methoxy species are hydrolyzed. Next, the reaction was allowed to proceed at steady state at a measured rate of  $0.88 \mu\text{mol}$



**Figure 2.** Transient, isotopically labeled kinetic experiments over Cu–Na–ZSM-5 (Cu/Al = 0.37, Na/Al = 0.26). Catalyst pretreatment: 5 h at 823 K under flowing  $\text{O}_2$ , cooled to 483 K under  $\text{O}_2$  flow and purged under He for 0.5 h. Initial  $\text{CH}_4$  oxidation: 0.5 h under  $2400 \text{ mL h}^{-1} \text{ g}_{\text{cat}}^{-1}$  of 17%  $^{13}\text{CH}_4/\text{He}$  at 483 K. Reaction conditions:  $T = 483 \text{ K}$ ,  $\text{WHSV} = 2400 \text{ mL h}^{-1} \text{ g}_{\text{cat}}^{-1}$ ,  $P_{^{12}\text{CH}_4} = 98.1 \text{ kPa}$ ,  $P_{\text{H}_2\text{O}} = 3.2 \text{ kPa}$ ,  $P_{\text{O}_2} = 0.0025 \text{ kPa}$  (25 ppm). After 31 h on-stream, WHSV was reduced to  $300 \text{ mL h}^{-1} \text{ g}_{\text{cat}}^{-1}$  represented by the dashed line. Gray area denotes 0.5 h pulse of  $P_{^{13}\text{CH}_4} = 98 \text{ kPa}$ ,  $P_{\text{H}_2\text{O}} = 3.2 \text{ kPa}$ ,  $P_{\text{O}_2} = 0.0025 \text{ kPa}$ .



**Figure 3.** Thermal pretreatments and onset of steady state CH<sub>4</sub> oxidation over Cu-Na-ZSM-5 (Cu/Al = 0.37). (A) Thermal pretreatments, reaction conditions for all pretreatments, and catalytic CH<sub>3</sub>OH production rates. The symbol ± denotes 95% confidence interval. (B) Evolution of catalytic CH<sub>3</sub>OH production for each pretreatment outlined in (A);  $t = 0$  denotes when the CH<sub>4</sub>/H<sub>2</sub>O/O<sub>2</sub> gas flow was started. Reaction conditions:  $T = 483$  K, WHSV = 2400 mL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>,  $P_{\text{CH}_4} = 98.1$  kPa,  $P_{\text{H}_2\text{O}} = 3.2$  kPa,  $P_{\text{O}_2} = 0.0025$  kPa.

CH<sub>3</sub>OH h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> for 21 h (equivalent to the production of 18.5  $\mu\text{mol g}_{\text{cat}}^{-1}$  of <sup>12</sup>CH<sub>3</sub>OH). At this point, the weight hourly space velocity (WHSV) was reduced from 2400 mL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> to 300 mL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, and the gas mixture was switched to <sup>13</sup>CH<sub>4</sub>/H<sub>2</sub>O/O<sub>2</sub> for 0.5 h before resuming the flow of the regular, unlabeled gas mixture. This effective pulse of labeled <sup>13</sup>CH<sub>4</sub> resulted in the production of labeled <sup>13</sup>CH<sub>3</sub>OH as evidenced by a detectable pulse of the  $m/z = 33$  signal without significantly altering steady state production of CH<sub>3</sub>OH (Figure 2). Similar <sup>13</sup>C enrichment profiles were observed for CO<sub>2</sub> during both isotope switching experiments (Figure S7). Analogous behavior was observed for similar experiments carried out over Cu-H-ZSM-5 (Figure S8). Control experiments using <sup>12</sup>CH<sub>4</sub> to populate the activated catalyst with unlabeled <sup>12</sup>C methoxy species did not generate a significant amount of <sup>13</sup>CH<sub>3</sub>OH in the stoichiometric or steady state regimes (Figures S6B, S8B), thereby ruling out artifacts or potential effects arising from natural abundance <sup>13</sup>CH<sub>4</sub> in the unlabeled gas stream. Kinetic measurements on Cu-Na-ZSM-5 at 483 K show first, half, and zero order dependencies with respect to CH<sub>4</sub>, H<sub>2</sub>O, and O<sub>2</sub>, respectively (Supporting Information Section S7, Figure S9). Importantly, replacing CH<sub>4</sub> with CD<sub>4</sub> in the extracting gas during steady state operation at a WHSV of 240 mL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> decreased the CH<sub>3</sub>OH production rate from 0.090 to 0.055  $\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$  (Figure S10). This change corresponds to a kinetic isotope effect (KIE) of  $1.6 \pm 0.1$ , thus indicating that C–H abstraction is a kinetically relevant step in the catalytic cycle. Taken together, the data from the transient <sup>13</sup>CH<sub>4</sub> pulse experiments, the reaction rate order dependencies, and the kinetic isotope effect confirm catalytic turnover.

Gas pretreatments were varied to gain insight into the origin of catalytic and stoichiometric sites in Cu-Na-ZSM-5 (see Figures 3, S11–12). Specifically, Cu-Na-ZSM-5 samples were subjected to three pretreatments at 873 K prior to regular CH<sub>4</sub> oxidation and extraction at 483 K: (i) calcination under O<sub>2</sub> and then under He (20 ppm of O<sub>2</sub>); (ii) calcination under He (20 ppm of O<sub>2</sub>); or (iii) calcination under He without O<sub>2</sub> (<0.1 ppm, Figure S11). In all cases, stoichiometric CH<sub>3</sub>OH production drastically diminished (98–100%), but catalytic CH<sub>3</sub>OH production was only moderately affected (0–60%)

(Figure 3). Treating activated Cu-Na-ZSM-5 with He above 723 K has been shown to eliminate the mono-( $\mu$ -oxo) dicupric cores for stoichiometric CH<sub>4</sub> oxidation.<sup>14</sup> The absence of the mono-( $\mu$ -oxo) dicupric sites during steady state methane oxidation was confirmed with UV–visible spectroscopic and online gas chromatographic measurements over Cu-Na-ZSM-5 (Cu/Al = 0.37) (Supporting Information Section S9, Figures S13–S15). Interestingly, van Bokhoven et al. observed a small fraction of H<sub>2</sub>O-tolerant sites in copper-exchanged mordenite (Cu-MOR) that did not require high temperature reactivation for stoichiometric CH<sub>4</sub> oxidation experiments after exposure to H<sub>2</sub>O.<sup>21,22</sup> However, in the present study, exposing Cu-Na-ZSM-5 to H<sub>2</sub>O/O<sub>2</sub>/He at 483 K prior to contacting it with CH<sub>4</sub> completely eliminated stoichiometric CH<sub>3</sub>OH production but did not affect catalytic CH<sub>3</sub>OH production. Note the onset of the catalytic regime was nearly identical for all samples (240 min on-stream) after exposure to CH<sub>4</sub>/H<sub>2</sub>O/O<sub>2</sub> irrespective of the pretreatment used. The similarity of catalytic rates and onset of CH<sub>3</sub>OH production for all pretreated Cu-Na-ZSM-5 samples implies the catalytic sites are different from those responsible for stoichiometric CH<sub>4</sub> oxidation, and the catalytic sites are either generated or activated when copper species are exposed to CH<sub>4</sub>, H<sub>2</sub>O, and O<sub>2</sub> at reaction conditions rather than during the high temperature pretreatment.

An induction period preceding the onset of catalytic CH<sub>4</sub> oxidation suggests that copper speciation changes under reaction conditions. The CH<sub>3</sub>OH production profile for a regular CH<sub>4</sub> oxidation and extraction experiment using Cu-Na-ZSM-5 pretreated at 823 K first with O<sub>2</sub> and then with He (20 ppm of O<sub>2</sub>) shows that catalytic production began after 240 min on-stream despite H<sub>2</sub>O breaking through the catalyst bed after 25 min (Figure S12). A comparable induction process was observed when Cu-Na-ZSM-5 was pretreated without O<sub>2</sub> and exposed to a CH<sub>4</sub>/H<sub>2</sub>O gas mixture at 483 K (Figure S11). In this case CH<sub>3</sub>OH was detected only ca. 300 min after O<sub>2</sub> was introduced into the system. Hydrated copper species are known to weakly associate with the zeolite framework, becoming mobile and easily oxidized.<sup>23</sup> In copper-exchanged zeolites with the chabazite topology (Cu-SSZ-13), hydrated Cu<sup>2+</sup> ions have been shown to migrate under flowing wet O<sub>2</sub>/N<sub>2</sub> (and trace NO and NH<sub>3</sub>) gas mixtures between 403–523 K during the

Table 1. Catalytic CH<sub>4</sub> Oxidation Rates for Various Zeolite Topologies<sup>a</sup>

material	framework	cage shape	cage size (Å) <sup>26</sup>	channel size (Å) <sup>27</sup>	Si/Al <sub>nom</sub> <sup>b</sup>	Si/Al <sub>tot</sub> <sup>c</sup>	Cu/Al <sub>tot</sub> <sup>d</sup>	specific activity <sup>e</sup>	STY (h <sup>-1</sup> × 10 <sup>-3</sup> ) <sup>f</sup>
H-ZSM-5	MFI			5.3 × 5.6 5.1 × 5.5	11.5	13.2	0.31	1.79 ± 0.02	5.2 ± 0.05
H-Beta	BEA			6.6 × 6.7 5.6 × 5.6	12.5	13.3	0.30	0.80 ± 0.01	2.4 ± 0.04
MCM-41	MCM-41			30	12	16.1	0.74	0.36 ± 0.02	0.6 ± 0.03
H-ZSM-5	MFI			5.3 × 5.6 5.1 × 5.5	11.5	13.9	0.13	0.84 ± 0.02	6.0 ± 0.17
H-mordenite	MOR			6.5 × 7 2.6 × 5.7	10	11.1	0.14	0.84 ± 0.01	4.6 ± 0.08
H-ferrierite	FER			4.2 × 5.4 3.5 × 4.8	10	10.6	0.12	0.44 ± 0.01	2.7 ± 0.04
Na-ZSM-5	MFI			5.3 × 5.6 5.1 × 5.5	11.5	13.6	0.37	0.88 ± 0.02	2.2 ± 0.04
Na-Y	FAU	spherical	9.6 × 9.6	7.4 × 7.4	5.1	4.6	0.45	0.30 ± 0.01	0.3 ± 0.01
Na-SAPO-34	CHA	ellipsoidal	9.4 × 9.4 × 12.7	3.8 × 3.8	0.3	0.6	0.02	0.84 ± 0.03	7.9 ± 0.29
Na-SSZ-13	CHA	ellipsoidal	9.4 × 9.4 × 12.7	3.8 × 3.8	15	13.8	0.50	3.12 ± 0.01	6.1 ± 0.03
CuO <sub>x</sub> -MFI <sup>g</sup>	MFI			5.3 × 5.6 5.1 × 5.5	∞	∞	∞	0	0
CuO <sub>x</sub> -BEA <sup>g</sup>	BEA			6.6 × 6.7 5.6 × 5.6	∞	∞	∞	0	0
H-ZSM-5 <sup>g</sup>	MFI			5.3 × 5.6 5.1 × 5.5	11.5	12.9	0	0	0

<sup>a</sup>Catalyst pretreatment: 5 h at 823 K under flowing O<sub>2</sub>, cooled to 483 K under O<sub>2</sub> flow and then purged under He for 0.5 h. Initial CH<sub>4</sub> oxidation: 0.5 h under 2400 mL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup> CH<sub>4</sub> at 483 K. Reaction conditions: T = 483 K, WHSV = 2400 mL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, P<sub>CH<sub>4</sub></sub> = 98.1 kPa, P<sub>H<sub>2</sub>O</sub> = 3.2 kPa, P<sub>O<sub>2</sub></sub> = 0.0025 kPa (25 ppm). <sup>b</sup>Si/Al<sub>nom</sub> denotes the nominal silicon to aluminum ratio in the zeolite based on commercial figures or ratios of SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> in synthesis procedures. <sup>c</sup>Si/Al<sub>tot</sub> denotes the ratio of silicon to aluminum atoms ratio within the zeolite calculated using data from inductively coupled plasma mass spectrometry (ICP-MS) measurements. <sup>d</sup>Cu/Al<sub>tot</sub> denotes the ratio of copper to aluminum atoms within the zeolite calculated using ICP-MS. <sup>e</sup>Specific activity = μmol<sub>CH<sub>3</sub>OH</sub> h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. <sup>f</sup>Site time yield (STY) defined as mol CH<sub>3</sub>OH (mol Cu)<sup>-1</sup> h<sup>-1</sup>. <sup>g</sup>T = 483 K, WHSV = 2400 mL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, P<sub>CH<sub>4</sub></sub> = 93.1 kPa, P<sub>H<sub>2</sub>O</sub> = 3.2 kPa, P<sub>O<sub>2</sub></sub> = 0.051 kPa. The ± symbol denotes 95% confidence intervals.

selective catalytic reduction (SCR) of NO<sub>x</sub><sup>24</sup> to form transient dimeric active sites.<sup>25</sup> The strong similarities between the reaction temperature and the gaseous atmosphere (H<sub>2</sub>O/O<sub>2</sub>) used during both the SCR of NO<sub>x</sub> and the oxidation of CH<sub>4</sub> could imply that mobile, hydrated copper species also rearrange into active sites for catalytic CH<sub>4</sub> oxidation as they do for the SCR of NO<sub>x</sub>.

Catalytic CH<sub>4</sub> oxidation was investigated as a function of the copper content and Brønsted acidity of the zeolite (see Table S1). A control experiment with H-ZSM-5 (Si/Al = 11.5) not subjected to copper exchange did not generate CH<sub>3</sub>OH (Table 1), thereby confirming that trace transition metal impurities in the zeolite are not responsible for catalytic behavior. Higher Cu/Al ratios in Cu-Na-ZSM-5 and Cu-H-ZSM-5 increased the steady state specific activity (defined as μmol<sub>MeOH</sub> h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>), but decreased the site-time yield (STY, defined as mol<sub>CH<sub>3</sub>OH</sub> mol<sub>Cu</sub><sup>-1</sup> h<sup>-1</sup>), suggesting that the number of active sites does not increase proportionally with the total amount of copper. The presence of Brønsted acid sites increased specific activity and STY for all samples with similar Cu/Al ratios. Indeed, different apparent activation energies (E<sub>a</sub><sup>app</sup>) were observed between the sodium and proton forms of Cu-ZSM-5 (Table S1). Density functional theory calculations over Cu-ZSM-5 have shown that Brønsted acid sites change the energetics of the formation of mono-(μ-oxo) dicupric cores with NO.<sup>28</sup> While mono-(μ-oxo) dicupric cores are likely not present under reaction conditions for catalytic CH<sub>4</sub> oxidation, Brønsted acid sites could impart similar changes in the energetics of formation of the catalytic sites.

The catalytic rates and E<sub>a</sub><sup>app</sup> values of CH<sub>4</sub> oxidation are heavily influenced by zeolite topology (see Table 1, Table S1). Cu-MOR, featuring 12-membered ring (MR) pores intersected by sinusoidal 8-MR pores, exhibited either comparable or lower activity at 483 K than that of Cu-H-ZSM-5 (Table S1). However, a significantly higher E<sub>a</sub><sup>app</sup> of 149 kJ/mol resulted in higher CH<sub>3</sub>OH rates at temperatures above 483 K when compared to those of Cu-H-ZSM-5 (Figure S16). These results suggest the site speciation and reaction environment within MOR may play a role in stabilizing kinetically relevant transition states. Other topologies, including ferrierite (FER), beta (BEA), Y (FAU), and caged-based SSZ-13 and SAPO-34 (CHA) also oxidize CH<sub>4</sub> into CH<sub>3</sub>OH but with different rates than those of ZSM-5. Zeolites with large pores at high Cu/Al (0.30–0.50) including BEA (12-MR, 6.6 × 6.7 Å and 5.6 × 5.6 Å) and FAU (7.4 × 7.4 Å windows) showed 50% and 70% lower overall activity when compared to MFI. MCM-41, an amorphous aluminosilicate with large pores of 30 Å, had nearly an order of magnitude lower STY than ZSM-5, indicating that a crystalline, microporous structure with small pores is preferable for catalytic CH<sub>4</sub> oxidation. At low Cu/Al (0.12–0.14), Cu-H-ZSM-5 has the highest specific activity and STY (Table 1), while FER (intersecting 10-MR [4.2 × 5.4 Å] and 8-MR [3.5 × 4.8 Å]) was half as active as ZSM-5. While Cu-ZSM-5 had the highest specific activity and STY compared to the small-pore zeolites tested, the cage-based aluminosilicate SSZ-13 and the silicoaluminophosphate SAPO-34 with the CHA topology (8-MR windows of 3.8 × 3.8 Å, ellipsoidal cages of 9.4 × 9.4 × 12.7 Å) featured higher STY of 6.1 × 10<sup>-3</sup> h<sup>-1</sup> and 7.9 × 10<sup>-3</sup> h<sup>-1</sup>, respectively, than those in Cu-Na-ZSM-5 or Cu-H-ZSM-5

at similar Cu/Al ratios (Table 1). These studies indicate the catalytic sites or the kinetically relevant transition states are sensitive to the zeolite topology, with materials featuring small pores or cage-based structures showing enhanced performance when compared to those with large pores.

Taking advantage of the large  $E_a^{\text{app}}$  for Cu-Na-SSZ-13 (Cu/Al = 0.50,  $100 \pm 2.1 \text{ kJ mol}^{-1}$ ), the reaction temperature was systematically increased to achieve higher catalytic rates. The site-time yield increased from  $2.2 \times 10^{-3}$  to  $31.6 \times 10^{-3} \text{ mol}_{\text{CH}_3\text{OH}} (\text{mol Cu})^{-1} \text{ h}^{-1}$  when increasing the temperature from 463 to 533 K before a decrease in rates was observed (Figure S17). The large  $E_a^{\text{app}}$  coupled with the stable  $\text{CH}_3\text{OH}$  production over a wide range of temperature suggest that Cu-SSZ-13 zeolites could be further engineered to enhance further catalytic rates. In summary, copper-exchanged zeolites offer a broad and robust platform for the low temperature, catalytic oxidation of  $\text{CH}_4$  into  $\text{CH}_3\text{OH}$  using  $\text{O}_2$ .

The nature of the catalytic active sites for  $\text{CH}_4$  oxidation into  $\text{CH}_3\text{OH}$  over copper-exchanged zeolites is currently unknown. A recent report by von Bokhoven et al. observed the formation of copper oxide clusters in Cu-MOR after the cyclic, isothermal, and stoichiometric oxidation of  $\text{CH}_4$  into  $\text{CH}_3\text{OH}$ .<sup>22</sup> It was hypothesized that these oxide clusters were active for isothermal cyclic  $\text{CH}_4$  oxidation. We did not observe steady state activity for large copper oxide nanoparticles supported on pure silica MFI between 483 and 543 K (average size 30 nm for  $\text{CuO}_x$ , Table 1, Figures S18–20) or on pure silica BEA (average size 60 nm for  $\text{Cu}_2\text{O}$ , 41 nm for  $\text{CuO}$ , Table 1, Figures S21–22). However, we cannot rule out that ultrasized copper oxide clusters, or copper species stabilized by aluminum in the zeolite framework or in defect sites are responsible for catalytic activity. Diffuse reflectance UV–visible spectroscopic measurements show peaks forming at 20 800, 26 800, and 30 000  $\text{cm}^{-1}$  during steady state  $\text{CH}_3\text{OH}$  production (Figure S15C.1–2, D.1–2), possibly corresponding to copper oxide species<sup>29</sup> generated during reaction. Future work will focus on identifying and characterizing the catalytic site(s) as well as devising strategies to maximize catalytic activity.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.6b00139.

Experimental details, product identification for catalytic  $\text{CH}_4$  oxidation over Cu-Na-ZSM-5, simulation of high conversion  $\text{CH}_4$  oxidation over Cu-Na-ZSM-5, control experiments for isotopically labeled kinetic experiments, kinetic order of reactants over Cu-Na-ZSM-5, thermal and gas pretreatments on Cu-Na-ZSM-5, in-situ UV–visible spectra of Cu-Na-ZSM-5, kinetic data of  $\text{CH}_4$  oxidation over Cu-ZSM-5 and Cu-MOR,  $\text{CH}_4$  oxidation vs temperature over Cu-Na-SSZ-13, powder X-ray diffraction patterns and  $\text{CH}_4$  oxidation vs temperature over  $\text{CuO}_x$  on silica MFI and BEA, powder X-ray diffraction patterns of ZSM-5 and MOR, elemental composition, pore volume, and surface area of ZSM-5, MOR, and SSZ-13 (PDF)

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## Notes

The authors declare the following competing financial interest(s): The authors and MIT have filed a patent on the results presented herein.

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