

## Supporting Information

### 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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#### Synthesis of CHA-type aluminosilicate zeolite

The CHA-aluminosilicate zeolite was synthesized by organic-directing agents (OSDA)-free method based on our previous study by hydrothermal synthesis [1,2]. In a typical CHA as-made, aluminum isopropoxide (FUJIFILM Wako Pure Chemical Corporation), NaOH (FUJIFILM Wako Pure Chemical Corporation) and KOH (FUJIFILM Wako Pure Chemical Corporation) were added distilled water. Then, FAU zeolite (CBV720, Zeolyst) added to the mixture solution. The final synthesis gel with following molar composition 1 SiO<sub>2</sub>: 0.033 Al<sub>2</sub>O<sub>3</sub>: 0.30 Na<sub>2</sub>O: 0.05 K<sub>2</sub>O: 95 H<sub>2</sub>O. The resulting gel with seed crystals (20 wt%) was transferred to a Teflon lined stainless-steel autoclaves and heated at 423 K at its autogenous pressure under tumbling (40 rpm) for 2 days. The resulting solid was recovered by filtration and washed exhaustively with distilled water. The as-made sample was dried at 373 K overnight (CHA as-made).

#### Preparation of ion-exchange CHA

The ion-exchange was carried out twice to obtain NH<sub>4</sub><sup>+</sup> form using 2.5 M NH<sub>4</sub>NO<sub>3</sub> (FUJIFILM Wako Pure Chemical Corporation) aqueous solution with stirring at 353 K for 3 h. After collecting the solid by filtration, the resultant product was dried at 373 K overnight to obtain the NH<sub>4</sub><sup>+</sup>-form CHA (NH<sub>4</sub><sup>+</sup>/CHA). The resultant NH<sub>4</sub><sup>+</sup>/CHA was calcined in air at 773 K for 4 h to obtain the proton-form CHA (H/CHA). Cu ion-exchanged was performed at room temperature adding NH<sub>4</sub><sup>+</sup>/CHA to Cu(NO<sub>3</sub>)<sub>2</sub> trihydrate (FUJIFILM Wako Pure Chemical Corporation) solution (1.0 mM, 5.0 mM, 10 mM, 50 mM, 100mM) with stirring for 24 h. After the filtration, the sample was calcined at 773 K for 4 h (ion exchange at 1 mM is called Cu-H/CHA). Na ion-exchanged was performed three times at 353 K adding NH<sub>4</sub><sup>+</sup>/CHA to NaNO<sub>3</sub> (FUJIFILM Wako Pure Chemical Corporation) solution (2.5 M) with stirring for 3 h. After the filtration, the sample was calcined at 773 K for 4 h (Na/CHA). As a control, Cu ion-exchanged Na/CHA (Cu-Na/CHA) was also prepared by ion-exchange method.

## Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a RINT-Ultima III (Rigaku) using a Cu K $\alpha$  X-ray source (40 kV, 40 mA). SEM-energy dispersive X-ray spectroscopy (EDX) mapping images were conducted by an S-9000 microscope (Hitachi). Elemental analyses of the samples were performed on an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Shimadzu ICPE-9000). Diffuse reflectance UV-vis spectra were recorded by JASCO V-650 spectrometer. The absorbance of all spectra was converted to the Kubelka-Munk function. Ammonia desorption profiles were recorded on a MicrotacBEL Multitrack TPD equipment (BEL). The amount of organics incorporated inside the samples was determined using a thermogravimetric-differential thermal analysis (TG-DTA) analyzer (RigakuThermo plus EVO II, Rigaku). FTIR spectra were obtained using a Jasco FTIR-4100 spectrometer equipped with a MCM detector. The self-supporting zeolite wafer (~50 mg, 1 cm in diameter) was first evacuated at 500 °C for 1 hour. In the case of activation, the sample was oxidized at 350 °C for 1 hour by introducing 1.3 kPa of N<sub>2</sub>O. When it was cooled to room temperature, NO (5–1000 Pa) was introduced into the cell. The IR spectrum was measured after equilibrium pressure was reached.

## Oxidative CH<sub>4</sub> conversion reaction

Catalytic oxidative methane conversion reaction was performed in a continuous flow reactor under atmospheric pressure. Typically, 100 mg of catalysts were pretreated at 773 K for 1 h with Ar flow rate 30 mL min<sup>-1</sup>. The reaction was performed at 623 K in a flowing gas mixture with the composition of  $P_{\text{CH}_4} : P_{\text{N}_2\text{O}} : P_{\text{H}_2\text{O}} : P_{\text{Ar}} = 0.4 : 0.4 : 0.08 : \text{balance (atm)}$ , total flow rate 25 mL min<sup>-1</sup>. Reactants and products were analyzed with two online gas chromatographs (GC-2014, Shimadzu) equipped with a TCD or FID detector. One of the GCs was used with a packed column (Shimadzu, Shincarbon-ST 50/80, inner diameter 3 mm, length 6 m) and a TCD, while the other was equipped with a capillary column (Agilent, HP-PLOT Q, inner diameter 0.530 mm, length 30 m, film thickness 40.0  $\mu\text{m}$ ), a flame ionization detector (FID).

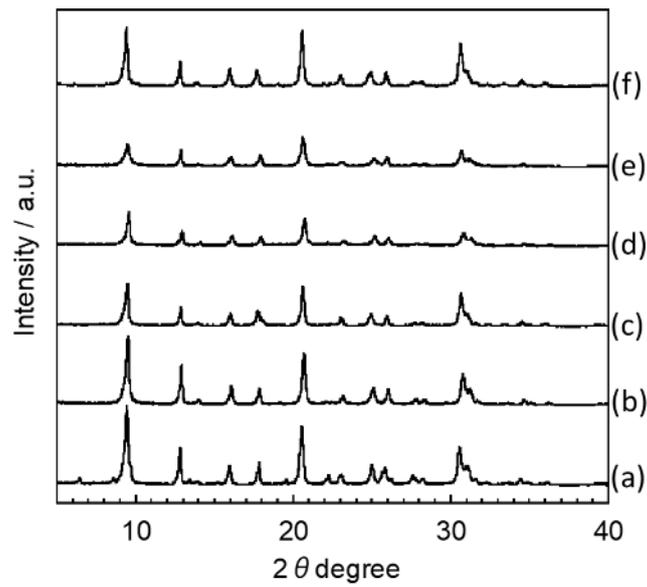
The selectivity to each product were calculated based on carbon basis with the following Supplementary equations (S. Eq. 1), (S. Eq. 2).

$$\text{Conversion of substrate (\%)} = \frac{\text{Moles of total carbon in products}}{\text{Moles of carbon in fed}} \times 100 \quad (\text{S. Eq. 1})$$

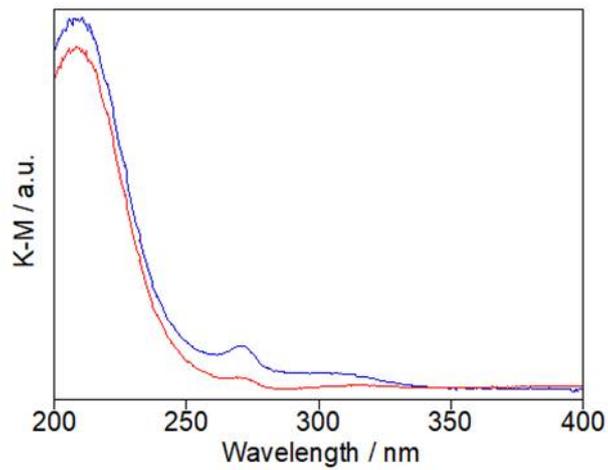
$$\text{Selectivity to product (\%)} = \frac{\text{Moles of total carbon in product defined}}{\text{Moles of carbon in substrate consumed}} \times 100 \quad (\text{S. Eq. 2})$$

## Supplementary References

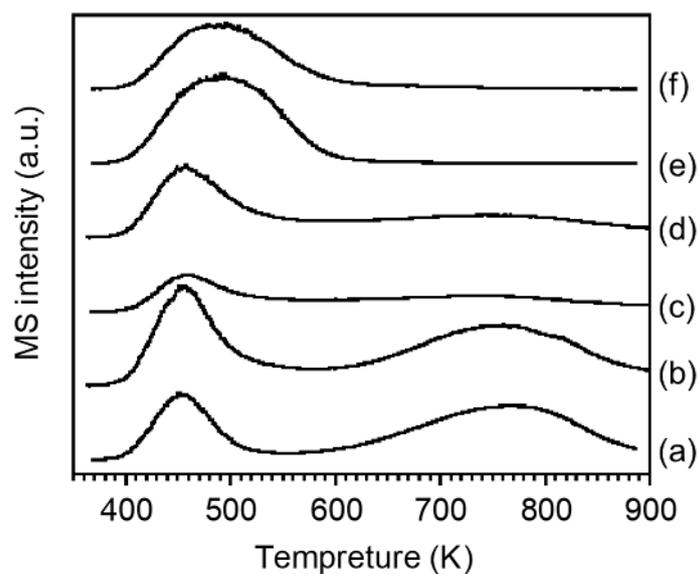
1. H. Imai, N. Hayashida, T. Yokoi, T. Tatsumi, “Direct crystallization of CHA-type zeolite from amorphous aluminosilicate gel by seed-assisted method in the absence of organic-structure-directing agents”, *Microporous Mesoporous Mater.* 2014, 196, 341–348.
2. Y. Wang, T. Nishitoba, Y. Wang, X. Meng, F.-S. Xiao, W. Zhang, B. Marler, H. Gies, D. de Vos, U. Kolb, M. Feyen, R. McGuire, A.-N. Parvulescu, U. Müller, T. Yokoi, “Cu-Exchanged CHA-Type Zeolite from Organic Template-Free Synthesis: An Effective Catalyst for NH<sub>3</sub>-SCR”, *Ind. Eng. Chem. Res.* 2020, 59, 16, 7375–7382.



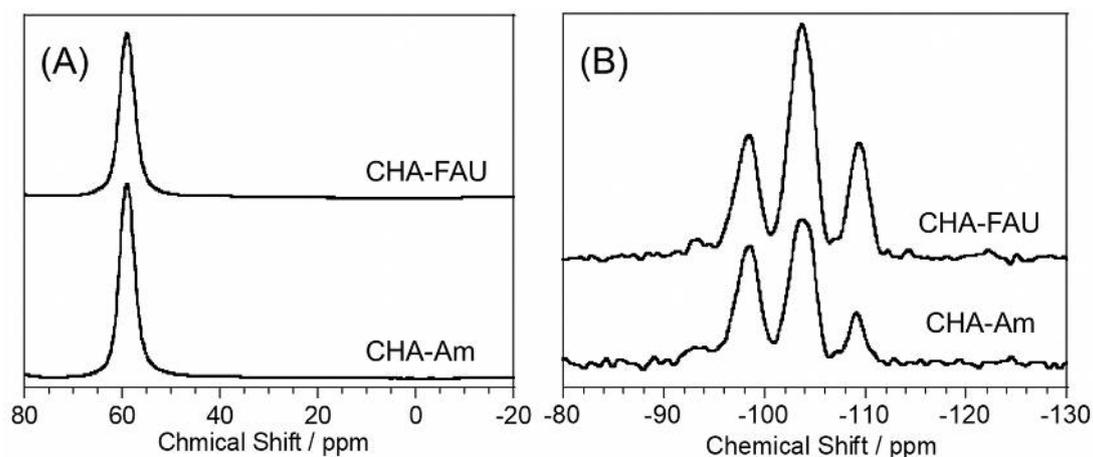
**Figure S1** XRD patterns of CHA samples. (a):  $\text{NH}_4^+$ /CHA-FAU; (b):  $\text{NH}_4^+$ /CHA-Am; (c): Na/CHA-FAU; (d): Cu-H/CHA-FAU; (e): Cu-H/CHA-Am; and (f): Cu-Na/CHA-FAU.



**Figure S2** UV-vis spectra of Cu-/CHA. (red: CHA-Am; blue: CHA-FAU)



**Figure S3** NH<sub>3</sub>-TPD profiles (intensity of  $m/z = 16$ ) of CHA samples. (a): NH<sub>4</sub><sup>+</sup>/CHA-FAU; (b): NH<sub>4</sub><sup>+</sup>/CHA-Am; (c): Cu-H/CHA-FAU; (d): Cu-H/CHA-Am; (e) Na/CHA-FAU; and (f) Cu-Na/CHA-FAU.



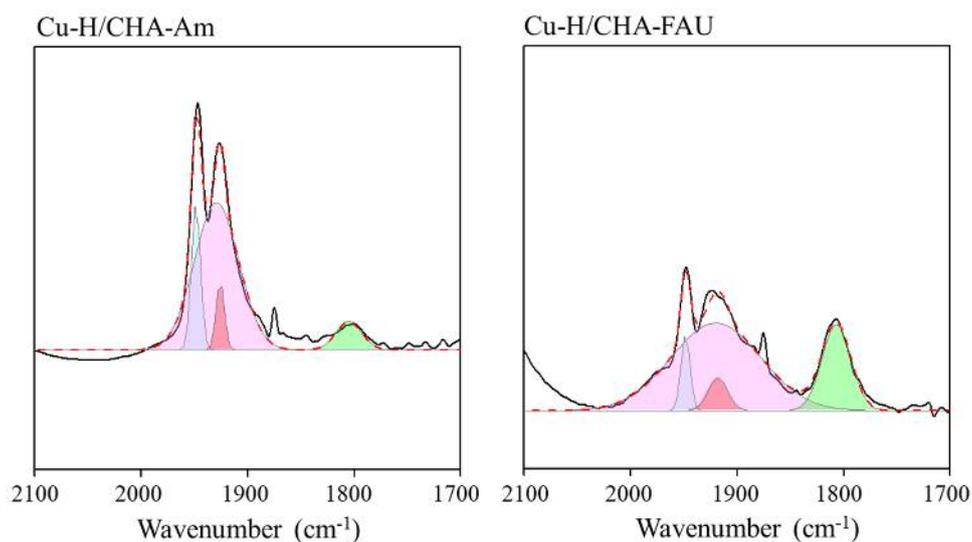
(C)

Sample	Proportion of Q <sup>4</sup> (nAl) and Q <sup>3</sup> (nAl) / %					Q <sup>4</sup> (2Al) / Q <sup>4</sup> (1Al)
	Q <sup>4</sup> (3Al)	Q <sup>4</sup> (2Al)	Q <sup>3</sup> (0Al)	Q <sup>4</sup> (1Al)	Q <sup>4</sup> (0Al)	
<b>CHA-FAU</b>	2.8	25.6	≤ 0.1	52	19.0	0.492
<b>CHA-Am</b>	2.3	30.9	≤ 0.1	48.4	18.6	0.638

**Figure S4** <sup>27</sup>Al (A) and <sup>29</sup>Si (B) MAS NMR spectra of the CHA catalysts and curve fitting result of <sup>29</sup>Si MAS NMR (C).

**Table S1** Quantitative evaluation of the distribution of framework Al atoms.

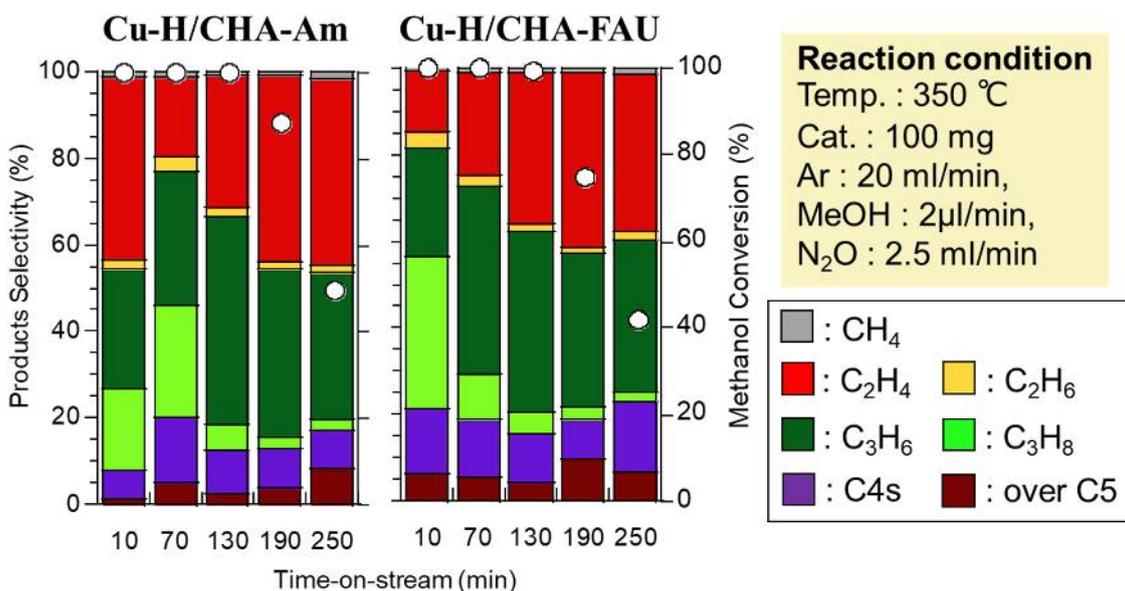
Samples	Si/Al	The amount of Al (mmol/g)	Quantities (mmol/g)	
			Q <sup>4</sup> (1Al)	Q <sup>4</sup> (2Al)
NH <sub>4</sub> <sup>+</sup> /CHA-FAU	3.8	3.47	1.66	1.58
NH <sub>4</sub> <sup>+</sup> /CHA-Am	3.1	4.06	1.70	1.95



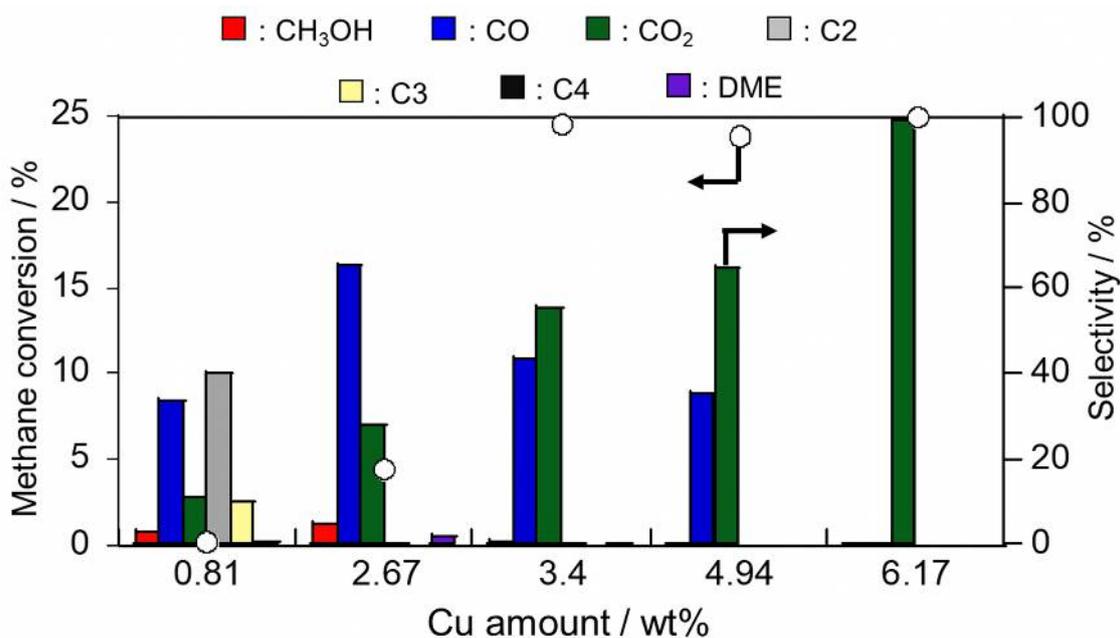
**Figure S5** Curve fitting results of in-situ NO adsorbed FT-IR in Cu-H/CHA-Am and Cu-H/CHA-FAU.

**Table S2** Quantitative evaluation of the distribution of Cu ions.

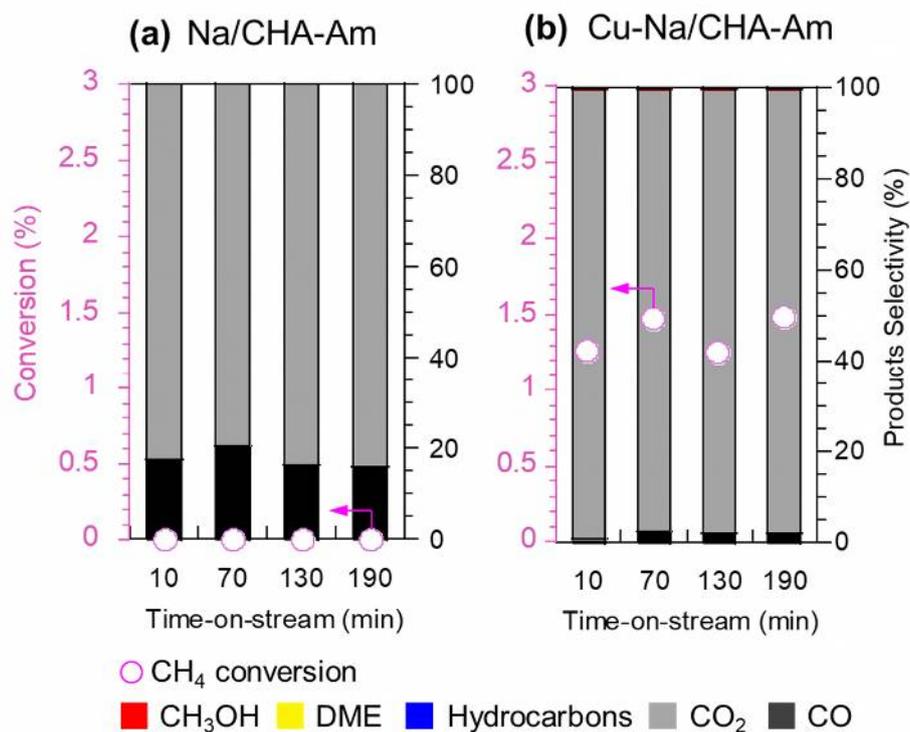
	Dimeric Cu <sup>2+</sup>	Isolated Cu <sup>2+</sup>	Cu <sup>+</sup>	Total
<b>Cu-H/CHA-Am</b>	14.4 %	77.7 %	7.9 %	
Quantities of Cu (mmol/g)	0.02	0.11	0.01	0.14
<b>Cu-H/CHA-FAU</b>	5.9 %	72.8 %	21.3 %	
Quantities of Cu (mmol/g)	0.01	0.09	0.03	0.13



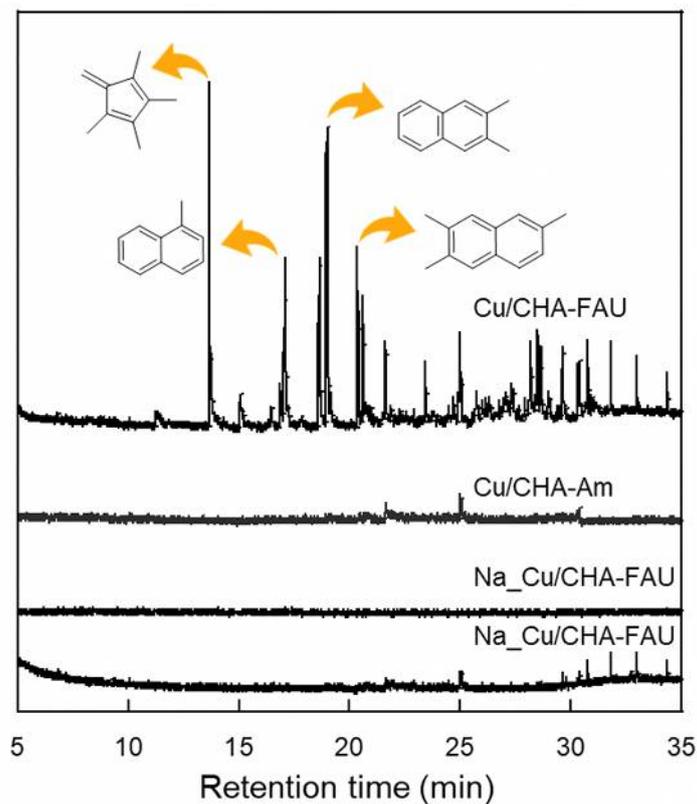
**Figure S6** MTO reaction in the presence of N<sub>2</sub>O over Cu-H/CHA and Cu-H/CHA-Am.



**Figure S7** Oxidative conversion of CH<sub>4</sub> with N<sub>2</sub>O over Cu-H/CHA-FAU catalysts with different Cu content. (○) Conversion of CH<sub>4</sub>, bars represent the selectivity to CH<sub>3</sub>OH, DME, C<sub>2</sub>-C<sub>4</sub>, CO and CO<sub>2</sub>, respectively. Reaction conditions: 100 mg catalyst; time-on-stream : 2 h; P<sub>CH<sub>4</sub></sub>: P<sub>N<sub>2</sub>O</sub>: P<sub>H<sub>2</sub>O</sub>: P<sub>Ar</sub> = 0.4:0.4:0.08: balance (atm); total pressure, 0.1 MPa; temperature, 623 K; SV = 1.5 × 10<sup>4</sup> mL h<sup>-1</sup> g<sup>-1</sup> and W/F = 3.7 g<sub>cat</sub> h mol<sup>-1</sup> CH<sub>4</sub>.



**Figure S8** Oxidative conversion of CH<sub>4</sub> with N<sub>2</sub>O over (a)Na/CHA-Am and (b)Cu-Na/CHA-Am. (○) Conversion of CH<sub>4</sub>, bars represent the selectivity to CH<sub>3</sub>OH, DME, hydrocarbons, CO and CO<sub>2</sub>.



**Figure S9** GC-MS results of catalysts after methane conversion reaction.