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Introduction

Methane, the main component of natural (and shale) gas, is one of the most abundant and inexpensive forms of fossil fuels and thus holds great potential to serve as a near-future source for energy and chemicals.^{1–3} The current industrial routes from methane to valuable products require the formation of syngas (CO and H₂) at high temperatures (>1000 K) and pressures (>4 MPa), which make them too costly and effective only in large-scale industries.⁴ The direct, low-temperature, and on-site conversion of methane into liquid oxygenates such as methanol is hence a highly desirable alternative green route for the efficient transportation and utilization of methane.^{5–7} Such a conversion is, however, extremely difficult to achieve, as it requires the cleavage of a strong C–H bond in methane and simultaneously needs to prevent methanol from further oxidation to CO_x .^{8–10}

In nature, methane monooxygenase enzymes (MMOs) that include iron or copper centers in active sites (soluble MMO^{11} or particulate $MMO^{12,13}$ respectively) have shown their own ability to oxidize methane directly and selectively to methanol with gaseous O₂ under mild conditions. Taking inspiration

Selective methanol formation *via* CO-assisted direct partial oxidation of methane over coppercontaining CHA-type zeolites prepared by one-pot synthesis[†]

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Direct conversion of methane into methanol at low temperature is a promising process for the efficient utilization of abundant methane as energy and chemical resources, and metal-loaded zeolites have been recently focused as a new candidate catalyst for this reaction. Here, catalytic CO-assisted direct conversion of methane into methanol was demonstrated over Cu-CHA zeolites. Methanol was selectively produced as a solo oxygenate, without the production of C2 oxygenates caused by CO insertion. For the preparation of the Cu-CHA zeolite catalyst, besides the conventional ion-exchange method, a one-pot synthesis approach using a Cu complex as a structure-directing agent was also applied. As both catalysts showed similar activation energies of 29–34 kJ mol⁻¹, the latter one was found to be more feasible resulting in a 1.5 times higher methanol production rate per gram of catalyst. The methanol production rate per Cu atom decreased with the increase of the Cu loading amount, indicating the necessity of low copper loadings for well-dispersed isolated single copper active sites, which would explain the improved result of the one-pot synthesis approach.

> from these enzymes, numerous research studies have been devoted towards developing synthetic catalysts and related processes for the partial oxidation of methane using O₂ as the ideal oxidant (CH₄ + $1/2O_2 \rightarrow CH_3OH$) at low temperatures. Accordingly, metal-containing zeolites have emerged as promising heterogeneous catalysts because of their capability to host comparable metal active sites to those found in biological systems. Many zeolites with different metal ions (Cu, Fe, and others) have been investigated for the direct conversion of methane.^{10,14-19} Particular interest in this regard has been focused on copper-containing zeolites that activate methane even with small concentrations of O2. Until recently, it was believed that the partial oxidation of methane over copper-containing zeolites could be realized only through a non-catalytic stepwise process (*i.e.*, chemical looping),²⁰⁻²⁴ which consists of three distinct stages operated at a wide range of temperature and requires several hours for one turnover. However, in 2016, Narsimhan et al. broke this ground by establishing a catalytic process for continuous methanol production in the gas phase. The study used various copper-containing zeolites (MFI, BEA, MOR, FER, FAU, and CHA-types) to convert methane into methanol by feeding a gas mixture of CH₄, H₂O, and O₂ at low temperatures (483-543 K).²⁵ Therein, copper-containing CHAtype zeolites (Cu-SSZ-13 and Cu-SAPO-34) with their small pore and cage-based structure revealed better catalytic performance than those having medium and large pores. Despite this, the low methanol production rates (~ 4.0×10^{-2} mol mol_{Cu}⁻¹ h⁻¹

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or ~6.0 μ mol g_{cat}⁻¹ h⁻¹)²⁶ achieved so far impede the industrial implementation of this continuous catalytic process.

On the other hand, Shan et al. and Tang et al. have recently developed another catalytic process for the partial oxidation of methane by using gaseous O2 with the assistance of CO at 423 K in an aqueous medium.^{27,28} Whilst this process initially proposed to employ rhodium-containing MFI-type zeolite (Rh-ZSM-5) as a catalyst, our group has broadened its application to other platinum group (Ru, Pd, Ir, and Pt) and transition metal (Fe, Co, Ni, and Cu) containing MFI-type zeolites.²⁹ It was noted that there is a peculiar requirement for CO to be present for the conversion of methane. And due to the presence of CO, other oxygenates such as formic acid and acetic acid besides methanol formed in appreciable amounts. In the study,²⁹ copper showed the highest methanol selectivity even though its reactivity was less than those of platinum group metals. Additionally, the catalyst showed a methanol production rate of 0.3 mol $\text{mol}_{\text{Cu}}^{-1}$ h⁻¹ (or 2.3 × 10 µmol g_{cat}⁻¹ h^{-1}), which outperformed the previously reported chemical looping processes over copper-containing zeolites. Although the CO-assisted reaction system over copper-containing zeolites offers significant advantages in the conversion of methane, it requires to be further investigated to enhance methanol formation as well as to obtain a better understanding of its mechanism and active sites.

As alluded to earlier, copper-containing CHA-type zeolites with their small pore cage-based structure (composed of $8 \times 8 \times$ 12 Å cages interconnected by windows with a maximum pore diameter of 3.8 Å)30 are superior catalysts for methanol production from methane compared to medium and large pore ones in either a stoichiometric stepwise or continuous catalytic manner. This is due to confinement effects in the small pore of the CHA structure that provides high stabilization of copper active species, which may expedite the conversion of methane to methanol.^{31,32} In view of this fact, we herein explore the COassisted direct conversion of methane into methanol over copper-containing aluminosilicate SSZ-13 as CHA-type zeolite catalysts (Cu-CHA). Different from our previous study on the MFI structure,²⁹ the present results demonstrate that the CHA structure becomes successful in suppressing the formation of other oxygenates and in producing methanol simultaneously as an only oxygenate with a trace of an unidentified product. Furthermore, by controlling the copper species and contents via different synthetic techniques along with optimizing the reaction temperature, the catalyst could achieve the highest methanol production rates reported so far for any copper-containing zeolites used in a catalytic process with O₂ as the oxidant.

Experimental section

Materials

The following raw materials were used as received: colloidal silica (Ludox® AS-40, 40 wt% suspension in water, Sigma-Aldrich) as a silica source, aluminum hydroxide (Al(OH)₃, Sigma-Aldrich) as an aluminum source, sodium hydroxide solu-

tion (NaOH, 50 wt% in water, Wako) as an alkali source, N,N,Ntrimethyl-1-adamantanamine hydroxide (25 wt% TMAdaOH in water, Sachem) as a crystallization organic structure-directing agent (OSDA), and deionized water. Moreover, Cu-TEPA solution was prepared as a cooperative OSDA to be used with TMAdaOH in the one-pot synthesis of CHA-type zeolites from the chemicals tetraethylenepentamine (TEPA, TCI) and copper sulfate pentahydrate (99.9 wt% CuSO₄·5H₂O, Wako).

One-pot synthesis of aluminosilicate Cu-CHA materials with different copper loadings

One-pot synthesis of aluminosilicate Cu-CHA materials was performed by a procedure similar to that described elsewhere³³ with reaction gel comprising 1.0SiO₂: 0.033Al₂O₃: xNaOH: 0.2TMAdaOH: yCu-TEPA: 20H₂O (where x = 0.1 and y = 0.01-0.1). Initially, Cu-TEPA as a copper complex of CuSO₄·5H₂O and TEPA was prepared in a molar ratio of 1:1, respectively. For doing that, CuSO4.5H2O was first dissolved in deionized water followed by dropwise addition of TEPA, and the final solution was stirred for 1 h. Separately, aluminum hydroxide was dissolved in an aqueous mixture of TMAdaOH and NaOH. The prepared Cu-TEPA was then added into this solution, and the mixture was further stirred for 10 min. After that, colloidal silica was slowly added, and the stirring was continued for 3 h to form an aluminosilicate reactant. The resulting mixture was then transferred into a stainless-steel autoclave (no. 4749, Parr Instruments) and subjected to hydrothermal treatment at 423 K for 14 days. The solid products were recovered by filtration, washed with deionized water, and dried overnight at 373 K. These solids were finally calcined at 823 K with a temperature ramp of 276 K min⁻¹ for 10 h to remove the occluded organic structure-directing agents in zeolites.

Preparation of aluminosilicate Cu-CHA materials by liquid ion-exchange

The conventional aluminosilicate CHA-type zeolite (SSZ-13) was synthesized from reaction gel with the following molar composition: 1.0SiO₂: 0.04Al₂O₃: 0.012NaOH: 0.2TMAdaOH: 20H₂O. First, aluminum hydroxide, TMAdaOH and NaOH were dissolved in deionized water under stirring for 10 min. Then, colloidal silica was slowly added, and the solution was homogenized under continuous stirring for 30 min. Later, the reaction mixture was placed in an autoclave, and heated at 433 K in an oven under rotation at 20 rpm for 5 days. After that, the solid products were recovered, purified, dried, and calcined by the same procedures as described above. The calcined CHA-type zeolite was then ionexchanged with 1 M NaNO3 solution for 24 h at room temperature (Na-CHA-IE). The Cu-CHA material was finally prepared by twice liquid ion-exchange of Na-CHA-IE with 0.01 M (CH3COO)2Cu solution for 24 h at room temperature. The solid Cu-CHA material was recovered by the same procedures as described above.

Characterization

Powder X-ray diffraction (XRD) patterns of solid products were recorded using a Rigaku Rint 2000 diffractometer with $CuK\alpha$ radiation (40 kV, 40 mA). The crystal sizes and morphologies

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of the resultant products were confirmed using a scanning electron microscope (SEM, Hitachi S-4500, 5 kV). Elemental analysis of the products was carried out with a Thermo Scientific iCAP-6300 inductively coupled plasma-atomic emission spectrometer (ICP-AES) system after dissolving the products in hydrofluoric acid and hydrochloric acid solutions, and a Jeol JSX-3100RII X-ray fluorescence (XRF) system with a Rh anode X-ray tube (50 kV). Nitrogen adsorption-desorption measurements were performed on a Quantachrome Quadrasorb-evo instrument at liquid nitrogen temperature with autogas pretreatment at 573 K for 3 h under vacuum. Diffuse reflectance (DR) UV-Vis spectra were recorded using a JASCO V-650 spectrometer in the 190-800 nm wavelength range at a scan rate of 100 nm min⁻¹ using BaSO₄ as a reference. Fourier transform infrared (FT-IR) spectroscopy was conducted on a Jasco FT-IR 4100 spectrometer equipped with a mercury cadmium telluride (MCT) detector (JASCO Corp., Japan). The powder sample was made into a self-standing wafer and pretreated at 423 K, and transmission spectra were collected at room temperature under 1 atm of CO.

CO-assisted direct partial oxidation of methane reactions over Cu-CHA materials

Methane oxidation reactions were carried out in a highpressure batch reactor. In a typical catalytic reaction, approximately 50 mg of zeolite catalyst and 5 mL of deionized water along with a stirrer were loaded into a 50 mL stainless-steel autoclave (Taiatsu Techno, TVS-N2-type). Initially, the reactors were purged with pure nitrogen flow for 10 min and evacuated with the help of a pump until the inner pressure reached around 0.05 MPa. Pure oxygen (O2, Taiyo Nippon Sanso), carbon monoxide (CO, Taiyo Nippon Sanso), and methane (CH₄, Taiyo Nippon Sanso) were then fed into the reactors with gas pressures of 0.20, 0.50 and 2.00 MPa, respectively. Following this, the reactors were immersed in preheated oil baths at temperatures of 423, 448, and 473 K for a certain period of time. The temperature profiles of the oil baths during heating-up to the described temperatures are presented in Fig. S2.[†] Additionally, all reactions were performed under stirring at 500 rpm that is fast enough to confirm both homogeneous heat distribution and homogeneous mixing of liquid and gas phases. After reaction for the given times, the reactors were placed in a cold-water bath for 15 min to cool down to

room temperature. Gaseous samples (CO, CO₂, and CH₄) were quantified using an on-line Shimadzu GC-8A gas chromatography (GC-FID) system equipped with an active carbon (2m, 4q \times 3 φ , 60/80) column and a methanizer (nickel on silica-alumina, Alfa-Aesar). The calculations for gaseous products were performed based on calibration lines which were presented in a previous work of our group.²⁹ Thereafter, the aqueous suspension was filtered, and the liquid samples that evolved during the catalytic reaction were analyzed using an off-line Shimadzu GC-14B gas chromatography (GC-FID) system with a Zebron phase ZB-1 (no. 198347) capillary column and ¹H-NMR with DANTE presaturation pulse. Methanol (CH₃OH) was the only liquid organic product that has been determined from the analyzing methods applied in this work, and its quantification was made based on the calibration curve which was constructed from the solutions with known CH₃OH concentrations and their relative peak areas in GC-FID (see Fig. S3[†]). Moreover, the catalytic reactions were performed with a CO partial pressure of 0.25-1.00 MPa, and without the assistance of CO by a procedure similar to that described above at 473 K for 3 h. Also, the reference reactions were carried out by a procedure similar to that described above without using O_2 and CH_4 .

Results and discussion

A series of Cu-CHA zeolites with different copper loadings were prepared through either a one-pot synthesis method using copper tetraethylenepentamine (Cu-TEPA) and 1-adamantanamine hydroxide (TMAdaOH) as cooperative structuredirecting agents (SDAs) in alkali media,³⁴ or liquid ionexchange of conventional aluminosilicate CHA-type zeolite. The obtained zeolite samples were designated depending on the preparation method used: one-pot synthesized as Cu-CHA-T(*x*) and ion-exchanged as Cu-CHA-IE(*x*), where "*x*" denotes the Cu/cage ratio as shown in Table 1. The Cu/cage ratios were calculated based on the equation given below.

$$Cu/cage = \frac{(Cu/Al) \times 36/((Si/Al) + 1)}{3}$$

The UV-Vis spectra of the as-synthesized samples disclosed that the Cu-TEPA complex was retained during crystallization

Table 1 Physicochemical properties of CHA-type zeolites prepared by the one-pot synthesis method with different copper loadings or liquid ionexchange

Sample ^a	$\mathrm{Si}/\mathrm{Al}^b$	Na/Al ^b	Cu/Al^b	Al/cage	Cu (wt%)	Cu/cage	$V_{\rm micro}^{c} (\rm cm^{3} g^{-1})$
Cu-CHA-T(0.1)	16.8	0.2	0.2	0.7	0.9	0.1	0.31
Cu-CHA-T(0.3)	15.8	0.3	0.5	0.7	2.3	0.3	0.30
Cu-CHA-T(0.5)	17.8	0.2	0.8	0.7	4.3	0.5	0.29
Cu-CHA-T(0.8)	16.8	0.2	1.2	0.7	6.5	0.8	0.26
Cu-CHA-IE(0.5)	14.0	n.a.	0.7	0.8	4.9	0.5	0.31

^{*a*} Cu-CHA-T(*x*) denotes the samples prepared from one-pot synthesis using TMAdaOH and Cu-TEPA as cooperative structure-directing agents, whereas Cu-CHA-IE(*x*) denotes the sample prepared by conventional liquid ion-exchange. The value *x* represents the number of Cu atoms per cage. ^{*b*} Si, Al, Na, and Cu contents were determined by ICP-AES and XRF measurements. ^{*c*} Micropore volumes were calculated by a *t*-plot method.

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and was encapsulated inside Cu-CHA-T(x) samples (Fig. S6†). All of the calcined Cu-CHA materials showed the calcined highly crystalline and pure phase of CHA as demonstrated by X-ray diffraction (XRD), SEM and nitrogen porosimetry (Fig. S4 and S5†). Additionally, no formation of large Cu_xO_y nanoparticles was observed from the XRD patterns along with the UV-vis spectra, indicating a dispersion of isolated copper species throughout zeolite crystals.

The catalytic performance of Cu-CHA zeolites was evaluated by CO-assisted direct conversion of methane over Cu-CHA-T (0.5) and Cu-CHA-IE(0.5) since their identical copper loadings allow the investigation of the effect of preparation methods on methanol production. According to the prior literature,²⁵⁻²⁷ methane conversion reactions were initially carried out at 423 K. As seen in Fig. 1, both zeolites demonstrated the formation of methanol in the presence of CO, where Cu-CHA-T (0.5) exhibited higher catalytic performance than Cu-CHA-IE (0.5) by yielding a methanol production rate of $2.1 \times 10 \ \mu mol$ g_{cat}^{-1} h⁻¹ almost similar to that of Cu-ZSM-5.²⁹ In both cases, unlike previously studied Cu-ZSM-5,²⁹ methanol was formed as the only liquid oxygenated product over Cu-CHA zeolites. No other potential chemicals such as formic acid, acetic acid, and formaldehyde, except a trace of an unidentified product, were observed by either GC-FID or ¹H-NMR analysis under our reaction conditions, indicating unprecedented high methanol selectivity of the CHA structure. As also shown in Fig. 1, when the reactions were carried out without CO, only a small amount of methanol was formed over both zeolites. These values are comparable to each other and the values obtained in the previous CO-free catalytic processes.^{25,26}

To study the impact of reaction conditions on methanol production, the CO-assisted reaction system was further investigated over Cu-CHA-T(0.5) and Cu-CHA-IE(0.5) zeolites. First, we carried out CO partial pressure optimization studies on Cu-CHA-T(0.5). CO pressure between 0.25 and 1.00 MPa was applied by a procedure similar to that described above and the results are presented in Fig. 2. As seen in Fig. 2, lower partial pressures (0.25–0.50 MPa) resulted in increased methanol formation rates, and the maximum methanol production



Fig. 2 Methanol production rates over the Cu-CHA-T(0.5) zeolite catalyst under different CO partial pressures ranging from 0.25 to 1.00 MPa (0.20 MPa O_2 , 2.00 MPa CH₄, 5 mL H₂O, 50 mg catalyst, 423 K, 3 h).

occurred at 0.5 MPa. However, further increasing the CO partial pressure up to 1.00 MPa resulted in a sharp decrease of methanol formation, which might be a result of overoxidation of CO in large amounts. Later, the reaction temperature and time were investigated at the optimized CO partial pressure of 0.50 MPa over both Cu-CHA-T(0.5) and Cu-CHA-IE(0.5) catalysts. As seen in Fig. 3(a) and (b), methanol yields of both zeolites increased with the increase of the reaction temperature from 423 to 473 K. Furthermore, when the reactions were conducted at 473 K, Cu-CHA-T(0.5) and Cu-CHA-IE(0.5) zeolites showed the highest initial methanol production rates of 5.3 \times 10 and $3.5 \times 10 \ \mu\text{mol g}_{cat}^{-1} \ h^{-1}$, respectively. To the best of our knowledge, at the time of writing this paper, these rates represent the highest values reported so far for any copper-containing zeolites from a catalytic reaction system with O₂ as the oxidant. The reason behind these high rates can be attributable to the fact that elevated temperatures generally improve the catalytic activity of reactants and catalysts,^{35,36} as well as the dissolution rates of these gaseous reactants of O₂, CO, and



Fig. 1 Methanol production rates (μ mol $g_{cat}^{-1} h^{-1}$) of direct conversion of methane over Cu-CHA-T(0.5) and Cu-CHA-IE(0.5) zeolite catalysts with and without the assistance of CO (0.20 MPa O₂, 0.50 MPa CO, 2.00 MPa CH₄, 5 mL H₂O, 50 mg catalyst, 423 K, 3 h).



Fig. 3 Methanol yields ($\mu_{mol} g_{cat}^{-1}$) versus the reaction time for CO-assisted direct conversion of methane at low temperatures of 423 K (light red), 448 K (red), and 473 K (dark red) over (a) Cu-CHA-T(0.5) and (b) Cu-CHA-IE(0.5) zeolite catalysts (0.20 MPa O₂, 0.50 MPa CO, 2.00 MPa CH₄, 5 mL H₂O, 50 mg catalyst).



Fig. 4 Arrhenius plots for Cu-CHA-T(0.5) and Cu-CHA-IE(0.5) obtained from methanol production rate measurements from 423 to 478 K (0.20 MPa O_2 , 0.50 MPa CO, 2.00 MPa CH₄, 5 mL H₂O, 50 mg catalyst, 3 h).

CH₄ into water (as shown in Fig. S7[†]). Based on the initial methanol production rates, the activation energies (E_a) were estimated over Cu-CHA-T(0.5) and Cu-CHA-IE(0.5) zeolites. Fig. 4 shows the Arrhenius plots within the temperature range of 423 to 473 K, and the corresponding effective E_a values. The calculations revealed activation energies of 34 ± 2 and 29 ± 2 kJ mol^{-1} for Cu-CHA-T(0.5) and Cu-CHA-IE(0.5) zeolites, respectively. These similar values point out that Cu-CHA-T(0.5) and Cu-CHA-IE(0.5) zeolites consisted of similar copper species as active sites. On the other hand, the amount of active sites within the CHA structure should be different since Cu-CHA-T (0.5) zeolite showed much higher methanol production rates than Cu-CHA-IE(0.5) despite the fact that the same metal loading and reaction conditions were applied (Fig. 1). After 24 h of reaction, methanol formation was suppressed and a non-linear CH₃OH yield was observed along with the increase in the reaction time (Fig. 3), even though it was far below the theoretical equilibrium. This might be a result of catalyst deactivation and/or the decrease of reactants by unintended side reactions. Additionally, overoxidation of methanol to CO_x might be another potential reason.

As it was stated previously,²⁹ the consumption of CO to form CO_2 is the major challenge for this catalytic system over Rh-ZSM-5. In order to evaluate this issue also for copper-containing zeolites, in Fig. S8,[†] CO consumption and CO₂ production are presented along with the increase in reaction time over Cu-CHA-T(0.5) and Cu-CHA-IE(0.5) zeolites at 473 K. As it can be seen over both catalysts, the behaviour of CO consumption has been found to be corresponding to that of CO_2 production. The calculated theoretical CO conversions (CO + 1/ $2O_2 \rightarrow CO_2$) approached 100% upon extending the reaction time to 24 h (i.e., theoretical maximum of CO consumption is 9.2 mmol determined by the total amount of O_2 gas fed in the batch reactor (4.6 mmol)). These results were consistent with the prior work performed by our group.²⁹ Additionally, it would be tough to estimate the total oxidation of methane into CO₂ owing to the far lower methane conversion. Apart from the CO oxidation reaction, other potential reactions including

the water-gas shift reaction (CO + $H_2O \rightarrow CO_2 + H_2$ or CO + $2H_2 \rightarrow CH_3OH$) might also occur over copper-containing zeolite catalysts at the reaction temperature between 423 K and 523 K. However, when the reference reactions were carried out in the absence of O_2 and CH_4 at 473 K, no formation of CO_2 and methanol could be determined by GC-FID, respectively, denying the evolution of other reaction paths (data not shown). Based on these results, it can be suggested that CO oxidation is mainly responsible for CO₂ formation in the COassisted direct conversion system. Since CO plays a critical role in methane activation to produce methanol with high rates, its consumption in large amounts through such a side reaction thwarts the efficiency of the reaction system. Therefore, it is significant to elucidate the role of CO in the conversion of methane into methanol, and to find an alternative substitute that can be replaced with CO to achieve possibly much higher production rates.

It is generally accepted that adsorption of CO can influence the energetics of a reaction, having a profound effect on the kinetics and thermodynamics of the system, regardless of whether these surface species are necessary for that elementary step or not. In a previous work, the presence of CO as a ligand and a reductant was proven for platinum group metals.²⁹ To obtain an insight into the role of CO for coppercontaining zeolites, the zeolites were studied by FTIR spectroscopy. As illustrated in Fig. 5, the coordination of CO on copper metal sites was confirmed over both Cu-CHA-T(0.5) and Cu-CHA-IE(0.5) zeolites. Two bands with maxima at 2135 and 2157 cm^{-1} are related to the stretching vibrations of C \Box O in carbonyl species adsorbed over two different Cu^I sites. According to the literature, the 2135 cm⁻¹ band corresponds to Cu⁺ in the constrained six-membered ring of the CHA structure whereas the 2157 cm⁻¹ band corresponds to Cu⁺ in the larger cages of the CHA structure.³⁷ Moreover, the 2135 cm⁻¹ band is generally assigned to Cu⁺ species near two Al sites in the six-membered ring together with Na⁺ or proton to balance the total charge, while the 2157 cm^{-1} band is near a single Al



Fig. 5 FT-IR spectra of Cu-CHA-T(0.5) and CO-coordinated Cu-CHA-T (0.5) (black, top two lines), and Cu-CHA-IE(0.5) and CO-coordinated Cu-CHA-IE(0.5) (grey, bottom two lines). CO coordination was conducted in the same reactor used for the catalytic test (0.50 MPa CO, 50 mg catalyst, 473 K, 3 h).

site in the six-membered ring.³⁸ The intensities of these bands are also attributed to the concentration of CO-coordinated copper species. As it was assumed from a synthetic point of view, these results suggested that Cu-CHA-T(0.5) possesses more isolated Cu⁺ species with CO coordination especially in isolated Al sites of the CHA framework. This clearly indicates that one-pot synthesis using Cu-TEPA is much efficient to fabricate isolated copper active species compared with the conventional ion-exchange method since the encapsulation of maximum one Cu-TEPA per cage structure could provide good dispersion of mononuclear copper atoms in CHA-type zeolite.³⁹

To evaluate the effect of copper contents on methanol production, the performance of Cu-CHA-T(x) zeolites with different copper loadings was also screened at 473 K for 3 h. Fig. 6 shows the methanol production rates per mol copper along with the copper amount per cage. The highest rate was achieved at the lowest copper content (Cu/cage = 0.1), and the rate decreased with the increase of the copper content (Fig. 6). This result indicates that increasing copper content does not necessarily lead to an increase in the methanol production rates, which is totally different from the conventional copperoxo studies realized in either stepwise stoichiometric or continuous catalytic processes. As it is well established by us and other groups,²⁷⁻²⁹ isolated mononuclear Rh species have gained high importance as active sites for CO-assisted partial oxidation of methane to methanol. In the case of copper, its high mobility through the small pore window of CHA-type zeolite has been discussed in the previous studies, and that allows the formation of di- and trinuclear metal-oxo species for CO-free methane conversion.^{12,16,20-26,32} In contrast, our result strongly suggested that the formation of a multi-nuclear cluster was not feasible for the CO-assisted methane conversion, and maintaining the isolated copper site would be the key to prepare active sites. On the basis of these speculations, it can be suggested that Cu-CHA materials prepared through



Fig. 6 Effect of copper loadings of Cu-CHA-T zeolite catalysts on methanol production rates from the CO-assisted direct conversion of methane into methanol (0.20 MPa O_2 , 0.50 MPa CO, 2.00 MPa CH₄, 5 mL H₂O, 50 mg catalyst, 473 K, 3 h). The dashed line was added to guide the eye.

one-pot synthesis with lower copper loadings might be promising for further improving the catalytic activity.

Conclusions

Cu-CHA zeolites, which were prepared through either one-pot synthesis or liquid copper ion exchange methods, exhibit excellent performance in the CO-assisted catalytic direct partial oxidation of methane into methanol. Methanol was observed as the one and only oxygenate product, indicating unprecedented high selectivity towards methanol. Methanol production rates of 5.3 \times 10 and 3.5 \times 10 μ mol g_{cat}⁻¹ h⁻¹ were obtained over Cu-CHA-T(0.5) and Cu-CHA-IE(0.5), respectively. These rates represented the highest values reported so far for any copper-containing zeolites. The content of active copper species in Cu-CHA zeolites varied with the synthetic strategies, among which one-pot synthesis is found to be more efficient to fabricate isolated copper active species. This also agreed with the gradual decrease in methanol production rates with the increase of copper loadings, which is opposite of conventional multi-nuclear copper-oxo studies. These results highlight the necessity of low copper loadings to direct the synthesis of well-dispersed isolated single copper active sites by a one-pot synthesis method.

Author contributions

Sibel Sogukkanli: catalyst preparation, catalytic test, analysis, writing the original draft, manuscript editing and review; Takahiko Moteki: project administration, conceptualization, data validation, supervision, manuscript editing and review; Masaru Ogura: supervision, funding acquisition, project administration, manuscript editing and review.

Conflicts of interest

There are no conflicts to declare.

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