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Dimethyl ether carbonylation to methyl acetate over highly crystalline zeolite-seed derived ferrierite

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ABSTRACT

Gas-phase carbonylation of dimethyl ether (DME) to methyl acetate (MA) was investigated on the ferrierite (FER) zeolite having different Si/Al molar ratios of 10.4 - 12.5 as well as high crystallinity synthesized by using various zeolite seed materials such as the MOR, ZSM-5 and USY. The enhanced crystallinity of the FER prepared by simply using the FER seed (denoted as FER@FER) having newly formed mesopore structures was responsible for an increased amount of the active Brønsted acid sites, which resulted in a higher MA productivity of 2.94 mmol/(g_{cat}·h) with MA selectivity above 99%. The highly crystalline FER@FER revealed the suppressed depositions of aromatic coke precursors due to the less presence of defect sites. Compared to other zeolite seed-derived FER zeolites, the less amount of defect sites (extra-framework Lewis acidic Al species, EFAL) on the FER@FER was successfully controlled through a recrystallization process. The active Brønsted acid sites for DME carbonylation reaction were mainly originated from the preferential formations of the stable tetrahedral Al sites (especially, T2 sites of the Al-O-Si-O-Al framework of FER) on the 8 and 10-membered ring channels of the FER@FER. On those stable T2 sites having proper acid strengths, the adsorbed methyl intermediates formed by the dissociation of DME can be transformed to acetyl adsorbates by a relatively faster CO insertion rate on the vicinal Brønsted acid sites, which are resulted in a high catalytic stability and activity of the highly crystalline FER@FER.

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Keywords: Carbonylation; Dimethyl ether (DME); Methyl acetate (MA); Ferrierite (FER); Brønsted acid sites.

1. Introduction

Liquid or gas-phase carbonylation reactions of methanol or dimethyl ether (DME) to acetic acid or methyl acetate (MA) has been intensively investigated to produce value-added useful chemical intermediates,¹⁻⁴ where MA can be further transformed to an alternative clean fuel of ethanol by subsequent hydrogenation.^{1,5-7} The MA has been widely used for petrochemical productions such as an acetic anhydride as well as acetyl cellulose.⁴ Even though a lot of environmentally-benign solid-acid zeolites were applied for DME carbonylation with CO to selectively produce MA, DME conversion on those heterogeneous solid-acid catalysts was relatively lower and deactivated significantly. These phenomena were much more significant on the MFI or BEA zeolites having a less amount of 8 membered-ring (8-MR) channels. Therefore, mordenite (MOR) or ferrierite (FER) zeolites having a lot of acidity in the 8-MR channels have been reported to be effective ones for a gas-phase carbonylation of DME.^{3,6,8-10} where DME can be produced by CO (or CO₂) hydrogenation using bifunctional Cu-ZnO-Al₂O₃/zeolites.¹⁰ The MOR zeolite has been well reported to have superior characteristics such as the structures connected by 8-MR of side pocket and 12 membered-ring (12-MR), where the former is known to be active sites and the latter is pathway of reactant and product transports for a higher DME conversion and MA selectivity.^{6,9} The number of OH groups in the 8-MR channels on the MOR has been well related with DME carbonylation activity since it can easily generate methyl groups by dissociate adsorption of DME resulted in forming surface acetyl (CH₃CO-) intermediates through a facile insertion of the adsorbed CO.^{3,6,9} However, the MOR zeolite showed severe deactivation phenomena by forming heavy coke precursors on the 12-MR channels selectively.^{6,9} Therefore, many studies have been focused on solving the coke depositions on the MOR by using post-treatments such as desilication, dealumination and metal ion exchanges such as copper, nickel, zinc or iron and so on.¹¹⁻¹⁴ Recently, the FER having structural characteristics of the side pockets of 8-MR channels

connected with the 10-MR channels, which is smaller than the 12-MR channels of the MOR, revealed a higher MA selectivity and stability due to a suppressed coke formation at a relatively lower activity than the MOR.^{5,15,16} Therefore, based on our previous research results,¹⁵ the gas-phase DME carbonylation was investigated by using a lab-made pristine FER with different Si/Al ratios to effectively prohibit the coke depositions, and the results revealed that a higher crystallinity of FER is responsible for a less coke deposition with a long-term stability and higher selectivity to MA during DME carbonylation.

In the present investigation, we tried to find new methods to shorten the preparation period and to further increase the crystallinity of as-prepared FER through a simple surface coating method using various zeolite seeds such as MOR, ZSM-5 and USY, which are known to be active for DME carbonylation as well. The higher crystallinity of the FER coated with previously synthesized FER seed zeolite showed a significantly improved catalytic activity and stability even for a less duration of FER synthesis period required. The enhanced catalytic performance on the highly crystalline FER was well related with its crystallinity and amount of active Brønsted acid sites, which were precisely analyzed by defining surface acidity and intermediates with the fine structural analyses through Rietveld refinement analysis of XRD and solid-state NMR.

2. Experimental section

2.1. Preparation procedures of seed-derived FER zeolites and activity measurements

The FER seed zeolite was previously synthesized through hydrothermal method at s fixed Si/Al molar ratio of 10.4 as described in our previous works.¹⁵ For more details, after mixing the separate precursors of silica and alumina such as a fumed silica (SiO₂) and sodium aluminate (NaAlO₂) with a structure directing agent of piperidine (hexahydropyridine, $C_5H_{11}N$) at a fixed molar ratio of SiO₂/NaAlO₂/piperidine/NaOH/DIW = 1:0.096:0.9:0.14:40,

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the solution mixtures were kept in a hydrothermal reactor with stirring for 7 days at 160 $^{\circ}$ C. The obtained gel after washing several times was subsequently calcined at 550 °C for 6 h, and as-prepared zeolite was denoted as the FER. For the preparation of the seed-derived FER zeolites coated by using various zeolite seeds such as commercially available MOR (Si/Al = 15), ZSM-5 (Si/Al = 25) and USY (Si/Al = 2.3), the same mixed solutions for a preparation of the FER seed was stirred for 1 h in the slurry of each zeolite seed before a hydrothermal treatment. However, while using the lab-made FER seed, the mixed solutions was added in a slurry of the lab-made FER seed without using the structure directing agent of piperidine due to their same surface structures of the FER seed. After a complete mixing again, the slurry was kept in a hydrothermal reactor for 4 days at 160 °C After the hydrothermal synthesis, the FER prepared from each zeolite seed was filtered, washed again using deionized water (DIW) followed by drying overnight. As-prepared white powder was calcined under air environment at 550 °C for 6 h. To convert Na-form zeolite to H-form ones, as-prepared seed-derived FER zeolites were stirred in 1 M NH₄NO₃ solution at 80 °C and washed with DIW for more than 6 times at the same temperature. The sample was further calcined at 550 °C for 3 h, and asprepared FER zeolites using different zeolite seeds were separately denoted as FER@FER, MOR@FER, ZSM-5@FER and USY@FER with respect to the different types of zeolite seeds. The weight ratio of the various zeolite seed material was fixed to 24 wt% based on total weight of the final as-prepared FER zeolites.

Catalytic activity measurements for a gas-phase carbonylation of DME to MA on the seedderived FER zeolites using various zeolite seeds were performed in a fixed bed tubular reactor having an inner diameter of 9 mm. For the activity measurement, the catalyst of 0.4 g was previously loaded into the reactor and it was pretreated at 500 °C under N₂ environment to remove any physisorbed contaminants. The gas-phase carbonylation reaction was carried out at T = 220 °C, P = 1.0 MPa, and space velocity (SV) of 2000 L/(kg_{cat}·h) for a reaction

time of 100 h using mixed gas reactants of DME/CO/N₂(mol%) = 5/45/50, where N₂ used as an internal standard gas at a higher N₂ concentration for a les coke deposition. 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. Conversion of DME and selectivity of MA with other byproducts were carefully calculated based on total carbonbalance due to an insignificant coke formation on the used catalysts for a long reaction duration of 100 h. The production rate (space time yield, STY) of MA was calculated using an averaged mole of MA produced [mmol/(g_{cat}·h)] at the reaction duration of 80 - 100 h, and turn-over frequency (TOF, s⁻¹) was defined as the MA produced at an initial reaction duration per Brønsted acid site and second [mmol/(mmol(B sites)·s)]. The deactivation rate (R_D, %/h) of the seed-derived FER zeolites was also calculated by the equation of [(maximum conversion of DME – conversion of DME at 100 h)/(reaction duration), which was further normalized using total Brønsted acid sites as well.

2.2. Characterization of the FER prepared by using various zeolite seeds

Wide-angle powder X-ray diffraction (XRD) patterns of the fresh seed-derived FER zeolites were obtained using a Bruker X-ray diffractometer (D8 Advance) with a Cu K_{α} radiation of 0.15406 nm at a scanning rate of 4°/min operated at 40 kV and 100 mA. The characteristic diffraction peaks of zeolites were measured in the range of 2 θ = 5 - 50°. The relative crystallinity of the seed-derived FER zeolites with various zeolite seeds was calculated by comparing the integrated areas of most intense two diffraction peaks of 2 θ = 9.3 and 25.2°, which are the characteristic diffraction peaks of FER, by assuming 100% crystallinity of the most highly crystalline FER@FER. The Si/Al molar ratios and Na contents of the fresh seedderived FER zeolites prepared from various zeolites seeds were measured by X-ray

fluorescence (XRF) using a Bruker S4 instrument operating at 60 kV and 150 mA. N_2 adsorption-desorption analysis of the seed-derived FER zeolites with various zeolite seeds was carried out by using a Micromeritics instrument (Tristar II) to characterize specific surface area (Brunauer-Emmett-Teller (BET) method), pore volume (t-plot method) and median pore diameter (Barrett-Joyner-Halenda (BJH) method from desorption branch) at liquid nitrogen temperature of -196 °C.

To verify the surface morphologies and crystalline sizes of the seed-derived FER zeolites, Field-emission scanning electron microscopy (FESEM) analysis was carried out by a JEOL scanning electron microscopy (JSM-7500F) operated at 1.4 nm guaranteed at 1 kV and at 0.6 nm guaranteed at 30 kV. Before the image analysis, the sample was previously coated with a conductive platinum metal on a conductive carbon tape substrate. High-resolution transmission electron microscopy (HRTEM) analysis was performed by a JEOL transmission electron microscopy (JEM-2100F) operated at 200 kV on the selected fresh FER and FER@FER only. To elucidate the detailed fine structures of the seed-derived FER zeolites, Rietveld refinement analysis from XRD data and solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) analysis were further carried out on the fresh FER zeolites. ²⁷Al and ²⁹Si MAS NMR analysis on all the fresh seed-derived FER zeolites were performed by using a 500 MHz solid state NMR (a Varian Unity INOVA instrument) at a resonance frequency of 130.26 MHz using a 3.2 mm Chemagnetics MAS probe head at a spinning rate of 10 kHz with a reference material of $Al(NO_3)_2$ and a delay time (D1) of 1 s at a number of scans of 4000 and $\pi/2$ pulse of 1.0 µs. The Rietveld refinement analysis of the seed-derived FER zeolites from the XRD data was performed by using a GSAS package and EXPGUI as an interface with a starting model in P42 space group with the isotropical refinements of all atoms, and the refined XRD peak shapes were described with a pseudo-Voigt function.

Temperature programmed desorption of NH₃ (NH₃-TPD) analysis was performed using 30

mg powder of the fresh seed-derived FER zeolites at the temperature range of 100 - 700 °C after the sample pretreatment at 350 °C for 1 h under He flow using a BELCAT-M instrument equipped with a thermal conductivity detector (TCD). Fourier transformed infrared spectra of pyridine (Py-IR) analysis were carried out using 30 mg sample, which was previously treated at 500 °C for 1 h under a vacuum condition to remove any contaminants and water adsorbed on the surfaces of the thin FER pellet. The Py-IR spectra were obtained after the adsorption of pyridine molecules for 15 min on the sample using a Nicolet 6700 FT-IR spectrometer with 4 cm⁻¹ resolution using a MCT detector at a fixed temperature of 220 °C to maximize the pyridine adsorption capacity on the small pores¹⁶ of the seed-derived FER zeolites. The formed surface intermediates and adsorption strengths of DME reactant on the fresh seedderived FER zeolites prepared with different zeolite seeds were characterized by in-situ Fourier transform infrared (FT-IR) analysis under a flow of reactant of DME and CO at various temperatures. Prior to the analysis, the sample was pretreated at 500 $^{\circ}$ C for 1 h under a vacuum condition to remove any contaminants adsorbed. After the DME and CO reactants were flowed into the lab-made FT-IR cell for 20 min, the physisorbed DME and CO molecules were removed at a vacuum evacuation for 10 min. The FT-IR spectra of the adsorbed chemical species were obtained at each temperature stages from 180 to 260 °C at an ambient pressure with an interval of 20 °C using a Perkin Elmer Frontier FT-IR spectrometer equipped with 4 cm⁻¹ resolution using a MCT detector as well. In addition, the successive adsorption characteristics of DME followed by CO molecules at 220 °C using a same instrument were further verified to confirm the different CO insertion rates on the selected FER and FER@FER.

Temperature-programmed surface reaction with H_2 (TPSR) analysis was carried out at the temperature range of 100 - 700 °C using a BELCAT-M instrument to confirm the types of

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coke precursors on the used seed-derived FER zeolites after the reaction for 100 h. The methane (m/z = 15), which can be formed by hydrogenation of coke precursors during the TPSR, was monitored by using a quadruple mass spectrometer (MS Pfeiffer QMS 200). Before the TPSR analysis, all samples were pretreated at 250 °C for 1 h under a He flow to remove any physically adsorbed contaminants. Thermogravimetric analysis (TGA) of the used seed-derived FER zeolites was conducted by a TA Instrument (Q50) to quantitatively identify the amount of coke precursors formed during the DME carbonylation for 100 h. In addition, for the further analysis of chemical species of the deposited cokes, the used catalyst was completely dissolved in a hydrofluoric acid (HF) solution, and it was subsequently dissolved in a 4 ml of dichloromethane solvent to completely extract the deposited cokes from the dissolved zeolite components. After a complete layer separation of the above mixed solution, the dichloromethane including coke precursors formed during DME carbonylation reaction for 100 h was analyzed by using GC/MS (a YoungLin instrument 6500 GC with YL6900 GC/MS system) equipped with a HP-5 capillary column having a specification of 15 m length x 0.25 um inner diameter x 0.25 mm coating thickness.

3. Results and discussion

3.1. Physicochemical properties of the FER prepared by various zeolite seeds

The well-synthesized FER structures with their higher crystallinity on all the fresh seedderived FER zeolites prepared by various zeolite seeds such as a pristine FER, MOR, ZSM-5 and USY were supported from the observed characteristic XRD peaks of FER^{15,17,18} without showing any characteristic XRD patterns of each seed zeolites as shown in **Figure 1(A)**. A relative crystallinity calculated from the most intense peaks of $2\theta = 9.3$ and 25.2° by assuming 100 % crystallinity of the highly crystalline FER@FER was summarized in **Table 1**. Compared with the FER seed, a relative crystallinity of the FER@FER was slightly increased from 94.7 to 100 % even for much shorter synthesis duration for 4 days. However, the crystallinity of the FER synthesized using other zeolite seeds such as MOR, ZSM-5 and USY was found to be lower in the range of 76.8 - 83.7 %. These lower crystallinities, except for the FER@FER, seem to be attributed to different crystalline phases of each zeolite seeds and its surface acidity due to different Si/Al ratios, which seems to prevent an easy growth of the FER structures. The different crystallinity of the seed-derived FER zeolites can generate different amounts and types of acidic sites with various morphologies, which resulted in a different DME carbonylation activity. In general, the post-synthesis of the FER for making a micro-mesopore zeolite structure largely altered surface properties by changing the defect site densities originated from Al(OH)₃ species (mainly responsible for Lewis acid sites).¹⁹⁻²² In addition, the Na content in the fresh seed-derived FER zeolites were found to be less than 0.07wt% on all the seed-derived FER zeolites from XRF analysis as summarized in **Table 1**, and the Si/Al molar ratios on the seed-derived FER zeolites were found to be similar in the range of 10 - 12.5 even though the original seed zeolites have various Si/Al ratios in the range of 2.3 to 25 due to the excess amounts of the coated FER zeolites on the zeolite seeds. We believe that a higher crystallinity of the FER@FER compared with other zeolites can be attributed to the reduced amounts of defect sites by the recrystallization process of the defect sites with insignificant contributions of Na residue and Si/Al ratios on the seed-derived FER zeolites even though the catalytic activity on the virgin zeolite seeds themselves were largely affected by their Si/Al ratios (higher initial activity on the USY zeolite having a smaller Si/Al ratio of 2.3) as shown in supplementary Figure S3. In addition, a lower crystallinity on the seed-derived FER zeolites prepared by MOR, ZSM-5 and USY seed can be also induced from the shortened intra-particular domain lengths from the different morphologies of seed zeolites with locally formed amorphous phases.²³

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The surface acidity with its types on the fresh seed-derived FER zeolites was verified by NH_3 -TPD and Py-IR, and these results are displayed in Figure 1(B) and Figure 1(C). The desorption peaks of the adsorbed NH₃ molecules at ~ 200 and 450 °C as shown in Figure 1(B) can be assigned to weak and strong acid sites, which are similar with the typical desorption patterns of many zeolites. As summarized in **Table 1**, the amounts of weak acid sites (assigned to the peak below 300 °C from NH₃-TPD) were found to be in the range of 0.40 -0.66 mmol/g with a larger value on the FER@FER. However, the amounts of strong acid sites (assigned to the peak at $350 \sim 550$ °C from NH₃-TPD) were found to be in the wide range of 0.44 - 0.70 mmol/g with a maximum value on the FER@FER. Therefore, the total acid sites were maximized on the FER@FER with the value of 1.36 mmol/g, and the acid strengths were modified by its selective depositions on the seed zeolites. In general, too stronger acid sites on the zeolites can be responsible for a preferential deposition of coke precursors by a facile decomposition of DME to hydrocarbons.^{10,15,18} The hypothesis was supported by maximum temperature shifts of T_{max} on the various seed-derived FER zeolites as shown in Figure 1(B). Compared with the FER seed with $T_{max} = 204$ °C, the T_{max} was shifted to lower ones such as T_{max} = 200 °C on the FER@FER and MOR@FER, and 191 °C on the ZSM-5@FER and USY@FER. Therefore, the types of those acid sites were further measured by Py-IR analysis, and a relative concentration of Brønsted and Lewis acid sites was reevaluated using total acid sites measured by NH₃-TPD. As shown in Figure 1(C), FT-IR peaks of adsorbed pyridines at 220 °C were observed with the characteristic absorption peaks at 1542 cm⁻¹ for Brønsted acid sites (assigned to B) and at 1454 cm⁻¹ for Lewis acid sites (assigned to L) with the combined acid sites at around 1480 cm⁻¹.²⁴ On the seed-derived FER zeolites, Brønsted acid sites originated 8-MR channels of the FER structures are known to be the most active sites for DME carbonylation.^{9,25} Even though the larger size of pyridine molecules seems not to be effective to quantitatively measure the acidic sites of 8-MR

channels of the FER due to the spatial size restriction effect of pyridine,^{16(b)} they can be possibly adsorbed on all the Brønsted acid sites through an increased lattice flexibility as well as kinetic energy of the pyridine at higher temperatures above 200 °C.^{25(b)} As summarized in Table 1, the ratio of Brønsted to Lewis acid site (B/L) on the outer zeolite surfaces was Published on 14 May 2018. Downloaded by University of Cambridge on 26/05/2018 03:36:24. maximized on the FER@FER with that of 84.1, which means a larger amount of Brønsted acid sites with 1.34 mmol/g. A relatively smaller outer surface B/L ratio in the range of 10.5 -16.4 with smaller amount of Brønsted acid sites of 0.79 - 0.85 mmol/g were observed on the MOR@FER, ZSM-5@FER and USY@FER. These Brønsted acid sites were known to be active through an easy formation of surface acetyl intermediates (CH₃CO-).^{3,6,9,25} Therefore. the FER@FER having abundant Brønsted acid sites by a selective removal of defect sites with a higher crystallinity seems to be the best catalyst, which was also supported by TEM images in **Figure 2** by showing a higher crystallinity on the FER@FER than the FER seed.

As shown by SEM images in **Figure 2**, the surface morphologies of all the seed-derived FER zeolites clearly showed the characteristic plate-like crystals with an irregular sizes and shapes of the typical FER morphology. Although the characteristic XRD patterns of the zeolite seeds on the seed-derived FER zeolites were not clearly observed in **Figure 1(A)** due to the partial disintegrations of the intrinsic structures of seed zeolites possibly, the intrinsic morphologies of each seed zeolites were maintained with the present FER morphology mainly. Interestingly, the FER@FER showed much smaller grain sizes of FER crystallites with an average crystallite size of ~ 1 μ m compared to the FER seed. The MOR@FER, ZSM-5@FER and USY@FER showed their original characteristic morphology of each seed zeolites FER crystallites. These smaller crystallite sizes on the FER@FER were responsible for the newly formed mesopores with its high crystallinity, which is beneficial for a higher DME conversion through an easy mass transport. The specific surface area, average pore diameter above mesopore size and pore volume are

summarized in **Table 1**. All the seed-derived FER zeolites showed similar mesopore characters in the range of $249 - 282 \text{ m}^2/\text{g}$, $0.16 - 0.17 \text{ cm}^3/\text{g}$ and 5.6 - 8.5 nm, respectively. As shown in supplementary **Figure S1**, N₂ adsorption-desorption isotherms on all catalysts showed the characteristic type IV isotherms with similar hysteresis patterns. A little bit larger average pore size and smaller surface area on the FER@FER seem to be originated from the newly formed inter-particular mesopores between the smaller plate-like FER crystallites (SEM images in **Figure 2**).²¹⁻²³ Interestingly, the mesopores above 3 nm in size on the seed-derived FER zeolites were responsible for the larger mesopore surface areas in the range of $20.5 - 32.0 \text{ m}^2/\text{g}$ with the maximized area of $32.0 \text{ m}^2/\text{g}$ on the highly crystalline FER@FER due to its well-developed inter-particular mesopores. The smaller surface area of $261 \text{ m}^2/\text{g}$ and larger acidic sites of $1.36 \text{ mmol NH}_3/\text{g}$ on the FER@FER than the pristine FER with the respective values of $282 \text{ m}^2/\text{g}$ and $1.10 \text{ mmolNH}_3/\text{g}$ can be attributed to the abundant presence of the newly formed inter-particular mesopores with its higher crystallinity.

3.2. Catalytic activity and product distribution for DME carbonylation reaction

The production rate of MA and DME conversions with product distributions on the labmade seed-derived FER zeolites and commercial FER zeolite are summarized in **Table 1** and supplementary **Table S1**. The catalytic activity at the selected reaction temperature of 220 °C was compared, which showed an insignificant initial deactivation rate based on the activity of the commercial FER (CFER, Si/Al ratio of 10.4 as shown in **Table S1**). The space time yield (STY, mmol/g_{cat}·h) with time on stream (h) on the seed-derived FER zeolites are also displayed in **Figure 1(D)**. Even though all the seed-derived FER zeolites showed a slight deactivation at the present reaction conditions of T = 220 °C, P = 1.0 MPa, and space velocity (SV) of 2000 L/(kg_{cat}·h), a higher DME conversion was kept for a longer time on the highly crystalline FER@FER compared to other seed-derived FER zeolites. The calculated

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production rate (STY) of MA at a steady-state was found to be in the range of 0.82 - 2.94mmol/(gcat h) with the maximum value on the FER@FER and minimum one on the USY@FER, which was similar with the previous work.⁶ A much higher STY at around reaction durations of 80 - 100 h was found to be 2.94 mmol/(g_{cat}·h) (equal to DME conversion of 71.5 %) with the MA selectivity of 99.2 % on the FER@FER (higher MA yield of 70.9%), which was much higher than the FER seed itself with the STY of 1.99 mmol/(gcat h), which can be attributed to the newly formed inter-particular mesopore structures and larger Brønsted acid sites. The relatively lower STYs in the range of 0.82 -1.34 mmol/(gcat h) were observed on the MOR@FER, ZSM-5@FER and USY@FER, where those catalysts possessed a smaller amount of Brønsted acid sites with a lower crystallinity. On all the seed-derived FER zeolites, the byproducts such as methanol and hydrocarbons (mainly, CH₄) were found to be below 4 %, except for the ZSM-5@FER since it has been well known for the active catalyst for methanol to gasoline (MTG) process by carbon pool mechanisms by decomposition or hydrogenolysis reactions of methanol and DME.^{26,27} In addition, the initial TOF (s⁻¹) (calculated from the active sites on the fresh seed-derived FER zeolites) was also found to be a higher on the FER@FER with the value of 4.90 x 10^{-4} s⁻¹ compared to other seed-derived FER zeolites in the range of $0.87 - 2.56 \times 10^{-4} \text{ s}^{-1}$. The variations of DME conversion and product distributions with time on stream with small initial deactivation rate are displayed in supplementary Figure S2 and the product distributions were stabilized after 30 h on stream without any significant changes on all the seed-derived FER zeolites. The deactivation rate (%/h) per the unit Brønsted acid sites on the seed-derived FER zeolites was calculated and summarized in **Table 1**. Even at an initially higher STY on the FER@FER compared to other seed-derived FER zeolites, the deactivation rate was found to be 0.07 on the FER@FER, which revealed much smaller deactivation than that of the MOR@FER of 0.23 from the very beginning of the reaction. Therefore, the types

of zeolite seeds revealed a significantly different surface properties and catalytic activity according to the crystallinity and density of Brønsted acid sites. These surface properties on the seed-derived FER zeolites synthesized with various zeolite seeds largely altered the deactivation mechanisms and adsorption properties as well. In addition, this coating procedure using the FER seed by recrystallization step of defect sites can significantly enhance the STY of MA with its selectivity without any significant byproduct formations rather than other zeolite seeds themselves such as MOR, ZSM-5 and USY as shown in supplementary Figure S3. All commercially available zeolites such as the MOR, ZSM-5 and USY themselves except for the lab-made FER seed without coating processes showed a fast deactivation with a lower MA selectivity with time on stream (supplementary Figure S3), which also revealed less significant contributions of the zeolite seeds themselves for altering the catalytic activity and stability by their physical mixing effects with the pristine FER. These modified zeolite surfaces by decorating with the FER structures, especially on the FER@FER can enhance the catalytic performances significantly by adjusting the surface properties. Therefore, we carried out the precise surface characterizations by using FT-IR and TPSR analysis and the fine structural analysis using XRD and solid-state NMR, which are to elucidate the behaviors of coke depositions and adsorption characteristics of DME as well as to verify the origins of Brønsted acid sites.

3.3. Adsorption properties of DME and CO with coke analysis on the synthesized FER

The adsorbed surface intermediates from DME/CO reactants were verified by using in-situ FT-IR analysis at adsorption temperature ranges of 180 - 260 °C. The FT-IR spectra in the wavenumber ranges of 2800 – 3100 for the adsorbed DME intermediates are displayed in **Figure 3** and supplementary **Figure S4** for one selected temperature at 200 °C. On the various types of Brønsted acid sites such as SiOH, AlOH and SiOHAl surface groups on the

zeolites, the absorption bands appeared at 3007, 2968, 2949 and 2840 cm⁻¹ can be possibly assigned to the hydrogen bonded DME on these Brønsted acid sites without showing any CO adsorption peaks. The absorption bands at 2968 and 2864 cm⁻¹ observed at a higher temperature above 220 °C can be possibly assigned to asymmetric and symmetric stretching vibration modes of the dissociatively adsorbed methyl (CH₃-) groups from the adsorbed DME.^{6,9,28-34} which can be fast reacted with CO molecules to selectively generate acetyl intermediate. In addition, the absorption bands appeared at 2949 and 2864 cm⁻¹ were attributed to the hydrogen-bonded DME on the defected surface sites such as SiOH and AlOH, respectively,³¹ which were found to be much larger intensity compared with that at 2968 cm⁻¹ on the lower crystalline zeolites such as the ZSM-5@FER and USY@FER rather than the highly crystalline pristine FER and FER@FER. Interestingly, the relatively smaller intensities of these peaks on the MOR@FER seem to be originated from a fast deactivation at the very beginning of reaction as shown in **Figure 1(D)** as well. In addition, the much weaker absorption band intensity of 2855 cm⁻¹ on the FER@FER in all temperature ranges compared with other seed-derived FER zeolites was mainly attributed to its higher crystallinity, which can be assigned to methyl groups adsorbed on the external silanol groups existing in the form of SiOCH₃.³² Therefore, the stable formations of hydrogen-bonded DME and methyl intermediates on the highly crystalline Brønsted acidic sites (SiOHAl) can enhance an easy insertion of CO molecules into the surface methyl groups to form surface acetyl groups selectively. Generally, the CO insertion step has been known to be kinetically controlled and possible rate determining step for DME carbonylation to MA.^{6,9,28,29} Furthermore, the extra framework Al species (EFAL) can act as Lewis acid sites,^{35,36} which can preferentially form the byproducts such as hydrocarbons through methanol-to-olefin reaction mechanisms by the well-known decomposition reaction of methanol and DME.^{27,37} Therefore, the highly crystalline FER@FER having larger amount of Brønsted acid sites instead of less active

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Lewis acid sites (defect EFAL sits) seems to be responsible for a higher STY and MA selectivity due to its optimal bond strengths of the adsorbed methyl intermediates appeared at 2968 cm⁻¹ for further fast CO insertion reaction. The observed lower activity on the less crystalline zeolites such as the MOR@FER, ZSM-5@FER and USY@FER, which revealed much larger absorption peak intensities at the absorption bands at 2949 and 2855 cm⁻¹ (strongly interacted methyl groups on the defect sites) can be explained by a relatively slow CO insertion rate to form acetyl groups due to too stronger adsorption characters of the methyl intermediates on the defect sites. These hypotheses were further supported by the characteristic absorption peaks of water molecules formed by methanol dehydration or hydrocarbon formation reactions during DME activation step on the Brønsted acid sites as shown in supplementary Figure S5 and Figure S6. The water absorption bands assigned to the separate peaks at 1640 and 3610 cm⁻¹ on the Brønsted acid sites originated from the 8 and 12-MR channels were found to be much smaller on the most active FER@FER and their intensities were decreased with an increase of adsorption temperatures due to the selective absorption natures of hydrogen-bonded DME molecules on those active Brønsted acidic O-H groups assigned to the acidic sites of the 8 and 12-MR channels^{6,9,29,38,39} or possible significant coke deposition such as polymerized alkenes³⁸ on the fast deactivated MOR@FER. Even though the characteristic absorption bands of C=O in acetyl groups at 1704 cm⁻¹ was not clearly observed due to a lower experimental pressure condition (0.1 MPa),^{6,9,29,39} the absorption bands appeared at 3660 cm⁻¹ and that at 1680 cm⁻¹, which can be respectively assigned to the defect sites of the EFAL²⁹ and C=O absorption band in aldehyde groups, was found to be larger on the less crystalline seed-derived zeolites, especially on the ZSM-5@FER and USY@FER. Therefore, we believe that the water formed by methanol dehydration reaction to DME or hydrocarbons⁹ on the Brønsted acid sites can be competitively adsorbed on the same acid sites,⁴⁰ which can prevent an easy DME activation

as well as CO insertion reaction to form acetyl groups. These competitive adsorptions of water molecules on the zeolite surfaces can largely alter the activity of methanol dehydration to DME, where the reaction was well correlated with the surface weak acid sites in two separate regions on the solid acid heterogeneous catalysts^{10,40} as shown in supplementary **Figure S7**.

In terms of the catalyst deactivation, the polyaromatic hydrocarbons have been considered as the inactive coke precursors to irreversibly deactivate solid-acid heterogeneous catalysts by being formed inside channels or external surfaces of zeolites.⁴¹ As shown in Figure 4(A) and Table 1, the weight loss (Wloss, %) measured by TGA can be correlated with deactivation rates since it was related with the total amounts of fully dehydrogenated graphitic or amorphous carbons.⁴² The deposited amount of coke precursors corresponding to the weight loss above ~ 400 °C, which can be possibly originated from the decomposition of DME through carbon pool mechanisms of methanol to gasoline process on the defect sites of the seed-derived FER zeolites, was found to be in the following orders of MOR@FER > ZSM- $5@FER \approx USY@FER > FER >> FER@FER$ with their respective values of 6.3, 5.4, 5.3, 4.7 and 3.6 % with the similar thermostability of the seed-derived FER zeolites. The more detailed analysis of the types of coke precursors was carried out by TPSR and GC/MS experiments, and the results are displayed in Figure 4(B) and Figure 4(C). The coke precursors deposited on the used zeolites can be categorized as the characteristic hydrogenation peaks with α , β , and γ coke precursors, which can be assigned to the TPSR peaks at ~ 350, 450, and 550 °C, respectively. The α -form coke precursor can be originated from the hydrogenation of dehydrogenated surface carbidic carbons, the β-form coke for amorphous hydrocarbons, and γ -form coke for inactive surface carbons, which can be removed hardly due to its natures of heavy cyclic polyaromatic hydrocarbons.⁴³ The relative peak intensities on the used seed-derived FER zeolites revealed the smallest intensity on the

FER@FER, and the extent of coke depositions follows the orders of MOR@FER \approx ZSM-5@FER > USY@FER > FER >> FER@FER. Interestingly, the peaks of the much harder coke precursors (assigned to γ -form) were found to be larger on the less active ZSM-5@FER and USY@FER. These deposited coke precursors were found to be the well-known aromatic heavy hydrocarbon species such as the tetramethyl benzene and tirmethyl benzene as characterized by GC/MS analysis as shown in **Figure 4(C)**, which were found to be more dominant on the MOR@FER showing a faster initial deactivation nature. Therefore, a facile coke deposition and lower catalytic activity with fast deactivation seems to be mainly attributed to the lower crystallinity and unstable Brønsted acid site (originated from defected Al sites) by selectively forming dehydrogenated heavy coke precursors instead of active acetyl intermediates.^{3,6,9,25,44}

3.4. Analyses of fine structures of FER zeolites and proposed reaction mechanisms

The more detailed analyses of crystalline structures were carried out by Rietveld refinement techniques^{45,46} from XRD data of the fresh seed-derived FER zeolites prepared by using various zeolite seeds. The distributions of tetrahedral sites (T sites) and their bond valences (BVs) with its bond energies were calculated, and the final results are displayed in **Figure 5(A)** and supplementary **Figure S8** with the summarized bone valences of T2 sites in **Table 1**. The more detailed results of BVs and crystallographic parameters are also summarized in **Table S2** and **Table S3**. The crystallographic parameters were found to be similar on all the fresh seed-derived FER zeolites with a space group of Immm, where they revealed the values of a = 1.88 nm, b = 1.41 nm and c = 0.74 nm with an acceptable R values below 10 $\%^{47,48}$ as summarized in supplementary **Table S2**. Although the similar BVs of T1, T3 and T4 sites were observed on all the seed-derived FER zeolites, the smaller BVs of T2 sites with the value of 3.76 was clearly observed on the FER@FER compared with other FER zeolites as

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summarized in supplementary **Table S3** and **Table 1**. This observation strongly suggests the stable presence of T2 sites in the 8 and 10-MR channels on the FER@FER, which are in line the observations of the previous work due to their hard removal characteristics from the framework tetrahedral Al species,⁴⁷ which was schematically summarized in Figure 5(A). In general, the number of Brønsted acid sites in the 8-MR channels of the FER has been reported to relate with DME carbonylation activity by easily generating the surface acetyl (CH₃CO-) intermediates via a facile insertion of the CO molecules.^{3,6,9} Therefore, the most stable T2 sites assigned to Brønsted acid sites of the Al-O-Si main frameworks^{6,9,28-34} on the FER@FER seem to be responsible for an increased activity and stability compared with other seed-derived FER zeolites. In addition, solid-state MAS NMR analysis of ²⁷Al and ²⁹Si on the fresh seed-derived FER zeolites was further performed to verify the structural characteristics and its environments. As shown in Figure 5(B), the ²⁷Al NMR peaks showed the characteristic chemical shifts of aluminum such as at ~ 54 ppm associated with the tetrahedral (4-coordinated) Al atoms (Al(OSi)₄) in the main framework of the FER and at ~ 0 ppm associated with the octahedral (6-coordinated) Al atoms, which is known as the extraframework Al species (EFAL) as possible defect sites. A shoulder peak at ~ 37 ppm indicates the penta-coordinated Al atoms or distorted tetrahedral EFAL species as well.⁴⁹⁻⁵¹ On the FER@FER having a highly crystalline structure with larger Brønsted acid sites at the stable T2 sites, the peak intensity of Al(OSi)₄ appeared at \sim 54 ppm was noticeably larger than other FER zeolites due to the stochastically abundant presences of the stable T2 sites with less defect sites in the 8 and 10-MR channels on the FER@FER. The ²⁹Si solid-state MAS NMR spectra on the seed-derived FER zeolites are also displayed in Figure 5(B) (supplementary Figure S9 for all synthesized FER zeolites) with the characteristic peaks at the chemical shifts of silicon of -99, -105, -111 and -115 ppm with a broad peak centered at -110 ppm. The peaks appeared at -99 and -105 ppm can be respectively related to the Si atoms bonded to two

Al atoms (Si(2AI)) or one Al atom (Si(1AI)) with a smaller peak intensity of Si(2AI), and the peaks at -111 and -115 ppm can be attributed to the Si atoms without any vicinal Al atoms (Si(0Al)) with the silanol groups (SiOH) on the FER surfaces appeared at -99 ppm.⁵²⁻⁵⁴ The chemical shift at -105 ppm assigned to the Si(1Al) was decreased on the FER@FER with a concomitant increase of the peak intensity at - 111 ppm compared to those of the FER. This observation can be possibly originated from the well-developed T2 sites with the homogeneous distribution of Al atoms on the FER@FER framework by preferentially forming the stable Al-O-Si-O-Al structures.⁵⁴ In addition, the smaller presence of the stable Si(0Al) sites seems to be related with the catalytic stability by showing a much fast deactivation on the MOR@FER having the smallest value (76 %) of (Si(0Al)) and largest amount of SiOH nest groups (7 %) as shown in supplementary Figure S9. It also suggests that the highly crystalline FER@FER has much smaller defect sites with the abundant presence of T2 sites assigned to Brønsted acid sites in the 8 and 10-MR channels of the FER structures compared to other seed-derived FER zeolites, which is responsible for its higher intrinsic catalytic performance since the activities were measured under the conditions of insignificant mass transfer limitations (more detailed calculations of those mass and heat transport limitations are further included in supplementary material) as well as far below the equilibrium conversion⁵⁵ as shown in Figure S10.

Finally, as shown in **Figure 5(C)** (scheme S1), the initial step of DME adsorption on the Brønsted acid sites of the seed-derived FER zeolites can easily occur to form surface methyl groups with a concomitant formation of methanol intermediate. However, the rate determining step of acetyl group formation by CO insertion reaction can be largely altered by the crystallinity (stable T2 sites) of the seed-derived FER zeolites by competing with its water adsorption natures formed by methanol dehydration to DME or hydrocarbons.⁹ Since the higher crystallinity of the FER@FER with less amounts of defect sites, which can be

originated from the isolated SiOH or AlOH groups or EFAL sites, can possibly generate larger amounts of the active Brønsted acid sites assigned to the stable T2 sites in the 8 and 10-MR channels of the FER@FER through their facile recrystallizations during the seedoriented preparation step. In addition, these stable Brønsted acid sites can enhance the formation rate of acetyl intermediates through a fast rate of CO insertion to the stable methyl surface groups. The fast CO insertion rate on the highly crystalline FER@FER having a larger amount of Brønsted acid sites instead of the pristine FER was further confirmed by comparing the variation of FT-IR peak intensity of the adsorbed methyl intermediates appeared at 2968 cm⁻¹ to the strongly interacted methyl groups on the defect sites for the band at 2949 cm⁻¹ (I₂₉₆₈/I₂₉₄₉) by a successive adsorption of DME followed by CO reactant as shown in supplementary Figure S11. As summarized in Figure 5(D), the observed much larger ratios of the integrated FT-IR peak area (I_{2968}/I_{2949}) on the FER@FER compared to pristine FER strongly revealed the more facile CO insertion on the highly crystalline active Brønsted acid sites assigned to the stable T2 sites in the 8 and 10-MR channels of FER structures. Finally, the formation MA can be finished by reacting with DME to regenerate the surface methyl groups as well as schematically summarized in Figure 5(C). Much strongly interacted methyl groups assigned to the absorption peaks at 2949 and 2855 cm⁻¹ in the FT-IR can be responsible for a coke and undesired byproduct formation, which can irreversibly deactivate the seed-derived FER zeolites such as ZSM-5@FER, USY@FER and MOR@FER. The possible rate determining step of acetyl formation by CO insertion step can be significantly increased on the highly crystalline FER@FER having a large amount of Brønsted acid sites (T2 sites) with fewer amounts of defect sites such as the EFAL. The newly formed large mesopore structures on the FER@FER with its higher crystallinity having a nature of Brønsted acidity can also suppress the formations of inactive heavy coke

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precursors irreversibly, and the crystallinity of the FER zeolite can be easily adjusted by using the previously synthesize FER seed even with a shorter zeolite synthesis duration.

4. Conclusions

The seed-derived FER zeolites with its Si/Al molar ratios of 10.0 - 12.5 prepared by simply using the various zeolite seed materials such as FER, MOR, ZSM-5 and USY were investigated for a gas-phase carbonylation of DME to MA to verify the effects of the crystallinity of the seed-derived FER zeolites with the number of active Brønsted acid sites. The largely enhanced crystallinity of the FER@FER through its possible recrystallization was mainly responsible for an increased amount of Brønsted acid sites assigned to stable T2 sites in the 8 and 10-MR channels of the FER@FER, which also showed higher STY and TOF of MA production with a higher selectivity above 99 %. The highly crystalline FER@FER revealed a lower deactivation rate due to the suppressed depositions of heavy aromatic coke precursors as well. The decreased amounts of defect sites assigned to an extra-framework Al species were observed on the highly crystalline FER@FER by the facile recrystallization natures compared with other seed-derived FER zeolites prepared from other zeolite seeds. The active Brønsted acid sites assigned to the stable T2 sites on the FER@FER effectively played as the important active sites for a selective formation of hydrogen-bonded DME intermediates by overcoming a competitive absorption of the water generated from dehydration of methanol on the Brønsted acid sites. These preferential formations of active Brønsted acidic sites were responsible for an enhanced activity of DME carbonylation with less coke depositions by easy transformations of the dissociatively adsorbed DME molecules to active acetyl adsorbates due to a relatively faster CO insertion rate on the vicinal Brønsted acid sites on the highly crystalline FER@FER.

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Supplementary Information

Additional information such as pore size distribution from N₂ sorption isotherms, FT-IR of the adsorbed intermediates, detailed catalytic activities including DME conversion with MA selectivity with time on stream (h), original XRD data for Rietveld refinement analysis and ²⁷Al and ²⁹Si NMR spectra on all the seed-derived FER zeolites are also included in supplementary material.

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Figure Captions

Figure 1. Bulk and surface properties and catalytic activity of the seed-derived FER zeolites synthesized by using various zeolite seeds; (A) XRD patterns, (B) NH₃-TPD profiles, (C) Py-IR spectra and (D) Space time yield (STY, mmol/(g_{cat} ·h)) with time on stream (h) at T = 220 °C, P = 1.0 MPa, and space velocity (SV) of 2000 L/(kg_{cat}·h) using a mixed gas reactant of DME/CO/N₂(mol%) = 5/45/50

Figure 2. SEM images of the seed-derived FER zeolites synthesized by using various zeolite seeds such as the FER, MOR, ZSM-5 and USY and TEM images of the fresh FER and FER@FER (upper middle figures)

Figure 3. FT-IR spectra of the adsorbed DME in the range of $2800 - 3100 \text{ cm}^{-1}$ at different temperatures on the fresh seed-derived FER zeolites synthesized from various zeolite seeds with the analyzing temperature profiles

Figure 4. Characterization of the seed-derived FER zeolites synthesized from various zeolite seeds; (A) TGA patterns, (B) TPSR patterns by measuring the methane formed (m/z = 15), and (C) Coke analysis by GC/MS

Figure 5. (A) Tetrahedral sites at 8 and 10-MR channels on the seed-derived FER zeolites analyzed by Rietveld refinement analysis from XRD data, (B) NMR spectra of the selected fresh FER and FER@FER with ²⁷Al MAS NMR spectra and ²⁹Si MAS NMR spectra, (C) Proposed reaction mechanisms on the highly crystalline FER@FER, and (D) variations of characteristic FT-IR peaks of the adsorbed methyl intermediates at 2968 cm⁻¹ to the strongly interacted methyl groups on the defect sites assigned to the band at 2949 cm⁻¹ (denoted as I_{2968}/I_{2949}) by a successive adsorption of DME followed by CO reactant for 10 minutes

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Notation	Seed zeolite	XRF	XRD (%) ^a	N_2 sorption ^b	NH ₃ -TPD (acid sites, mmolNH ₃ /g) ^c		Py-IR (acid sites, mmolNH ₃ /g) ^d			TGA (%) ^e	Activity (mol%) ^f		
		Si/Al ratio	D _{cryst} / T2(BV)	Sg (meso) / Pv / Dp	$\mathbf{S}_{\mathbf{W}}$ / $\mathbf{S}_{\mathbf{S}}$ / $\mathbf{S}_{\mathbf{T}}$	T _{max} (°C)	B/L ratio	В	L	W _{loss}	Rate (STY / TOF x 10^4)	Sel (MA)	R _D
FER	None	10.0	94.7/3.91	282 (23.4) / 0.17 / 5.8	0.58 / 0.52 / 1.10	204	40.5	1.07	0.03	4.7	1.99 / 1.88	95.4	0.12
FER@FER	FER	11.0	100/3.76	261 (32.0) / 0.17 / 8.5	0.66 / 0.70 /1.36	200	84.1	1.34	0.02	3.6	2.94 / 4.90	99.2	0.07
MOR@FER	MOR	10.4	83.7/3.86	274 (23.2) / 0.16 / 5.6	0.40 / 0.44 / 0.84	200	16.4	0.79	0.05	6.3	1.34 / 2.56	95.2	0.23
ZSM-5@FER	ZSM-5	12.5	76.8/3.81	279 (27.8) / 0.17 / 5.8	0.47 / 0.46 / 0.93	191	11.7	0.85	0.08	5.4	0.82 / 0.87	89.7	0.14
USY@FER	USY	12.4	80.3/3.98	249 (20.5) / 0.16 / 7.9	0.48 / 0.44 / 0.91	191	10.5	0.82	0.09	5.3	1.00 / 1.01	94.2	0.13

Table 1. Bulk and surface properties of the seed-derived FER zeolites synthesized by using various zeolite seeds with their catalytic activity

^aThe relative crystallinity (D_{cryst}) of the FER using various zeolite seeds (Ferrierite(FER), Modernite(MOR), ZSM-5 and USY) was calculated by comparing the integrated areas of the most intense two diffraction peaks of $2\theta = 9.3$ and 25.2° , which are the characteristic diffraction peaks of FER, by assuming 100% crystallinity of the most highly crystalline FER@FER. The bond valences (BV) of the T2 sites on the fresh FER-based zeolites were calculated by the Rietveld refinement analysis of the XRD data.

^bThe abbreviations of Sg represent the specific surface area (m^2/g) with that of mesopore (meso), Pv for pore volume (cm^3/g) , and Dp for average pore diameter (nm).

^cThe acid sites were denoted as the S_w (weak acid sites assigned to NH₃-TPD peak below 300 °C), S_S (strong acid sites assigned to NH₃-TPD peak below 300 – 450 °C) and S_T for total acid sites, and the T_{max} represents the maximum desorption peaks of NH₃.

^dThe relative surface acid sites such as Brønsted (B) and Lewis (L) acid sites from Pyridine IR (Py-IR) analysis were calculated by using the total acid sites from NH_3 -TPD analysis with the ratios of B/L from Py-IR with the assumption of pyridine molecules being accessible to the small pores of the seed-derived FER zeolites.

^eThe weight loss (W_{loss}) from TGA analysis of the used catalysts denotes the weight decreases from ~400 to 700 °C, which can be assumed as the weight loss from the deposited coke combustion possibly.

^fThe production rate (space time yield, STY) of MA was defined as the averaged mole of MA produced at the reaction duration of 80 - 100 h $[mmol/(g_{cat}\cdot h)]$, and the Sel(MA) represents the selectivity of methyl acetate (MA). The turn-over frequency (TOF, s⁻¹) was defined as the MA produced at an initial reaction duration per Brønsted acid site (mmol) and second $[mmol/(mmol(B \text{ sites}) \cdot s)]$. The deactivation rate (R_D, %/h) of the various zeolites coated with FER was calculated by using the equation of [(maximum conversion of DME – conversion of DME at 100 h)/(reaction duration), which was further normalized using total Brønsted acid sites on the fresh seed-derived FER zeolites.

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Figure 1. Bulk and surface properties and catalytic activity of the seed-derived FER zeolites synthesized by using various zeolite seeds; (A) XRD patterns, (B) NH₃-TPD profiles, (C) Py-IR spectra, and (D) Space time yield (STY, mmol/(g_{cat} ·h)) with time on stream (h) at T = 220 °C, P = 1.0 MPa and space velocity (SV) of 2000 L/(kg_{cat}·h) using a mixed gas reactant of DME/CO/N₂(mol%) = 5/45/50

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Figure 2. SEM images of the seed-derived FER zeolites synthesized by using various zeolite seeds such as the FER, MOR, ZSM-5 and USY and TEM images of the fresh FER and FER@FER (upper middle figures)



Figure 3. FT-IR spectra of the adsorbed DME in the range of 2800 – 3100 cm⁻¹ at different temperatures on the fresh seed-derived FER zeolites synthesized from various zeolite seeds with the analyzing temperature profiles



Figure 4. Characterization of the seed-derived FER zeolites synthesized from various zeolite seeds; (A) TGA patterns, (B) TPSR patterns by measuring the methane formed (m/z = 15) and (C) Coke analysis by GC/MS



Figure 5. (A) Tetrahedral sites at 8 and 10-MR channels on the seed-derived FER zeolites analyzed by Rietveld refinement analysis from XRD data, (B) NMR spectra of the selected fresh FER and FER@FER with ²⁷Al MAS NMR spectra and ²⁹Si MAS NMR spectra, (C) Proposed reaction mechanisms on the highly crystalline FER@FER, and (D) variations of characteristic FT-IR peaks of the adsorbed methyl intermediates at 2968 cm⁻¹ to the strongly interacted methyl groups on the defect sites assigned to the band at 2949 cm⁻¹ (denoted as I₂₉₆₈/I₂₉₄₉) by a successive adsorption of DME followed by CO reactant for 10 minutes

Dimethyl ether carbonylation to methyl acetate over highly crystalline zeolite-seed derived ferrierite

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