Catalysis Today 164 (2011) 425–428

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

A new method of ethanol synthesis from dimethyl ether and syngas in a sequential dual bed reactor with the modified zeolite and Cu/ZnO catalysts

Guohui Yang[a], Xiaoguang San[a], Nan Jiang[a,c], Yuki Tanaka[a], Xingang Li[d], Quan Jin[a], Kai Tao[a], Fanzhi Meng[a], Noritatsu Tsubaki[a,b,*]

[a] Department of Applied Chemistry, School of Engineering, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan
[b] JST, CREST, Sanbancho 5, Chiyoda-ku, Tokyo 102-0075, Japan
[c] School of Chemical Engineering, Dalian University of Technology, Dalian 116012, PR China
[d] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China

ARTICLE INFO

Article history:
Available online 4 November 2010

Keywords:
Ethanol
Dimethyl ether
Carbonylation
Hydrogenation
Zeolite

ABSTRACT

Ethanol was directly synthesized from dimethyl ether (DME) and syngas ($CO + H_2$) with the combination of Cu-modified H-Modernite (H-MOR) zeolite catalyst and metallic Cu/ZnO catalysts in a dual-catalyst bed reactor. The methyl acetate (MA) was firstly formed by DME carbonylation on the upper zeolite catalyst layer, and then was subsequently hydrogenated on the lower Cu/ZnO catalyst layer to be converted into ethanol accompanying with methanol. A copper doped H-MOR catalyst prepared by ion-exchange method exhibited better catalytic activity compared with the pure H-MOR catalyst in the single DME carbonylation reaction, and the influence of reaction temperature was investigated in detail, confirming that the optimal reaction temperature for this copper doped H-MOR catalyst was 493 K. For ethanol synthesis in the dual catalyst bed reactor, the combination of copper doped H-MOR catalyst with Cu/ZnO catalyst effectively improved the DME conversion, enhanced the ethanol selectivity in the final products remarkably, if compared with the combination of pure H-MOR catalyst with Cu/ZnO catalyst.

1. Introduction

Ethanol, an important starting feedstock for the production of a number of chemicals, is mainly synthesized by catalytic hydration of ethylene [1], where the ethylene is from petroleum cracking. In order to reduce the dependence on crude oil, cut down greenhouse gas emissions and avoid food shortage at the same time, more attentions have been paid to the ethanol synthesis by non-petroleum route based on other alternative resources, such as natural gas or biomass. At present, some potential routes for ethanol synthesis are widely investigated. Such as the direct synthesis of ethanol from syngas on the various metals loaded heterogeneous catalysts [2–5], or the ethanol direct synthesis by the methanol homologation method [6,7]. Another interesting method is the carbonylation of methanol to form acetic acid, where the formed acetic acid will be converted to acetate ester by esterification, followed by the hydrogenolysis of acetate ester to produce ethanol [8]. However, the use of noble metal as catalyst or promoter, non-environmentally friendly reaction, very high operating pressure and/or the lower selectivity of ethanol prevent them from commercialization.

Dimethyl ether (DME) can be one-step synthesized from syngas ($CO + H_2$) with the elevated maximum conversion, which make it a promising candidate as clean and high efficiency energy. In our previous work, a new method for ethanol synthesis from the DME and syngas using a dual-catalyst bed reactor was briefly introduced [9,10], and the whole reaction processes and possible reaction mechanism had also been presented [11]. In this method, the DME was firstly converted to methyl acetate (MA) through carbonylation on the H-MOR catalyst, and then the formed MA is hydrogenated to ethanol on Cu/ZnO catalyst. This proposed process had a high ethanol selectivity and productivity. In this report, a new copper doped H-MOR catalyst was prepared by ion-exchange method and used for ethanol direct synthesis by its combination with Cu/ZnO catalyst in a dual-catalyst bed reactor. And the effect of reaction temperature for DME carbonylation on this copper doped H-MOR was also investigated in detail.

2. Experimental

2.1. Catalyst preparation

The commercial H-MOR zeolite (Tosoh Corporation, $SiO_2/Al_2O_3 = 17.3$, $S_{BET} = 343\ m^2\ g^{-1}$) was used for DME car-

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[*] Corresponding author at: Department of Applied Chemistry, School of Engineering, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan. Tel.: +81 76 445 6846; fax: +81 76 445 6846.
E-mail address: tsubaki@eng.u-toyama.ac.jp (N. Tsubaki).

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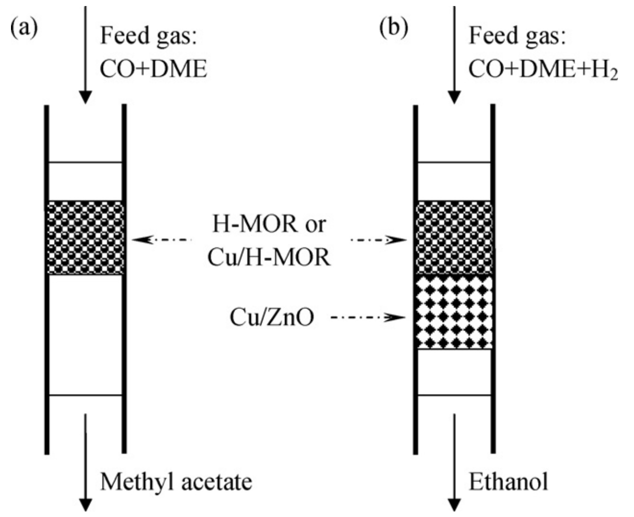
doi:10.1016/j.cattod.2010.10.027



Scheme 1. Illustration of catalyst loading in reactor: (a) the single zeolite catalyst for DME carbonylation and (b) the dual-catalyst bed reactor for ethanol synthesis.

bonylation reaction in this report as a reference. The copper doped H-MOR catalyst, named as Cu/H-MOR, was prepared by the ion-exchange method. The commercial H-MOR zeolite was mixed with an aqueous solution of copper nitrate, and then the mixture was heated at 353 K for 2 h. The obtained sample was washed by deionized water for several times and dried at 393 K for 12 h. This ion-exchange process might be repeated in order to get a desired copper amount on H-MOR zeolite. The final sample was calcined at 773 K in air for 2 h, followed by granulating into the size of 60–120 mesh. The copper loading amount of Cu/H-MOR catalyst was 4.7 wt% by weight, as determined by ICP. The calculated value of ion-exchange percentage of this Cu/H-MOR zeolite catalyst was about 0.58.

The Cu/ZnO catalyst (Cu/Zn = 1:1, molar ratio) was prepared by a conventional co-precipitation method. The copper nitrate and zinc nitrate solutions were mixed with sodium carbonate solution at 333 K, keeping the pH value of mixture at 8.5. The slurry was aged overnight and then filtrated, washed with deionized water thoroughly. The obtained precipitate was dried at 393 K for 12 h, and calcined in air at 623 K for 1 h, followed by being pelletized and screened to the size of 20–40 mesh.

Before loading the catalysts into reactor, the Cu/H-MOR and Cu/ZnO were firstly reduced by a flow of pure hydrogen at 573 K for 10 h, and then passivated by 1% oxygen diluted in nitrogen at room temperature for 1 h.

2.2. *Catalyst characterization*

Powder X-ray Diffraction (XRD) patterns of the H-MOR zeolite, passivated catalyst Cu/H-MOR and Cu/ZnO, were collected using a Rigaku RINT 2400 X-ray Diffractometer equipped with a Cu-Kα radiation ($\lambda = 0.154$ nm). The X-ray tube was operated at 40 kV and 40 mA. The actual elemental composition of catalyst was measured by a JEOL JSM-6360LV scanning electron microscope (SEM) with a JED-2300 energy dispersive spectroscopy (EDS).

2.3. *Catalytic reactions*

A packed-bed stainless steel reactor (9.5 mm OD) was adopted for the followed reactions. For the single DME carbonylation, 0.5 g of H-MOR or Cu-H-MOR was loaded into the middle of reactor as shown in Scheme 1(a), and then the reactor was heated at 773 K under flowing nitrogen (80 ml min^{-1}) for 1 h. After being cooled to the reaction temperature, the reactants gas (Ar 3.09%/DME 2.03%/CO 94.88%) with 1.5 MPa was introduced. In order to investigate the influence of hydrogen in feed gas, also as a reference for the following ethanol synthesis reaction, another feed gas (Ar 1.54%/DME 1.02%/CO 47.44%/H_2 50%) was also adopted for DME carbonylation on the Cu/H-MOR catalyst.

For ethanol synthesis, the reaction was conducted with the same packed-bed stainless steel reactor to the above-mentioned single DME carbonalytion reaction. But there was a dual-catalyst bed in the reactor as shown in Scheme 1(b), the first catalyst bed was H-MOR or Cu/H-MOR zeolite catalyst of 0.5 g used for DME carbonylation to produce methyl acetate (MA), the formed MA was then hydrogenated on the followed Cu/ZnO of 0.5 g catalyst, being converted to ethanol.

The effluent products from the reactor outlet were first analyzed by an online gas chromatograph (TCD detector and Porapak Q column). Liquid products collected by an ice-water trap were analyzed using another FID gas chromatograph with a connected dual column (packing materials: Gaskuropack 54 and Porapak N). In this report, all of the selectivity values in the tables are calculated in molecular selectivity, instead of carbon molar base.

3. Results and discussion

3.1. *Catalyst characterization*

The actual Cu/Zn ratio for Cu/ZnO catalyst measured by EDS was 0.96:1 very close to the designed molar recipe. The XRD patterns of the H-MOR zeolite, Cu/H-MOR and Cu/ZnO catalyst are presented in Fig. 1. For the Cu/ZnO catalyst after reduction, there are only two phases, Cu and ZnO, can be found obviously. And the average crystallite size of the Cu and ZnO calculated by Scherrer equation was about 7.7 nm and 6.3 nm respectively. Comparing the XRD pattern of H-MOR catalyst with that of Cu/H-MOR, it is difficult to find some obvious peaks assigned to copper, which should be due to the lower Cu loading amount (4.7%) on zeolite catalyst together with the location exchange of proton with Cu^{2+} after ion-exchange treatment. Furthermore, it should be noted that the relative crystallinity of Cu/H-MOR zeolite catalyst decreased slightly compared with the pure H-MOR zeolite catalyst.

3.2. *DME carbonylation on the Cu/H-MOR catalyst*

As a reference, the H-MOR zeolite catalyst for DME carbonylation was also investigated, as shown in Table 1. The DME conversion for this pure H-MOR zeolite catalyst was 63.7% with a higher MA selectivity of 96.8%. A small amount of CO_2 as the by-products was

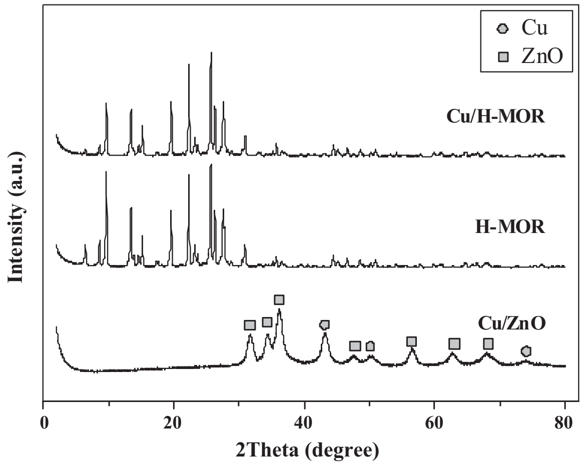


Fig. 1. XRD patterns of Cu/ZnO, H-MOR and Cu/H-MOR catalysts.

Table 1
DME carbonylation on H-MOR catalyst and Cu/H-MOR catalysts.[a]

Catalyst	Conversion (%)		Selectivity (%)			
	DME	CO	MA	MeOH	EtOH	CO_2
H-MOR	63.7	1.1	96.8	0	0	3.2
H-MOR[b]	46.3	0.43	100	0	0	0
Cu/H-MOR	98.2	1.6	96.2	0	0	3.8
Cu/H-MOR[b]	63.7	1.6	96.4	0	0	3.6

[a] Reaction conditions: temperature = 493 K, $weight_{H\text{-}MOR}$ = 0.5 g; $weight_{Cu/H\text{-}MOR}$ = 0.5 g; reaction gas, Ar 3.09%/DME 2.03%/CO 94.88%; pressure = 1.5 MPa; F_{CO+DME} = 40 ml min^{-1}; MA = methyl acetate.

[b] The feed gas used for this experiment was Ar 1.55%/DME 1%/CO 47.45%/H_2 50%; pressure = 1.5 MPa; F_{CO+DME} = 40 ml min^{-1}; F_{H_2} = 40 ml min^{-1}.

Table 2
Effect of various temperatures on DME carbonylation by Cu/H-MOR catalyst.[a]

Temp. (K)	Conv. (%)	Productivity (mmol kg^{-1} h^{-1})	Selectivity (%)	
	DME	MA	MA	CO_2
423	1.6	23.3	100	0
453	43.7	616.7	97.7	2.3
473	65.5	1106.6	97.1	2.9
493	98.2	1994.3	96.2	3.8
513	99.1	1390.7	72.7	27.3[b]

[a] Reaction conditions: $weight_{Cu/H\text{-}MOR}$ = 0.5 g; reaction gas, Ar 3.09%/DME 2.03%/CO 94.88%; pressure = 1.5 MPa; F_{CO+DME} = 40 ml min^{-1}; MA = methyl acetate.

[b] The by-products include CO_2 and some other hydrocarbons.

detected in the final products, which should be attributed to the Water Gas Shift (WGS) reaction. Ethanol or methanol cannot be generated by DME carbonylation on this single pure zeolite catalyst.

The Cu/H-MOR catalyst was conducted for DME carbonylation under the same reaction conditions to H-MOR catalyst. With only a small amount of copper modification, the Cu/H-MOR catalyst exhibited very higher catalytic activity, as shown in Table 1. The DME conversion on Cu/H-MOR catalyst was 98.2%, very higher than the 63.7% of H-MOR catalyst, keeping a stable MA selectivity 96.2% at the same time. Iglesia and co-workers [12] reported that the CO insertion into methyl groups occurs selectively within the eight-membered ring H-MOR zeolite channels, where the functional groups and acid forms actually control the carbonylation rate [13]. The metallic elements introduced into H-MOR zeolite by ion-exchange method could effectively alter the zeolite physical properties, such as acid sites, acidity strength and structure composition [14], which should be beneficial to the formation and/or adsorption of methoxy groups on a BrØnsted acid sites [15]. The activated CO at the metallic sites very near the aluminum framework could easily attack the adsorbed methoxy species, thus speeding up the DME conversion.

It should be noticed that the hydrogen will be used in the following dual-catalyst bed reactor for MA hydrogenation on the Cu/ZnO catalyst to form ethanol, and the hydrogen together with CO and DME in feed gas would firstly pass through the Cu/H-MOR catalyst layer in reactor. Therefore, a new feed gas containing hydrogen was also adopted to investigate the influence of H_2 for DME carbonylation on Cu/H-MOR catalyst, as listed in Table 1. The conversion of DME was 63.7%, lower than that of the case without hydrogen in feed gas because of the higher gas flow rate and lower partial pressure of CO + DME. However, the selectivity of MA was still stable, similar to that of cases without hydrogen in feed gas, indicating that the addition of H_2 had only little influence on DME carbonylation over Cu/H-MOR catalyst, at least under this reaction conditions.

3.3. *Effect of reaction temperature on DME carbonylation*

The effect of various temperatures on DME carbonylation over single Cu/H-MOR catalyst was exhibited in Table 2. The DME conversion and MA productivity increased linearly with the increase of reaction temperature from 423 K to 493 K, and reached 98.2% and 1994.3 mmol kg^{-1} h^{-1} respectively at 493 K. However, the selectivity of MA decreased slightly along with increasing reaction temperature, which should be attributed to the fact that higher reaction temperatures accelerated the formation of CO_2 by WGS reaction. It can be also found that the productivity and selectivity of MA increased up to 493 K and then decreased quickly with increasing reaction temperature. Therefore, the 493 K at which the optimized catalytic performance for DME carbonylation to produce MA on the Cu/H-MOR catalyst was obtained, and this result was also similar to our previous finding [9].

3.4. *Ethanol synthesis with the combination of H-MOR or Cu/H-MOR and Cu/ZnO catalyst*

The ethanol synthesis process was conducted using the combination of H-MOR or Cu/H-MOR catalyst with Cu/ZnO catalyst in a dual-catalyst bed reactor. The feed gas containing hydrogen firstly passed through the H-MOR or Cu/H-MOR catalyst layer, where the MA was produced by DME carbonylation, and then the formed MA and hydrogen continued its route to reach the followed Cu/ZnO catalyst layer, and was successively converted into ethanol and methanol by its hydrogenation. The reaction results were showed in Table 3.

For the combination of pure H-MOR catalyst with Cu/ZnO catalyst, the CO conversion was 56.3% and the selectivity of ethanol was 39.3%. The MA selectivity in final products was only 0.3%, very lower than that in the case of DME carbonylation on single H-MOR zeolite catalyst, indicating that the formed MA from upper catalyst layer was almost converted completely on the followed Cu/ZnO catalyst. It should be noted that methanol as the main by-product with the selectivity of 55.3% was produced by MA hydrogenation, but here the methanol can be easily recycled into DME on acid solid catalysts, realizing a green and economical process with only tiny loss in theory.

A higher DME conversion of 93.8% was achieved in the dual-catalyst bed reactor, where Cu/H-MOR catalyst was used to substitute the pure H-MOR zeolite. And it seems that the Cu/MOR catalyst in the dual-catalyst bed reactor was more active than the single catalyst in reactor for the sole DME carbonylation under the same reaction condition. The latter case presented a lower DME conversion of 63.7%, as shown in Table 1. These results should be due to the synergistic effect of two sequential reactions, the preliminary carbonylation and the followed hydrogenation. The MA

Table 3
The combination of H-MOR or Cu/H-MOR catalyst with Cu/ZnO catalyst for ethanol synthesis.

Catalysts	Conversion (%)		Productivity (mmol kg^{-1} h^{-1})			Selectivity (%)				
	DME	CO	MA	MeOH	EtOH	MA	EA	MeOH	EtOH	CO_2
H-MOR and Cu/ZnO	56.3	1.6	4.1	690.5	491.8	0.3	0	55.3	39.3	5.1
Cu/H-MOR and Cu/ZnO	93.8	1.9	71.2	1047.2	1011.4	3.1	4.6	45.7	44.1	2.5

Reaction conditions: temperature = 493 K; $weight_{H\text{-}MOR\ or\ Cu/H\text{-}MOR}$ = 0.5 g, $weight_{Cu/ZnO}$ = 0.5 g; reaction gas, Ar 1.55%/DME 1%/CO 47.45%/H_2 50%; pressure = 1.5 MPa; F_{CO+DME} = 40 ml min^{-1}, F_{H_2} = 40 ml min^{-1}; MA = methyl acetate; EA = ethyl acetate; MeOH = methanol; EtOH = ethanol.

hydrogenation on the lower Cu/ZnO catalyst layer could effectively promote DME carbonylation on the upper Cu/H-MOR catalyst [10]. Compared with the above dual-catalyst bed reaction using pure H-MOR zeolite catalyst, the ethanol selectivity of this new catalyst combination was increased from 39.3% to 44.1% accompanying by the decrease of selectivity of methanol from 55.3% to 45.7%, which indicated that the Cu/H-MOR catalyst was more beneficial to ethanol synthesis under this reaction conditions. Furthermore, other tiny by-products, such as MA and EA, were also found in the final products, but could be easily hydrogenated to ethanol only by increasing the Cu/ZnO catalyst loading amount or hydrogen partial pressure.

4. Conclusions

The direct ethanol synthesis from DME and syngas on the combination of Cu/H-MOR zeolite catalyst and Cu/ZnO catalyst in a dual-catalyst bed reactor was proposed and studied. The Cu/H-MOR catalyst prepared by ion-exchange method effectively enhanced its catalytic activity for DME carbonylation compared with the pure H-MOR zeolite catalyst, keeping the stable and high methyl acetate selectivity at the same time. The effect of reaction temperature on the DME carbonylation using single Cu/H-MOR catalyst was investigated in detail. Higher reaction temperature favored DME conversion, but the selectivity of by-products increased gradually. The 493 K was identified as the optimal reaction temperature for DME carbonylation on Cu/H-MOR catalyst. For ethanol synthesis in dual-catalyst bed reactor, the combination of Cu/H-MOR catalyst with Cu/ZnO catalyst exhibited promoted performance, not only on catalytic activity, but also on the selectivity and productivity of ethanol, much better than that of the combination of pure H-MOR catalyst with Cu/ZnO catalyst. The novel ethanol synthesis route reported here, using DME and syngas as reactants and the catalyst combination of copper doped H-MOR zeolite with metallic catalyst, was effective and environmentally friendly, acting as a new and promising alternative ethanol synthesis method for chemical or energy industry.

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