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Synthesis of mesoporous ZSM-5 zeolites and catalytic cracking of ethanol and oleic acid into light olefins

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Highlights

- Mesoporous ZSM-5 is synthesized by utilizing template.
- Light olefins are produced from catalytic cracking of ethanol and oleic acid over mesoporous ZSM-5.
- Mesoporous ZSM-5 shows better catalytic activity than traditional microporous ZSM-5.
- Mesoporous ZSM-5 shows better anti-coking ability than traditional ZSM-5.

Abstract: Conversion of biomass-derived chemicals into light olefins is a promising method to maintain sustainable development of light olefin industry. In this study, three mesoporous ZSM-5 zeolites (MZSM-5-A, MZSM-5-B and MZSM-5-C) with major pore diameter about 4.8 nm, 16 nm and 22 nm were synthesized using a hydrothermal method by utilizing different templates. The catalytic activity of catalysts was studied by catalytic cracking of ethanol and oleic acid. The influence of reaction temperature on conversion and product selectivity was investigated. The characterization of ZSM-5 samples showed that the orders of the external surface area and mesopore volume were MZSM-5-C > MZSM-5-B > MZSM-5-A > conventional HZSM-5. In ethanol to light olefin reaction, MZSM-5-C achieved the highest light olefin yield (318.3 mL \cdot g⁻¹) and ethylene selectivity (42.3%) at 400 °C. In oleic acid to light olefin reaction, MZSM-5-B achieved a complete conversion of oleic acid at 500 °C, and obtained the highest light olefin selectivity (38.1%) at 550 °C. The difference may be relevant to the size and chemical structure of feedstock molecular as well as the acidity of catalysts. Regardless of ethanol or oleic acid as feedstock, introduction of mesopore in zeolites significantly enhanced the light olefin yield and selectivity.

Keywords: mesoporous ZSM-5; ethanol; oleic acid; light olefins; catalytic cracking

1. Introduction

Light olefins, such as ethylene, propylene and butene, are an important raw material in petrochemical industry. At present, the main commercial techniques for producing light olefins are steam cracking (SC) or catalytic cracking of naphtha, light diesel oil and other petroleum products [1, 2]. With light olefins demand increasing and petroleum resources supply dwindling, exploiting new non-petroleum raw materials to produce light olefins has attracted significant research attention. Light olefins have been produced from catalytic cracking of biomass [3, 4], bio-methanol [5], bio-ethanol [6], fatty acids and triglycerides [7].

Catalytic cracking is an efficient way to produce light olefins from various resources. For catalytic cracking process, catalyst is a key factor affecting process efficiency and target product selectivity. Zeolite Y is the main component of typical FCC catalyst, but possesses low activity for production of light olefins. When zeolite ZSM-5 was mixed with zeolite Y, and used as catalyst for FCC of vacuum gasoil, more gasoline molecules were converted into light olefins [8]. Cracking of low value C4-C8 olefinic streams coming from steam cracking with ZSM-5-based catalysts showed that the propylene/ethylene (P/E) ratio in products was significantly improved [9, 10]. ZSM-5 was used in "Methanol to Olefins" (MTO) reaction, finding that ZSM-5 was stable and gave propylene as main product [11]. Butenes were produced by dehydro-isomerization of *n*-butane on Pt supported ZSM-5 (SiO₂/A1₂O₃=480), consequently butenes selectivity around 45% was obtained even at high conversion (80%) [12]. The outstanding catalytic activity and selectivity for light olefin production of ZSM-5 was attributed to the proper acidic property and pore structure dependent-shape selectivity. However, the relatively small size of the pore of ZSM-5 zeolite and

zeotype materials (maximum pore size is typically, 1.2 nm), may significantly limit the possibilities of upgrading of crude oil and transformations of numerous bulky compounds into fine chemicals [13, 14]. Recently, the synthesis of zeolites with new structures, in particular those with large channels where bigger molecules can diffuse into the zeolite crystallite, is an active field of research.

Early mesoporous materials such as MCM-41 and SBA-15 were synthesized using the organic-template-assisted approach, in which self-assembled molecular aggregates or supramolecular assemblies were used as structure-directing agents. These molecular sieves had well-defined pores up to about 30 nm in diameter [15, 16]. However, the disadvantages of these materials were low acidity (owing to the low concentration of aluminum) and insufficient thermal stability (due to the amorphous structure). This is unfavorable for cracking of bulky molecules at an elevated temperature. Afterwards, a number of researchers started work on preparation of micro/mesoporous composites to improve surface acidity and hydrothermally stability. In this case, ZSM-5/MCM-41, zeolite Y/MCM-41, zeolite Beta/MCM-48 and mesoporous ZSM-5 single crystals were prepared according to either recrystallization of amorphous pore walls in presence of structure-directing agent, or the use of zeolite seeds as framework-building units, which can self-organize in mesoporous matrices, or direct assembly of nano-clustered aluminosilicate precursors-zeolite seeds in crystalline zeolite structures, or utilization of small particle of organic or inorganic particles (carbon black) as substrate templates [16]. The resulting mesoporous zeolite-based materials exhibited larger pore volume, higher acidity and hydrothermal stability. In another research, mesoporous ZSM-5 was directly synthesized from the normal synthesis gel of ZSM-5 under microwave heating and addition of carbon particles as template [17]. Addition of 40 wt% of carbon led to the formation of mesoporous ZSM-5 (MW-40) with high external surface

area (383 m²/g) and mesoporous volume (0.82 cm³/g). The MW-40 exhibited eight times higher conversion than corresponding standard ZSM-5 without mesopores in the transformation reaction of 2',4'-dimethoxyacetophenone with 4-methoxybenzaldehyde into vesidryl. Besides, mesopores can be generated by steaming and acid treatment [18], alkali treatment [19] and heat treatment [20]. However, these methods trend to generate nonuniform mesopores, and the skeleton structure of the zeolites is frequently destroyed during treatment process.

Most of the synthetic porous zeolites were obtained via solvothermal synthesis by use of different reaction conditions, reactants, and structure-directing agents. Ahmadpour and Taghizadeh [21] prepared hierarchical porous ZSM-5 with different pore size by using different templates, e.g. tetrapropyl ammonium hydroxide (TPAOH), cetyltrimethyl ammonium bromide (CTAB) and dimethyl octadecyl [3-(trimethoxysilyl)propyl]ammonium chloride (TPOAC), demonstrating that, in comparison to conventional microporous ZSM-5, the hierarchical porous ZSM-5 with the secondary porosity centered at ~16 nm achieved a longer catalytic lifetime and a higher propylene selectivity in MTP reaction. Wen et al. [22] synthesized hierarchical porous ZSM-5 by using 3-triethoxysilypropylmercaptan (CPTES) as a template for catalytic conversion of chloromethane into light olefins. The obtained mesopore-abundant ZSM-5 improved light olefin selectivity by 24% and extended the catalytic lifetime by 4.5 times compared to the traditional ZSM-5. The above results indicate that the introduction of mesopores into ZSM-5 to some extent enhances catalytic activity and light olefin selectivity, especially when smaller molecules e.g. methanol and chloromethane are used as feedstocks. However, so far, a few of work has been done to clarify the effect of pore structure of catalysts on catalytic cracking of a long-chain large molecule reactant. In this work, three mesoporous ZSM-5 with different pore sizes were synthesized by using different templates. The obtained ZSM-5 samples were used to catalyze small molecule ethanol and

long-chain large molecule oleic acid (both are renewable resources) to produce light olefins. The effects of pore structure of zeolites and process conditions on conversion and light olefin selectivity were discussed.

2. Experimental

2.1. Materials

Colloidal silica (Ludox, 40%, Guangzhou Suize Co. Ltd), sodium aluminate (NaAlO₂, Al₂O₃ wt.% = 50%, Sinopharm Chemical Reagent Co. Ltd), sodium hydroxide (NaOH, 96%, Aladdin Reagents), ammonium nitrate (NH4NO3, analytical grade), tetrapropyl ammonium bromide (TPABr, 98%, Aladdin), tetrapropyl ammonium hydroxide (TPAOH, 25%, Aladdin), hexadecyl trimethyl ammonium bromide (CTAB. 99%. Aladdin). dimethyl octadecyl [3-(trimethoxysilyl)propyl]ammonium chloride (TPOAC, 65%, Macklin Chemical Reagent), and sulfuric acid (H₂SO₄, 98%) were used as received. H-type ZSM-5 zeolite (SiO₂/Al₂O₃=227) was supplied by Nankai University Catalyst Corporation (Tianjin, China) and activated at 110 °C for 6 h before use.

2.2. Preparation of catalysts

Three mesoporous ZSM-5 samples with different pore size were synthesized according to a hydrothermal method [23-25]. The final molar composition of three synthesis mixtures was 200SiO₂–1.0Al₂O₃–27.8NaOH–10TPABr–3.5TPOAC–14.5H₂SO₄–3000H₂O for MZSM-5-A, 200SiO₂–1.0Al₂O₃–27.8NaOH–5.0TPABr–10CTAB–14.5H₂SO₄–3000H₂O for MZSM-5-B, and 200SiO₂–1.0Al₂O₃–27.8NaOH–10TPAOH–10CTAB–14.5H₂SO₄–3000H₂O for MZSM-5-C. A typical synthesis process was as follows: first, a certain amounts of NaOH and NaAlO₂ were

dissolved in H₂O to form solution A. A certain amount of Ludox and templates were dispersed in H₂O to form solution B. Then, solution A was added into solution B drop by drop with agitation to form gel mixture. A certain amount of moderate concentrated H₂SO₄ was added to the mixture to adjust gel pH to 7, and continuously stirred for 4 h. Finally, the resultant gel was transferred into a stainless-steel Teflon-lined autoclave and crystallized at 180 °C for 48 h. The solid product was filtered, washed with distilled water until the pH of the filtrate was 7, and then dried at 105 °C overnight. The product was afterwards calcined at 550 °C for 6 h to remove the organic templates. The obtained sample was defined as Na-ZSM-5 zeolite. HZSM-5 zeolite was obtained by ion-exchanging Na-ZSM-5 zeolite three times with 1 M NH₄NO₃ solution (liquid/solid = 10/1 (g/g)) at 90 °C for 2 h. The solid sample was filtered, dried at 105 °C overnight, and calcined at 550 °C for 6 h. The HZSM-5 was tableted, granulated and sieved to obtain 20-30 mesh catalyst.

2.3. Characterizations of catalysts

The crystalline structure and pore structure of the synthesized ZSM-5 were determined by X-ray diffraction (XRD) and N₂ adsorption-desorption method, respectively. The acidic properties were analyzed by the temperature-programmed desorption of ammonia (NH₃-TPD) and infrared adsorption of pyridine (Py-IR). The detail about determination was revealed in previous study [26]. The analysis of Py-IR is as follows. Catalysts samples were activated at 500 °C under vacuum (10⁻³ Pa) for 1.5 h and cooled to room temperature in an IR cell prior to the adsorption of pyridine. Pyridine adsorption proceeded at ambient temperature for 30 min and followed by desorption at 150 °C or 300 °C for 20 min. After cooling to room temperature, IR spectra were collected using an FT-IR spectrometer (Thermo Nicolet380). The concentrations of Brønsted acid and Lewis acid sites were calculated from the integral intensities of individual adsorption bands at 1540 cm⁻¹

(Brønsted acid sites) and 1446 cm⁻¹ (Lewis acid sites) [27]. The actual SiO₂/Al₂O₃ molar ratio was determined by inductively coupled plasma optical emission spectroscopy (ICP–OES, Agilent 7700e).

2.4. Catalytic performance tests

Catalytic performance of catalysts was evaluated by catalytic cracking of ethanol and oleic acid in a fixed-bed quartz tube reactor (inner diameter: 20 mm; length: 380 mm). As a typical run, the catalyst (0.5 g) was loaded into reactor, and heated to a desired temperature in N₂ stream (the flow rate: 40 mL/min). The feedstock (0.87 g) was then injected into the reactor by a syringe pump. After flowing out from the reactor, the reaction products were cooled. Liquid products were weighed and analyzed by GC-MS (QP5000, Shimadzu, Japan) equipped with a DB-WAX fused silica capillary column (30 m ×0.25 mm × 0.25 µm). The gaseous product was collected with a gas collecting bag, and analyzed by GC referring to the method as described in our previous study [26].

The amount of coke deposition on the catalysts was calculated from weight loss during calcination of the used catalysts at 550 °C for 3 h. 0.5 g of the used catalysts were dispersed in 2 mL dichloromethane, and the dichloromethane-dissolved compounds (soluble coke) were analyzed by GC-MS. Temperature programmed oxidation (TPO) of carbon deposition was performed to determine the properties of coke [26].

The yields of total gas production (Y_{TGP}) and light olefins (Y_{LO}), the selectivity to light olefins (S_{LO}), feedstock conversion and coke yield (Y_{coke}) were calculated by the following equations, respectively:

$$Y_{\text{TGP}}\left(\text{mL/g}\right) = V_{\text{TGP}}/M_0 \tag{1}$$

$S_{\text{LO}}(\%) = x(C_2H_4) + x(C_3H_6) + x(C_4H_8)$	(2)
$Y_{\rm LO} (mL/g) = Y_{\rm TGP} \cdot S_{\rm LO}$	(3)
<i>Conversion</i> (%) = $[1 - (M_u/M_0)] \times 100\%$	(4)
Y_{coke} (%) = (M _{c0} – M _{c1})/M ₀ × 100%	(5)

where V_{TGP} is the total volume of gas product excluding N₂ (mL), M₀ is the mass of the feedstock, *x* is the molar percentage content of light olefins in the gas product (%), M_u is the mass of the unreacted feedstock, M_{c0} is the mass of the used catalysts before calcination (g), and M_{c1} is the mass of the used catalyst after calcination (g). The data of *Y*_{TGP}, *Y*_{LO}, *S*_{LO}, *Conversion* and *Y*_{coke} are the average value of three parallel experiments.

2.5. Stability experiments of catalysts

The stability of the catalysts was determined by ten continuous cracking-regeneration tests. The used catalyst was regenerated by calcination at 550 °C for 3 h in air atmosphere to remove the deposited coke.

3. Results and discussion

3.1. Characterization of the catalysts

The low-angle and the wide-angle XRD patterns of the catalyst samples are indicated in Fig. 1. The main peaks observed in the XRD patterns ($2\theta = 7.8$, 8.8, 23.2 and 23.8°) of all samples are assigned to the ZSM-5 orthorhombic structure [23]. The lattice parameters of the three ZSM-5 samples were calculated and depicted in Table 1, which were compared with that of conventional HZSM-5. The relative crystallinity (was calculated based on the sum of peak areas between $2\theta = 22.5-25^{\circ}$ from XRD pattern of ZSM-5 samples compared to that of conventional HZSM-5) is 85.8%

for MZSM-5-A, 71.1% for MZSM-5-B and 54.7% for MZSM-5-C. The decrease in crystallinity of the synthesized ZSM-5 is probably attributed to the weaker interaction between templates (TPOAC and CTAB) and aluminosilicate species, which leads to a more difficult deposition of aluminosilicate species on templates. Some amorphous species were likely formed during the hydrothermal crystallization process [28, 29]. The crystal sizes of zeolites were calculated with Scherrer Equation using XRD data. The crystal sizes of the synthesized ZSM-5 are 37~69 nm (shown in Table 1), which are larger than MFI nanozeolite as reported in Valtchev and Mintovas' research [30], but smaller than the referential conventional ZSM-5 (89 nm). The smaller crystal sizes are thought to be more favorable for shortening diffusion path and increasing diffusion rate of the reactants and products molecules.

The N₂ adsorption-desorption isotherms and the pore size distribution for each sample are illustrated in Fig. 2. As can be seen, the conventional HZSM-5 presents a typical I-type isotherm without any hysteresis loop even at a high relative pressure, indicating the existence of microporous structure [13, 24]. For the three synthesized ZSM-5, N₂ adsorption amounts increase significantly and an IV-type isotherm with a hysteresis loop at a high relative pressure (P/P₀=0.7-0.99) are observed. In particular, MZSM-5-B and MZSM-5-C show a larger hysteresis loop than MZSM-5-A, indicating that there are more mesoporous structure in MZSM-5-B and MZSM-5-C. Fig. 2(b) shows the pore size distributions of the four ZSM-5 obtained by using Barrett-Joyner-Halenda (BJH) method [31]. As can be seen, the pore size distribution broadens in this order: HZSM-5 < MZSM-5-A < MZSM-5-B < MZSM-5-C. The major pore diameter is 2.5 nm for HZSM-5, 4.8 nm for MZSM-5-A, 16 nm for MZSM-5-B, and 22 nm for MZSM-5-C. Table 2 summarizes the textural properties of all ZSM-5 samples. All ZSM-5 samples show a high specific surface area (> 400 m²·g⁻¹). Compared with HZSM-5, external surface areas (S_{ext}), total

pore volumes (V_{total}), mesopore volumes (V_{meso}), and average pore diameter (D_{aver}) of the synthesized ZSM-5 significantly increase, indicating that TPOAC and CTAB as templates substantially improve the mesopore formation in catalysts. We deduce that mesostructure could be generated by aggregation of the surfactant molecules, whereas the crystallization of microporous ZSM-5 is directed by quaternary ammonium groups within the mesoporous structure [29]. Mesoporous domain in fact plays an important role in scattering microporous zeolites and active sites. Although the S_{BET} and S_{ext} of the synthesized ZSM-5 in our work are lower than those of two-dimensional MCM-36 and ITQ-2, but are much higher than those of MCM-22P and MCM-56 MWW zeolites [32]. Furthermore, S_{ext} occupies >57% of total surface area of the fabricated ZSM-5 zeolites, thus, mesoporous structure in present study are expected to play an important role in contributing on catalytic activity and selectivity.

The NH₃-TPD profiles of the ZSM-5 samples are illustrated in Fig. 3 and Table 3. As can be seen, two obvious NH₃ desorption peaks appeared at 100–200 °C and 400 °C are observed for all ZSM-5 samples, which are ascribed to the desorption of NH₃ adsorbed on the weak acid sites and strong acid sites, respectively [33, 34]. All ZSM-5 samples exhibit a similar total acidity, indicating that the kinds of template and pore structure have little effect on the total acidity, and the acidity is mainly determined by the SiO₂/Al₂O₃ ratio.

Fig. 4 shows the Py-IR spectra of the ZSM-5 samples at different desorption temperature. As can be seen in Fig. 4(a), three characteristic bands at 1446 cm⁻¹, 1490 cm⁻¹ and 1540 cm⁻¹ of all samples are observed. The IR band at 1446 cm⁻¹ is attributed to Lewis (L) acid sites, mainly derives from Lewis aluminum, being an electron pair acceptor (binding pyridine in a coordination fashion). The IR band at 1540 cm⁻¹ can be ascribed to Brønsted (B) acid sites, mainly deriving from PyrH⁺ created by protonation. Infrared band appearing at 1490 cm⁻¹ is related to the vibration

of the pyridine ring on both B and L acid sites [24]. The concentrations of B and L acid sites determined based on the intensity of these bands are shown in Table 4. As can seen, the concentration of B acid sites is much lower than that of L acid sites for all samples, and with increasing the desorption temperature to 300 °C, the concentration of all acid sites substantially decrease (Fig. 4b). This indicates that the ZSM-5 samples prepared in present study are L acid-dominant materials, and among them, MZSM-5-B possesses more B acid sites.

3.2. Catalyst Performance

3.2.1 Conversion of ethanol into light olefins

In ethanol to light olefins (ETO) reaction, ethanol was catalytically cracked at 200–500 °C in N₂ stream over four ZSM-5 samples. Conversion and Y_{LO} are exhibited in Fig. 5. As can be seen in Fig. 5, at the lowest temperature, 200 °C, the conversions for four ZSM-5 samples are lower than 60%, but the Y_{LO} are less than 20 mL·g⁻¹. At the highest temperature, 500 °C, the conversions from the synthesized ZSM-5 are higher than 95%, but the conversion from conventional HZSM-5 reaches only 89%. Meanwhile, the conversion increases with the rise of the pore size of catalysts, and meets the maximum value over MZSM-5-C (99.4%) at 500 °C. As shown in Fig. 5(b), the Y_{LO} from different catalysts increase with raising reaction temperature until 300 °C, and maintain a constant value at a higher temperature. Sample MZSM-5-C gives the highest Y_{LO} (> 310 mL·g⁻¹) whereas the conventional HZSM-5 obtains the lowest value (about 262 mL·g⁻¹) at 300–500 °C. These results demonstrate that introduction of mesopore into zeolites significantly enhanced ethanol conversion and light olefin selectivity.

Fig. 6 shows the gaseous product selectivity from cracking of ethanol at different temperature over the synthesized ZSM-5 samples. As shown in Fig. 6(a), the selectivity to ethylene increases

with the rise of reaction temperature, and meets the maximum value (42.3%) over MZSM-5-C at 400 °C. It is worth noting that the propylene/ethylene mass ratios (P/E values) in products for all catalysts are less than 1.0, and dramatically decrease with increasing reaction temperature. This indicates that ethylene is the main light olefin product from cracking of ethanol at the tested temperature range. Meanwhile, as can be seen in Fig. 6(b), a little amount of C_1 - C_4 alkanes are formed, and the selectivity slightly increases with raising temperature. CO and CO₂ were not detected in this reaction likely due to the extremely low content. Some other gas components such as *n*-pentane, isobutylene and butadiene, were also probably produced but could not be identified with the present standard gas.

It is thought that ethanol conversion is controlled by a single-site surface reaction, and strongly depends on the diffusion of reagents and products in the catalyst particles [35]. MZSM-5-C contains larger mesopore structure (major pore diameter is 22 nm) than other synthesized ZSM-5. This provides an accessible tunnel for diffusion of feedstock and products molecular. The high S_{ext} of MZSM-5-C allows exposing more active sites and helping reactants better access to active sites [36]. Coke formation is restrained owing to the medium acidity of catalyst as well as the diminishing secondary reaction (due to the low diffusion resistance of product molecules). The suitable porous structure and acidic properties would account for the high catalytic activity of the synthesized MZSM-5-C in ETO reaction.

3.2.2. Conversion of oleic acid into light olefins

In oleic acid to light olefins (OATO) reaction, oleic acid was catalytically cracked at 380-600 °C in N₂ stream over the four ZSM-5 samples. Conversion and Y_{LO} are shown in Fig. 7. The rapid conversion of oleic acid occurs in two temperature ranges: $380 \sim 400$ °C and $450 \sim$

550 °C. At 380 ~ 400 °C, oleic acid rapidly evaporates, which is accompanied by the preliminary cracking, decarbonylation and decarboxylation reaction. At 450 ~ 550 °C, cracking and decarbonylation reactions of oleic acid amplify, evidenced by the release of a large of light olefins and CO (Fig. 8). At a high temperature e.g. > 500 °C, the conversions on different catalysts are all higher than 90%, indicating that a temperature higher than 500 °C is needed for effective cracking of oleic acid. MZSM-5-B achieves a complete conversion at a temperature from 500 to 600 °C, indicating the high activity of MZSM-5-B. Contrarily, the conversion over HZSM-5 reaches the maximum value (98%) at 550 °C, and then drops at a higher temperature. This may be attributed to the fact that the relative small pore size trends to cause fast deactivation of catalyst at a high temperature [37]. Among the four tested ZSM-5 samples, MZSM-5-B achieved the highest conversion and Y_{LO} (Fig. 7b), indicating that the porosity with main pore size about 16 nm would be the most suitable for mass transfer of oleic acid molecular and providing reaction sites.

The gaseous product distribution from cracking of oleic acid at different temperature over different ZSM-5 samples is presented in Fig. 8. For all ZSM-5 samples, S_{LO} increase significantly with raising reaction temperature, indicating that reaction temperature plays an important role to determine product yield and selectivity. At 550 °C, three mesoporous ZSM-5 samples give the maximum S_{LO} , and the S_{LO} for four ZSM-5 samples are in the order: MZSM-5-B (38.1%) > MZSM-5-A (36.7%) > MZSM-5-C (36.2%) > HZSM-5 (31.3%). Conversion, Y_{LO} and S_{LO} considered, MZSM-5-B is the best catalyst for cracking of oleic acid into light olefins. Besides, it is found that the P/E values are higher than 1.0, indicating that propylene is the main light olefin product, which is different from that of ETO reaction. The P/E values decrease dramatically with increasing reaction temperature, indicating that secondary decomposition of C_3H_6 could occur, consequently leading to the formation of more C_2H_4 [38, 39].

3.2.3. Coke analysis

After cracking reaction, the used catalysts were collected, and calcined at 550 °C. The amount of coke deposited on the catalysts was calculated from weight loss of the catalysts during calcination. The results are shown in Table 5. As can be seen, for both ETO and OATO reactions, the coke yields on the three synthesized ZSM-5 are lower than conventional HZSM-5, indicating that the anti-coking ability of catalysts was markedly improved by introduction of mesopores into zeolites [21, 40]. The TPO profiles of the used HZSM-5, MZSM-5-C and MZSM-5-B, collected from cracking ethanol and oleic acid are shown in Fig. 9. As seen in Fig. 9(a), in comparison to HZSM-5, MZSM-5-C releases less CO and CO₂ (as evidenced by the weaker peaks), indicating less coke deposited on MZSM-5-C. In the case of cracking of oleic acid (in Fig. 9b), the total peak area of CO and CO₂ from MZSM-5-B is much less than that from HZSM-5, indicating less coke deposited on MZSM-5-B. The temperature corresponding to peak height (Tp) on TPO curve of HZSM-5 is 545 °C, which is little lower than Tp on MZSM-5-B (560 °C). This indicates that more thermo-oxidative-sensitive light compounds were deposited on HZSM-5. It is worth noting that the CO peak on the TPO curve of HZSM-5 is much stronger than that of CO₂, suggesting that the small pore in traditional ZSM-5 could affect the diffusion of O₂, consequently leading to incomplete oxidation of coke. In addition, the catalysts derived from cracking of oleic acid produce a much stronger oxidation peaks than that from ethanol, indicating that more coke was formed on catalysts when large molecule oleic acid was used as feedstock. The results are also coincident with the analysis on Y_{coke} as shown in Table 5.

The dissoluble components of coke from cracking of ethanol and oleic acid at 500 °C are presented in Table 6. As can be seen, ethanol-derived coke mainly consists of hydrocarbons, while the composition of oleic acid-derived coke is complicated, including hydrocarbons, aromatics,

esters and ketones. It is also found that some heavier coke compounds are easily formed when oleic acid is used as feedstock compared to ethanol.

3.2.4. Liquid product analysis and cracking reaction mechanism

The liquid products from cracking of ethanol at 500 °C over MZSM-5-C mainly contain o-xylene (28.5%), 2-methylpropyl-cyclopentane (19%) and 3, 5, 5-trimethyl-cyclohexene (16.2%). Combined with the results of previous research, the reaction path for ethanol is concluded, as shown in Scheme 1. Ethanol is converted to C_2H_4 directly via an intramolecular dehydration or undergoes an intermolecular dehydration to form $CH_3CH_2OCH_2CH_3$, and $CH_3CH_2OCH_2CH_3$ is then converted to C_2H_4 . Ethanol can be converted to C_3H_6 via oligomerization reaction between ethylene and carbene species, and converted to C_4H_8 via ethylene dimerization [41]. C_3H_6 and C_4H_8 subsequently produce cycloparaffins and aromatics via cyclization, dehydrogenation and aromatization reactions. The presences of o-xylene, 2-methylpropyl-cyclopentane and 3, 5, 5-trimethyl-cyclohexene in liquid product, as well as chain- and cyclo-paraffins in coke confirm the above speculation.

Liquid products from cracking of oleic acid (Table 7) at 500 °C over MZSM-5-B contain about 97.1% aromatic hydrocarbons and a small amount of esters. Combined with the current reports, the reaction pathway of oleic acid is illustrated in Scheme 2. Breaking of C–C bond in oleic acid could occur at β position of C=C bond and α position of –COOH [7], which leads to the formation of light olefins and short-chain paraffins with a simultaneous release of CO₂ and CO. Subsequently, these short-chain paraffins could be converted to light olefins via further cracking reaction. Besides, those light olefins and paraffins could also produce aromatic hydrocarbons through series further reactions in the pores of the ZSM-5 zeolites, such as cyclization,

dehydrogenation and aromatization [4]. H₂ could be released from the above dehydrogenation and aromatization reaction, which would react with CO to produce methanol. The resultant methanol would subsequently react with oleic acid on the surface of catalysts (H⁺ site) to form esters. Therefore, a lot of aromatic hydrocarbons are present in liquid products while a considerable amount of ester compounds are present in oleic acid-derived coke.

3.3. Stability of the catalysts

The stability of the catalysts was determined by repeating the cracking and regeneration experiments 10 times using ethanol and oleic acid over the optimized catalyst. The results are shown in Fig. 10 and Fig. 11. As seen in Fig. 10, Y_{LO} and S_{LO} from ethanol decrease by less than 10% after ten cycles. Meanwhile, C_2H_4 selectivity decreases from 42% to 36% after ten cycles. For MZSM-5-B, as shown in Fig. 11(a), the Y_{TGP} after several cycles are higher than that of the fresh catalyst, while Y_{LO} keeps at a constant value (200 mL·g⁻¹). Besides, the S_{LO} , C_3H_6 and C_2H_4 selectivity decrease slightly with increasing the cycle number (Fig. 11(b)). These results show that the synthesized catalyst MZSM-5-B and MZSM-5-C have good stability and reusability.

Based on the above study, it is clear that regardless of ETO and OATO reactions, the synthesized ZSM-5 with mesopore structure showed a higher catalytic activity than conventional ZSM-5. However, there are some differences in the selected optimum catalyst for cracking of ethanol and oleic acid. MZSM-5-C and MZSM-B exhibited the best catalytic performance in ETO and OATO reaction, respectively. The difference may be relevant to the size and chemical structure of feedstock molecular as well as the acidity of catalysts. For cracking of large oleic acid molecular, a catalyst with both large pore channel and moderate acid sites (B acid sites) is required. The large pore channel is helpful for quick mass and heat diffusion, while the B acid sites are the

active sites for cracking and deoxygenation reaction. Therefore, MZSM-B is the most suitable for OATO reaction.

Table 8 lists the comparison between our obtained results and those reported in current literatures. In Wang's research [23], the mesoporous ZSM-5 with pore size centered around 3.0 nm showed the higher light olefin selectivity (40.9%) to that of micro-ZSM-5 (31.0%) in MTO reaction. Compared to Wang's research, MZSM-5-C (major pore diameter about 22 nm) in this work achieved higher light olefin selectivity (47.2%), including C_2H_4 (42.3%). In Bi's study [6], ethanol as feedstock obtained a higher selectivity to C_2H_4 . This is essentially in agreement with our results. Furthermore, the light olefin yields obtained in present study are 0.32–0.34 kg of olefins/kg of ethanol and oleic acid, namely 32–34 wt%, which are much higher than those from cracking of oleic acid [26], bio-oil [38] and cellulose [39]. Besides, C_3H_6 selectivity of OATO reaction in this study is 5.3% higher than Li's study [26]. The high Si/Al₂ ratio (> 200) led to the formation of weak acid-dominant ZSM-5 zeolite in this study. The weak acidity and mesoporous structure maybe help to restrain coking and thus prolong the lifetime of catalysts [23].

4. Conclusion

Three kinds of ZSM-5 zeolites with different pore structure (MZSM-5-A, MZSM-5-B and MZSM-5-C) were successfully synthesized using a hydrothermal method by utilizing different templates. The resultant ZSM-5 zeolites were used for production of light olefins from catalytic cracking of ethanol and oleic acid. The synthesized ZSM-5 zeolites contained abundant mesopore, and had higher external surface area and mesopore volume than conventional ZSM-5. In ETO reaction, MZSM-5-C (major pore diameter about 22 nm) obtained the highest light olefin yield (318.3 mL·g⁻¹) and C₂H₄ selectivity (42.3%) at 400 °C. In OATO reaction, MZSM-5-B (with major

pore diameter about 16 nm) achieved a complete conversion at 500 °C, and obtained the maximal light olefin selectivity (38.1%) at 550 °C. The difference may be relevant to the size and chemical structure of feedstock molecular as well as the acidity of catalysts.

Notes

The authors declare no competing financial interest.

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Samples	Relative	Lat	tice constant	ts (nm)	$\mathbf{V} = (mm^3)$	Crystal size ^a	
	crystallinity (%)	а	b	с	V cell (fiffi)	(nm)	
HZSM-5	100	2.003	1.995	1.328	5.306	89	
MZSM-5-A	85.8	2.004	1.983	1.331	5.291	56	
MZSM-5-B	71.1	2.004	1.984	1.336	5.310	69	
MZSM-5-C	54.7	2.004	1.982	1.328	5.276	37	

Table 1 Lattice parameters of four different ZSM-5 zeolites.

^aThe crystal size was calculated by using Scherrer equation: $D=K\lambda/(B\cos\theta)$, where K is a constant, λ is X ray wavelength, B is half width and θ is diffraction angle ($2\theta=23.2^{\circ}$).

Samples	$\frac{S_{BET}^{a}}{(m^{2}\cdot g^{-1})}$	$\frac{S_{micro}^{b}}{(m^2 \cdot g^{-1})}$	$\frac{S_{ext}}{(m^2 \cdot g^{-1})}$	V_{total}^{c} (cm ³ ·g ⁻¹)	V_{micro}^{b} (cm ³ ·g ⁻¹)	V_{meso}^{d} (cm ³ ·g ⁻¹)	D _{aver} ^e (nm)
HZSM-5	459	258	201	0.35	0.13	0.22	3.1
MZSM-5-A	439	188	251	0.40	0.09	0.31	4.0
MZSM-5-B	469	132	337	0.52	0.06	0.46	4.5
MZSM-5-C	405	0	405	0.76	0	0.76	7.5

Table 2 Textural properties of four different ZSM-5 zeolites.

^aS_{BET} (BET surface area) was obtained from the adsorption isotherm.

 ${}^{b}S_{micro}$ (micropore surface areas) and S_{ext} (external surface areas) and V_{micro} (micropore volumes) were calculated using t-plot method.

 $^{c}V_{total}$ (total pore volumes) was obtained at the relative pressure (p/p₀) = 0.99.

 $^{d}V_{meso} = V_{total} - V_{micro.}$

^eD_{aver} (average pore diameter) was obtained from average pore size.

	n(SiO ₂)/	Total acid	Percentage of acid		
Samples	$n(Al_2O_3)^a$	(mmol/g)	Weak acid	Strong acid	Strong/weak
HZSM-5	227	0.52	69.2	30.8	0.44
MZSM-5-A	222	0.53	56.6	43.5	0.77
MZSM-5-B	212	0.56	67.7	32.1	0.47
MZSM-5-C	226	0.51	78.4	21.6	0.28

^aSiO₂/(Al₂O₃) molar ratio of the four ZSM-5 zeolites was determined by ICP-OES.

Samples	150 °C desorption				300 °C desorption		
Samples	B(mmol/g)	L (mmol/g)	B/L	Ι	B(mmol/g)	L (mmol/g)	B/L
HZSM-5	0.01	0.21	0.05		0	0.03	0
MZSM-5-A	0.01	0.18	0.06		0	0.04	0
MZSM-5-B	0.02	0.18	0.11		0.01	0.04	0.25
MZSM-5-C	0.01	0.14	0.07		0	0.03	0

 Table 4 Quantitative analysis of acidic sites types of ZSM-5 samples by Py-IR spectra.

B-Brönsted acid amount; L-Lewis acid amount

Somplag	Y _{coke} ((%)
Samples	Ethanol	Oleic acid
HZSM-5	0.73 ± 0.04	1.17 ± 0.03
MZSM-5-A	0.28 ± 0.06	0.66 ± 0.08
MZSM-5-B	0.16 ± 0.03	0.90 ± 0.02
MZSM-5-C	0.70 ± 0.04	0.82 ± 0.03

Table 5 Coke yield (Y_{coke}) from catalytic cracking of ethanol and oleic acid over thesynthesized ZSM-5 at 500 °C, WHSV=4.5h⁻¹.^a

^aThe data is reported as mean values \pm standard deviation, n = 3.

Name of compound	Mologular formula	Structural formula	Area %		
Name of compound	Wolecular formula	Suuctural formula	HZSM-5	MZSM-5-C	
Catalytic cracking of ethanol					
Octane, 3,5-dimethyl-	$C_{10}H_{22}$		25.23	_	
Nonane, 3,7-dimethyl-	$C_{11}H_{24}$		8.33	8.70	
Cyclododecane	$C_{12}H_{24}$	\bigcirc	_	34.77	
Decane, 2,3,5-trimethyl-	$C_{13}H_{28}$	\mathbf{y}^{1}	16.67	13.04	
1-Pentadecene	$C_{15}H_{30}$	$\qquad \qquad $	8.14	-	
Others		No hit compound	41.64	43.48	
		Č	HZSM-5	MZSM-5-B	
Catalytic cracking of oleic acid					
Methyl octyl ketone	C ₁₀ H ₂₀ O		21.62	_	
Octane, 3,4,5,6-tetramethyl-	$C_{12}H_{26}$		_	10.72	
Benzene, undecyl-	$C_{17}H_{28}$		27.03	-	
Methyl n-hexadecyl ketone	$C_{18}H_{36}O$	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	10.81	6.93	
Heptadecanoic acid, methyl ester	$C_{18}H_{36}O_2$	~~~~~lo	5.41	-	
Octadecanoic acid, methyl ester	$C_{19}H_{38}O_2$	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	-	47.06	
Others		No hit compound	35.13	35.29	

 Table 6 Components of soluble coke formed from catalytic cracking of ethanol and oleic acid at

500 °C.

			Molecular	Sample (area%)
NO.	RI (min)	Name of compound	formula	Oleic acid
1	4.980	benzene	C ₆ H ₆	3.5
2	5.939	Toluene	C_7H_8	8.1
3	8.291	Ethylbenzene	C_8H_{10}	6.4
4	8.665	p-Xylene	C_8H_{10}	21.5
5	9.128	o-Xylene	C_8H_{10}	6.3
6	10.732	Benzene, 1,2,3-trimethyl-	C_9H_{12}	3.4
7	11.487	Benzene, 1-ethyl-2-methyl-	$C_{9}H_{12}$	5.0
8	12.347	Indane	C_9H_{10}	3.9
9	12.550	Indene	C_9H_{10}	4.6
10	13.253	(E)-1-Phenyl-1-butene	$C_{10}H_{12}$	2.4
11	14.361	1H-Indene, 2,3-dihydro-5-methyl-	$C_{10}H_{12}$	1.1
12	14.550	1H-Indene, 1-methyl-	$C_{10}H_{10}$	3.3
13	14.695	2-Methylindene	C ₁₀ H ₁₀	4.4
14	15.282	Naphthalene	$C_{10}H_{8}$	5.8
15	15.941	Benzene, (1,2-dimethyl-1-propenyl)-	$C_{11}H_{14}$	2.2
16	16.534	Naphthalene, 1,2,3,4-tetrahydro-	$C_{10}H_{12}$	3.9
17	17.120	Naphthalene, 1-methyl-	$C_{11}H_{10}$	5.0
18	18.769	Naphthalene, 2,6-dimethyl-	$C_{12}H_{12}$	1.4
19	18.939	Naphthalene, 2,3-dimethyl-	$C_{12}H_{12}$	1.9
20	24.978	Indane, 1-nonyl-	$C_{16}H_{24}$	1.8
21	25.588	Naphthalene, 1-hepty-1,2,3,3-tetrahydro	$C_{18}H_{28}$	1.4
22	26.677	9,12-Octadecadiennoic acid, methyl ester	$C_{19}H_{34}O_2$	2.7

Table 7	Compounds	in liquid	products from	catalytic	cracking	of oleic aci	d over MZSM-5-B

701 5	Ess data alar	Desetion and discul	S	S	Y _{LO}	Ref.
ZSM-5	Feedstocks	Reaction condition	(C_2H_4/C_3H_6)	(total olefins)		No.
Nanosized	ethanol	400°C, 3 h ⁻¹	43.9% ^b	74.5%	-	[6]
(Si/Al ₂ =26)						
Mesoporous	methanol	450 °C, 6.0 h ⁻¹	20.8% ^c	40.9%	4.79 wt.%	[23]
(Si/Al ₂ =40)						
Mesoporous	methanol	470 °C, 2.0 h ⁻¹	46.3% ^c	75.3%	-	[25]
(Si/Al ₂ =336)						
6 wt.%	oleic acid	600 °C,	13.6% ^c	35.3%	0.21 kg olefins/(kg bio-oil)	[26]
La/ZSM-5		catalyst/feed= 0.6				
$(Si/Al_2 = 16)$						
6 wt.%	bio-oil	550 °C, 1.0 h ⁻¹	-	55.7 C-mol%	0.25 kg olefins/(kg bio-oil)	[37]
La/ZSM-5						
$(Si/Al_2 = 50)$						
Fe-ZSM-5	cellulose	600 °C,	2.0 C-mol% ^c	7.5 C-mol%	4.36 wt.%	[38]
$(Si/Al_2 = 50)$		catalyst/feed = 2				
Mesoporous	ethanol	400 °C, 4.5 h ⁻¹	42.3% ^b	47.2%	0.34 kg olefins/(kg ethanol)	this
(Si/Al ₂ =226)						work
Mesoporous	oleic acid	550°C, 4.5 h ⁻¹	18.9% ^c	38.1%	0.32 kg olefins/(kg bio-oil)	this
(Si/Al ₂ =212)						work

Table 8 Comparison of catalytic cracking of different feedstocks to produce light olefins.

^aReaction condition mainly includes reaction temperature, weight hourly space velocity and catalyst/feed ratio.

 b The selectivity to C₂H₄.

 c The selectivity to C₃H₆.

FIGURE CAPTIONS

- Fig. 1. XRD patterns of four ZSM-5 samples.
- **Fig. 2.** N₂ adsorption-desorption isotherms (a) and pore size distributions (b) of conventional ZSM-5 and the synthesized zeolites with different templates.

Fig. 3. NH₃-TPD profiles of four ZSM-5 samples with different pore size.

Fig. 4. Py-IR spectra of four samples: (a) desorption at 150 °C; (b) desorption at 300 °C.

- **Fig. 5**. Conversion (a) and olefin light yield (b) obtained from cracking of ethanol at different reaction temperature over different ZSM-5 samples, WHSV=4.5h⁻¹.
- Fig. 6. Product selectivity obtained from cracking of ethanol at different temperature over the synthesized ZSM-5 samples, WHSV= $4.5h^{-1}$. (a) selectivity to C₂H₄; (b) selectivity to C₁-C₄ alkanes.
- **Fig. 7.** Conversion (a) and the light olefin yield (b) obtained from cracking of oleic acid at different temperature over the synthesized ZSM-5 samples, WHSV=4.5h⁻¹.
- Fig. 8. Gaseous product selectivity from cracking of oleic acid at different temperature over the different ZSM-5 samples, WHSV=4.5h⁻¹. (a) selectivity to light olefins; (b) selectivity to C₁-C₄ alkanes; (c) selectivity to CO; (d) selectivity to CO₂.

Fig. 9. TPO profiles of the used catalysts from cracking of ethanol (a) and oleic acid (b) at 500 °C.

- Fig. 10. (a) Total gas production and light olefin yield and (b) gaseous product selectivity with cycle number from cracking of ethanol over MZSM-5-C at 400 °C, WHSV = 4.5 h^{-1} .
- Fig. 11. (a) Total gas production and light olefin yield and (b) gaseous product selectivity with cycle number from cracking of oleic acid over MZSM-5-B at 550 °C, WHSV = 4.5 h^{-1} .



Fig. 1. XRD patterns of four ZSM-5 samples



Fig. 2. N₂ adsorption-desorption isotherms (a) and pore size distributions (b) of conventional ZSM-5 and the synthesized zeolites with different templates.



Fig. 3. NH₃-TPD profiles of four ZSM-5 samples with different pore size.



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Fig. 6. Product selectivity obtained from cracking of ethanol at different temperature over the synthesized ZSM-5 samples, WHSV= $4.5h^{-1}$. (a) selectivity to C₂H₄; (b) selectivity to C₁-C₄ alkanes.



Fig. 7. Conversion (a) and the light olefin yield (b) obtained from cracking of oleic acid at different temperature over the synthesized ZSM-5 samples, WHSV=4.5h⁻¹.



Fig. 8. Gaseous product selectivity from cracking of oleic acid at different temperature over the different ZSM-5 samples, WHSV= $4.5h^{-1}$. (a) selectivity to light olefins; (b) selectivity to C₁-C₄ alkanes; (c) selectivity to CO; (d) selectivity to CO₂.



Fig. 9. TPO profiles of the used catalysts from cracking of ethanol (a) and oleic acid (b) at 500 °C.



Fig. 10. (a) Total gas production and light olefin yield and (b) gaseous product selectivity with cycle number from cracking of ethanol over MZSM-5-C at 400 °C, WHSV = 4.5 h^{-1} .



Fig. 11. (a) Total gas production and light olefin yield and (b) gaseous product selectivity with cycle number from cracking of oleic acid over MZSM-5-B at 550 °C, WHSV = 4.5 h^{-1} .



Scheme 1 Postulated pathways for ethanol conversion.



Scheme 2 Postulated reaction pathway for catalytic pyrolysis of oleic acid.