



Short communication

Selective carbonylation of dimethyl ether to methyl acetate on Ferrierite

So Young Park^a, Chae-Ho Shin^b, Jong Wook Bae^{a,*}^a School of Chemical Engineering, Sungkyunkwan University (SKKU), Suwon, Gyeonggi-do 440-746, Republic of Korea^b Department of Chemical Engineering, Chungbuk National University (CNU), Cheongju, Chungbuk 361-763, Republic of Korea

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ABSTRACT

Synthesis of methyl acetate (MA) by carbonylation of dimethyl ether (DME) was investigated using laboratory-made H-form Ferrierite (FER) zeolite with different Si/Al molar ratios. The synthesized H-FER with a Si/Al ratio of 12 (FER(12)) revealed a higher DME conversion as well as MA selectivity. The observed higher catalytic performance on the FER(12) was mainly attributed to a higher ratio of Bronsted to Lewis acid sites as well as the higher crystallinity with the less coke formation. The superior properties of the FER(12) having a higher ratio of Bronsted to Lewis acid sites and crystallinity efficiently suppressed the formation of inactive coke precursors.

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1. Introduction

Carbonylation reaction of dimethyl ether (DME) with CO has been largely investigated to selectively synthesize an important petrochemical intermediate or alternative clean fuels [1,2]. The carbonylation reactions of methanol or DME have been well known to produce acetic acid using rhodium or iridium organometallic homogeneous catalysts or to synthesize methyl acetate (MA) on the zeolites, respectively [3–5]. An application of heterogeneous catalysts for carbonylation reaction has large advantages of facile catalyst separation [6–8]. MA is also known to be one of important chemical intermediates for the production of acetic anhydride for paint additive or acetylcellulose [6,8]. MA produced by DME carbonylation with a subsequent hydrogenation to ethanol can be also one of the alternative routes in comparison with traditional production processes of ethanol [9,10].

The carbonylation of DME on the zeolites especially for H-MOR, which consists of 8-membered ring (MR) channels connected with 12-MR channels, can produce MA selectively on the active 8-MR channels by forming an intermediate of surface acetyl ($\text{CH}_3\text{CO}-$) species through CO insertion to an adsorbed methyl (CH_3-) species originated from DME [3,10,11]. Based on the proposed mechanism of DME carbonylation [11,12], a possible initiation step of DME carbonylation can be the activation of DME on the Bronsted acid sites by forming a hydrogen-bonded DME with a successive formation of CH_3 species and methanol. And, methylated Bronsted acid sites can further produce an acetyl species by an insertion of CO molecule to produce MA product which is known as a rate determining step [10–12], and the active sites

can be finally regenerated by forming an adsorbed methyl group [12,13]. Interestingly, the micropores of the H-form Ferrierite (H-FER), which has one-dimensional channels of 8-MR with perpendicularly intersected channels of 10-MR structures, seem to be effective for DME carbonylation to MA or direct DME synthesis from syngas [3,10,11,14]. One-dimensional 10-MR channels in the H-FER can preferentially reduce the hydrocarbon depositions by restricting the diffusion of reactants due to the steric hindrance effects of those channels [6] compared with the H-MOR zeolite [10]. Furthermore, H-form zeolites can be further modified by pre-adsorption of pyridine [2] or by metal-ion exchange [15] to modify acid sites and micropore structures with a high stability. However, the effects of Si/Al ratio and amount of the acid sites with a crystallinity on the H-FER have not been well studied till now for DME carbonylation to MA. In the present study, we prepared H-FER with different Si/Al ratios to explain different activities under a low CO/DME ratio of around 9 in terms of the crystallinity, types of acid sites of the H-FER and coke analysis on the used H-FER.

2. Experimental section

2.1. Preparation of H-FER with different Si/Al ratios and activity measurement

H-FER zeolites with different Si/Al ratios were prepared through a hydrothermally synthesis method. The as-prepared H-FER was denoted as FER(9), FER(12), FER(14), and FER(16) for an Si/Al ratio of 8.2, 11.4, 14.1, 15.5 of the H-FER, respectively. The carbonylation reaction of DME to MA was carried out in a fixed bed tubular reactor. The reaction was performed at $T = 220^\circ\text{C}$, $P = 1.0\text{ MPa}$, and space velocity of $2000\text{ L}/(\text{kg}_{\text{cat}}\cdot\text{h})$ for around 30 h using a mixed gas containing 5%DME/45%CO/50N₂ and

* Corresponding author.

E-mail address: finejw@skku.edu (J.W. Bae).

Table 1
Physicochemical properties of H-FER and distribution of separate acid sites.

Notation ^a	XRF	N ₂ sorption ^b	NH ₃ -TPD (acid sites, mmolNH ₃ /g)		Pyridine IR (acid sites, mmolNH ₃ /g) ^c		
	Si/Al ratio	Sg/Pv/Dp	Weak	Strong	B/L ratio	Bronsted	Lewis
FER(9)	8.7	288/0.13/9.6	1.09	0.64	14.7	1.62	0.11
FER(12)	11.7	287/0.07/7.4	0.89	0.63	18.0	1.44	0.08
FER(14)	14.0	263/0.07/7.2	0.77	0.62	11.6	1.28	0.11
FER(16)	15.6	276/0.12/10.1	0.66	0.64	9.0	1.17	0.13

^a H-form Ferrierite (H-FER) was denoted as FER(x), where x represents a molar ratio of Si/Al with an intended ratios of 8.2, 11.4, 14.1 and 15.5 during the H-FER synthesis, respectively.

^b Sg stands for surface area (m²/g), Pv for pore volume (cm³/g) and Dp for average pore diameter (nm) of the fresh H-FER.

^c The acid site ratio of Bronsted(B) to Lewis(L) was denoted as B/L measured by pyridine IR, and the separate acid site of Bronsted and Lewis acid sites was calculated using total acid sites measured from NH₃-TPD by multiplying the ratio of B/L.

the effluent gases were analyzed using an on-line gas chromatography (Younglin, YL6100). The more detailed synthesis procedures of H-FER preparation and activity test are summarized in supplementary material.

2.2. Catalyst characterizations

Powder X-ray diffraction (XRD) patterns of the as-prepared H-FER were obtained using a Bruker X-ray diffractometer (D8 Advance). The crystallinity of the H-FER was calculated by using the ratio of the sum of the integrated peak areas at the diffraction peaks of $2\theta = 9.3$ and 25.2° on each H-FER to that of the most intense peaks of the FER(14), which was done by assuming 100% crystallinity. The chemical composition of the H-FER was further verified by X-ray fluorescence (XRF) spectrometry (Bruker AXS S4 Pioneer). The surface area, pore volume and average pore diameter of the as-prepared H-FER were characterized by Brunauer–Emmett–Teller (BET) method using a Tristar II instrument (Micromeritics).

Temperature programmed desorption of ammonium (NH₃-TPD) analysis was performed by BELCAT-M instrument equipped with a thermal conductivity detector (TCD) at a temperature range of 100–600 °C. Fourier transformed infrared (FT-IR) spectra of pyridine (Py-IR) were obtained on the as-prepared H-FER after pyridine adsorption using Nicolet 6700 FT-IR spectrometer. Temperature-programmed surface reaction with hydrogen (TPSR) analysis was conducted using U-shape quartz tube reactor to verify the type of coke precursors on the used H-FER. The formed CH₄ ($m/z = 15$) by the hydrogenation of coke precursors was measured by using quadruple mass spectrometer (MS Pfeiffer QMS 200). Thermo gravimetric (TG) analysis of the used H-FER was conducted by Seiko Exstar 6000 (TG/DTA6100) to confirm the quantity of deposited cokes. The more detailed characterization methods are included in supplementary material.

3. Results and discussion

3.1. Textural and acidic properties of as-prepared FER

The specific surface area, pore volume, average pore diameter and the molar ratio of Si/Al measured by N₂ sorption and XRF on the as-prepared H-FER are summarized in Table 1. The surface area, pore volume and average pore diameter on the FER were in a range of 263–288 m²/g, 0.07–0.13 cm³/g and 7.2–10.1 nm, respectively. As shown in supplementary Figs. S1 and S2, N₂ adsorption-desorption isotherms revealed the characteristic type IV isotherm. The observed larger average pore diameter above 7 nm seems to be possibly attributed to a possible formation of inter-particle pores of zeolite particles by showing a maximum intensity of the pore diameter at around 4 nm in size on all H-FER. The Si/Al ratio of the as-prepared H-FER measured by XRF analysis showed similar value with the intended Si/Al ratio for the synthesis of the various H-FER. The characteristic diffraction peaks of the H-FER (Fig. S3) were observed at $2\theta = 9.3$, 25.2° and 25.7° on all H-FER. At lower Si/Al ratio, the crystallinity was significantly decreased to 63.3% on the FER(9) by maintaining it above 83% on other H-FER as summarized in Table 1. This suggests that one dimensional micropore

channels on the H-FER having 8-MR channels with perpendicularly intersected 10-MR channels [6,12,13] are well synthesized on the FER(14) and FER(12).

In general, the active sites of DME carbonylation to MA have been well known as the Bronsted acid sites by easily forming hydrogen-bonded DME [11,12]. As shown in Fig. 1, NH₃-TPD patterns showed the characteristic desorption peaks at maximum temperatures of around 280 and 530 °C which can be assigned to weak and strong acid sites, respectively [14]. Interestingly, the first desorption peak assigned to the weak acid sites was slightly decreased with an increase of Si/Al ratio on the H-FER from 288 °C on the FER [9] to 266 °C on the FER(16). The amount of acid sites is also summarized in Table 1, and the amount of weak acid sites was decreased with an increase of Si/Al ratio from 1.09 mmolNH₃/g on the FER(9) to 0.66 mmolNH₃/g on the FER(16) by maintaining similar amount of the strong acid sites. To further verify the amount and type of the different acid sites, Py-IR analysis was carried out on the H-FER as displayed in Fig. S4 and Table 1. The characteristic absorption peaks of pyridine can be assigned to Bronsted acidic sites (B) at the wave number of 1550 cm^{−1}, Lewis acidic sites (L) at that of 1450 cm^{−1}, and combined Bronsted and Lewis acid sites (B + L) at that of 1480 cm^{−1} [16]. The B/L ratios shown (Table 1) were maximized on the FER(12) and minimized on the FER(16), and the amount of Bronsted acid sites was increased with the decrease of Si/Al molar ratio in the range of 1.17–1.62 mmol/g.

3.2. Effects of acidity and coke deposition on the activity

The catalytic performances on the H-FER are summarized in Table 2 and it showed the DME conversion in the range of 11.1–17.6% and MA selectivity in the range of 90.6–93.3%. The catalytic activity on the H-FER was measured at somewhat higher temperature of 220 °C and lower CO/DME feed molar ratio of 9 compared with the previous works [10,11] to clearly verify the effect of coke deposition. DME

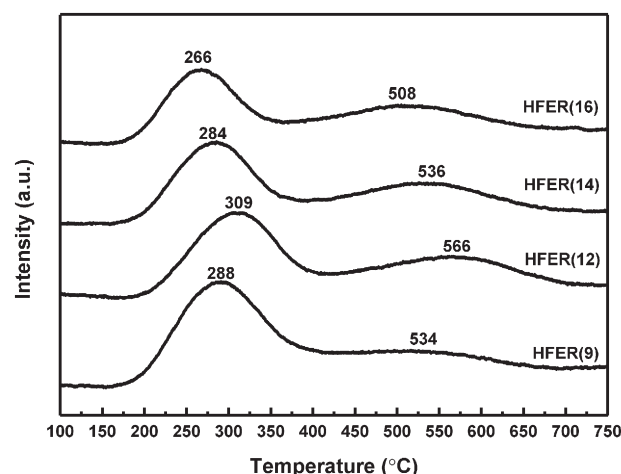


Fig. 1. NH₃-TPD profiles of parent H-form FER with different Si/Al ratios.

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