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Cu-Erionite Zeolite Achieves High Yield in Direct Oxidation of Methane to Methanol by Isothermal Chemical Looping

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ABSTRACT: We herein report that a copper-ion-exchanged erionite zeolite (Cu-ERI) exhibited a methanol yield as high as 147 µmol/g-zeolite, equaling 0.224 µmol/µmol-Cu, in the direct oxidation of methane to methanol. Moreover, this high methanol yield was achieved using an isothermal chemical looping with both oxygen activation and reaction with methane carried out at 300 °C, in contrast to the conventional stepwise protocol where activation is performed at high temperature (450 °C and above) and the methane reaction at lower temperature (typically 200 °C). Under isobaric condition (1 bar), the Cu-ERI still gave a high yield of 80 µmol/g-zeolite after a single aqueous extraction of the methanol. Such improvements indicate that high yields can be obtained over Cu-ERI in the direct conversion of methane to methanol by a chemical looping without any temperature or pressure swing.

INTRODUCTION

Methane, the major component of natural gas, is both abundant and cheap and is thus considered to hold promise to replace other fossil fuels (such as oil and coal) as a source of energy and chemicals.[1-3] The direct conversion of methane to methanol is a highly desirable route for efficient utilization of methane, but, it has remained a longstanding challenge in hydrocarbon chemistry.[4-6] The chemical properties of methane and methanol make selective oxidation of methane to methanol extremely difficult.[7,8] The higher chemical reactivity of methanol, compared to that of methane, favors deep oxidation to unwanted products such as CO and CO_2, which complicates this process.[9-11]

Numerous researchers have explored the stepwise conversion of methane to methanol using copper-exchanged materials.[12-40] The most-studied zeolites for direct oxidation of methane to methanol are mordenite[16-20,22-25] and ZSM-5,[12,13,15,27-29] and, since 2005,[13] the overall methanol yields have increased significantly. Based on these findings, a wide range of zeolites, such as BEA[31], FAU[32] and MAZ[35], and non-crystalline oxides, such as silica[36,37] and alumina,[38] have been found to yield methanol directly from methane when doped with copper. Very recently, it was reported that, Cu-CHA[33], a small-pore zeolite, exhibited methanol yields up to 125 µmol/g-zeolite after four reactive cycles. The reactivity of the Cu-CHA system was related to confinement effects in the 8-membered ring (8MR) of CHA, which stabilizes highly dispersed copper-oxo active species and which then may facilitate the conversion of methane to methanol.[39] Earlier work by Lobo *et al.*, which focused on a series of copper-containing small-pore zeolites for this reaction, also suggested that small-pore zeolites are promising materials for methane oxidation.[34]

In the conventional step-wise reaction protocol, copper-based zeolites are activated with oxygen at temperatures above 450 °C followed by the reaction with methane at a considerably lower temperature (about 200 °C). Methanol is subsequently extracted using water at ambient temperature, or by steaming at an elevated temperature (Figure 1(a) and Figure S1). The repeated heating and cooling cycles involved in this conventional approach are significant barriers to the development of a practical process. Tomkins *et al.* reported an isothermal process over Cu-MOR zeolite, where the temperature for both oxygen activation and methane reaction was constant. However, this comes at a price. Only half the amount of methanol was produced in that isothermal procedure compared with the amount achieved in the conventional procedure, even when a high methane pressure of 36 bar was applied.[40] An isothermal conversion of methane to methanol without pressure swings was demonstrated recently for Cu-Faujasite (Cu-FAU), emphasizing the importance of making temperatures of oxygen activation and methane reaction equal.[32] Here, we report that copper-ion-exchanged erionite zeolite (Cu-ERI), a small-pore zeolite, can lead to a high methanol yield in the direct oxidation of methane to methanol using an isothermal procedure (Figure 1(b)). Our results demonstrate that oxygen activation at high temperature (above 450 °C) is not a prerequisite for achieving a high methanol yield. With an optimal Cu/Al ratio of 0.3, a methanol yield of 147 µmol/g-zeolite can be achieved within the isothermal protocol. This is equivalent to the yield obtained under conventional conditions with high-temperature activation.

EXPERIMENTAL SECTION

Materials. The following materials were used as received: aluminum sec-butoxide (Al[OCH(CH₃)C₂H₅]₃, 97%, Aldrich) as an aluminum source, colloidal silica (LUDOX® AS-40, 40 wt.% suspension) as a silica source, potassium hydroxide solution (Wako Pure Chemical Industries, Ltd., 30 wt%) as an alkali source, hexamethonium bromide (Tokyo Chemical Industry, Ltd., >98 wt%) as the crystallization organic structure-directing agent. ERI seed crystals were synthesized according to the charge density mismatch (CDM) method.

Zeolite Synthesis. ERI zeolite was prepared, but not according to the CDM approach, with a reactant mixture comprising 1.63 RBr_2/7.8 KOH/0.8 Al_2O_3/16 SiO_2/258 H_2O, where TPAOH and

RBr2 represent tetrapropylammonium and hexamethonium bromide, respectively. First, aluminum sec-butoxide was dissolved in potassium hydroxide solution, followed by the dropwise addition of a solution containing hexamethonium bromide dissolved in deionized water. Colloidal silica was then slowly added to form an aluminosilicate reactant. The reactant mixture was homogenized for 2 h and aged for 24 h in an oven at 95 °C. After aging, 10 wt% ERI seed crystals, synthesized according to the recipe in Ref. 41, were added to the reactant mixture and stirred for 10 min. The resulting reactant was fed into a sealed pipe reactor and heated at 210 °C for 2 h. The solid products were recovered by centrifugation, washed with de-ionized water and dried at 80 °C.

Preparation of Cu-ERI Materials with Different Copper Loadings. The synthesized ERI zeolite was calcined at 550 °C for 8 h to remove the organic structure-directing molecules occluded in the zeolite. The calcined ERI zeolite was then ion-exchanged twice with 1 M NH_4NO_3 solution at 90 °C for 5 h. Cu-ERI material was prepared by liquid ion exchange of NH_4-ERI with $(CH_3COO)_2Cu$ solution at 90 °C for 30 min. After centrifugation and drying in an oven, the obtained Cu-ERI zeolite was calcined at 550 °C for 3 h. Cu-ERI materials with different copper loadings were readily controlled by varying the concentration of $(CH_3COO)_2Cu$ aqueous solutions.

Characterizations. The crystallinity of all the solid products was identified with a Panalytical X'Pert Pro MPD instrument (λ = 0.15406 nm, 40 kV, 40 mA) at a scan rate of 4 °/min. The crystallinity of the solid product was calculated based on the area of the peaks ranging from 20° to 30°. The crystal size and morphology of the solid products were confirmed with scanning electron microscopy (Zeiss Gemini 1530) at an acceleration voltage of 5 keV.

Elemental analysis of the products was carried out using a SpectraAA 220FS atomic absorption spectrometer. Fifteen milligrams of Cu-ERI were dissolved with 2 ml hydrofluoric acid and 3 ml nitric acid and then diluted to 50 ml with deionized water. Nitrogen adsorption–desorption measurements were performed to evaluate the micropore volume of the zeolite products using a Quantachrome Autosorb-iQ at −196 °C. Prior to the measurements, all samples were preheated at 325 °C for 6 h under vacuum.

FTIR spectroscopy was performed on a Thermo Nicolet iS50 spectrometer with a MCT detector. Optical adsorption data were collected from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} and with 128 scans. The Cu-ERI sample (20 mg) was pressed into a self-supporting disc and activated in the IR cell with 300 torr of oxygen at 400 °C for 1 h. The system was then evacuated and cooled down prior to measurement. 300 torr of CH_4 was then introduced into the cell and reacted with the Cu-ERI sample at 300 °C. Spectra of surface species were obtained by subtracting the reacted sample from the activated Cu-ERI before the reaction with the OMNIC 9.1 software package. For nitrogen monoxide adsorption, the activated sample was cooled to 77K with liquid nitrogen. Nitrogen monoxide was dosed into the cell with subsequent acquisition of IR spectrum. The dosing was stopped until the saturation of the sample with NO.

Thermogravimetric and differential thermal analyses (TG-DSC) were performed on a STA 449 C (Jupiter) thermo-microbalance from 30 °C to 800 °C at a heating rate of 10 °C/min in a flow (200 ml/min) of air.

Methane Oxidation Reaction over Cu-ERI Materials. Methane oxidation reaction measurements were carried out in a high-pressure reactor. Approximately 300 mg of Cu-ERI material were loaded into a stainless-steel autoclave. The sample was activated in a pure flow of O_2 (25 ml/min) at the target temperature (450 °C with the conventional method and 300 °C with the isothermal method) for 1 h. The reactor system was cooled to 300 °C after activation and purged with a pure helium flow for 20 min. Then, pure methane was fed into the reactor at the same temperature. After the reaction with methane at 300 °C for 30 min, the reactor was then cooled down to room temperature with a flow of pure helium.

The obtained methanol was extracted offline by adding 2 ml deionized water to the reacted Cu-ERI sample, and the resulting suspension was stirred for 1 h at room temperature. The aqueous suspension was then filtered and analyzed with a gas chromatograph (Agilent 6890). Butanol was added as the external standard solution. Only one extraction was performed on each Cu-ERI sample for the calculation of methanol yield. In the multiple extraction, the solid sample was collected after the previous extraction and the process was repeated until no more methanol was detected by the gas chromatograph.

RESULTS AND DISCUSSION

The Cu-ERI samples were prepared by aqueous ion-exchange of the ERI zeolites synthesized using a previously described ultrafast method.[41] Cu-ERI materials with different copper loadings (Table 1) were prepared by varying the concentration of the copper acetate solution used for ion exchange. The Si/Al ratio was 5.6, the Cu/Al ratios 0.1, 0.2, 0.3 and 0.4, and the K/Al ratio 0.21 in all cases, as measured by AAS analysis. The samples were designated Cu-ERI(x), where "x" denotes the Cu/Al ratio. All the Cu-ERI materials were highly crystalline, as demonstrated by the XRD and nitrogen adsorption-desorption isotherms (Figure S2). The SEM image reveals that the parent ERI zeolite had a particle size of *ca.* 1 μm (Figure S3).
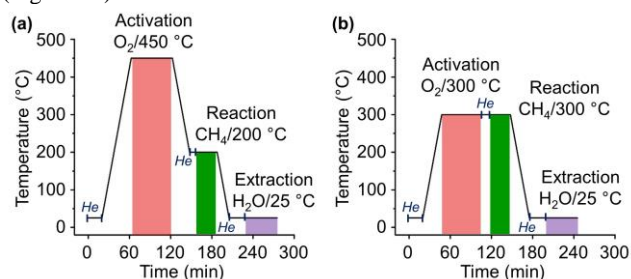

Figure 1. Comparison of (a) the conventional procedure and (b) the isothermal procedure of the stepwise oxidation of methane to methanol with off-line water extraction.

Table 1. Chemical composition of the Cu-ERI materials.

Sample	Si/Al[b]	K/Al[c]	Cu/Al[d]	Cu (wt%)	V_{micro} (cm^3/g)[e]
Cu-ERI(0.1)[a]	5.6	0.21	0.1	1.6	0.19
Cu-ERI(0.2)	5.6	0.21	0.2	3.1	0.19
Cu-ERI(0.3)	5.6	0.21	0.3	4.2	0.20
Cu-ERI(0.4)	5.6	0.21	0.4	5.9	0.19

[a]Cu-ERI(x), x represents Cu/Al ratio. [bcd]Measured by AAS. [e]Calculated with t-plot method.

The performance of the Cu-ERI materials was first evaluated by the conventional procedure (activation at 450 °C and reaction with methane at 200 °C) (Figure 1(a)). Figure 2(a) shows the methanol yields per gram of zeolite obtained over the Cu-ERI materials with different copper loadings. At a methane pressure of 1 bar, Cu-ERI exhibited a nearly linear increase in methanol yield with the copper loading, showing a maximum at about 28 μmol/g-zeolite for Cu-ERI(0.4). This result probably suggests that only part of the copper species participated in methane activation under low methane pressure (at 200 °C) and that the amount of this type of active sites increased linearly with copper loading. FTIR spectroscopy of adsorbed NO (Figure S4) show that different copper species were present in the activated Cu-ERI samples. The band at 1908 and 1958 cm^{-1} are believed to be due to copper monomeric species and aggregate copper species (especially dimeric copper), respectively.[25] It seems that copper loading did not alter the nature of copper species in the samples. The density of each type of copper species, however, varied with increasing the copper loading.[24,42] An ele-
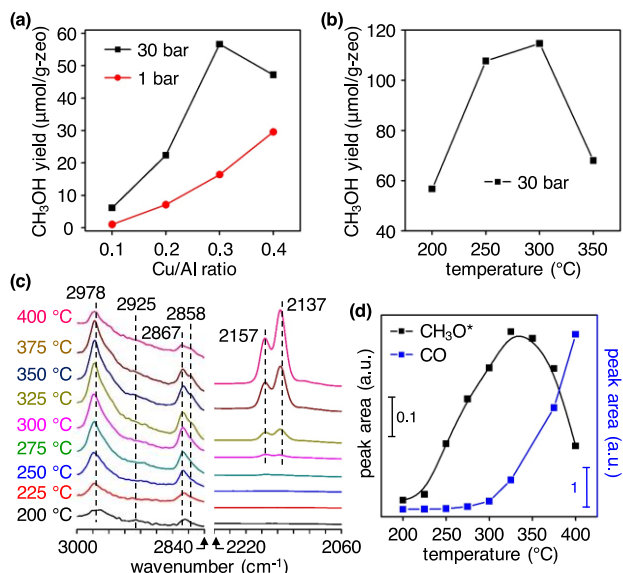
Figure 2. Direct oxidation of methane to methanol over the Cu-ERI zeolites according to the conventional procedure with oxygen activation at 450 °C. **(a)** Methanol yield of the Cu-ERI zeolites with different copper loadings and different methane partial pressures at 200 °C. **(b)** Methanol yield of Cu-ERI(0.3) at different reaction temperatures ranging from 200 °C to 350 °C. **(c)** In-situ FTIR spectra of surface species formed after the reaction with 300 torr of methane at different temperatures for 30 min. **(d)** Comparison of the relative intensity of the bands of methoxy species and that of carbon monoxide formed after the reaction with methane at different temperatures for 30 min.

Figure 3. Effect of copper loading on the direct oxidation of methane to methanol over the Cu-ERI zeolites. **(a)** Methanol yield on the Cu-ERI zeolites with different copper loadings at 300 °C and methane partial pressure of 30 bar. **(b)** Multiple methanol extraction performed on the Cu-ERI(0.3) material. **(c)** In-situ FTIR spectra of surface species formed on the Cu-ERI zeolites with different copper loadings after the reaction with 300 torr of methane for 30 min (Cu-ERI(x) was abbreviated to Cu-(x) for clarity). **(d)** Comparison of the relative intensity of the bands of methoxy species and that of carbon monoxide formed on the Cu-ERI zeolites with different copper loadings after the reaction with methane for 30 min.

vated methane pressure of 30 bar led to a greater participation of copper species in methane activation, and correspondingly, an enhancement of productivity. In particular, when the copper loading was optimal (Cu/Al=0.3), the Cu-ERI gave the highest methanol yield of 56 μmol/g-material. The methanol yield normalized by the copper content (mol/mol, Figure S5) demonstrated a similar trend. Cu-ERI(0.3) was selected to optimize the methane reaction temperature. Figure 2(b) shows that the methanol productivity doubled (from 56 μmol/g- zeolite to 109 μmol/g-zeolite) when the reaction temperature was increased from 200 °C to 250 °C, and the highest yield of 114 μmol/g-zeolite was achieved at 300 °C. A further increase in the reaction temperature to 350 °C led to a lower methanol yield.

In-situ Fourier-transform infrared spectroscopy (FTIR) was employed to study the surface species formed after the reaction of methane over activated Cu-ERI materials and to understand the effect of the reaction temperature, which strongly affects selectivity and, thus, impacts the methanol yield.[17,30,32,33] Figure 2(c) presents the spectra of surface species formed during the reaction with 300 torr of methane. The bands at 2978 cm^{-1} (v_{as}CH$_3$), 2867 cm^{-1} (v_sCH$_3$) are assigned to vibrations of methoxy species. The band at 2925 cm^{-1} and 1598 cm^{-1} are due to formate species (Figure S6) and those at 2858 cm^{-1} and 1469 cm^{-1} (Figure S6) correspond to the methanol formed by the hydrolysis of methoxy species.[22,25,32,43-45] The bands at 2157 cm^{-1} and 2137 cm^{-1} are related to the stretching vibrations of carbon monoxide adsorbed at two different Cu^I sites. The spectra acquired at different temperatures indicate that Cu-ERI displays superior selectivity, because no by-products, such as carbon monoxide and formate (Figure S6), were found up to 300 °C. The intensity of the band attributed to surface methoxy increases with temperature up to 350 °C. From these temperature-dependent observations of product formation, the optimal temperature regime for the operations of Cu-ERI in direct methane conversion to methanol was de-
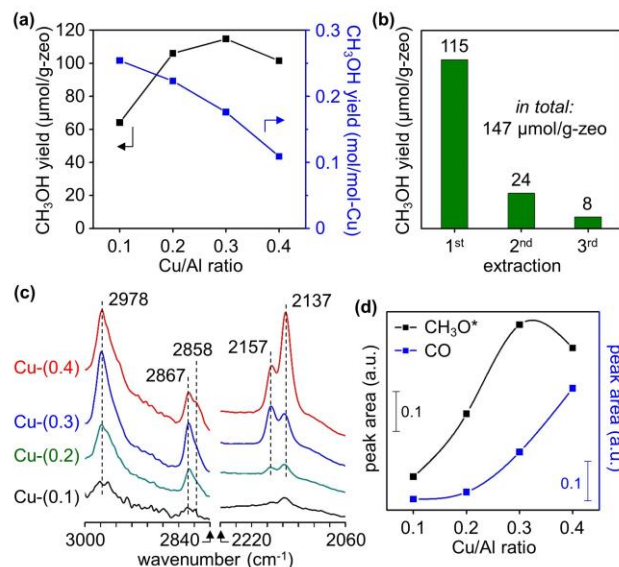
termined to be around 300 °C (Figure 2(d)), which is consistent with the reaction results shown in Figure 2(b). The species formed as gas phases in the reaction were also studied by in-situ FTIR to calculate the selectivity over Cu-ERI. As shown in Figure S7, a selectivity of 87% was achieved after reacting with methane for 30 min at 300 °C. This optimal reaction temperature is 100 °C higher than that generally reported for other types of zeolites[16,20,24,34,39,40,46], with the exception of copper-exchanged faujasite (Cu-FAU) which also exhibits a high selectivity to methoxy and strong stabilization of these species up to 360 °C[32]. The attainment of high selectivity at these reaction temperatures might be ascribed to the strong stabilization of methoxy species by Brønsted acid sites, which could prevent further oxidation of methoxy species to carbon monoxide, formate, and carbon dioxide.[43] Meanwhile, the confinement within the small-pore structure could likely exert a positive effect, particularly on C-H bond cleavage toward methanol formation, and possibly on stabilization of methoxy species and disfavoring over oxidation as well.[34,39,43] These results discussed above further demonstrate the importance of interplay between operation conditions and material properties.

After screening the reaction temperature, the performance of Cu-ERI zeolites with different copper loadings was evaluated at 300 °C under 30 bar of methane. Figure 3(a) shows that a similar trend of methanol yield per gram zeolite versus copper loading was obtained at 300 °C as compared with the results at 200 °C. Cu-ERI(0.3) displayed the highest methanol yield of 115 μmol/g-zeolite, and a value as high as 147 μmol/g-zeolite, equivalent to 0.224 μmol/μmol-Cu, was achieved when three consecutive extractions were carried out (Figure 3(b)). A higher copper loading (Cu/Al=0.4) led to a decrease in the methanol yield. In-situ FTIR spectroscopy demonstrated the effect of copper loading on the methanol yield. Figure 3(c) depicts the spectra of surface species formed on Cu-ERI samples with different copper loadings after the reaction with methane at 300 °C. The intensity of the band attributed to carbon
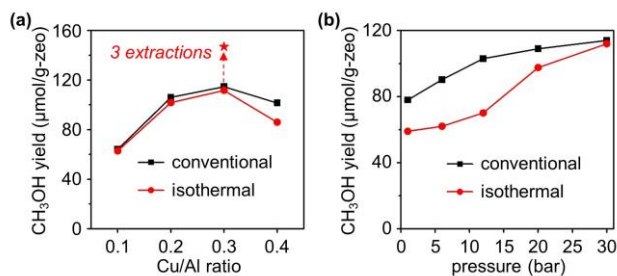
Figure 4. Comparison of the methanol yields obtained over the Cu-ERI zeolites according to the conventional procedure and the isothermal procedure. (**a**) Methanol yield of the Cu-ERI zeolites with different Cu loadings after activation at 450 °C (conventional procedure) and 300 °C (isothermal procedure. The red asterisk denotes the methanol yield after three extractions). (**b**) Dependence of methanol yield on methane pressure after activation at 450 °C (conventional procedure) and 300 °C (isothermal procedure), respectively.

monoxide increased with copper loading, whereas the intensity of the bands due to surface methoxy species reached its maximum at Cu-ERI(0.3) and decreased for Cu-ERI(0.4). This result indicates that increasing the copper loading does not necessarily lead to an increase in the methanol yield; there is a critical copper loading, which, when exceeded, lowers selectivity to methanol due to over-oxidation (Figure 3(d)).

The fact that a relatively high methane reaction temperature can be applied to the Cu-ERI suggests the feasibility of establishing an isothermal operation regime, similar to that shown for Cu-FAU.[32] Figure 4(a) presents the methanol yields obtained with the conventional procedure (Figure 1(a)) and those with the isothermal procedure (Figure 1(b)). All Cu-ERI materials with different copper loadings achieved a high methanol yield in the isothermal approach, which was comparable to the yield obtained in the conventional approach. According to previous studies, pretreatment at a high temperature above 450 °C is a prerequisite to producing the maximum concentration of active sites.[33,34,46] Activation at lower temperatures reduces the yield of methanol, probably as a result of the incomplete removal of water.[17] However, as demonstrated by the TG-DTA (Figure S8), Cu-ERI is almost completely dehydrated at 300 °C; thus, there is no reason to perform activation at higher temperatures with this zeolite. The methanol yield obtained at 30 bar of methane is the same for both activation procedures (Figure 4 (a)). The effect of methane partial pressure on the methanol productivity was investigated by means of two different procedures. The plots in Figure 4(b) demonstrate that elevating the methane pressure increased the production of methanol in both procedures. A similar trend was observed on the MOR, MAZ and CHA zeolites, where an increase in the methane partial pressure was shown to increase the fraction of copper active species that participate in C-H cleavage.[33,40,47] After high-temperature oxygen activation at 450 °C, the methanol yield was almost saturated at 15 bar of methane (Figure 4(b)), while in the isothermal procedure, a higher methane pressures are required to produce the maximum amount of methanol. This might be associated with the small amount of water retained in the zeolite after activation at 300 °C (Figure S8). However, the yield is only slightly lower than in the conventional procedure, indicating that high-temperature activation in oxygen is not a prerequisite for the conversion of methane to methanol in the Cu-ERI system. From a practical perspective, the decrease in activation temperature is attractive, as it enables isothermal methane partial oxidation at 300 °C and, thus, would facilitates the process design.[32,48] Furthermore, a multicycle experiment performed over Cu-ERI(0.3) with off-line extraction at room temperature showed a stable meth-

anol yield of 113±2 μmol/g-zeolite over four reactive cycles (Figure S9), which is probably attributable to the high hydrothermal stability of the Cu-ERI zeolite.[41] XRD patterns (Figure S10) and TEM images (Figure S11) of the Cu-ERI(0.3) before and after methane oxidation confirm that the zeolite structure was maintained and that no (XRD visible) copper oxide particles formed.

CONCLUSIONS

In summary, the Cu-ERI zeolite exhibits excellent performance in the direct oxidation of methane to methanol, and a high selectivity was observed even at a relatively high methane reaction temperature of 300 °C, which is 100 °C higher than the optimal reaction temperature for most of the copper-containing zeolites. With an optimized copper loading and under elevated methane partial pressure, Cu-ERI led to a methanol yield of as high as 147 μmol/g-zeolite at 30 bar of methane under conventional conditions. Thanks to its high activity and selectivity at 300 °C, an equivalently high methanol yield was achieved by means of the isothermal procedure with both oxygen activation and reaction with methane carried out at 300 °C. Due to its high hydrothermal stability, Cu-ERI zeolite exhibited a stable methanol yield of 113±2 μmol/g-zeolite per cycle. These results reveal that the Cu-ERI zeolite has the potential to emerge as a competitive material in the direct oxidation of methane to methanol. Further studies focusing on ERI samples with a variety of properties (e.g. different Si/Al ratios, cations and morphologies) are ongoing, which will help reveal the structure-performance relationship of Cu-ERI zeolites and explore a more feasible protocol to achieve a high methanol yield over this small-pore zeolite.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Characteristics of the Cu-ERI materials revealed XRD patterns, SEM images and nitrogen adsorption-desorption isotherm. In-situ FTIR spectra of species formed during the reaction with methane.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.
Notes
There are no conflicts of interest to declare.

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Cu-Erionite achieves a high methanol yield (147 μmol/mol/g-zeolite, or 0.224 μmol/μmol-Cu) in an isothermal chemical looping with both the oxygen activation and methane reaction carried out at 300 °C, which is comparable to the yield obtained in the conventional approach requiring high-temperature oxygen activation.