

## Supporting Information

### Continuous selective conversion of methane to methanol over Cu-KFI zeolite catalyst using water-O<sub>2</sub> mixture as the oxygen source

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## Content

S1. Materials and method .....	3
S1.1. Zeolite synthesis .....	3
S1.2. Ion-exchanged procedures .....	3
S1.3. Characterization methods .....	5
S1.4. Catalytic continuous MTM conversion tests .....	5
S1.5. Temperature-programmed surface reaction (TPSR) coupled with isotope labelling .....	6
S2. Characterization results .....	7
S2.1. Structure and morphology of KFI and CHA zeolites.....	7
S2.2. HAADF-STEM and H <sub>2</sub> -TPR of Cu-KFI .....	9
S3. Reaction results .....	10
S4. References .....	15

## S1. Materials and method

### S1.1. Zeolite synthesis

**KFI:** The molar ratio of the synthetic gel was  $\text{SiO}_2 : 0.38 \text{ KOH} : 0.2 \text{ Al(OH)}_3 : 0.01 \text{ Sr(OH)}_2 : 15 \text{ H}_2\text{O}$ . 4.98 g of KOH ( $\geq 85\%$ , Shanghai Macklin Biochemical Co., Ltd) was dissolved in 10 g of  $\text{H}_2\text{O}$ . 3.12 g of  $\text{Al(OH)}_3$  (99%, Shanghai Macklin Biochemical Co., Ltd) was added into the above KOH solution, and it was heated to 100 °C until clear, then it was cooled down to the room temperature and denoted as alkali solution. 0.531 g of  $\text{Sr(OH)}_2 \cdot 8 \text{ H}_2\text{O}$  (95%, Sinopharm Chemical Reagent Co., Ltd) was dissolved in 14 g of  $\text{H}_2\text{O}$ , and  $\text{Sr(OH)}_2$  solution was added dropwise in 40 g of Silica solution (30%, Sigma-Aldrich) to form a homogenous viscous gel. The above alkali solution was poured into the homogenous viscous gel, and 4g of  $\text{H}_2\text{O}$  was applied to transfer the residual alkali solution into the homogenous viscous gel, then it was stirred vigorously to obtain homogenous gel. The obtained gel was poured into the PTFE-lined autoclave and transferred into a high-temperature oven for crystallization under 145 °C for 120 h. After the crystallization process, the autoclave was taken out to cool down naturally. Finally, the obtained zeolite was separated, washed and dried overnight.

**CHA (SSZ-13):** In order to synthesize SSZ-13 with low SAR (Si/Al ratio), SSZ-13 seed was synthesized with template-free method. The molar composition of gel was  $0.38 \text{ KOH} : 0.017 \text{ Sr(OH)}_2 : 0.2 \text{ Al(OH)}_3 : 1 \text{ SiO}_2 : 39 \text{ H}_2\text{O}$ . The gel was poured to a PTFE-lined autoclave and placed into rotation oven at 175 °C for 24 h. Finally, the seeds were recovered with centrifugation, tilting, washing and drying under the same conditions with the synthesis of KFI.

**Other zeolites:** The other zeolites such as H-MOR (Si/Al = 11), H-ZSM-5 (MFI-type, Si/Al = 15), H-SSZ-39 (AEI-type, Si/Al = 10) and H-SSZ-13 (CHA-type, Si/Al = 10) were commercial purchase.

### S1.2. Ion-exchanged procedures

**$\text{NH}_4^+$ -exchange:** The  $\text{NH}_4^+$ -exchange of the synthesized KFI and CHA zeolites was

performed in 100 mL of 0.1 M  $\text{NH}_4\text{NO}_3$  (99 wt%) aqueous solution (100 mL deionized water and 0.8 g  $\text{NH}_4\text{NO}_3$ ). The solution was stirred at 80 °C for 6 h during the ion-exchange process. After  $\text{NH}_4^+$ -exchange, the ion-exchanged zeolites were separated and washed via centralization for 3-5 times using deionized water, and then dried at 80 °C for a day. The same exchange procedure was repeated for 3 times using the above exchanged zeolites in a new  $\text{NH}_4\text{NO}_3$  solution under the same conditions. The final  $\text{NH}_4^+$ -zeolites were calcined at 500 °C for 5 h after drying at 80 °C for a day to obtain H-type zeolites.

**$\text{Cu}^{2+}$ -exchange:** 2 g of zeolite powder was stirred in 100 mL of copper(II) nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , 99.99%, Sinopharm Chemical Reagent Co., Ltd) at 80 °C. The loading amount of copper and the Cu/Al ratios were determined by controlling the concentration of copper(II) nitrate solutions and the ion-exchange time. Subsequently, the suspension was centrifugalized and rinsed 3-4 times with deionized water (50 mL each time) to remove the surplus copper ions and ensure the pores in zeolites only contained the exchanged copper ions. The copper-exchanged samples were finally dried at 60 °C for a day and calcined in static air at 550 °C for 6 h with a heating rate of 1 °C  $\text{min}^{-1}$ . Copper (Cu), aluminum (Al) and silicon (Si) contents were measured by wavelength dispersive X-ray fluorescence (WDXRF) on a S8 TIGER X-ray fluorescence spectrometer (Bruker, Germany). The X-ray fluorescent spectra of Cu-zeolite samples were collected under vacuum condition with the working voltage of 60 kV and the electric current of 40 mA.

**Table S1.** The composition of Cu-exchanged zeolites.

Cu-zeolite	Si/Al	Cu loading (wt%)	Cu/Al
Cu-KFI	3.5	0.45	0.037
Cu-KFI	3.5	2.04	0.17
Cu-CHA	4.1	1.9	0.18
Cu-CHA	10	2.1	0.43
Cu-MOR	11	2.1	0.47
Cu-SSZ-39	10	2.2	0.45
Cu-ZSM-5	15	1.7	0.51

### **S1.3. Characterization methods**

X-ray diffraction (XRD) patterns of Cu-zeolite samples were measured on Rigaku Ultima IV using Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm, 40 kV, 40 mA). Morphology of the as-prepared KFI zeolite was measured through Scanning Electron Microscopy (SEM) on a QUANTA 400F Field Emission microscope operated at 20 kV. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was carried out to confirm the presence of copper atoms located on Cu-KFI catalyst on a FEI Talos electron microscope. XPS (X-ray photoelectron spectroscopy) measurement of Cu-KFI was conducted on the AXIS Ultra DLD (Shimadzu Kratos Ltd., JPN) to obtain the chemical states of surface Cu species. Temperature-programmed reduction with hydrogen (H<sub>2</sub>-TPR) was performed using TCD as detector to identify the copper species confined in KFI zeolite. Prior to H<sub>2</sub>-TPR, the Cu ion-exchanged KFI (50 mg) was pretreated at 400 °C in the flowing He (30 ml min<sup>-1</sup>) for 30 min, then cooled down to room temperature (RT), H<sub>2</sub>-TPR was carried out in the flowing 5% H<sub>2</sub>/Ar (30 mL min<sup>-1</sup>) at a ramp of 8 °C/min. The signal of H<sub>2</sub> consumption was recorded by TCD detector. FTIR spectra of Cu-KFI samples were measured on a Nicolet IS50 FTIR spectrometer in the diffuse reflectance mode equipped with a high sensitivity mercury-cadmium-telluride (MCT) detector and a high-temperature reaction cell with KBr window. The sample was first pretreated at 400 °C in the flowing He for 30 min, then the temperature was controlled to 200 °C and the IR spectrum of the sample was recorded using KBr powders as the background. Diffuse reflectance UV-Vis spectra of Cu-zeolite samples were measured to identify copper species on a Cary Series UV-Vis spectrophotometer (Agilent Technologies) in the diffuse reflectance mode equipped with a high-temperature reaction cell. The sample was firstly pretreated in the flowing He (30 ml min<sup>-1</sup>) at 400 °C for 30 min, then cooled down to RT and the spectrum was collected, using BaSO<sub>4</sub> as the background.

### **S1.4. Catalytic continuous MTM conversion tests**

Continuous MTM conversion was carried out in a tubular reactor (U-shaped quartz

tube, I.D. 8.0 mm) with a continuous flow of 15 ml min<sup>-1</sup> (GHSV = 9000 ml g<sub>cat.</sub><sup>-1</sup> h<sup>-1</sup>) under 1 bar pressure. The reactor was heated through a single-zone furnace. K-type thermocouple was mounted into the oven and used to control the reaction temperature. 100 mg of Cu-KFI zeolite (40-60 mesh, 0.3-0.45 mm) were packed between quartz wool plugs in the reactor and placed in the furnace heating zone. The reaction gas mixture, i.e., 90% CH<sub>4</sub>, 3.2% H<sub>2</sub>O, 100 ppm O<sub>2</sub>, He as the balance, was fed into the reactor and their flow rates were controlled by independent mass flow meters (Bronkhorst). The steam was introduced into the reactor through a saturator maintained at 25 °C. In the continuous MTH conversion process, the Cu-exchanged zeolite was firstly pretreated in the flowing helium (15 ml min<sup>-1</sup>) at 400 °C for 30 min with a heating rate of 5 °C min<sup>-1</sup> and then exposed in the reaction gas mixture in a reaction temperature range of 200-550 °C. The effluent products were identified and quantified on a mass spectrometer (MS, ThermoStar, GSD320, Shanghai, China) based on MS signals of methanol (CH<sub>3</sub>OH), formaldehyde (HCHO), dimethyl ether ((CH<sub>3</sub>)<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>) at m/z = 31, 30, 45 and 44. The space-time yields (STYs) of the products were calculated as follows:

$$Y_i = \frac{k_i \times M_{Cu}}{m \times x\%} \int_0^{60} I_i dt$$

where  $Y_i$ ,  $k_i$ ,  $I_i$ ,  $M_{Cu}$ ,  $m$ ,  $x\%$  and  $t$  refer to the space-time yield of  $i$ -product (mol mol<sub>Cu</sub><sup>-1</sup> h<sup>-1</sup>), the calibration coefficient, the MS intensity of  $i$ -product, the molar mass of copper (g mol<sup>-1</sup>), the mass of Cu-zeolite used for methane-steam conversion (0.1 g), the content (wt.%) of copper in per gram catalyst and the continuous reaction time (min), respectively.

The selectivity of methanol ( $S_{CH_3OH}$ ) was calculated as the following equation:

$$S_{CH_3OH} = \frac{Y_{CH_3OH}}{\sum iY_i}$$

### **S1.5. Temperature-programmed surface reaction (TPSR) coupled with isotope labelling**

Temperature-programmed surface reaction (TPSR) coupled with deuterium and <sup>18</sup>O

labelling experiments were performed in a fixed-bed reactor to reveal the oxygen source of MTM. 100 mg of Cu-zeolite sample (40-60 mesh, 0.3-0.45 mm) was placed in a U-shape quartz reactor (I.D. 8.0 mm) and pretreated at 400 °C in He flow (15 ml min<sup>-1</sup>) for 30 min. After the temperature dropped to 120-150 °C, the reaction gas mixtures including CH<sub>4</sub> (~96.8%) + D<sub>2</sub>O (3.2%) + O<sub>2</sub> (100 ppm) and CH<sub>4</sub> + H<sub>2</sub><sup>18</sup>O + O<sub>2</sub> (100 ppm) were fed to the reactor with the total flow rate of 15 ml min<sup>-1</sup>. In the TPSR mode, the sample was heated from 150 to 700 °C at a rate of 8 °C min<sup>-1</sup>. The reaction outlet composition was analyzed on-line on the MS (Pfeiffer Omnistar GSD320, Shanghai, China) based on the time-dependent evolution of m/z signals of the products.

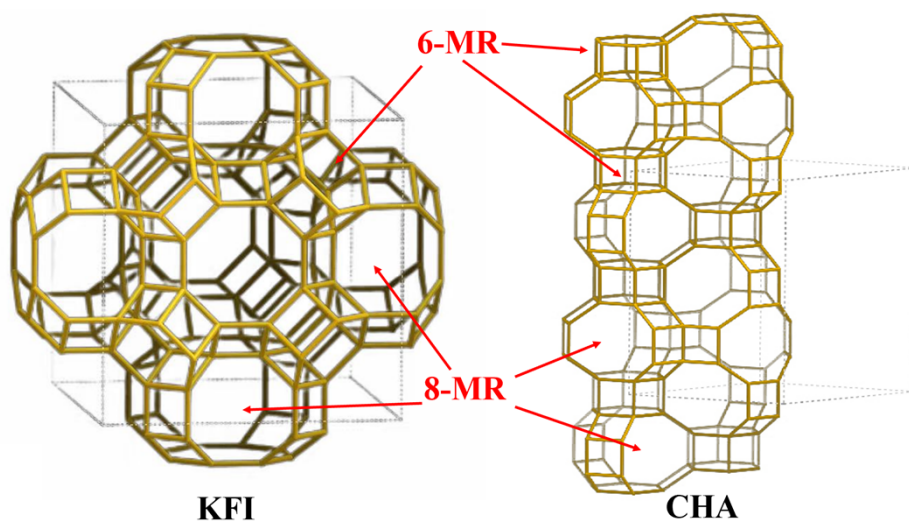
The m/z values for the chemicals used in this study and their relative intensities.

Chemicals	m/z	Chemicals	m/z
H <sub>2</sub>	2 (100%), 1 (1%)	CH <sub>4</sub>	16 (100%), 15 (85%), 14 (16%)
D <sub>2</sub>	4 (100%), 2 (1%)	CH <sub>3</sub> OH	31 (100%), 32 (74%), 29 (43%)
HD	3 (100%), 2 (1%), 1 (1%)	CH <sub>3</sub> OD	32 (100%), 33 (74%), 29 (43%)
H <sub>2</sub> O	18 (100%), 17 (21%), 16 (1%)	CH <sub>3</sub> <sup>18</sup> OH	33 (100%), 34 (74%), 31 (43%)
H <sub>2</sub> <sup>18</sup> O	20 (100%), 19 (21%), 18 (%)	CO <sub>2</sub>	44 (100%), 28 (50%), 16 (50%)
D <sub>2</sub> O	20 (100%), 18 (21%), 16 (1%)	C <sup>18</sup> O <sub>2</sub>	48 (100%), 30 (50%), 18 (50%)
HDO	19 (100%), 18 (21%), 16 (1%)	CH <sub>3</sub> OCH <sub>3</sub>	45 (100%), 46 (61%), 29 (39%)
CH <sub>3</sub> D	17 (100%), 16 (76%)	O <sub>2</sub>	32 (100%), 16 (22%)

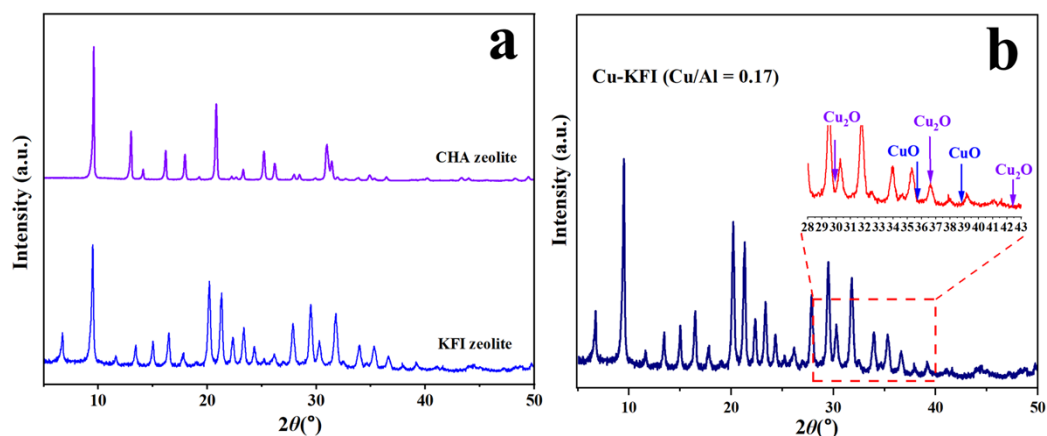
Indicative m/z values shown in red; relative intensities shown in parentheses.

## S2. Characterization results

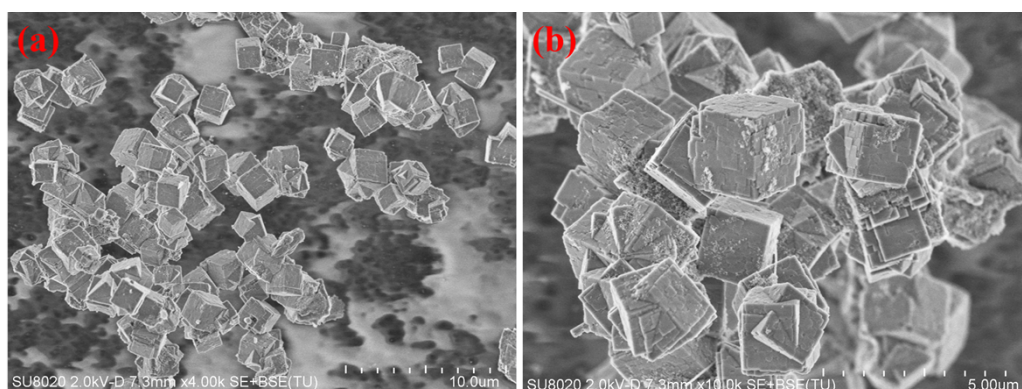
### S2.1. Structure and morphology of KFI and CHA zeolites



**Fig. S1.** Framework structure of KFI and CHA zeolites. Both the zeolites show a similar ring structure, mainly including double 6MR and 8MR.



**Fig. S2.** XRD pattern of the as-prepared KFI and CHA zeolites. The result confirms that the zeolites were successfully synthesized.



**Fig. S3.** SEM images of the as-prepared KFI zeolite.



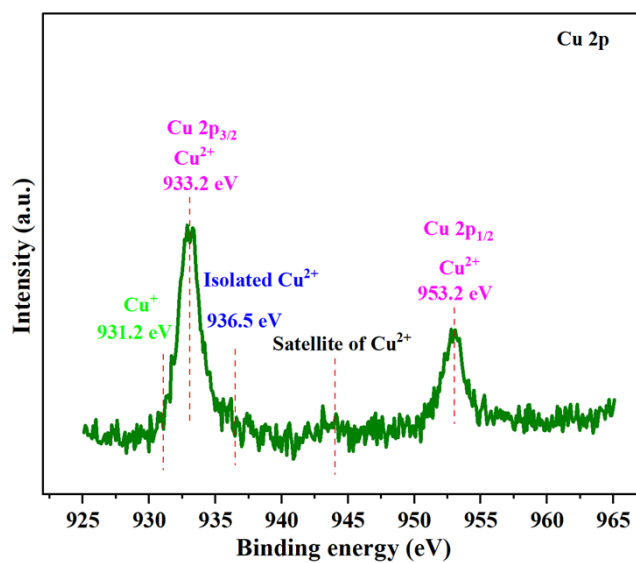


Fig. S4. Cu 2p XP spectrum of Cu-KFI (Cu/Al = 0.17).

## S2.2. HAADF-STEM and H<sub>2</sub>-TPR of Cu-KFI

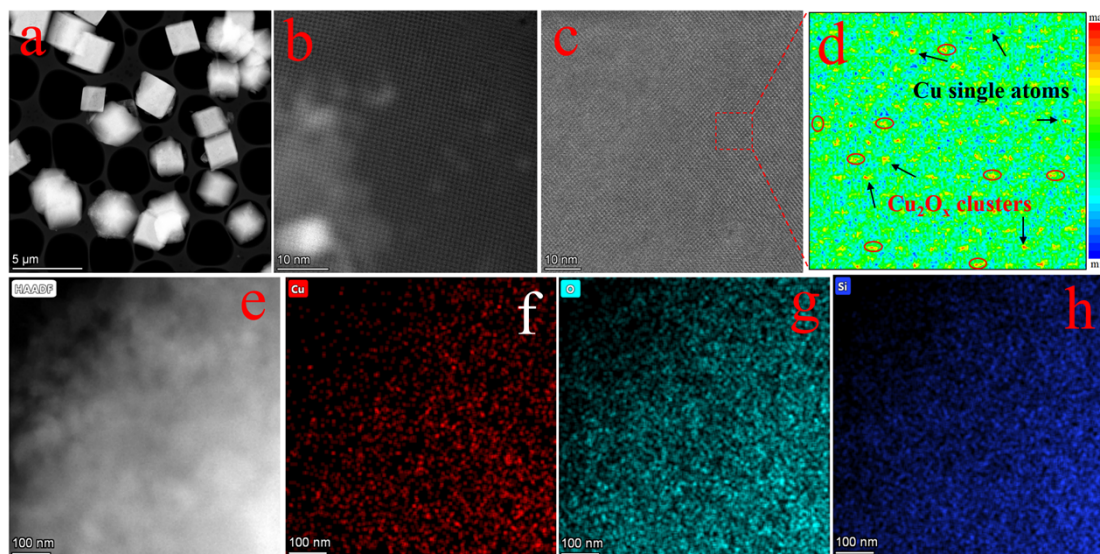


Fig. S5. HAADF-STEM images of the as-prepared Cu-KFI zeolite (a-c), d showing the energy distribution map obtained through image-matrix transformation for the red box in c and the EDX elemental mapping of Cu, O and Si (e-h).

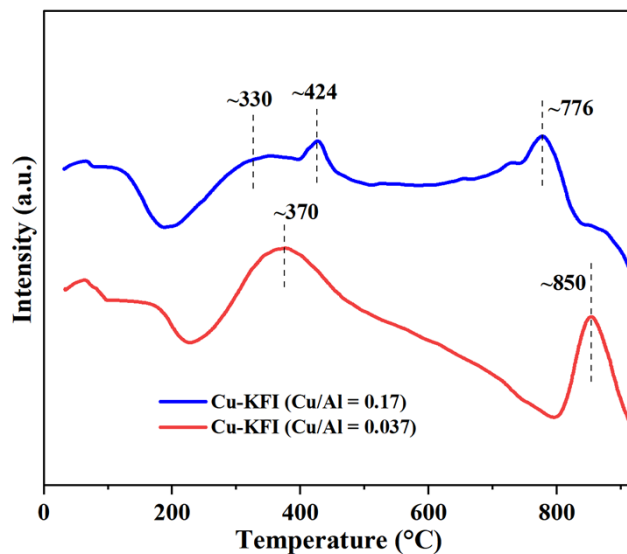


Fig. S6. H<sub>2</sub>-TPR profiles of Cu-KFI zeolites with Cu/Al = 0.037 and 0.17.

### S3. Reaction results

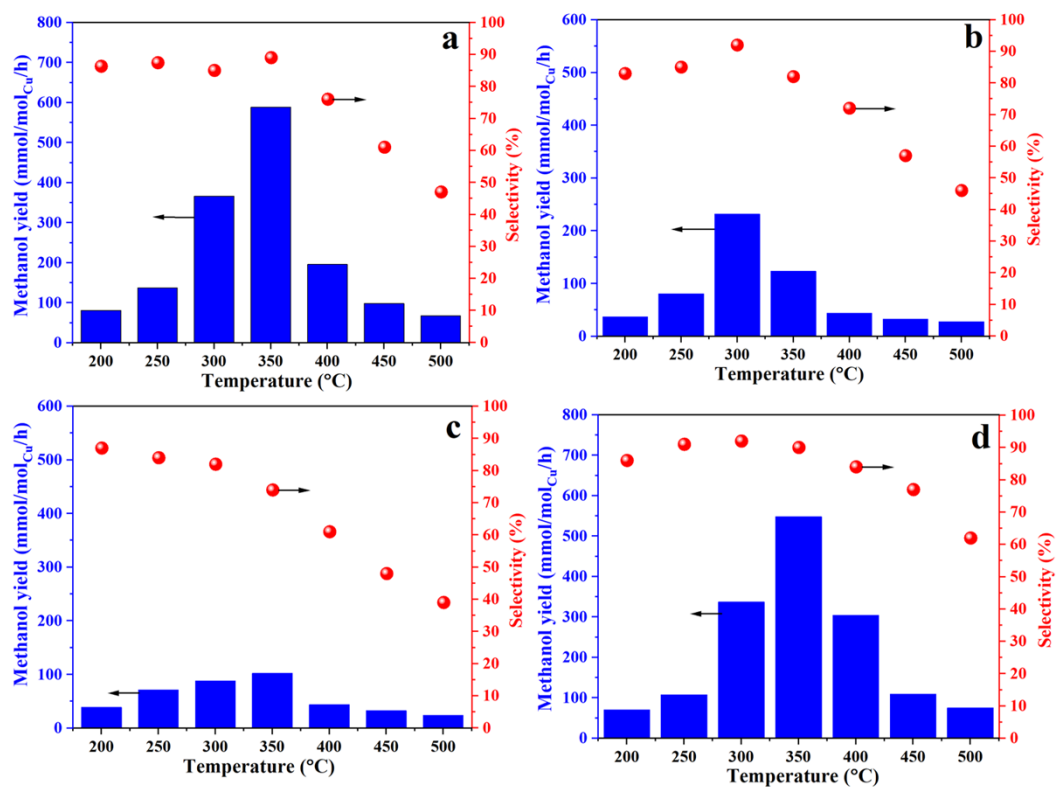


Fig. S7. Selective methane conversion to methanol on **a** Cu-SSZ-13 (Cu/Al = 0.43, Si/Al = 10), **b** Cu-MOR (Cu/Al = 0.47, Si/Al = 11), **c** Cu-ZSM-5 (Cu/Al = 0.51, Si/Al = 15) and **d** Cu-SSZ-39

(Cu/Al = 0.45, Si/Al = 10) under reaction gas mixture of 90% CH<sub>4</sub> + 100 ppm O<sub>2</sub> + 3.2% H<sub>2</sub>O upon elevating reaction temperatures from 200 to 500 °C. Blue bars and red points refer to methanol yield (mmol mol<sub>Cu</sub><sup>-1</sup> h<sup>-1</sup>) and methanol selectivity (%), respectively.

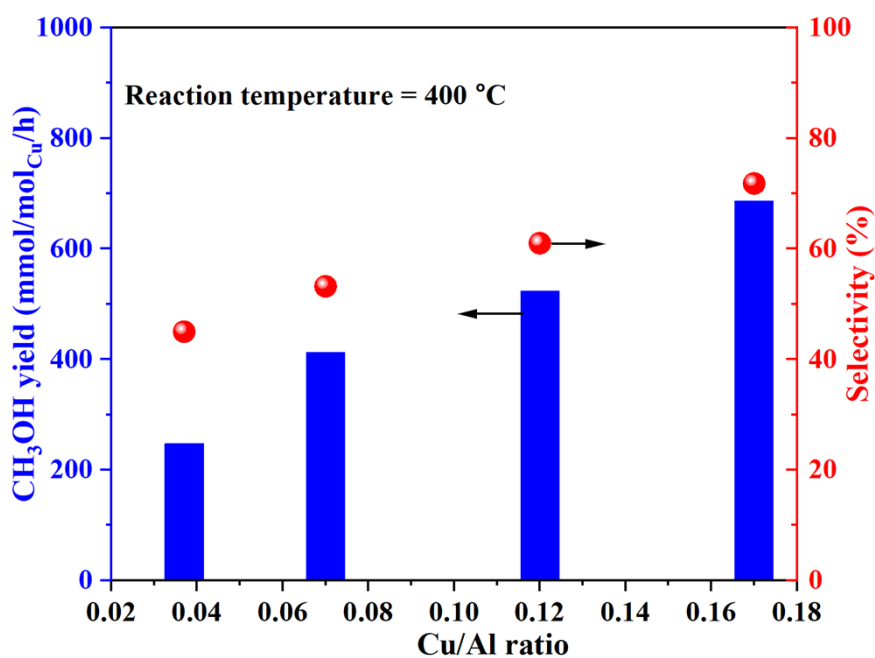
**Table S2.** The comparative activities of continuous MTM reaction on various Cu-zeolites.

Cu-zeolite	Si/Al	Cu/Al	Reaction conditions	CH <sub>3</sub> OH yield (mmol mol <sub>Cu</sub> <sup>-1</sup> h <sup>-1</sup> )	Selectivity (%)	Ref. <sup>b</sup>
Cu-MOR	7.5	0.145	33 mol% CH <sub>4</sub> , 67 mol% steam, 350 °C	~17	/	1
Cu-MOR	15	0.185	33 mol% CH <sub>4</sub> , 67 mol% steam, 350 °C	~22	/	1
Cu-SSZ-39	6.3	0.22	$P_{\text{CH}_4} = 40.5$ kPa, $P_{\text{N}_2\text{O}} = 15.2$ kPa, $P_{\text{H}_2\text{O}} = 4.0$ kPa, 325 °C	~1020	34	2
Cu-SSZ-13	9.7	0.10	$P_{\text{CH}_4} = 40.5$ kPa, $P_{\text{N}_2\text{O}} = 10.1$ kPa, $P_{\text{H}_2\text{O}} = 2.6$ kPa, 300 °C	157	59	2
Cu-MOR	8.9	0.15	$P_{\text{CH}_4} = 40.5$ kPa, $P_{\text{N}_2\text{O}} = 10.1$ kPa, $P_{\text{H}_2\text{O}} = 2.6$ kPa, 300 °C	220	54	2
Cu-CHA	17.8	0.8	0.20 MPa O <sub>2</sub> , 0.5 MPa CO, 2.0 MPa CH <sub>4</sub> , 5 mL H <sub>2</sub> O, 200 °C	~80	/	3
Cu-SSZ-13	10	0.33	$P_{\text{CH}_4} = 49.5$ kPa, $P_{\text{O}_2} = 0.025$ kPa, $P_{\text{H}_2\text{O}} = 2.3$ kPa, 225 °C	13	/	4
Cu-SSZ-13	23	0.22	$P_{\text{CH}_4} = \sim 72$ kPa, $P_{\text{O}_2} = 0.09$ kPa, $P_{\text{H}_2\text{O}} = 3.14$ kPa, 270 °C	130	/	5
Cu-SSZ-13	11	0.23	98% CH <sub>4</sub> , 400 ppm O <sub>2</sub> , 2% H <sub>2</sub> O, 300 °C	540	91	6

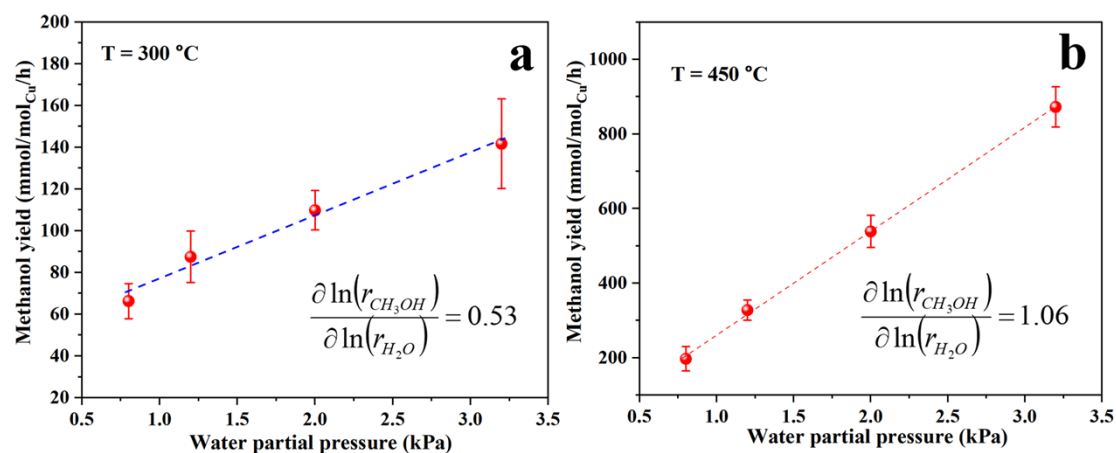
Cu-MOR	10.9	0.27	98% CH <sub>4</sub> , 400 ppm O <sub>2</sub> , 2% H <sub>2</sub> O, 300 °C	~15	~18	6
Cu- ZSM-5	12.8	0.27	98% CH <sub>4</sub> , 400 ppm O <sub>2</sub> , 2% H <sub>2</sub> O, 300 °C	~100	~18	6
Cu-MOR	10	/	48 ml min <sup>-1</sup> CH <sub>4</sub> , 2 ml min <sup>-1</sup> O <sub>2</sub> , 50 ml min <sup>-1</sup> N <sub>2</sub> , 0.5 g h <sup>-1</sup> H <sub>2</sub> O, 300 °C	310	< 50%	7
Cu-CHA	5	~0.13	CH <sub>4</sub> /O <sub>2</sub> /H <sub>2</sub> O (g)/N <sub>2</sub> = 48/2/10/50 ml min <sup>-1</sup> , 300 °C	~700	~79	8
Cu-CHA	10	~0.08	CH <sub>4</sub> /O <sub>2</sub> /H <sub>2</sub> O (g)/N <sub>2</sub> = 48/2/10/50 ml min <sup>-1</sup> , 300 °C	~900	~88	8
Cu-KFI	3.5	~0.03 7	90% CH <sub>4</sub> , 100 ppm O <sub>2</sub> , 3.2% H <sub>2</sub> O, 400 °C	~250	~45	This work
Cu-SSZ- 13	4.1	0.18	90% CH <sub>4</sub> , 100 ppm O <sub>2</sub> , 3.2% H <sub>2</sub> O, 400 °C	~327	~81	This work
Cu-MOR	11	0.47	90% CH <sub>4</sub> , 100 ppm O <sub>2</sub> , 3.2% H <sub>2</sub> O, 300 °C	231.6	92	This work
Cu-SSZ- 13	10	0.43	90% CH <sub>4</sub> , 100 ppm O <sub>2</sub> , 3.2% H <sub>2</sub> O, 350 °C	588.7	89	This work
Cu- ZSM-5	15	0.51	90% CH <sub>4</sub> , 100 ppm O <sub>2</sub> , 3.2% H <sub>2</sub> O, 350 °C	102.4	74	This work
Cu-SSZ- 39	10	0.47	90% CH <sub>4</sub> , 100 ppm O <sub>2</sub> , 3.2% H <sub>2</sub> O, 400 °C	548.3	90	This work
<b>Cu-KFI</b>	<b>3.5</b>	<b>~0.17</b>	<b>90% CH<sub>4</sub>, 100 ppm O<sub>2</sub>, 3.2% H<sub>2</sub>O, 450 °C</b>	<b>~880.3</b>	<b>~83</b>	<b>This work</b>

**Table S3.** Turnover number (TON) and methanol selectivity of Cu-KFI zeolite (Cu/Al = 0.17) at reaction temperature of 450 °C with different reaction time.

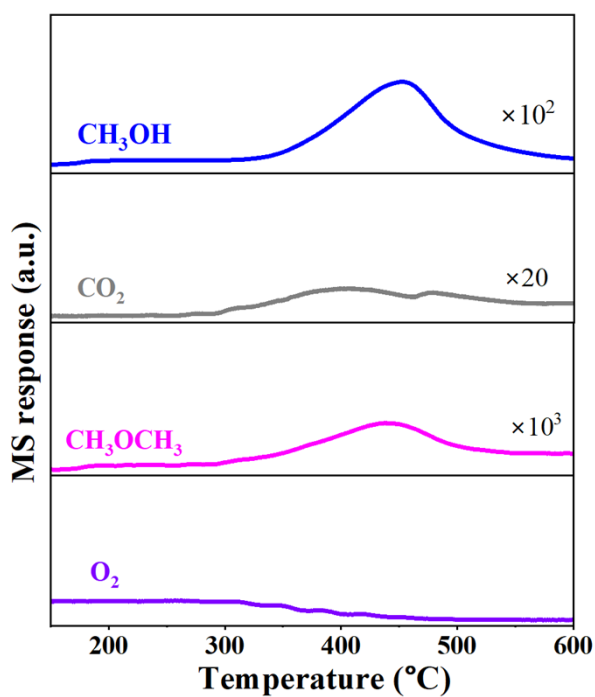
Reaction time (min)	Methanol yield ( $\mu\text{mol}/\text{g}_{\text{cat.}}$ )	TON	Selectivity (%)
30	137.5	0.43	84
60	288.9	0.91	82
120	566.2	1.77	85
240	1083.5	3.40	85
360	1641.9	5.15	82
600	2761.9	8.66	81



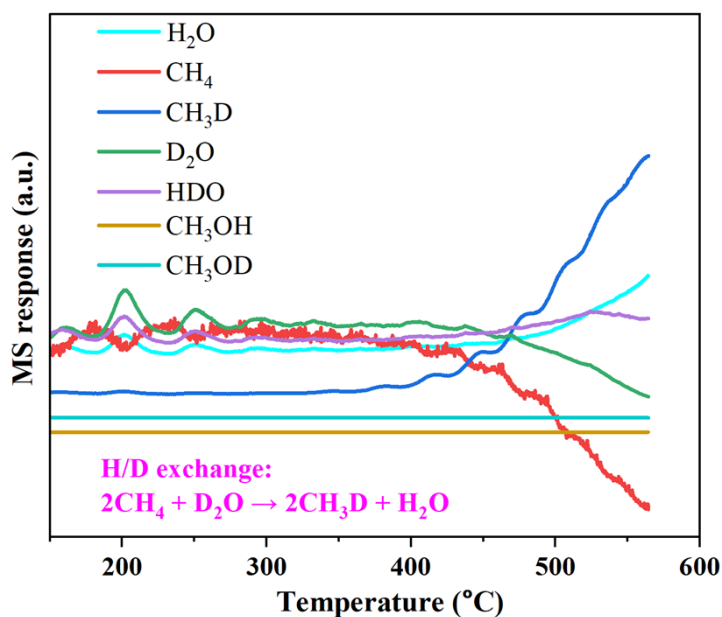
**Fig. S8.** Selective methane conversion to methanol on Cu-KFI zeolites with different Cu/Al ratios under reaction gas mixture of 90% CH<sub>4</sub> + 100 ppm O<sub>2</sub> + 3.2% H<sub>2</sub>O at the reaction temperature of 400 °C. Blue bars and red points refer to methanol yield (mmol mol<sub>Cu</sub><sup>-1</sup> h<sup>-1</sup>) and methanol selectivity (%), respectively.



**Fig. S9.** Kinetic results of methane continuous conversion to methanol over Cu-KFI (Cu/Al = 0.17), which show the different reaction orders on water at different reaction temperatures.



**Fig. S10.** Temperature-programmed surface reactions (TPSR) of continuous MTM on Cu-KFI (Cu/Al = 0.17). Reaction conditions: 100 mg catalyst was heated from 150 to 600 °C, heating rate = 8 °C min<sup>-1</sup>, total flow rate = 15 ml min<sup>-1</sup>; 96.8% CH<sub>4</sub>, 3.2% H<sub>2</sub>O, 100 ppm O<sub>2</sub>.



**Fig. S11.** Temperature-programmed surface reactions (TPSR) of the KFI zeolite without Cu species. Reaction conditions: 100 mg KFI was heated from 150 to 600 °C, heating rate = 8 °C min<sup>-1</sup>, total flow rate = 15 ml min<sup>-1</sup>; 10% CH<sub>4</sub>, 3.2% D<sub>2</sub>O, He as the balance gas. The result shows that the H/D exchange between CH<sub>4</sub> and D<sub>2</sub>O occurred and CH<sub>3</sub>OH and CH<sub>3</sub>OD were not detected.

## S4. References

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