

Continuous methanol synthesis directly from methane and steam over Cu(II)-exchanged mordenite

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(Received 27 July 2018 • accepted 12 September 2018)

Abstract—The formation of methanol directly from methane and steam was observed over Cu ion-exchanged mordenite. Furthermore, the continuous production of methanol was achieved by co-feeding methane and steam over Cu-mordenite. The methanol production rate was comparable to that reported in the stepwise process in which activation, methane reaction, and extraction of methanol were carried out separately.

Keywords: Methane Activation, Methanol, Copper, Mordenite, Steam

INTRODUCTION

Methane has recently become a common chemical feedstock and energy resource because of an upsurge in shale gas production [1]. Currently, methane is commercially utilized as a raw material for various chemicals indirectly via syngas ($\text{CO} + \text{H}_2$), which is typically produced through energy-intensive processes such as steam-reforming ($\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$, $\Delta H_{298\text{ K}}^\circ = 206 \text{ kJ/mol}$) [2]. The direct conversion of methane into value-added chemicals can be cost-effective as long as a high selectivity for the target product is maintained at a high methane conversion rate [3,4].

Among a variety of target chemicals from methane, methanol is an important platform chemical because it can be easily transported and converted into other chemicals [5]. Until now, various routes have been examined to synthesize methanol directly from methane [6,7]. Recently, metal ion-exchanged zeolites have been intensively investigated for the production of methanol directly from methane [7]. However, all the reported schemes follow a stepwise process comprising activation, methane reaction, and extraction of methanol, which results in a discontinuous methanol synthesis process. In this scheme, metal ion-exchanged zeolites work as a reactant rather than a catalyst.

To the best of our knowledge, there is no report in which methanol is continuously produced directly from methane and steam over a heterogeneous catalyst under mild conditions. In this communication, we report the first direct formation of methanol from methane and steam over Cu-mordenite in a continuous process.

EXPERIMENTAL

1. Catalyst Preparation

Cu-mordenite was prepared by an aqueous ion-exchange method. In 1.37 L of distilled water, 2.77 g of copper(II) acetate monohydrate

($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, Junsei Chem.) was first dissolved. To this solution was added 17.5 g of H-mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 18$, Tosoh Corp.), following which the mixture was stirred at a speed of 450 rpm for 24 h at room temperature. The resultant slurry was filtered and the cake was dried at 110°C for 12 h. The recovered powder was ion-exchanged two more times following the same procedure except for the use of the recovered powder instead of H-mordenite. The final cake after the third ion exchange was washed with 750 mL of distilled water, dried at 110°C for 12 h, and then calcined in air at 400°C for 3 h. The Cu content was determined to be 3.1 wt% by inductively-coupled plasma-atomic emission spectroscopy (ICP-AES), and the molar ratio of Cu/Al was calculated to be 0.3.

2. Catalyst Characterization

The catalyst was characterized by N_2 physisorption and powder X-ray diffraction (XRD). The detailed procedure for each characterization technique is described in the supporting information.

3. Catalytic Activity Tests

Two different reactor systems were used to carry out the methanol synthesis reaction from methane and steam. One is the Micromeritics Autochem 2910 equipped with a vapor generator, thermal conductivity detector, and mass spectrometric detector (MSD). Cu-mordenite (0.3 g) was loaded into a U-type quartz reactor and pre-treated with air at 450°C for 1 h. The gas was then switched to methane and the catalyst was contacted with methane at a flow rate of 30 mL/min at various temperatures. A pulsed injection of 10 μL of distilled water was carried out several times at various time intervals in order to monitor the products. The ion signals recorded at m/z ratios of 2, 18, 31, and 44 were utilized for monitoring desorbed H_2 , H_2O , CH_3OH , and CO_2 . The continuous production of methanol was also monitored with this reactor system. Methane gas with a flow rate of 30 mL/min was passed through the vapor generator, which was filled with distilled water and maintained at 73°C . This gas mixture of methane and steam was flowed into the reactor charged with Cu-mordenite at 350°C . The product stream was also analyzed by MSD.

The other reactor system is a fixed-bed stainless-steel reactor (O.D.=9.525 mm, I.D.=7.745 mm) with a length of 370 mm. The

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flow rate of each gas was controlled with a mass flow controller (MFC; Brooks Instruments). The reaction temperature was monitored with a thermocouple located just above the catalyst bed. Water was fed into the reactor with a syringe pump (ISCO MODEL 260D). Continuous methanol production was carried out by co-feeding methane and steam at flow rates of 30 mL (STP)/min and 60 mL (STP)/min, respectively, into the reactor loaded with 0.3 g of Cu-mordenite at various temperatures. All the lines were heated above 120 °C with a heating tape to avoid water condensation. The liquid product was condensed with a cold trap maintained at -1 °C and collected in a reservoir. The liquid product was analyzed by ¹H-NMR spectroscopy, recorded at room temperature on a Jeol Resonance ECZ600R (¹H 599.7 MHz), and quantified with a 0.1% trimethylsilylpropanoic acid (TMSP)/D₂O standard (Euriso-top). Typically, 0.7 mL of sample and 0.1 mL of D₂O were placed in an NMR tube along with the standard. A solvent suppression program was run to minimize the signal arising from the solvent.

RESULTS AND DISCUSSION

1. Pulsed Water Injection to Produce Methanol from Methane

There was no noticeable difference in the textural properties of H-mordenite and Cu-mordenite (Table S1), and no bulk Cu oxides could be found in the XRD data of Cu-mordenite (Fig. S1), which indicates that Cu(II) ions were successfully ion-exchanged into H-mordenite. While flowing methane at a constant temperature, 10 μL of water was injected into the reactor loaded with Cu-mordenite while monitoring the product. As shown in Fig. 1, the simultaneous formation of methanol, hydrogen, and carbon dioxide was

observed at each injection of water. It is notable that steady-state formation of methanol can be observed after several injections of water (Figs. S1 and S2). Sushkevich et al. first reported that methanol could be formed through a cyclic process in which methane, steam, and helium are contacted with Cu-mordenite in a stepwise manner [8]. They claimed that the high-temperature He-treatment was essential to remove water completely from the zeolite surface because the formation of methoxy species during the methane reaction can be hindered in the presence of water molecules [8]. However, methanol formation was confirmed by addition of steam in the methane flow at a constant temperature. To determine the effect of residual water on the catalyst surface, the time interval between injections of water was decreased from 2 h to 20 min while monitoring the products. As shown in Fig. 2, there was no decrease in the peak intensity in the mass spectroscopy data corresponding to methanol in the product stream, even after repeated injections of water at short time intervals. This implies that there are active Cu species for methanol synthesis from methane and steam even in the presence of water.

2. Continuous Production of Methanol from Methane and Steam

The product gas was monitored while contacting Cu-mordenite with a gas mixture in which methane gas with a flow rate of 30 mL/min was saturated with water vapor at 73 °C. As shown in Fig. 3, the formation of methanol, water, hydrogen, and carbon dioxide was observed at ~250 °C in the absence of water in the feed (stage I in Fig. 3) while increasing temperature in the presence of methane. This formation of methanol in the absence of water in the feed might be due to the presence of residual water in the zeo-

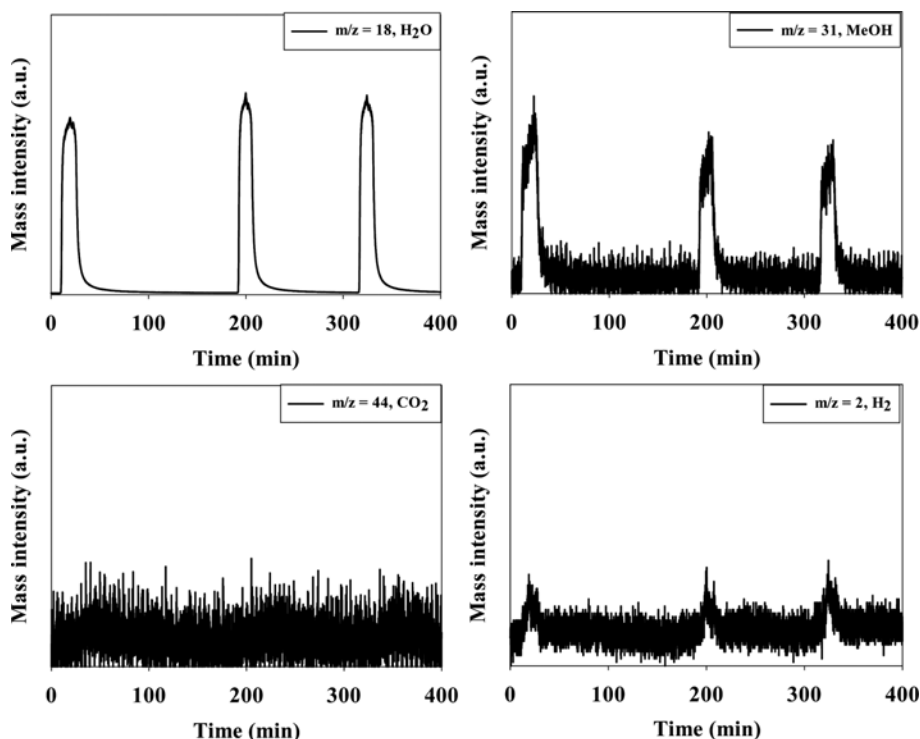


Fig. 1. Mass spectroscopy data as a function of time during water injection experiment. 0.30 g of 3.1 wt% Cu-mordenite was contacted with methane at a flow rate of 30 mL/min at 250 °C while injecting 10 μL of water.

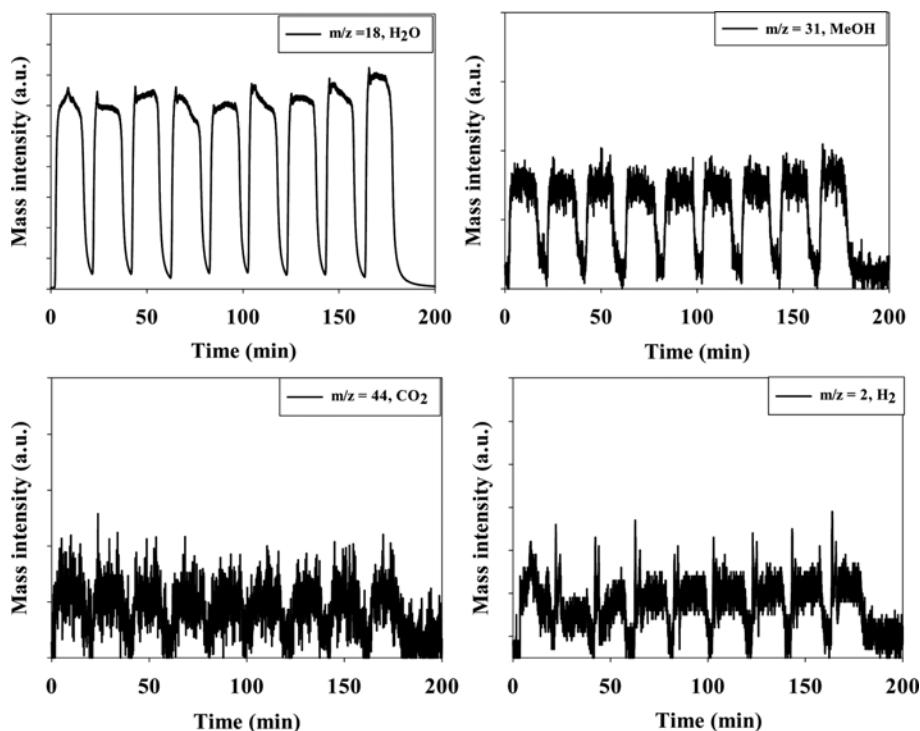


Fig. 2. Mass spectroscopy data as a function of time during water injection experiment. 0.30 g of 3.1 wt% Cu-mordenite was contacted with methane at a flow rate of 30 mL/min at 350 °C and 10 μL of water were injected every 20 min.

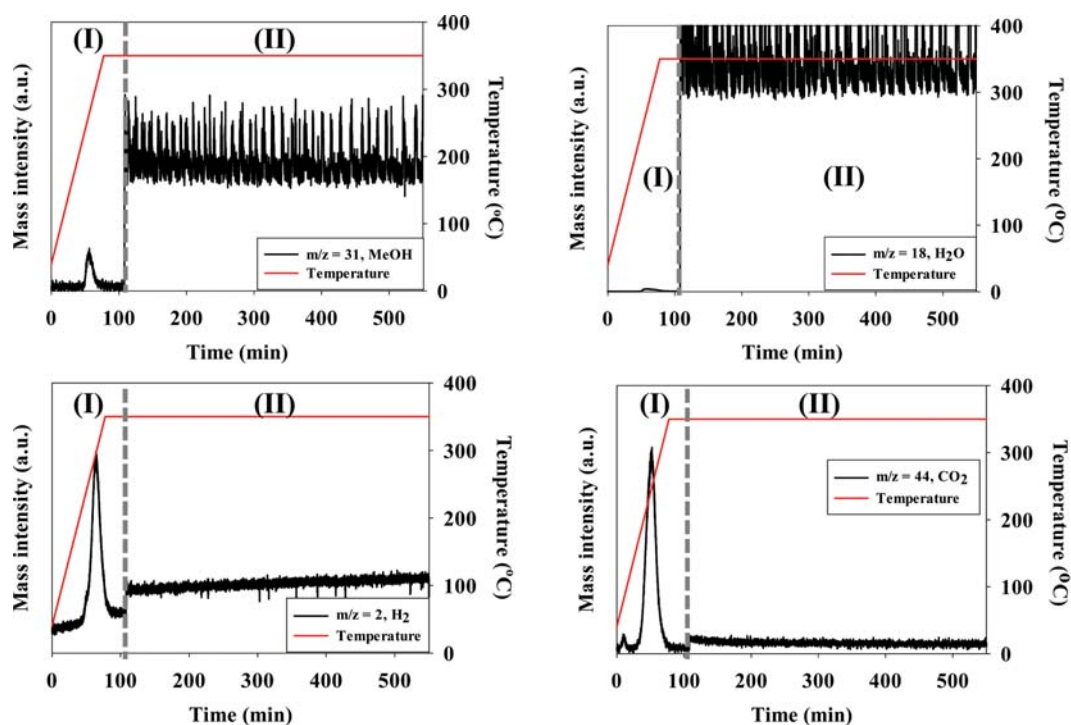


Fig. 3. Mass spectroscopy data as a function of time during methanol synthesis from methane and water at 350 °C. 0.10 g of 3.1 wt% Cu-mordenite was contacted first with methane at a flow rate of 30 mL/min (I) and then with a gas mixture composed of methane saturated with water at 73 °C (II).

lite. The formed methoxy species can be decomposed into CO_2 and H_2 in the absence of water in the feed. However, their forma-

tion was not continuous even with a continuous feed of methane. On the other hand, the continuous formation of methanol, hydro-

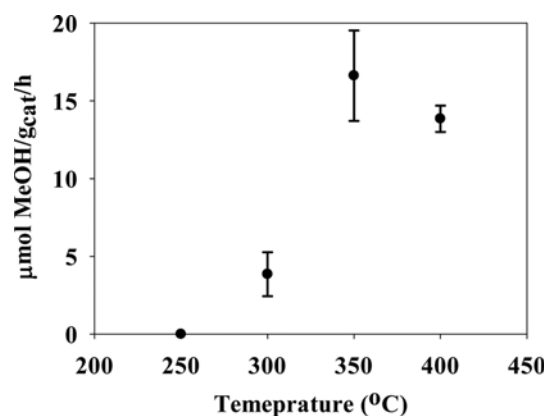


Fig. 4. Steady-state production rate of methanol over 3.1 wt% Cu-mordenite at various temperatures. The feed is composed of 33 mol% methane and 67 mol% steam. 0.3 g of catalyst was contacted with the feed gas at a flow rate of 90 mL (STP)/min.

gen, and carbon dioxide was confirmed at 350 °C in the co-presence of methane and steam (stage II in Fig. 3). This implies that there exists a catalytic cycle over Cu-mordenite in the co-presence of methane and steam.

Similar experiments were also carried out by co-feeding methane and steam at 1 atm pressure. The formation rate of methanol decreased initially but reached a steady-state value. The leaching of Cu was not observed after a reaction. As shown in Fig. 4, the methanol formation rate increased with reaction temperature from 250 to 350 °C, showing a maximum value at 350 °C, and then decreased with a further increase in temperature up to 400 °C. This is closely

related to the competitive adsorption of water molecules on the active sites and to the stability of the methoxy species. At low temperatures, the strong adsorption of water molecules on the active site prevents the adsorption of methane molecules. The formation of methoxy species can be facilitated with increasing temperature. However, the formed methoxy species can be easily decomposed into CO₂ and H₂O at high temperatures. This is why the formation rate of methanol is dependent on the reaction temperature. The rate of methanol formation in the continuous process is comparable to that reported previously in the cyclic process in which activation, methane reaction, and extraction of methanol are carried out separately (Table 1).

The main reaction ($\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \leftrightarrow \text{CH}_3\text{OH}(\text{g}) + \text{H}_2(\text{g})$) is a thermodynamically unfavorable ($\Delta G_{298\text{ K}}^\circ = 117 \text{ kJ/mol}$) and endothermic reaction ($\Delta H_{298\text{ K}}^\circ = 116 \text{ kJ/mol}$). This can explain the low methanol formation rate. However, this methanol production rate is comparable to that obtained in various cyclic processes. To overcome this thermodynamic limitation, it is required to oxidize the hydrogen formed in the main reaction. Recently, Narsimhan et al. [13] reported the continuous production of methanol from methane, oxygen, and steam using Cu-zeolites. However, its formation rate is so low that further work should be done to improve the catalytic activity.

CONCLUSIONS

An isothermal two-step process for methanol synthesis was realized over Cu-mordenite by feeding methane and steam alternately. Furthermore, continuous methanol production was confirmed from methane and steam over Cu-mordenite. Even though the produc-

Table 1. Comparison of methanol yield using Cu-mordenite among different processes

Entry	Catalyst	Pretreatment (gas/pressure/ temperature/ holding time)	Reaction with methane (gas/pressure/ temperature/ holding time)	Methanol extraction (gas/pressure/ temperature/ holding time)	Methanol yield ($\mu\text{mol/g}_{\text{cat}}$)	Methanol yield ($[\text{MeOH}]/[\text{Cu}]$)	Reference
1	Cu-mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3=18$)	-	33% CH_4 +67% H_2O / 1 bar/350 °C/10 h	-	161±15	0.330	In this work
2	Cu-mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3=13$)	He/1 bar/ 400 °C/1 h	CH_4 /7 bar/ 200 °C/0.5 h	2.4% steam in He/ 1 bar/200 °C/2-4 h		0.204	[8]
3	Cu-mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3=92$)	O_2 /1 bar/ 400 °C/1 h	CH_4 /7 bar/ 200 °C/0.5 h	2.4% steam in He/ 1 bar/200 °C/2-4 h		0.316	[9]
4	Cu-mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3=40$)	10% N_2O / 1 bar/ 600 °C/2 h	CH_4 /1 bar/ 150 °C/1 h	7% steam in N_2 / 1 bar/135 °C/NA ^a	97	0.312	[10]
5	Cu-mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3=40$)	O_2 /1 bar/ 450 °C/2 h	CH_4 /1 bar/ 150 °C/1 h	7% steam in N_2 / 1 bar/135 °C/NA ^a	67	0.215	[10]
6	Cu-mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3=17$)	O_2 /1 bar/ 450 °C/4 h	5% CH_4 /1 bar/ 200 °C/0.5 h	Liquid water/ 1 bar/25 °C/2 h	19	0.029	[11]
7	Cu-mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3=17$)	O_2 /1 bar/ 450 °C/4 h	5% CH_4 /1 bar/ 200 °C/0.5 h	10 g·h ⁻¹ steam in He/ 1 bar/200 °C/NA ^a	13	0.020	[11]
8	Cu-mordenite ($\text{SiO}_2/\text{Al}_2\text{O}_3=17$)	O_2 /1 bar/ 450 °C/4 h	CH_4 /1 bar/ 200 °C/0.5 h	Liquid water/ 1 bar/25 °C/3 h	29.8	0.061	[12]

^aNot available

tion rate of methanol was very low due to thermodynamic limitations, the formation rate of methanol is comparable to that previously reported in the cyclic process in which activation, methane reaction, and extraction of methanol are carried out separately.

ACKNOWLEDGEMENTS

This work was supported by C1 Gas Refinery Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (2015M3D3A1A01064899). This work was also supported by the Human Resources Program in Energy Technology (No. 20154010200820) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), which is granted financial resources from the Ministry of Trade, Industry and Energy of the Republic of Korea.

NOMENCLATURE

ΔH : Enthalpy of reaction [kJ/mol]

ΔG : Gibbs free energy [kJ/mol]

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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Supporting Information

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(Received 27 July 2018 • accepted 12 September 2018)

EXPERIMENTAL

Catalyst Characterization

The specific surface area of the catalysts was measured on a Micromeritics ASAP 2020 instrument and calculated using the Brunauer-Emmett-Teller (BET) method. Prior to measurement, the

samples were degassed under vacuum for 6 h at 200 °C.

Powder X-ray diffraction (XRD) experiments were performed on a Rigaku D/Max instrument with a Cu K α source.

The metal content was confirmed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Thermo Scientific iCAP 6500).

Table S1. The physical properties of mordenite and Cu-mordenite

Sample	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Micropore surface area ^a (m ² /g)	External surface area ^a (m ² /g)	Micropore volume ^a (cm ³ /g)
Mordenite	409	0.227	383	26	0.177
Cu-mordenite	431	0.238	394	37	0.182

^aThe data were obtained by the t-plot method

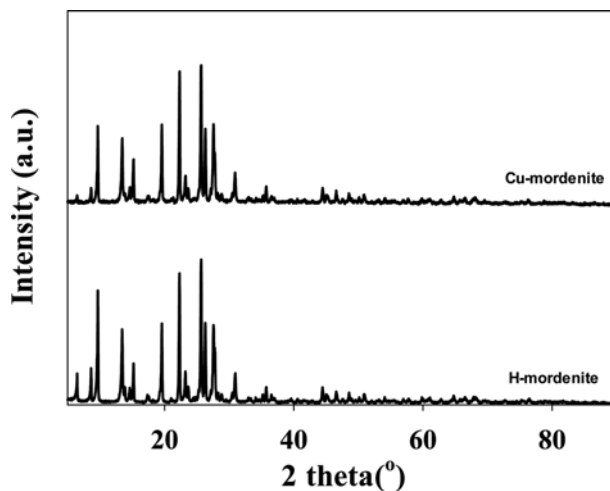


Fig. S1. X-ray diffraction pattern of H-mordenite and Cu-mordenite.

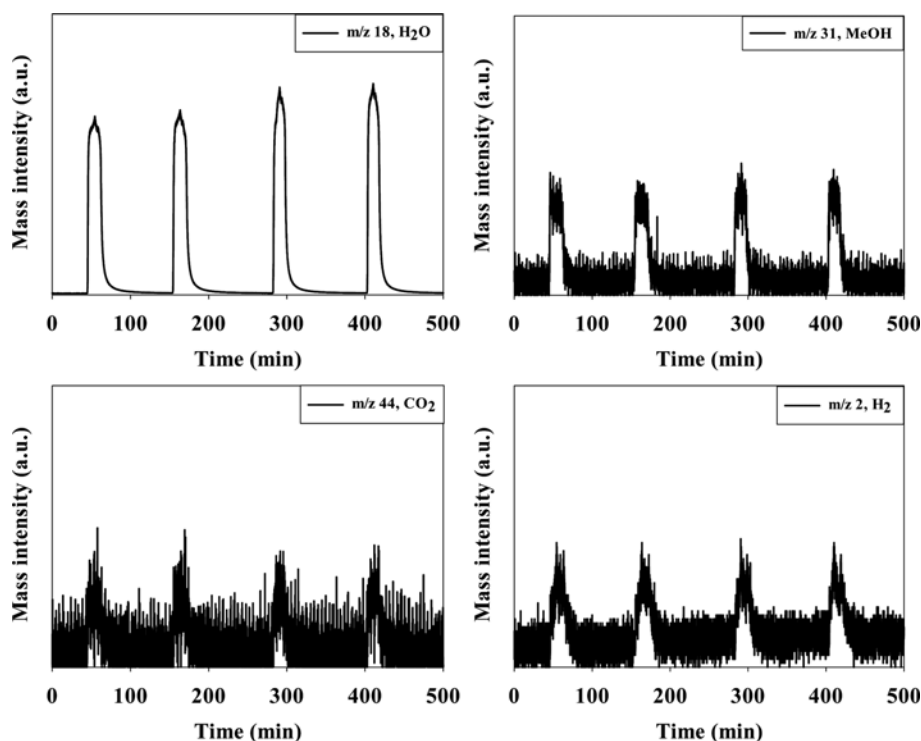


Fig. S2. Mass spectroscopy data as a function of time during water injection experiment. 0.30 g of 3.1 wt% Cu-mordenite was contacted with methane at a flowrate of 30 mL/min at 300 °C. 10 μ L of water was injected at every 2 h.

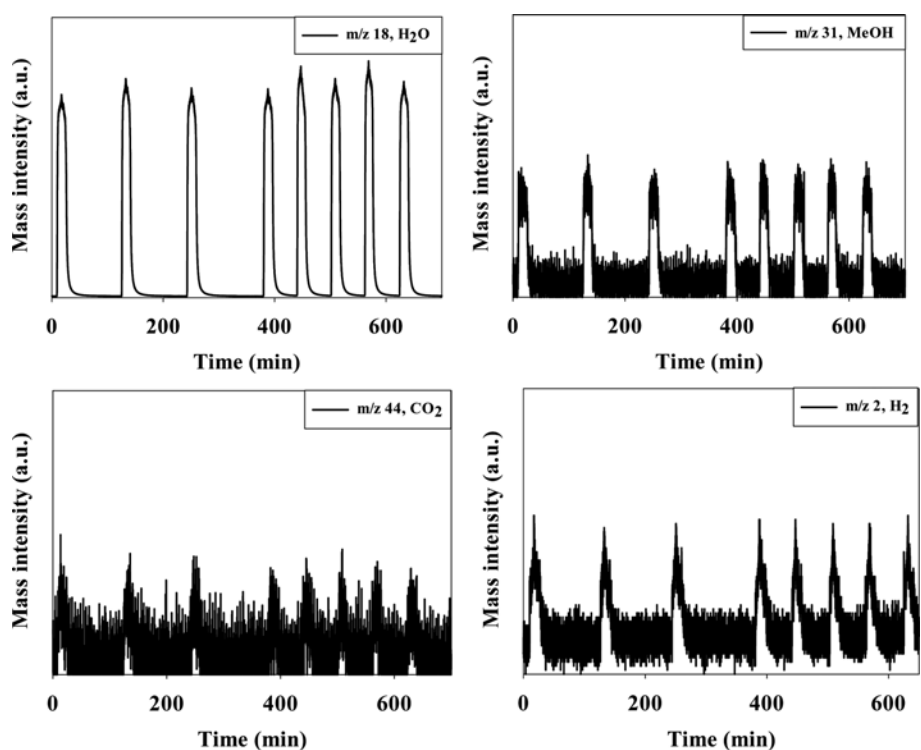


Fig. S3. Mass spectroscopy data as a function of time during water injection experiment. 0.30 g of 3.1 wt% Cu-mordenite was contacted with methane at a flowrate of 30 mL/min at 350 °C. 10 μ L of water was injected at every 2 h or 1 h.