Impacts of framework Al distribution and acidic properties of Cu-exchanged CHA-type zeolite on catalytic conversion of methane into methanol followed by lower hydrocarbons

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Complete List of Authors:	Nakamura, Kengo; Tokyo Institute of Technology Xiao, Peipei; Tokyo Institute of Technology Osuga, Ryota; Tohoku University, Institute of Multidisciplinary Research for Advanced Materials Wang, Yong; Tokyo Institute of Technology, Chemical Resources Laboratory Yasuda, Shuhei; Tokyo Institute of Technology, Innovative Research Matsumoto, Takeshi; Tokyo Institute of Technology Institute of Innovative Research, Nanospace Catalysis Unit Kondo, Junko; Tokyo Institute of Technology, Chemical Resources Laboratory Yabushita, Mizuho; Tohoku University, Institute of Multidisciplinary Research for Advanced Materials Muramatsu, Atsushi; Tohoku University, Institute of Multidisciplinary Research for Advanced Materials; Japan Science and Technology Agency, Core Research for Evolutional Science and Technology Gies, Hermann; Ruhr-Universitat Bochum, Geologie, Mineralogie und Geophysik Yokoi, Toshiyuki; Tokyo Institute of Technology, Innovative Research

COMMUNICATION

Impacts of framework Al distribution and acidic properties of Cu-exchanged CHA-type zeolite on catalytic conversion of methane into methanol followed by lower hydrocarbons

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Kengo Nakamura,[a] Peipei Xiao,[a] Ryota Osuga,[b] Yong Wang,[a] Shuhei Yasuda,[a] Takeshi Matsumoto,[a] Junko N. Kondo,[a] Mizuho Yabushita,[c] Atsushi Muramatsu,[b] Hermann Gies,[a,d] and Toshiyuki Yokoi*[a]

This work highlighted the significance of the Al distribution in the CHA-type zeolite to the formation of active Cu species for oxidative conversion of CH_4; isolated Al atoms in the zeolite framework are found to be advantageous for producing CH_3OH. The acid sites also played an important role in the production of hydrocarbons; produced CH_3OH is converted into hydrocarbons over the acid sites.

The use of CH_4 as the carbon source for producing value-added chemicals has attracted much attention in the last decade. The development of a catalytic process that can directly convert CH_4 into useful chemical feedstocks such as CH_3OH and C2-C4 hydrocarbons has extensively been pursued.[1-6] Among various types of heterogeneous catalysts, Cu-containing zeolites have extensively been investigated as a catalyst for the methane to methanol (MTM) reaction; small pore-zeolites such as CHA, AEI, and AFX frameworks exhibit a better CH_4 reactivity and CH_3OH selectivity than medium-(MFI) and large-(*BEA and MOR) ones.[7-11] Regarding the active Cu species, the density functional theory (DFT) studies by Yoshizawa and co-workers has confirmed that the activation energy required for the cleavage of the C–H bond of CH_4, which is the rate-limiting step, is governed by the Cu-O-Cu angle and also depends on the crystallographic position in zeolite cavity.[12-15] Very recently, the role of zeolite lattice constraints on methane activation over the Cu–O–Cu active site has been proposed.[16] However, the catalytic performance is still insufficient in terms of CH_4 conversion and CH_3OH yield. Apart from the high stability of CH_4 molecule, one of the reasons is that produced CH_3OH is very easily over-oxidized to carbon dioxide under oxidative atmosphere; there is a trade-off between CH_4 conversion and CH_3OH selectivity.[17,18] Hence, the study on the MTM reaction has still been challenging.

Focusing on the production of hydrocarbons from CH_4, oxidative coupling of methane has been well-recognized as a catalytic process for producing hydrocarbons from CH_4, while this exothermic reaction requires high temperature, more than 973 K.[19,20] The catalytic process that can directly produce hydrocarbons from CH_4 under mild conditions has also been challenging, and not fully been developed to date.

We have found that the importance of Al distribution in zeolite framework for physicochemical and catalytic properties[21]. The CHA-type zeolite has one unique nonequivalent tetrahedral site (T site) in double 6- ring (D6R) building unit. Hence, the Al distribution in the CHA-type zeolite has been discussed in terms of the number of Al atoms connecting to ≡OSi moiety, "Q^4(1Al) and Q^4(2Al)", where "Q^4(nAl)" is $Si(OSi)_{4-n}(OAl)_n$. We have reported that the starting materials affected the Al distribution in the CHA-type zeolite.[21,22]. Moreover, regarding metal-exchanged zeolites, the metal cations exist around Al^{3+} species to balance the negative charge. Very recently, we have found that the Al distribution has greatly affected the state and location of the metal species introduced and catalytic activities [23,24]. However, the impact of the Al distribution in the CHA-type zeolite on Cu-exchanged zeolites and their catalytic performance in the MTM reaction has not been clarified to date.

Here, we report a novel catalytic process for the selective and effective production of hydrocarbons from CH_4 under mild conditions. Our strategy is that produced CH_3OH from CH_4 is

Table 1 Physicochemical properties of CHA samples.

Samples	Si/Al[a]	Na/Al[a,b]	Cu/Al[a]	Number of acid site[c] (mmol g^{-1})
NH_4^+/CHA-FAU	3.8	-	-	1.98
NH_4^+/CHA-Am	3.1	-	-	2.63
Cu-H/CHA-FAU	3.6	-	0.04	1.33
Cu-H/CHA-Am	2.8	-	0.03	2.03
Na/CHA-FAU	4.6	0.92	-	< 0.01
Cu-Na/CHA-FAU	4.2	1.07	0.04	0.024

[a]Determined by ICP. [b]Determined by AAS. [c]Determined by NH_3-TPD

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[a] *Institute for Innovative Research, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan.*

[b] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan.*

[c] *Department of Applied Chemistry, School of Engineering, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan.*

[d] *Institute of Geology, Mineralogy und Geophysics, Ruhr-University Bochum, Bochum 44780, Germany*

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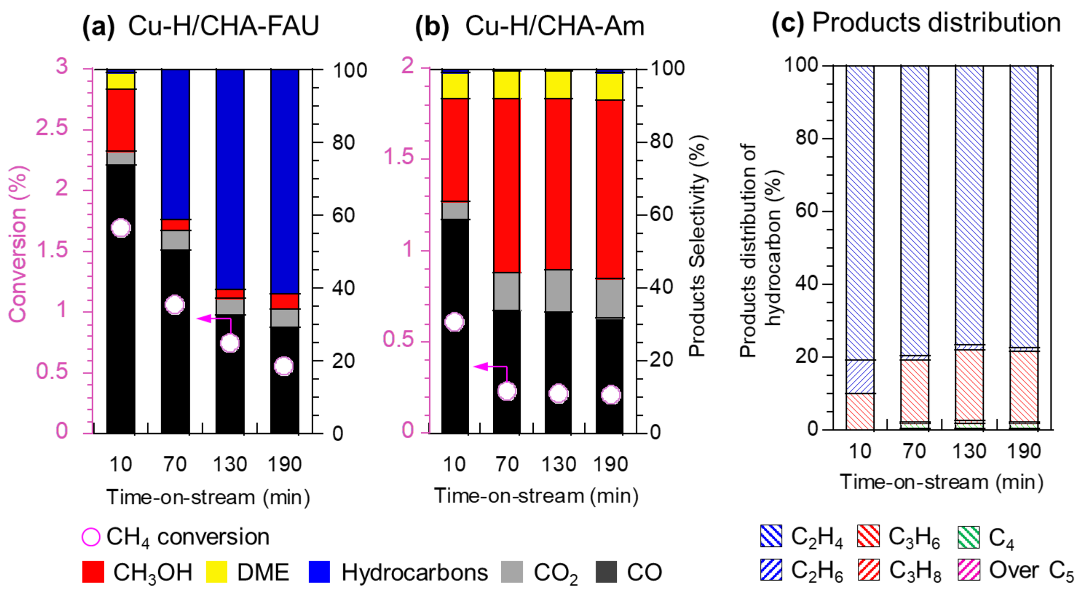

Figure 1 Oxidative conversion of CH_4 with N_2O over CHA zeolite catalysts: a Cu-H/CHA-FAU and b Cu-H/CHA-Am; (○) Conversion of CH_4, the bars represent the selectivity to CH_3OH, hydrocarbons, CO and CO_2, respectively. c Products distribution of hydrocarbons in "a Cu/CHA-FAU" results; Reaction conditions: 100 mg catalyst; P_{CH4}: P_{N2O}: P_{H2O}: P_{Ar} = 0.4:0.4:0.08: balance (atm); total pressure, 0.1 MPa; temperature, 623 K; SV = 1.5×104 mL h^{-1} g^{-1} and W/F = 3.7 $g_{\text{-cat}}$ h $mol^{-1}{}_{CH4}$.

immediately converted to hydrocarbons by methanol to olefins (MTO) reaction before over-oxidation of CH_3OH. For this strategy, we have tackled the design and synthesis of the zeolite catalyst enabling the production of lower olefins from CH_4 under oxidative atmosphere through the optimization of the Al distribution and the creation of both active sites for the MTM and MTO reaction in single zeolite catalyst.

First, to investigate the impact of the Al distribution, aluminosilicate-type CHA zeolite with the Al distribution controlled were synthesized from different starting materials under the organic structure-directing agent (OSDA)-free conditions; the details were described in Supporting Information. Here, the CHA zeolites synthesized from amorphous silica-alumina and FAU were designated as CHA-Am and CHA-FAU, respectively. Cu species were introduced into the NH_4^+-form zeolites (NH_4^+/CHA) by ion-exchange method (Cu-H/CHA-Am and Cu-H/CHA-FAU).

The XRD patterns of the Cu-containing samples showed typical diffraction patterns originated from the CHA-type structure (Figure S1), and also did not show any diffractions attributed to Cu species, implying the high dispersion and/or small amount of Cu species (metal cation and oxides). The high dispersibility of the Cu species were also supported by their UV-vis spectra (Figure S2). The acid amount of the samples was estimated by NH_3-TPD profiles (Figure S3). The physicochemical properties of the obtained samples are summarized in Table 1. From the ^{27}Al MAS NMR spectra (Figure S4-A), all samples exhibit an intense peak at 58 ppm corresponding to tetrahedrally coordinated aluminum in the zeolite framework. There was no marked difference in the presence of defect sites between CHA-FAU and CHA-Am by ^{29}Si CP/MAS NMR spectra. Hence, the Al distribution was evaluated based on the ^{29}Si MAS NMR spectra (Figure S4-B)[21,22], indicating that CHA-FAU gave a significantly lower Q^4(2Al) proportion than CHA-Am; CHA-FAU contained more isolated Al atoms compared to CHA-Am. We quantitatively evaluated the amounts of Q^4(1Al) and Q^4(2Al) species (Table S1, S2, Figure S5).

Oxidative conversion of CH_4 with N_2O were carried out by using Cu-H/CHA-Am and Cu-H/CHA-FAU. In this work, in order to enhance the MTM reaction, oxidative conversion of CH_4 was carried out in the presence of steam and highly active oxidant N_2O (Figure 1). For both catalysts, the conversions of CH_4 and N_2O were decreased along with time on stream (TOS), while Cu-H/CHA-FAU gave a higher CH_4 conversion than Cu-H/CHA-Am. Note, there were clear differences in the products' distribution. Interestingly, for Cu-H/CHA-FAU, in addition to CH_3OH, hydrocarbons were produced. On the other hand, Cu-H/CHA-Am mainly produced CH_3OH and CO, and hardly produced the hydrocarbons. For Cu-H/CHA-FAU, the selectivity to CH_3OH was decreased but that to hydrocarbons was increased along with time on stream (TOS) (Figure 1), suggesting that the CH_4 is converted to the hydrocarbons *via* CH_3OH and/or CH_3OH derivates. The distribution of the hydrocarbons was shown in Figure 1 (c), indicating that lower hydrocarbons such as C2-C4 were selectively produced; the main products were ethylene followed by propylene. This is a typical feature of the MTO reaction over CHA-type zeolite. We carried out the MTO reaction in the presence of N_2O over Cu-H/CHA and Cu-H/CHA-Am (Figure S6), indicating. both catalysts selectively produced lower olefins even when N_2O was co-fed. Hence, these results strongly suggest a new route to the production of the hydrocarbons from CH_3OH, which is produced by oxidative conversion of CH_4. Consequently, it is concluded that the Al distribution greatly affected the oxidative conversion of CH_4 and that Q^4(1Al) species would be advantageous for this reaction.

To clarify thus observed difference in the catalytic activity between Cu-H/CHA-Am and Cu-H/CHA-FAU, the chemical state of Cu species was characterized by *in-situ* NO adsorbed FTIR measurement (Figure 2). The measurements were carried out with and without the activation with N_2O for 1 h at 623 K to

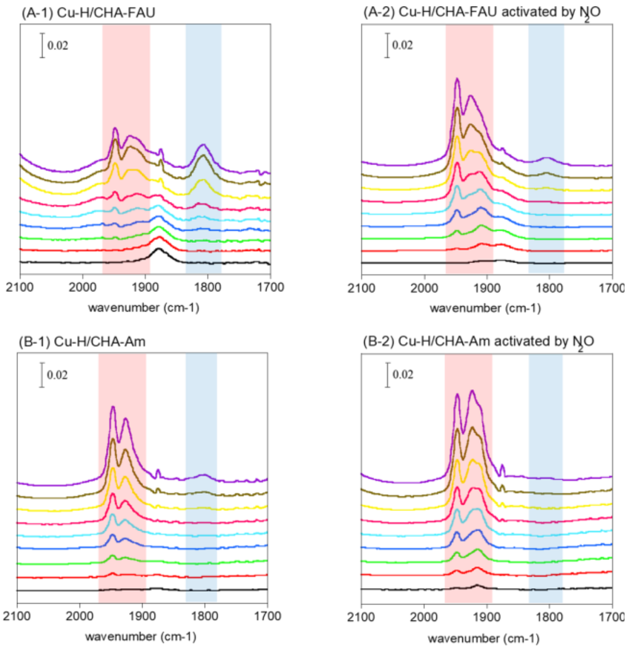

Figure 2 NO adsorption FTIR spectra over Cu-H/CHA-Am (A-1) and Cu-H/CHA-FAU (B-1), and the same spectra after activation with N_2O over Cu-H/CHA-Am (A-2) and Cu-H/CHA-FAU (B-2). (NO (5-1000 Pa) was adsorbed at RT.)

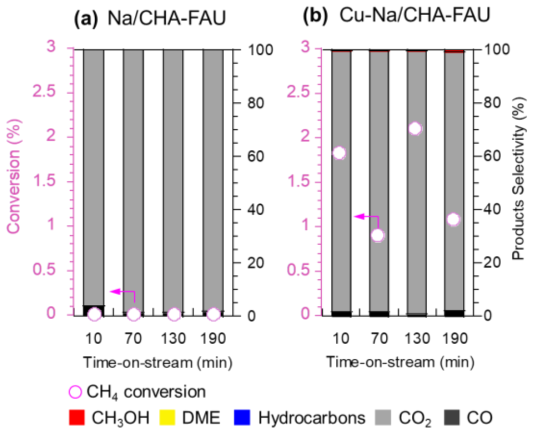

Figure 3 Oxidative conversion of CH_4 with N_2O over (a)Na/CHA-FAU and (b)Cu-Na/CHA-FAU. (○) Conversion of CH_4, bars represent the selectivity to CH_3OH, DME, hydrocarbons, CO and CO_2, respectively. Reaction conditions: 100 mg catalyst; P_{CH4}: P_{N2O}: P_{H2O}: P_{Ar} = 0.4:0.4:0.08: balance (atm); total pressure, 0.1 MPa; temperature, 623 K; SV = 1.5×104 mL h^{-1} g^{-1} and W/F = 3.7 g_{-cat} h $mol^{-1}{}_{CH4}$.

observe the active site; the peak around 1800 cm^{-1} (blue zone) was associated with NO bound to Cu^+ site, and the peaks at 1900~1970 cm^{-1} (red zone) were assigned to Cu^{2+} species.[25] Focusing on the band at 1800 cm^{-1}, this band was clearly observed in Cu-H/CHA-FAU (A-1) compared to Cu-H/CHA-Am (B-1); CHA-FAU captured Cu species as Cu^+ as well as Cu^{2+} species, while CHA-Am produced mainly Cu^{2+}. Hence, it is concluded that the Al distribution remarkably affected the state of Cu species. For both samples, after the activation with N_2O, the bands at 1800 cm^{-1} decreased but the band at 1900~1970 cm^{-1} increased, indicating that some Cu^+ sites were activated by N_2O, converting to Cu^{2+} sites. We have considered that such changeable Cu species from Cu^+ to Cu^{2+} by the activation with N_2O would contribute to the formation of $[Cu(II)\text{-}O\text{-}Cu(II)]^{2+}$ and $[Cu(II)\text{-}OH]^+$, which are considered to be an active site for the MTM reaction[15,26]. Note that the change in the valence was significant in Cu-H/CHA-FAU, resulting in the different catalytic performance. The further investigation on the influence of spatial distribution of Al atoms in the framework is ongoing.

As a control, Na/CHA-FAU and Cu-Na/CHA-FAU were prepared and their catalytic performance were evaluated (Figure 3). When the Cu loading was increased, the CH_4 conversion but the main product was CO_2. (Figure S7). Na/CHA-FAU did not show any catalytic performance, while Cu-Na/CHA-FAU gave an almost similar CH_4 conversion to Cu-H/CHA-FAU, indicating that Cu species would be indispensable for CH_4 activation. However, the main product was CO_2 and no hydrocarbon formation was observed. Na/CHA-Am and Na-Cu/CHA-Am also gave the same trends (Figure S8). These results strongly suggest that the acid sites played an important role in both the production of methanol and the conversion of CH_3OH into the hydrocarbons, and that the cooperative effect of Cu and H^+ leads to the direct production of the hydrocarbons from CH_4.

In order to estimate the production mechanism of the hydrocarbons, the catalyst after the reaction was dissolved and the extracted solution was analyzed by GC-MS technique (Figure S9). Organic residual was hardly detected in Cu-Na/CHA-FAU and Na/CHA-FAU after the reaction, while hydrocarbons, mainly aromatics, were observed in Cu-H/CHA-FAU. This is a typical feature of the MTO reaction; the hydrocarbons are produced by dissociation and desorption of the side chains of aromatic hydrocarbons formed by the "carbon pool" and/or "dual cycle" mechanism.[27,28,29] The catalytic interaction between Brønsted acid sites and methanol molecules is essential for realizing the formation of aromatic hydrocarbons. At this time, we have considered that Cu-H/CHA-FAU produced more methanol, and the methanol molecules produced were effectively converted into the lower hydrocarbons via aromatic hydrocarbons.

In conclusion, the Cu-exchanged CHA-type aluminosilicate zeolites "with the Al distribution controlled" were successfully synthesized. We have successfully found the Al distribution greatly affected the state of the Cu species, and the catalytic performance in oxidative conversion of CH_4 and that "isolated Al atoms" would be advantageous for producing CH_3OH. In addition, the acid sites played an important role in the production of hydrocarbons; the CH_3OH produced from CH_4 is converted into hydrocarbons over the acid sites. Our findings will give us important insights on the catalytic conversion of CH_4, and will contribute to the effective utilization of CH_4 as carbon resource.

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Conflicts of interest

There are no conflicts to declare.

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