Recent Progress in Direct Conversion of Methane to Methanol Over Copper-Exchanged Zeolites

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The conversion of methane into an easily transportable liquid fuel or chemicals has become a highly sought-after goal spurred by the increasing availability of cheap and abundant natural gas. While utilization of methane for the production of syngas and its subsequent conversion via an indirect route is typical, it is cost-intensive, and alternative direct conversion routes have been investigated actively. One of the most promising directions among these is the low-temperature partial oxidation of methane to methanol over a metal-loaded zeolite, which mimics facile enzymatic chemistry of methane oxidation. Thus mono-, bi-, and trinuclear oxide compounds of iron and copper stabilized on ZSM-5 or mordenite, which are structurally analogous to those found in methane monooxygenases, have demonstrated promising catalytic performances. The two major problems of these metal-loaded zeolites are low yield to methanol and batch-like non-catalytic reaction systems challenging to extend to an industrial scale. In this mini-review, attention was given to the direct methane oxidation to methanol over copper-loaded zeolite systems. A brief introduction on the catalytic methane direct oxidation routes and current status of the applied metal-containing zeolites including the ones with copper ions are given. Next, by analyzing the extensive experimental and theoretical data available, the consensus among the researchers to achieve the target of high methanol yield is discussed in terms of zeolite topology, active species, and reaction parameters. Finally, the recent efforts on continuous methanol production from the direct methane oxidation aiming for an industrial process are summarized.

Keywords: methane oxidation, methanol, zeolite, copper, process schemes

INTRODUCTION

Natural gas will be a major energy resource in the transition period from the current petroleum-based energy economy to a renewable energy society in the future. Natural gas is presently used as a fuel for power generation or transportation, but often merely flared to the atmosphere without being utilized. Various attempts have been made to convert methane, which
accounts for 70–90% of natural gas, to a more useful liquid fuel or chemicals (Periana et al., 1998; McFarland, 2012; Sushkevich et al., 2017). Thus, syngas is produced by steam reforming of methane (CH\textsubscript{4} + H\textsubscript{2}O → CO + 3H\textsubscript{2}, \(\Delta H\textsubscript{298K} = +266.2 \text{ kJ mol}^{-1}\)), and this can be followed by either a Fischer-Tropsch process to hydrocarbons or methanol synthesis (CO + 2H\textsubscript{2} → CH\textsubscript{3}OH, \(\Delta H\textsubscript{298K} = -41.2 \text{ kJ mol}^{-1}\)). However, this indirect route is highly energy consuming and also accompanied by multi-stage processes including a unit for water gas shift reaction (CO + H\textsubscript{2}O → CO\textsubscript{2} + H\textsubscript{2}, \(\Delta H\textsubscript{298K} = -90.7 \text{ kJ mol}^{-1}\)). Therefore, it is strongly desirable to develop a low-cost, small-scale direct conversion process that can replace the indirect route.

Methane is a highly stable molecule difficult to activate due to its low electron and proton affinity, low polarity, high ionization energy, and strong C-H bond (∼440 kJ mol\(^{-1}\)) (Periana et al., 1998). The C-H bond of methane can be kinetically and thermodynamically activated by oxidation. However, the C-H bond (∼47 kJ mol\(^{-1}\)) in methanol which is one of the oxidative intermediates is weaker than that of methane, and thus completely oxidized to carbon dioxide under the reaction condition for methane activation. Therefore, it is desirable to develop an appropriate catalytic means to produce methanol selectively by direct methane oxidation. Methanol, incidentally, is a vital platform molecule to synthesize dimethyl ether, formaldehyde, light olefins, and even to gasoline through the methanol-to-gasoline (MTG) process (Tian et al., 2015; Yarulina et al., 2018).

One promising pathway for direct conversion of methane to methanol is via partial oxidation of methane over a metal-containing zeolite catalyst (CH\textsubscript{4} + 0.5SO\textsubscript{2} → CH\textsubscript{3}OH, \(\Delta H\textsubscript{298K} = -126.2 \text{ kJ mol}^{-1}\)), which mimics the methane oxidation by an enzyme (Kondratenko et al., 2017; Ravi et al., 2017; Tomkins et al., 2017; Dinh et al., 2018; Kulkarni et al., 2018; Mahyuddin et al., 2018a). As shown in Figure 1A, a mono-, bi- or tri-nuclear copper or iron complex similar to that of methane monoxygenases (MMOs) can be stabilized in the zeolite micropore structure such as ZSM-5 (framework type MFI) or mordenite (MOR) by ion-exchange of zeolite followed by successive activation with an oxidant (Snyder et al., 2018). The electrophilicity of the active metal oxide species allows methanol production by readily activating the strong C-H bond of methane even at a relatively low temperature. However, these metal-containing zeolite systems exhibit stoichiometric and non-catalytic reaction characteristics destitute of the continuous desorption of product such that a high methanol selectivity can only be achieved under the conditions of methane conversions <0.1% (Ravi et al., 2017; Dinh et al., 2018). These problems have to be resolved to extend the reaction to an industrial scale.

Although many studies on the direct conversion of methane over a zeolite containing transition metal ions of Fe, Co, Ni, Cu, and Zn and using N\textsubscript{2}O, H\textsubscript{2}O\textsubscript{2}, O\textsubscript{2}, and recently H\textsubscript{2}O as oxidants have been reported, the Cu-zeolite system with O\textsubscript{2} or H\textsubscript{2}O has been regarded to be most promising for industrial application (Sushkevich et al., 2017; Lee et al., 2018). Cu-zeolites can be activated by both N\textsubscript{2}O and O\textsubscript{2}, unlike the Fe-zeolites on which methane activation sites cannot be formed with O\textsubscript{2}. The use of N\textsubscript{2}O and other oxidants (e.g., HNO\textsubscript{3}, H\textsubscript{2}SO\textsubscript{4}, NaClO, NaClO\textsubscript{2}, H\textsubscript{2}O\textsubscript{2}, etc.) cannot compete against freely available and environmentally friendly O\textsubscript{2} and H\textsubscript{2}O. In this mini-review, therefore, the focus will be made on the direct methane oxidation to methanol on Cu-zeolite systems. After a short overview of this reaction system, the efforts made to obtain high methanol yields, and recent efforts for continuous methanol production are summarized.

**MULTISTEP METHANE PARTIAL OXIDATION OVER CU-ZEOLITES**

Copper has been used as a catalyst for various oxidation reactions and, in particular, CuO is well-known as a catalyst for methane oxidation (Elwell et al., 2017). As shown in Figure 1B, the initially proposed direct methane to methanol conversion over a Cu-zeolite is carried out by a three-step cyclic process of oxygen activation, methane reaction, and methanol extraction (Ravi et al., 2017; Tomkins et al., 2017). In typical operation, Cu-zeolite is activated for several hours at near 450°C in an oxygen atmosphere and treated with an inert gas such as He to remove the O\textsubscript{2} used in the activation of Cu-zeolite. Then methane is reacted for some time at about 200°C, and the produced methanol or methoxy group is desorbed or extracted from the Cu-zeolite using a solvent such as water to obtain.
methyl. A variety of Cu-zeolite catalysts have been evaluated during the last decade for such a multistep cyclic process, and the representative results are summarized in Table 1. An initial study using Cu-ZSM-5 showed a methanol yield of about 8.2 μmol g_{cat}^{-1} with a methanol selectivity of over 98% with negligible carbon dioxide and carbon monoxide (Groothaert et al., 2005). More recently, much higher methanol yields were achieved, for example, ca. 125 and 169 μmol g_{cat}^{-1} using Cu-SSZ-13 (CHA) and Cu-mordenite, respectively (Pappas et al., 2017, 2018; Dyballa et al., 2019). The methanol selectivity close to 100% was attained as a result of inert gas treatment between the oxygen activation and the methane reaction to prevent the excess oxidation of generated methanol in an O2-free atmosphere.

The methanol formed inside the zeolite pores can be extracted by two processes (Kulkarni et al., 2018). As shown in Figure 1C, one is a process in which methanol is produced by hydrolysis of a Bronsted methoxy group bonded to a zeolite framework oxygen atom with water. The other is a process in which the methyl radical of methane activated at the Cu-oxo site is directly adsorbed to a zeolite framework oxygen, and methanol is replaced by water used as a solvent. According to Kulkarni et al. who calculated the adsorption energies between methanol and different metal active species, it is difficult to spontaneously desorb the methanol molecules formed inside zeolite pores in most zeolite structures, but it is possible to desorb them using water. Theoretically, the adsorbed methanol could be desorbed with low water vapor pressure from almost any zeolite structures.

Although the structure of copper-oxo active species inside zeolite pores involved in the methanol production has been proposed since the beginning of the investigation, it remains controversial. The detailed spectroscopic and computational analyses for the active species are available in other reviews (Kulkarni et al., 2018; Snyder et al., 2018). Cu-mordenite, Cu-ZSM-5, and Cu-SSZ-13 have been studied extensively, and various active species such as monocopper (e.g., [CuOH]^+) (Grundner et al., 2015, 2016; Li et al., 2016), dicopper (e.g., mono(μ-oxo)dicopper, [Cu2(μ-O)2]^{2+} and bis(μ-oxo)dicopper, [Cu2(μ-O)]^{2+}) (Groothaert et al., 2005; Woertink et al., 2009; Tsai et al., 2014; Mahyuddin et al., 2018b,c), tricopper (e.g., tris(μ-oxo)tricopper, [Cu3(μ-O)3]^{2+}) (Grundner et al., 2015; Markovits et al., 2016; Vogiatzis et al., 2017; Dandu et al., 2018; Mahyuddin et al., 2018b,c), and even sub-nanometer copper oxide clusters (Tomkins et al., 2017; Doan et al., 2018) have been proposed (Figure 1A). An early study of Cu-ZSM-5 showed a peak in the UV/Vis spectrum at 22,700 cm^{-1} corresponding to a bis(μ-oxo)dicopper site (Groothaert et al., 2005). On the other hand, using UV/Vis and Raman spectroscopies, the active species formed inside Cu-ZSM-5 pores was also claimed as a mono(μ-oxo)dicopper site (Woertink et al., 2009). The UV/Vis result for Cu-mordenite also detected the presence of the μ-oxo-dicopper site, but other active species were also proposed to be involved in methanol production (Alayon et al., 2012). Recently, EXAFS analysis of Cu-mordenite reported that a trimuclear copper-oxo cluster is the active species (Grundner et al., 2015; Markovits et al., 2016). For other zeolites such as Cu-beta (*BEA) and Cu-ferrierite (FER), despite only with a small amount of methanol formed, no active species like μ-oxo-copper clusters were observed (Smeets et al., 2005). These different results seem to indicate that there could be various active species depending on the zeolite structure, composition, and activation conditions.

METHANE REACTIVITY AND METHANOL YIELD IN CU-ZEOLITE SYSTEM

Various factors such as structure and composition of the zeolite used, the structure of copper active species, and reaction conditions should be considered to produce methanol selectively by direct partial oxidation of methane. Depending on the structure of the zeolite, different environment in which oxygen or methane is stabilized at the active copper species can be formed (Kulkarni et al., 2016; Zhao et al., 2016; Pappas et al., 2017; Liu et al., 2018). The C-H bond activation barrier energy of methanol depending on the type of metal active species present in the zeolite pores was estimated (Kulkarni et al., 2018). The activation barrier energy decreased significantly among the transition metals from left to the right in the periodic table (Fe, Co, Ni, and Cu), and the energy by the μ-oxo-dicopper species was 107 kJ mol^{-1} lower than that by iron. Therefore, it was predicted that copper ion has a better reactivity to methane than the other transition metal ions. It was also claimed that activation barrier energy changes depending on the zeolite structures; the aluminum position and its bonding structure with metal cations affected the M-O-M angle, which influenced the activation barrier energy.

Recently, Cu-zeolites with small-pores such as SSZ-13, SSZ-16 (AFX), SSZ-39 (AEI), and SAPO-34 (CHA) were reported to exhibit better methane reactivity and methanol selectivity than the conventional Cu-ZSM-5 and Cu-mordenite (Wulfers et al., 2015; Ipek and Lobo, 2016; Kulkarni et al., 2016; Ipek et al., 2017; Pappas et al., 2017; Oord et al., 2018). These small-pore Cu-zeolites produced almost twice as much methanol per Cu-atom than the medium- and large-pore zeolites. It was reported that the activation energy necessary for breaking the C-H bond of methane, which is the rate determining step in the methane conversion, is controlled by the Cu-O-Cu angle, which is dependent on the crystallographic location in a zeolite structure and copper active species (Mahyuddin et al., 2017, 2018b). DFT calculations indicated that the activation energies for C-H bond dissociation by [Cu2(μ-O)2]^{2+} formed inside the small-pore zeolites (SSZ-13, SSZ-16, and SSZ-39) are lower than those for medium- (Cu-ZSM-5) and large-pore (Cu-mordenite) zeolites. Also, the 8- ring side pocket of mordenite zeolite was claimed to stabilize the catalytically active trinuclear copper-oxo clusters owing to the structural environment similar to that of the MMO (Grundner et al., 2015).

Park et al. prepared Cu-zeolites with 12 different structure types (i.e., MOR, EON, MAZ, MEI, BPH, FAU, LTL, MFI, HEU, FER, SZR, and CHA), and compared their methanol productivity by direct conversion of methane based on the
copper content, activation temperature in an oxygen flow, zeolite structure, and zeolite precursor type (Park et al., 2017). The Cu-omega with MAZ structure showed the highest methanol yield among the zeolites. This was explained as a result of copper-oxo active species distributed in the three-dimensional 8-ring small-pore channel only available in the MAZ structure. In-situ UV/Vis analysis after catalyst activation under high temperature and oxygen atmosphere revealed that there exist various copper active species rather than a single copper active state. Four main factors contributing to obtain high methanol yield were suggested: (i) highly dispersed copper-oxo active species, (ii) copper active species formed in small-pore channels, (iii) appropriate level of activation temperature, and (iv) Cu$^{2+}$ ion-exchanged from an H$^+$-form zeolite. Cu-mordenite and Cu-omega catalysts prepared from their H$^+$-form precursor showed the highest methanol yield up to 169 $\mu$mol g$^{-1}$ cat. However, Cu-mordenite prepared by liquid phase ion-exchange with methane and extraction of methanol proceed at a relatively lower temperature of 200$^\circ$C to prevent the methanol from excessively oxidized to CO or CO$_2$.

At the beginning of the investigation using a Cu-zeolite system, an off-line extraction method was employed for methanol recovery. After the second step of methane reaction is completed, the reacted Cu-zeolite was recovered from the reactor, and the methanol was extracted by adding a solvent such as water. Subsequently, a closed multistep cyclic process that continuously extracts methanol by using on-line generated steam was proposed (Alayon et al., 2012). The cycling experiments showed successful regeneration of Cu-zeolite in a cyclic batch-wise operation; the catalyst deactivation can occur primarily due to sintering or leaching of Cu at high activation temperatures. The crucial problem of the multistep cyclic process was that these production steps proceed at different temperatures such that the first step of activating the copper in zeolite pores in an oxygen atmosphere is carried out at a high temperature of 450$^\circ$C, and the contact with methane and extraction of methanol proceed at a relatively lower temperature of 200$^\circ$C. This low temperature was necessary to prevent the methanol from excessively oxidized to CO or CO$_2$.

CONTINUOUS METHANOL PRODUCTION OVER A CU-ZEOLITE SYSTEM

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CONTINUOUS METHANOL PRODUCTION OVER A CU-ZEOLITE SYSTEM

TABLE 1 | Representative Cu-zeolite performances reported for the gas-phase direct methane oxidation to methanol$^a$.

| IZA code | Cu, wt% | Cu/Al | Oxidant | Temp., $^\circ$C | Methanol yield $\mu$mol g$^{-1}$ cat. | References |
|----------|---------|--------|---------|---------------|-------------------------------------|------------|
| MFI | 4.0 | - | $O_2$ | 450 | 200 | 8.2 | Groothaert et al., 2005$^b$ |
| MOR | 4.3 | 0.4 | $O_2$ | 450 | 200 | 13 | Alayon et al., 2012 |
| MFI | 1.9 | - | NO | 150 | 150 | 0.63 | Sheppard et al., 2014 |
| CHA | 4.9 | 0.4 | $O_2$ | 450 | 200 | 31 | Wulfers et al., 2015 |
| AFI | 2.5 | 0.3 | $O_2$ | 450 | 200 | 36 | Wulfers et al., 2015 |
| AFX | 5.0 | 0.3 | $O_2$ | 450 | 200 | 39 | Wulfers et al., 2015 |
| MOR | 3.2 | - | $O_2$ | 450 | 200 | 160 | Grundner et al., 2015 |
| CHA | 3.2 | 0.4 | $O_2$ | 450 | 200 | 45 | Ipek and Lobo, 2016 |
| CHA | 3.2 | 0.4 | $N_2O$ | 450 | 200 | 35 | Ipek and Lobo, 2016 |
| MOR | 3.0 | - | $O_2$ | 200 | 200 | 56 | Tomkinc et al., 2016$^c$ |
| MFI | - | 0.3 | $O_2$ | 550 | 210 | 82 | Narsimhan et al., 2016$^d$ |
| MFI | 3.3 | 0.5 | $O_2$ | 450 | 200 | 89 | Markovits et al., 2016 |
| MOR | 3.1 | 0.2 | $O_2$ | 450 | 200 | 30 | Park et al., 2017$^b$ |
| CHA | 4.5 | 0.8 | $O_2$ | 450 | 200 | 30 | Park et al., 2017$^b$ |
| MAZ | 6.0 | 0.3 | $O_2$ | 450 | 200 | 86 | Park et al., 2017$^b$ |
| CHA | 3.9 | 0.5 | $O_2$ | 500 | 200 | 125 | Pappas et al., 2017 |
| MOR | 2.0 | 0.4 | $N_2O$ | 600 | 150 | 97 | Kim et al., 2017 |
| MOR | - | 0.4 | $H_2O$ | 400 | 200 | - | Sushkevitch et al., 2017$^e$ |
| MOR | 3.1 | 0.3 | $H_2O$ | 350 | 350 | 161 | Lee et al., 2018$^f$ |
| MOR | 2.3 | 0.2 | $O_2$ | 500 | 200 | 169 | Pappas et al., 2018 |

$^a$All experiments were performed in a closed three-step cyclic process under atmospheric pressure that continuously extracts methanol by using on-line generated steam unless otherwise stated.

$^b$Off-line methanol extraction with 1:1 water/acetonitrile mixture or water.

$^c$Methane pressure of 37 bar.

$^d$Methanol extraction by flowing a gas mixture comprised of 3.2 kPa of $H_2O$, 0.0025 kPa $O_2$, and balance $CH_4$.

$^e$Activation in He flow.

$^f$Continuous one-step methanol production using 33% $CH_4$ and 67% $H_2O$.  

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was very low due to the thermodynamic limitation. For this reaction \((\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{g}) + \text{H}_2(\text{g}))\), there is a thermodynamic restriction with \(\Delta G_{298K}^\circ \approx 117\ \text{kJ/mol}\), and the equilibrium methanol formation level is low.

**CONCLUSION AND OUTLOOK**

In this mini-review, we examined the recent progress in methanol synthesis by direct methane oxidation over a Cu-zeolite catalyst. There have been various characterization and computational studies to identify the Cu-oxo active species involved in methanol production, and various types of mono-, di-, tricopper, and even sub-nanometer copper oxide clusters were proposed. Although there are several factors related to methane conversion, selection of a suitable zeolite is crucial to obtain the high methanol yield. It has been reported that Cu-zeolites with small-pores have shown the higher methanol yields than medium- and large-pore Cu-zeolites. The activation of methane C-H bond, which is considered to be the rate-determining step during the methane conversion, and Cu-oxo formed in the small-pores was calculated to have the lowest C-H bond activation energy. There has been considerable progress in continuous methanol production from direct methane conversion over Cu-zeolites, i.e., steady-state cyclic reaction with the simultaneous introduction of methane and steam with or without oxygen. However, considering the hourly production rate, the current status is just around one-hundredth of the methanol production rate via syngas from the commercially available indirect methane transformation. Therefore, it is necessary to both maximize the total number of copper active species in the zeolite catalyst and to reduce the time required for each cycle of the multistep process. There have been only limited attempts for isothermal oxidative activation and methane reaction, which can be an alternative but still needs a significant breakthrough for future implementation.

**AUTHOR CONTRIBUTIONS**

MP planned the contents and wrote the draft. EP did consulting and feedback on process data. W-SA initiated and supervised the work.

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**REFERENCES**

Alayon, E. M., Nachtegaal, M., Ranocchiari, M., and van Bokhoven, J. A. (2012). Catalytic conversion of methane to methanol over Cu-mordenite. *Chem. Commun.* 48, 404–406. doi: 10.1039/c1cc13584f

Dandu, N. K., Reed, J. A., and Odoh, S. O. (2018). Performance of density functional theory for predicting methane-to-methanol conversion by a tri-copper complex. *J. Phys. Chem. C* 122, 1024–1036. doi: 10.1021/acs.jpcc.7b09284

Dinh, K. T., Sullivan, M. M., Serna, P., Meyer, R. J., Dincă, M., and Román-Leshkov, Y. (2018). Viewpoint on the partial oxidation of methane to methanol using Cu- and Fe-exchanged zeolites. *ACS Catal.* 8, 8306–8313. doi: 10.1021/acscatal.8b01180

Doan, H. A., Li, Z., Farha, O. K., Hupp, J. T., and Snurr, R. Q. (2018). Theoretical insights into direct methane to methanol conversion over supported dicopper oxo nanoclusters. *Catal. Today* 312, 2–9. doi: 10.1016/j.cattod.2018.03.063

Dybulla, M., Pappas, D. K., Kvande, K., Borfecchia, E., Arstad, B., Beato, P., et al. (2019). On how copper mordenite properties govern the framework stability
Wulfers, M. J., Teketel, S., Ipek, B., and Lobo, R. F. (2015). Conversion of methane to methanol on copper-containing small-pore zeolites and zeotypes. Chem. Commun. 51, 4447–4450. doi: 10.1039/c4cc09645b

Yarulina, I., Chowdhury, A. D., Meier, F., Weckhuysen, B. M., and Gascon, J. (2018). Recent trends and fundamental insights in the methanol-to-hydrocarbons process. Nat. Catal. 1, 398–411. doi: 10.1038/s41929-018-0078-5

Zhao, Z.-J., Kulkarni, A., Vilella, L., Nørskov, J. K., and Studt, F. (2016). Theoretical insights into the selective oxidation of methane to methanol in copper-exchanged mordenite. ACS Catal. 6, 3760–3766. doi: 10.1021/acscatal.6b00440

Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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