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# Effect of Active Sites Structure on Activity of Copper Mordenite in Aerobic and Anaerobic Conversion of Methane to Methanol

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**Abstract:** Zeolite mordenite with different Si/Al ratio was used to synthesize the materials with monomeric and oligomeric copper sites active in the process of direct conversion of methane into methanol. Comparison of two reactivation protocols with oxygen (aerobic oxidation) respectively water (anaerobic oxidation) revealed that such copper-oxo species possess different reactivity towards methane and water. We have shown for the first time that copper oligomer species exhibit high activity under both aerobic and anaerobic activation conditions, whereas copper monomer sites produce methanol only in aerobic process.

Conversion of methane to methanol is an industrially very important process, as it provides a sustainable route from an abundant and clean component of natural gas to one of the main precursors for chemicals synthesis.<sup>[1]</sup> A promising stepwise process over copper-exchanged zeolites has been suggested; however, a detailed understanding of the mechanism of such a zeolite-catalyzed conversion is still missing.<sup>[2-4]</sup> One of the ongoing debates in studying copper-exchanged zeolites is the exact configuration of the available active sites.<sup>[1-4]</sup> Another open question is the role of the nature of the oxidant, and the mechanism of methane oxidation and regeneration of the copper oxide active site.<sup>[5-8]</sup> Most crucially, the existing methods often suffer from low selectivity or costliness of oxidants.<sup>[9-12]</sup>

We have recently proposed an alternative solution to the above problem by showing that selective anaerobic oxidation of methane is possible,<sup>[13]</sup> where water can be used both to provide oxygen to regenerate the zeolite active centers, and to facilitate stabilization of the reaction intermediate, which uniquely occurs in the copper zeolite, to drive the otherwise endothermic Cu(I) oxidation reaction.<sup>[14,15]</sup> Instead of using oxygen, only the presence of water is required, while the reactivation of the zeolite material is done in an inert atmosphere. Such a water-facilitated redox process requires at least two copper atoms to stoichiometrically oxidize methane into methanol, thus suggesting the presence of active sites containing several copper atoms, such as dimers<sup>[5-7]</sup> and trimers,<sup>[8]</sup> stabilized by the framework aluminum atoms.

While the existence of smaller active sites has been

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inspired by natural enzymes<sup>[16]</sup> and proven experimentally,<sup>[2,5-8]</sup> the possibility of formation of larger clusters has also been suggested theoretically based on thermodynamic stability.<sup>[3,17-19]</sup> Copper monomers, on the other hand, are believed to require the formation of copper hydrides to facilitate the methane oxidation, which is energetically unfavorable.<sup>[20]</sup> The intrinsic activity of copper species of different size is still a subject of debate. Furthermore, recent reports suggest the possibility of formation of a mixture of active sites,<sup>[2-4]</sup> and even give evidence to their dynamic structural behavior.<sup>[21,22]</sup>

At the same time, copper species of variable size are expected to form during the synthesis via conventional ion exchange of parent zeolites. As such, in the materials with high Si/Al ratio (i.e. low Al content) the probability of the formation of copper monomeric species is significantly higher than that for the materials with low Si/Al (i.e. high Al content, high concentration of Al pairs).<sup>[23]</sup> This method can thus be used for modulation of the size of active copper clusters in zeolites and their performance.

Herein we demonstrate the influence of Si/Al ratio of the zeolite on the possible configurations of the active copper oxide sites, and therefore on the activity of the material in the process of aerobic and anaerobic conversion of methane into methanol. We show that the samples with high Si/Al ratio (low Al content) preferentially contain isolated copper cations leading to higher methanol yield on a copper ion basis and selectivity. Such stabilization comes at a price of a poor activity in the water reactivation reaction, preventing these sites from stabilizing and releasing molecular hydrogen while oxidizing Cu(I) into Cu(II). The samples with lower Si/Al ratios, on the other hand, both provide sufficient methanol yield, and facilitate an energetically less costly release of hydrogen, thus offering optimal conditions for the efficient selective direct methane conversion without oxygen.

The samples were prepared by conventional ion exchange of commercial zeolite mordenite with Si/AI ratio 6.5, 10 and 46 using copper nitrate solution followed by calcination in a flow of dry air at 773 K (Table 1). They are denoted as CuMOR(x), where x corresponds to Si/AI molar ratio in the parent zeolite. Activation and reaction with methane was carried out using two different procedures: i) standard pretreatment in oxygen ("aerobic" activation), and ii) recently discovered activation in inert gas ("anaerobic" activation).<sup>[13]</sup> The details on sample synthesis, activation protocols and reaction conditions are given in Supporting Information.

First, the activity of the samples activated in oxygen has been studied (Figure 1, blue lines). After interaction with methane at 473 K and 7 bars, and subsequent introduction of water-containing helium flow, desorption of methanol starts after a certain induction period, which is associated with gradual saturation of the samples with water. During the first 10 minutes, the concentration of methanol in the stream reaches its COMMUNICATION

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maximum and gradually decreases for the next 2–4 h. Only traces of dimethyl ether were observed in the stream by mass spectrometry, possibly due to the high partial pressure of water with respect to methanol, which shifts the dehydration reaction equilibrium. In the case of samples with Si/AI ratio of 6.5 and 10 the slowed desorption of methanol is related to the higher amount of aluminum and residual Brønsted sites that can interact with methanol molecules, hence possessing high affinity to polar molecules. No hydrogen formation was observed after the introduction of water on  $O_2$ -activated samples (insets in Fig. 1), which is in line with our previous study.<sup>[11]</sup>

#### Table 1. Materials characteristics.

Sample		CuMOR(6.5)	CuMOR(10)	CuMOR(46)
Si/Al molar ı	atio	6.5	10	46
Cu/Al molar ratio		0.377	0.399	0.603
Aerobic	Methanol yield, mol(MeOH)/ mol(Cu)	0.142	0.216	0.316
protocol	Selectivity towards methanol, %	87	91	98
Anaerobic activation	Methanol yield, mol(MeOH)/ mol(Cu)	0.204	0.187	~0
protocol, 3 <sup>rd</sup> cycle	Selectivity towards methanol, %	97	98	

Quantitative assessment of the amount of methanol formed over different samples (Table 1) points to the gradual increase of the methanol yield per mole of copper with increase of Si/Al ratio which is paralleled with different selectivity of methane conversion over these samples. To address this point, in situ infrared spectroscopy was used, which allowed observing the surface species. The spectra obtained after the interaction of methane at 473 K with oxygen-activated samples followed by evacuation are given in Figures 2a, S4. The reaction with methane led to appearance of three groups of bands attributed to molecular methanol, carbon monoxide and surface methoxy and formate species. IR intensities of the bands assigned to  $\delta$ (CH<sub>3</sub>) vibrations increase in the following order: CuMOR(46) < CuMOR(10) < CuMOR(6.5), which is in line with the copper content in these samples (Table 1). However, the intensities ratio of the bands due to methanol overoxidation products, CO, and formates to the bands of methanol increase in the same order, indicating higher selectivity of the reaction in the case of the CuMOR(46) sample. The quantitative analysis made by the temperature-programmed desorption of carbon dioxide (Fig. S5) after the reaction confirmed this, giving the highest selectivity of 98% to CuMOR(46), while for CuMOR(6.5) it amounted to only 87%.

Higher selectivity observed for CuMOR(46) may point to different sites being present in the samples due to different probabilities of formation of Al pairs in the structure of zeolite, hence stabilizing the formation of copper  $Cu_xO_y$  oligomeric structures with  $x \ge 2$ . To access the structure of copper sites,

infrared spectroscopy of adsorbed NO was used<sup>[24]</sup> (Figure 2b). The bands at 1804 and 1826, 1730 cm<sup>-1</sup> are attributed to Cu(I) mono- and dinitrozyls, respectively.<sup>[24-27]</sup> Similarly, the bands in the region 2000-1900 cm<sup>-1</sup> with three main peaks centered at 1995, 1950 and 1908 cm<sup>-1</sup> are generally attributed to Cu(II) interacting with NO. The bands with low vibration frequencies (~1900 cm<sup>-1</sup>) are believed to be due to the copper monomeric species, while the bands at high frequencies starting from 1940 cm<sup>-1</sup> belong to oligomeric species interacting with NO.<sup>[28,29]</sup> The small shoulder at ~1880 cm<sup>-1</sup> corresponds to NO interacting with zeolite surface (Figure S6). The formation of Cu(I) species in the oxygen-activated samples is associated with the so-called "autoreduction" process,<sup>[30]</sup> which implies the thermo-induced conversion of Cu(II) into Cu(I) during the short evacuation at 673K after the oxidation in O<sub>2</sub>.



Figure 1. Methanol desorption profiles from a) CuMOR(6.5), b) CuMOR(10) and c) CuMOR(46) after the reaction with methane following aerobic (blue lines) and anaerobic protocols measured by on-line mass-spectrometry (MS) immediately after the introduction of water stream (2.6 vol% in He). The reaction conditions: methane pressure 7 bars, 30 min contact time at 473 K. The inserts represents corresponding MS response of molecular hydrogen.

While the spectra of adsorbed NO for CuMOR(6.5) and CuMOR(10) are very similar, revealing the presence of identical bands with close intensities, the CuMOR(46) sample shows dramatic changes in the spectrum. In the region of Cu(II)

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species, only one intense band at 1908 cm<sup>-1</sup>, with a small shoulder at 1950 cm<sup>-1</sup> was observed, hence indicating the dominant formation of copper monomeric species, in contrast to the samples with Si/Al ratio higher than 10, where different copper sites were detected (Figure 2b). Unfortunately, the quantification of the amount of different copper species from the IR data was not possible due to the unknown extinction coefficients for each site.

As such, the difference in the nature of copper sites could lead to different redox properties. In order to assess this, we used temperature-programmed reaction of copper mordenite samples with methane monitored by means of in situ XANES (Figures 2c, S7-S10).<sup>[31]</sup> It can be clearly seen that the reduction of all samples starts at ~400 K and then progressively accelerates with the rise of temperature. CuMOR(6.5) and CuMOR(10) demonstrated similar redox properties, with almost full reduction of Cu(II) into Cu(I) at 500 K. On the contrary, the reduction of CuMOR(46) material showed a more gradual reduction until the temperature of 600 K. This indicates lower reactivity of copper monomeric species of CuMOR(46) towards methane.



**Figure 2.** a) *in situ* FTIR spectra of surface species formed after interaction of methane with CuMOR samples; b) FTIR spectra of NO adsorbed over CuMOR samples at 77K; c) results of linear combination fitting of XAS data obtained in the temperature-programmed reaction of CuMOR materials with methane at 1 bar; d) FTIR spectra of H<sub>2</sub> adsorbed over CuMOR samples at 77K and 20 torr. All samples prior to the measurements were activated in oxygen at 673 K for 1 h followed by evacuation at 673K for 20 min to remove the traces of water.

In the next experiments, the reaction of different CuMOR samples with different nature of copper species was carried out using the anaerobic activation protocol in three consecutive cycles (Figure 1). Being activated in a flow of He, CuMOR(6.5) in the first cycle revealed methanol yield which is slightly lower than that achieved for the oxygen-activated sample. However, in the next two cycles, methanol yield increased by ~20%, which is associated with the increase of selectivity due to avoiding overoxidation (Fig. S11).<sup>[13]</sup> Shortly after water contact with the methane reacted materials, hydrogen was observed in all three cycles (insets in Figure 1).[13-15] Similarly, CuMOR(10) showed the presence of methanol and hydrogen during the cycling of the material in methane and water vapors. Treatment in oxygenfree environment leads also to a significant impact of autoreduction process resulting in formation of additional amount of Cu(I) as evidenced by FTIR of adsorbed NO (Figure S12).

On the contrary, the CuMOR(46) sample demonstrated very low methanol yield in any cycle when activated without oxygen. No hydrogen was observed, indicating that this sample does not

> undergo reoxidation with water. The rather small methanol desorption peak could be attributed to either a small impact from residual copper oligomeric species in CuMOR(46) sample or to oxygen impurities in the flow of helium.

> Therefore, it appears that monomeric copper (II) species can interact with oxygen and methane yielding methanol with high selectivity, but the copper (I) species formed cannot interact with water. On the contrary, copper-oxo oligomeric sites exhibit high efficiency in the synthesis of methanol from methane in both aerobic and anaerobic protocols with satisfactory yields and selectivity.

> We have shown that over the CuMOR sample with high Si/Al ratio neither the release of hydrogen during interaction with water (Figure 1) nor copper reoxidation (Figure S13) was observed. Such a configuration of copper sites does not allow water activation. Therefore, we introduced the infrared spectroscopy of adsorbed hydrogen to probe the affinity of copper sites in different samples towards molecular H2. The spectra given in Figure 2d showed the presence of the bands at 4100, 4063 and 4031  $\text{cm}^{-1}$ . The first band is assigned to hydrogen interacting with Brønsted acid sites of the zeolite, while the bands at lower frequencies are due to H<sub>2</sub> adsorbed over the copper sites of the materials.<sup>[32,33]</sup> The CuMOR(6.5) and CuMOR(10)

samples containing copper-oxo oligomeric species showed intense bands for Cu sites interacting with hydrogen. This observation is in line with the NO adsorption infrared spectroscopy and the data on reactivity towards water. On the contrary, CuMOR(46) shows the presence of a very low intensity peak at 4031 cm<sup>-1</sup> due to the copper oligomers, which was also present in the spectra of adsorbed NO (Figure 2b), indicating that molecular hydrogen cannot be stabilized over copper monomeric species. This fact is in direct correlation with

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the data on methane oxidation in anaerobic conditions: CuMOR(46) does not generate hydrogen and cannot undergo reoxidation with water in any cycle (Figures 1, S13).

To get a deeper insight into thermodynamic feasibility of the CuMOR interaction with methane and reoxidation with water, we carried out DFT calculations with copper sites modelling copperoxo species in AI poor and AI rich mordenite. We compared a "conventional" mono(µ-oxo)dicopper species located in the 8member ring pore of mordenite with the system of two monomers in the larger 12-member ring pore that can interact with each other. It should be emphasized that the formation of structured multicopper active sites is governed by the probability of AI distribution, which might be especially restrictive for the samples with higher Si/Al ratios. However, such structures are statistically possible (see Supporting Information), with probability greatly increased by the potential effects of dynamic structural behavior.<sup>[21]</sup> In our previous work we have shown that the presence of multiple copper atoms is essential for the twoelectron process of methane transformation into methanol and subsequent copper reoxidation.[13] Whereas the presence of isolated monomeric species leads to high energy barriers up to 175 kJ/mol and therefore renders the process energetically unfeasible,<sup>[17]</sup> the presence of two copper atoms in a form of a dimer facilitates the water-mediated release of methanol with the barrier as low as 85 kJ/mol.<sup>[13]</sup> Such a substantial energetic difference between the two systems is caused by the large distance between the two copper atoms in the case of individual monomeric species, making the formation of bridging species, and, subsequently, the efficient proton transfer, impossible. We therefore assumed the possibility of formation of the system of



two copper monomers in the same zeolite pore. While the 8member ring pore is too small to accommodate such a system, the 12-member ring pore turned out to be of a suitable size (Figures S14, 15).

**Figure 3.** Calculated reaction profiles and the corresponding intermediates of the process of anaerobic oxidation of methane to methanol for the CuMOR systems based on copper monomer (red lines) and dimer (blue lines). Zeolite framework is omitted for the sake of clarity (Fig. S16). Full reaction cycle leading to regeneration of original active centers is presented in Fig. S17. Corresponding reaction profile for trimers is presented in Fig. S19.

Figure 3 shows that the methane activation step is similar for both the pair of monomers and the dimer, with the monomer system exhibiting higher stabilization of the methoxy species (214 kJ/mol vs 134 kJ/mol for the dimer). Such stabilization can be explained by the larger number of hydrogen bonds formed in the case of the monomeric system. Such an additional stabilization makes it more energetically costly to remove the products at the later steps of the reaction. Furthermore, the larger distance between the two copper atoms in the case of monomer system will necessarily lead to larger activation barriers. Thus, the single water molecule cannot initiate the reaction of copper reoxidation and simultaneous hydrogen release. We model the formation of hydrogen with the subsequent stabilization of the formed species with three additional water molecules, according to the stabilization model described in our previous work.<sup>[14]</sup> This is consistent with the experimentally observed amount of water added to the system. Thus, the formation of hydrogen involves the increase of  $\Delta G$  in the case of monomers, while the corresponding energy profile for dimers rapidly goes down due to possible formation of very stable bis(dihydroxy)dicopper sites. Although the energy of the final water-stabilized species depends on the number of water molecules, it is clearly much easier to stabilize the dimer structure, following the release of hydrogen. Similar tendency was observed for copper oxo trimers (Figure S19). This agrees with the experimental evidence for the low yield of the reaction products in the case of the samples with high Si/Al ratio.

The full reaction cycle corresponds to the net reaction of  $CH_4 + H_2O \rightarrow CH_3OH + H_2$ , and is completed only after the removal of all water molecules, as strong adsorption of water competes with the reaction of methane. This is achieved by purging the CuMOR material in dry helium at 673 K. During this process, fractions of water are removed from active sites step by step, thus transforming a strong endothermal effect of the net reaction (121 kJ/mol at 473 K) to a set of thermodynamically feasible steps (Fig. S17 and Ref. 12), helped by the strong entropy gain upon water desorption.

To conclude, our study shows that the Si/Al ratio can be used to tune the configurations of the active sites in copper zeolites, thus allowing direct control over the activity of the materials in the conversion of methane to methanol. The nature and redox properties of these sites can be assessed by infrared spectroscopy of adsorbed nitric oxide and hydrogen, as well as by X-ray absorption spectroscopy. Monomeric and oligomeric copper species possess different activity towards methane in both aerobic and anaerobic pathways; and towards water under anaerobic conditions.

I This difference is most probably associated with the stabilization effect of the water molecules interacting with active copper sites. Altogether, these data can serve as a basis for the further improvement of existing and design of novel materials for direct conversion of methane into methanol: for the anaerobic methane conversion the materials must contain aggregated copper oxo sites, while for aerobic conversion it is reasonable to design the materials with, for instance, isolated copper monomers.

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**Keywords:** methane to methanol conversion • copper zeolite • Al loading • FTIR • XAS

- C. Hammond, S. Conrad, I. Hermans, *ChemSusChem* 2012, *5*, 1668-1686.
- [2] D. K. Pappas, E. Borfecchia, M. Dyballa, I. Pankin, K. A. Lomachenko, A. Martini, M. Signorile, S. Teketel, B. Arstad, G. Berlier, C. Lamberti, S. Bordiga, U. Olsbye, K. P. Lillerud, S. Svelle, P. Beato, *J. Am. Chem. Soc.* 2017, 139, 14961-14975.
- P. Tomkins, A. Mansouri, S. E. Bozbag, F. Krumeich, M. B. Park, E. M. C. Alayon, M. Ranocchiari, J. A. van Bokhoven, *Angew. Chem. Int. Ed.* 2016, *55*, 5467-5471.
- [4] P. Tomkins, M. Ranocchiari, J. A. van Bokhoven, Acc. Chem. Res. 2017, 50, 418-425.
- [5] M. H. Groothaert, J. A. van Bokhoven, A. A. Battiston, B. M. Weckhuysen, R. A. Schoonheydt, J. Am. Chem. Soc. 2003, 125, 7629-7640.
- [6] P. J. Smeets, M. H. Groothaert, R. A. Schoonheydt, Catal. Today 2005, 110, 303-309.
- J. S. Woertnik, P. J. Smeets, M. H. Groothaert, M. A. Vance, B. F. Sels, R. A. Schoonheydt, E. I. Solomon, *Proc. Natl. Acad. Sci. U. S. A.* 2009, *106*, 18908-18913.
- [8] S. Grundner, M. A.C. Markovits, G. Li, M. Tromp, E. A. Pidko, E. J.M. Hensen, A. Jentys, M. Sanchez-Sanchez, J. A. Lercher, *Nat. Commun.* 2015, *6*, 7546.
- [9] M. Ravi, M. Ranocchiari, J. A. van Bokhoven, Angew. Chem. Int. Ed. 2017, 56, 16464-16483.
- [10] M. B. Park, S. H. Ahn, A. Mansouri, M. Ranocchiari, J. A. van Bokhoven, ChemCatChem, 2017, 9, 3705-3713.
- [11] Y. Kim, T. Y. Kim, H. Lee, J. Yi, Chem. Commun., 2017, 53, 4116-4119.
- [12] H. Schwarz, Angew. Chem. Int. Ed. 2011, 50, 10096-10115.
- [13] V. L. Sushkevich, D. Palagin, M. Ranocchiari, J. A. van Bokhoven, Science 2017, 356, 523-527.
- [14] V. L. Sushkevich, D. Palagin, M. Ranocchiari, J. A. van Bokhoven, Science 2017, 358, eaan6083.

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- [15] S. Docao, A. R. Koirala, M. G. Kim, I. C. Hwang, M. K. Songa, K. B. Yoon, *Energy Environ. Sci.* 2017, *10*, 628-640.
- [16] R. Balasubramanian, S. M. Smith, S. Rawat, L. A. Yatsunyk, T. L. Stemmler and A. C. Rosenzweig, *Nature* 2010, 465, 115–119.
- [17] A. A. Verma, S. A. Bates, T. Anggara, C. Paolucci, A. A. Parekh, K. Kamasamudram, A. Yezerets, J. T. Miller, W. N. Delgass, W. F. Schneider, F. H. Ribeiro, *J. Catal.* **2014**, *312*, 179–190.
- [18] D. Palagin, A. J. Knorpp, A. B. Pinar, M. Ranocchiari, J. A. van Bokhoven, *Nanoscale* 2017, 9, 1144-1153.
- [19] M. Mahyuddin, A. Staykov, Y. Shiota, M. Miyanishi, K. Yoshizawa, ACS Catal., 2017, 7, 3741-3751.
- [20] A. R. Kulkarni, Z.-J. Zhao, S. Siahrostami, J. K. Nørskov, F. Studt, ACS Catal. 2016, 6, 6531-6536.
- [21] C. Paolucci, I. Khurana, A. A. Parekh, S. Li, A. J. Shih, H. Li, J. R. Di lorio, J. D. Albarracin-Caballero, A. Yezerets, J. T. Miller, W. N. Delgass, F. H. Ribeiro, W. F. Schneider, R. Gounder, *Science* 2017, 357, 898-903.
- [22] C. W. Andersen, E. Borfecchia, M. Bremholm, M. R. V. Jørgensen, P. N. R. Vennestrøm, C. Lamberti, L. F. Lundegaard, B. B. Iversen, Angew. Chem. Int. Ed. 2017, 56, 10367-10372.
- [23] M. J. Rice, A. K. Chakraborty, A. T. Bell, J. Catal. 2000, 194, 278-285.
- [24] S. Bordiga, C. Lamberti, F. Bonino, A. Travert, F. Thibault-Starzyk, Chem. Soc. Rev., 2015, 44, 7262-7341.
- [25] F. Giordanino, P.N.R. Vennestrøm, L.F. Lundegaard, F.N. Stappen, S. Mossin, P. Beato, S. Bordiga, C. Lamberti, *Dalton Trans.* 2013, 42, 12741-12761.
- [26] F. X. Llabrés i Xamena, P. Fisicaro, G. Berlier, A. Zecchina, G. T. Palomino, C. Prestipino, S. Bordiga, E. Giamello, C. Lamberti, J. Phys. Chem. B. 2003, 107, 7036-7044.
- [27] E. Borfecchia, K. A. Lomachenko, F. Giordanino, H. Falsig, P. Beato, A. V. Soldatov, S. Bordiga, C. Lamberti, *Chem. Sci.* 2015, 6, 548-563.
- [28] M. Tortorelli, K. Chakarova, L. Lisi, K. Hadjiivanov, J. Catal. 2014, 309, 376-385.
- [29] W.Z. Zhang, H. Yahiro, N. Mizuno, J. Izumi, M. Iwamoto, *Langmuir* 1993, 9, 2337-2343.
- [30] G.D. Lei, B.J. Adelman, J. Sarkany, W.M.H. Sachtler, Appl. Catal. B 1995, 5, 245-252.
- [31] A. Martini, E. Borfecchia, K. A. Lomachenko, I. A. Pankin, C. Negri, G. Berlier, P. Beato, H. Falsig, S. Bordiga, C. Lamberti, Chem. Sci., 2017, 8, 6836-6851.
- [32] A. I. Serykh, V. B. Kazansky, Phys. Chem. Chem. Phys. 2004, 6, 5250-5255.
- [33] V. B. Kazansky, J. Catal. 2003, 216, 192-202.

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Effect of Active Sites Structure on Activity of Copper Mordenite in Aerobic and Anaerobic Conversion of Methane to Methanol

Copper-exchanged zeolite mordenite with different Si/AI ratios was used to study a direct conversion of methane into methanol in aerobic and anaerobic regimes. Al loading can be used to modulate the nature of the copper sites and the activity of the material.