

Catalytic applications of highly crystalline seed-derived ferrierite zeolite for syngas conversion to value-added chemicals

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Abstract: The seed-derived ferrierite (FER) with a high crystallinity was applied for a gas-phase dimethyl ether (DME) carbonylation to methyl acetate (MA), and it was further applied for the direct syngas conversion to DME on the bifunctional Cu-ZnO-Al₂O₃/FER. The observed higher catalytic activity and stability were mainly attributed to the larger amounts of active Brønsted acid sites with less defected sites of the FER.

Keywords: Highly crystalline FER, DME carbonylation, CO hydrogenation, hybrid Cu-ZnO-Al₂O₃/FER.

1. Introduction

A gas-phase carbonylation of dimethyl ether (DME) to methyl acetate (MA) on the solid acid zeolites has been intensively investigated to produce value-added useful chemical intermediates [1-3], where MA can be further transformed to an alternative clean ethanol fuel by hydrogenation [1,4,5]. Although a lot of solid-acid zeolites such as MFI, BEA, or MOR were applied for DME carbonylation to produce MA, DME conversion on those heterogeneous solid-acid catalysts was relatively lower and deactivated significantly [4], where DME can be produced by CO and CO₂ hydrogenation using the bifunctional hybrid Cu-ZnO-Al₂O₃/zeolites [6,7], where the larger amounts of surface acidic sites of zeolites as well as meal surface area of copper species have been known to be crucial factors to get a higher catalytic activity. Based on our previous research results [8], DME carbonylation was investigated by using a lab-made FER with high crystallinity to prohibit the coke depositions effectively for a stable long-term activity in terms of the crystallinity and dispersion of active metallic sites on the FER-based catalysts.

2. Experimental sections

The FER zeolite seed was previously synthesized according to our previous work [8], the seed-derived FER with a fixed amount of FER seed of 24wt% was further prepared at different hydrothermal duration from 24 to 96 h at a fixed Si/Al molar ratio of 10.4, which showed a higher crystallinity than other ratios of the FER. The bifunctional Cu-ZnO-Al₂O₃/FER(10.4) for syngas conversion to DME was prepared by coprecipitation methods [6] at a fixed weight ratio of CuO/ZnO/Al₂O₃ = 7/3/1 and CuO/FER = 3, which was calcined at 350 °C for 3 h before activity measurement. The effluent gases from the reactor were analyzed using an on-line gas chromatography (Younglin GC, YL6100) installed with a flame ionization detect (FID) with DB-WAX capillary column to analyze the hydrocarbons, methanol, DME, MA and other byproducts and thermal conductivity detector (TCD) for detecting inflammable gases. The seed-derived FER and Cu-ZnO-Al₂O₃/FER(10.4) catalysts were characterized by N₂-sorption, XRD, XPS, TEM and solid-state MAS NMR analysis to verify the bulk and surface properties of the fresh and used catalysts.

3. Results and discussion

As summarized in **Table 1**, the catalytic activity of CO and CO₂ hydrogenation on the bifunctional Cu-ZnO-Al₂O₃/FER(10.4) was found to be higher than 85% with DME selectivity above 95% at 250 °C, which was found to be much higher than the commercial FER zeolite [6,7] due to the larger amounts of Brønsted acid sites attributed to the high crystallinity of the home-made FER (**Figure 1(A)**). In addition, DME carbonylation to MA on the seed-derived FER at the duration of hydrothermal synthesis around 96 h (much less time required compared to pristine FER for 168 h) was found to be more active than the pristine FER with DME conversion above 70% and MA selectivity above 99% due to the abundant presence of active Brønsted acid sites (T2 sites in 8 and 10-membered ring channels of FER as shown in **Figure 1(B) and (C)**). In addition, the bifunctional

Cu-ZnO-Al₂O₃/FER prepared by the hybridized two functions (**Figure 1(D)**) showed the much higher thermal stability of the supported copper nanoparticles on the acidic surfaces (**Figure 1(E)**) which also showed higher CO conversion by synergy effects of CO₂ addition at an optimal CO/(CO+CO₂) = ~0.6 (**Figure 1(F)**).

Table 1. Catalytic activities on the highly crystalline seed-derived FER and Cu-ZnO-Al₂O₃/FER hybrid catalysts

(1) Syngas conversion to DME on the Cu-ZnO-Al ₂ O ₃ /FER(10.4)						
Reaction T (°C)	CO conversion (mol%)	CO ₂ conversion (mol%)	Selectivity (mol%)			
			Methanol	DME	hydrocarbons	
220	25.6	-2.9	9.9	89.9	0.2	
250	85.5	-20.4	4.2	95.6	0.2	
280	90.6	-19.9	4.2	95.0	0.8	

(2) DME carbonylation to MA on the FER(10.4) using 24wt%FER seed						
Duration of hydrothermal synthesis (h)	DME conversion (mol%)	MA formation rate (mmol _{MA} /g _{Al} ·h)	Selectivity (mol%)			
			Methanol	MA	hydrocarbons	
24	6.6	3.9	18.2	72.2	9.6	
48	49.6	40.7	0.8	98.9	0.3	
72	57.4	47.1	0.7	99.0	0.3	
96	71.5	58.8	0.5	99.2	0.3	

(1) Reaction conditions: P = 5.0 MPa, SV=2000 L/(kg_{cat}·h), CO/CO₂/H₂/N₂ = 21/9/66/4 (H₂/(CO+CO₂) = 2.2) with 0.4 g catalyst

(2) Reaction conditions; T = 220 °C, P = 1.0 MPa, SV = 2000 L/(kg_{cat}·h), N₂/CO/DME = 50/45/5 with 0.4 g catalyst

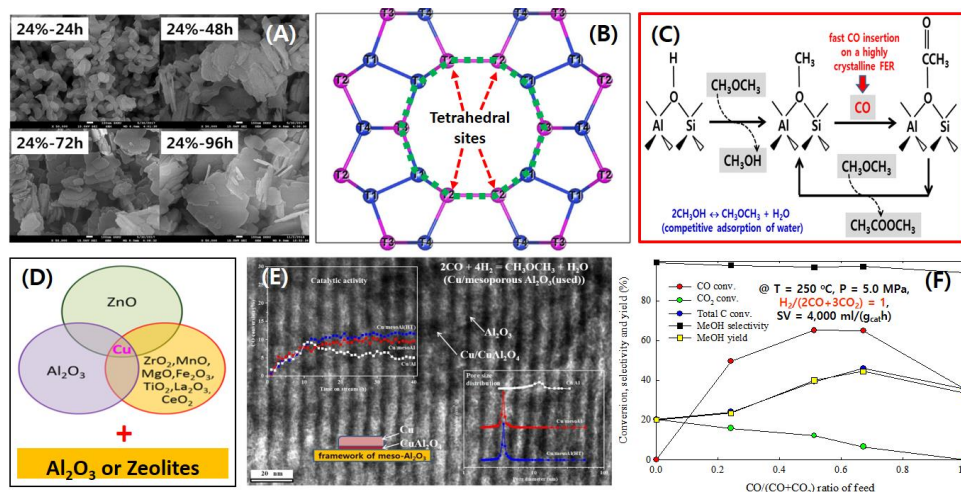


Figure 1. (A) SEM images of the seed-derived FER (with 24wt% seed FER) according to the duration (h) of hydrothermal synthesis, (B) active T2 sites in the 10-membered ring channels of seed-derived FER, (C) reaction mechanisms of DME carbonylation, (D) schemes of bifunctional catalyst preparation, (E) schemes of thermally stable copper nanoparticles in the solid acid mesoporous material and (F) synergy effects of CO₂ during CO hydrogenation at an optimal CO/(CO+CO₂) = ~0.6

4. Conclusions

These superior catalytic activities on the seed-derived FER and the bifunctional Cu-ZnO-Al₂O₃/FER catalysts were mainly attributed to the large amounts of Brønsted acidic sites on the highly crystalline FER zeolite, which can simultaneously increase the catalytic activity of DME carbonylation to MA on the FER zeolite as well as direct CO and (or) CO₂ hydrogenation to DME on the well-dispersed and thermally stable copper nanoparticles on the acidic sites of the FER zeolite (or mesoporous Al₂O₃) as well.

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