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Conversion of methanol to propylene over nano-sized ZSM-5 zeolites aggregates synthesized by modified seed-induced method with CTAB

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Abstract

A facile and economical route to synthesize nano-sized ZSM-5 zeolites aggregates with mesopores was developed by a modified seed-induced method using silicate-1 (S-1) as seeds without additional templates in the presence of trace amount of cetyltrimethylammonium bromide (CTAB). The effect of the amounts of CTAB and S-1 on the morphologies and textural properties were studied in detail, and the possible formation mechanism was proposed. The primary crystal sizes of the ZSM-5 zeolites could be adjusted and mesopores were generated in a certain range. The resulting ZSM-5 zeolites showed a uniformly conglobate morphology with particle sizes of 400-600 nm, aggregated with 20-50 nm crystallites, possessing large external surface area and abundant inter-crystallite mesopores under the optimum synthesis conditions (CTAB to total SiO₂ molar ratio was 0.02 and SiO₂ in S-1 gel took up 8% to the total SiO₂). The catalytic performance of nano-sized ZSM-5 zeolites in methanol to propylene reaction exhibited high stability and high propylene selectivity.

Keywords: Mesoporous ZSM-5; CTAB; Seed; Nano-sized; MTP

1. Introduction

Propylene is one of important organic raw materials in the petrochemical industry, widely used for the production of propylene derivatives.¹⁻³ In the past decade, Lurgi company has successfully developed a methanol to propylene (MTP) technology based on ZSM-5 zeolites catalysts, demonstrating that it is a promising process for the production of propylene from non-petroleum

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sources such as coal and natural gas.^{4,5} However, the microporous characteristic of ZSM-5 often leads to intra-crystalline diffusion limitations and a rapid deactivation associated with coke depositions,⁶ which severely hinders its practical applications.^{7,8}

To overcome these disadvantages of the pure microporosity in ZSM-5, two main strategies have been developed in recent years. One strategy is to reduce the crystal sizes of ZSM-5.⁹ The decrease in the crystal sizes from the micrometer to nanometer scale could increase the external surface area and decrease the diffusion path length, which is conducive for the enhancement of catalytic stability.¹⁰ Within the past few decades, nano-sized ZSM-5 zeolites have been successfully synthesized by the hydrothermal crystallization.¹¹⁻¹³ However, zeolite crystals of particles no bigger than 100 nm might be thermodynamically unstable due to high surface energy and vast amounts of surface defects.¹⁴ Meanwhile, nanocrystals are difficult to handle and have low yields during synthesis, in which the majority of the building units are left unused in the mother liquid. Another strategy is to prepare ZSM-5 with both micropores and mesopores, which are usually referred to as mesoporous ZSM-5 or hierarchical structured ZSM-5.15 To this end, various attempts to synthesize mesopores ZSM-5 zeolites have been reported, including mainly post treatments and indirect templating methods.¹⁶ Post treatments can be divided into steaming dealumination¹⁷⁻¹⁹, acid dealumination²⁰⁻²² and base desilication²³⁻²⁶. Though mesopores can be developed, the etching of zeolites is often accompanied by the loss of crystallinity, which leads to pernicious effects on the catalytic performance. Indirect templating method is to add a lot of meso-template agents in the synthetic gels with the micropore template of tetrapropylammonium hydroxide (TPAOH).²⁷⁻³⁰ In 2009. Choi et al.³¹ developed MFI zeolite nanosheets with a thickness of 2.5 nm along the b-axis by designing a di-quaternary ammonium-type surfactant, and the MFI zeolite nanosheets dramatically suppressed the catalyst deactivation through coke deposition in methanol-to-gasoline conversion.

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Recently, Kim et al.³² also reported that MFI zeolite nanosheets synthesized with multiammonium surfactants showed greater activity and selectivity to propylene and longer lifetimes than commercial ZSM-5 in the MTP reaction, this was attributed to the well-developed nanosheet structure with a high specific surface area and a large mesopore volume. Zhang et al.³³ developed a hierarchical ZSM-5 zeolite with b-oriented thinner dimension in fluoride medium, and the obtained material displayed a greatly longer catalytic lifetime and higher propylene selectivity in MTP reaction than conventional ZSM-5 catalysts, due to the superior diffusivity of thinner b-axis path and intracrystal secondary mesopores. However, with these methods, the large usage of TPAOH and mesoporogens makes the ZSM-5 zeolites expensive and produces environmental pollution.

A seed-induced method is an interesting alternative to synthesize the nano-sized ZSM-5 zeolites since its low consumption of templates and rapid crystallization of ZSM-5 zeolites.^{34,35} Nevertheless, the intergrowth and secondary growth of crystals usually occur, leading to the formation of compact aggregates with larger crystal sizes in respect to the seed particles.³⁴ To overcome the problem, the effort has been done to develop seed-induced method in the presence of various mesoporogens such as cationic surfactants and special organosilanes. Frunz and co-workers³⁶ reported that the mesoporous ZSM-5 crystals were synthesized by aging of ZSM-5 synthesis solution to form the protozeolitic seeds, and subsequently adding a surfactant of cetyltrimethylammonium chloride (CTACl). Nearly identical method was adopted to synthesize hierarchical mesoporous ZSM-5 using cetyltrimethylammonium bromide (CTAB) instead of CTACl by Zhu et al.¹⁴ and Gonçalves et al.³⁷. However, in these methods, a large number of TPAOH and CTAB were still used. Recently, Gao et al.³⁸ prepared a series of ZSM-5 nanozeolites with hierarchical seed-assisted addition porositv by а method and the of phenylaminopropyltrimethoxysilane (PATMOS) into the medial synthesis system. The molar ratio

of TPAOH introduced by the addition of seeds to total SiO_2 (TPAOH/SiO₂) is 0.05-0.1, much lower than above methods, but the use of expensive organosilanes restricts its wide range of applications in industry.

Herein, nano-sized ZSM-5 zeolite aggregates were directly synthesized by a facile and economical approach using silicalite-1 (S-1) as seeds in the presence of CTAB. The obtained ZSM-5 zeolites display high crystallinity, large specific surface area and external surface area, abundant intercrystal mesoporosity due to self-assembled nanocrystallites and a markedly improvement in the stability and propylene selectivity in MTP reaction. Moreover, the synthesis method has the advantage of low TPAOH and CTAB consumption (TAPOH/SiO₂=0.018, CTAB/SiO₂= 0.02).

2. Experimental

2.1. Materials

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The reagent grade chemicals including sodium aluminum (NaAlO₂, AR), CTAB (AR), Sodium hydroxide (NaOH, AR), ethanol (EtOH, AR), TPAOH (24.8 wt.% in water) and methanol (AR) were obtained from Tianjin Guangfu Fine Chemical Research Institute Co., Ltd. Tetraethyl orthosilicate (TEOS, 98 wt.%) was obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. Silica sol (40 wt% suspension in water) was purchased from Qingdao Haiyang Chemical Co., Ltd. Ammonium nitrate (NH₄NO₃, AR) was purchased from Guangdong Xilong Chemical Co., Ltd. A commercial ZSM-5 zeolites (SiO₂/Al₂O₃=160) was purchased from the Catalyst Plant of Nankai University for comparison.

2.2. Synthesis of the S-1 gel

S-1 gel used as seeds with a molar composition of 100 SiO₂: 24 TPAOH: 800 EtOH: 2400 H_2O was prepared according to our previous work.³⁹ 10.98 g of TEOS, used as silica source, was added

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dropwise into 10.37 g of TPAOH solution mixed with 15.0 g deionized water and 9.71 g EtOH while stirring. After homogenizing at room temperature for 2 h, the mixture was transferred to a Teflon-lined autoclave, sealed, and hydrothermally treated at 100 °C for 96 h. After cooling, the obtained S-1 gel was directly used for the synthesis of ZSM-5 zeolites without any treatments.

2.3. Preparation of nano-sized ZSM-5 aggregates

To synthesize the nano-sized ZSM-5 aggregates, silica sol was used as silica source and NaAlO₂ was used as aluminum source. NaOH was added to adjust the pH. In a typical run, 0.6782 g NaOH, 0.0887 g NaAlO₂ and 0.664 g CTAB were dissolved in 30 g H₂O. After vigorously stirring for 0.5 h, 6.3755 g S-1 gel and 12.446 g silica sol were dropwise added into the clear solution in sequence under stirring. Then, the mixture with a molar composition of 100 SiO₂: 0.6 Al₂O₃: 10 Na₂O: 2500 H₂O: 2 CTAB: 8 S-1(SiO₂ molar content in respect to total SiO₂) was stirred at ambient temperature for 2 h, and transferred into Teflon-lined autoclave, aging at 120 °C for 12 h and subsequent crystallization at 170 °C for 24 h were carried out. The products were centrifuged and washed with distilled water until the pH reached about 7, dried at 120 °C for 12 h, and calcined at 550 °C for 6 h. The obtained samples were denoted N-ZSM-5.

To better investigate the effect of CTAB added in the precursor solution on the properties of the final ZSM-5 products, five samples with different CTAB/SiO₂ ratios (0.005, 0.015, 0.02, 0.03 and 0.05, respectively) were synthesized with the same synthesis method of N-ZSM-5, and they were denoted as Z-xC-0.08S (x represents the CTAB/SiO₂ molar ratio). Here, N-ZSM-5 (CTAB/SiO₂=0.02) was re-synthesized in order to prove the reliability of this synthesis method, and denoted as Z-0.02C-0.08S. For comparison, conventional ZSM-5 (denoted as Con-ZSM-5) was synthesized under the same condition of N-ZSM-5, but in the absence of CTAB. Both

representative N-ZSM-5 and Con-ZSM-5 zeolites were ion exchanged three times in 1 M NH₄NO₃ solution at 80 °C for 2 h, and then calcined at 550 °C to obtain the H-type ZSM-5.

Similarly, to investigate the effect of seeds on the properties of ZSM-5 zeolites, four samples with different S-1/SiO₂ ratios (0.005, 0.02, 0.04 and 0.06, respectively) were synthesized with the same synthesis method of N-ZSM-5, and they were denoted as Z-2C-yS (y represents the S-1/SiO₂ ratio).

2.4. Catalyst characterization

Scanning electron microscopy (SEM) and transmission electron microscope (TEM) were used to determine the size of the crystals and particles and the morphology of the ZSM-5 samples. SEM images were recorded on an S-4800 field emission scanning electron microscopy with an accelerating voltage of 3 kV. TEM was carried on a JEM-2100F instrument operating at 200 kV. For the TEM image, the specimens were dispersed in ethanol and placed on holey copper grids.

X-ray diffraction (XRD) patterns were obtained at room temperature on a Rigaku D/max2500 diffractometer employing the graphite filtered Cu K α radiation ($\lambda = 0.1542$ nm) with a scanning rate of 8° min⁻¹ in the 2 θ ranges from 5° to 55°.

Nitrogen adsorption and desorption isotherms of the samples were measured at liquid N₂ temperature (77 K) on a Micromeritics TriStar 3000 automated physisorption instrument. Prior to the measurements, all the samples were degassed at 300 °C for 4 h. The total specific surface area (S_{BET}) was derived from the Brunauer-Emmett-Teller (BET) equation. The micropore surface area (S_{micro}) was derived from the t-plot method, and external surface area (S_{ext}) was calculated by subtracting S_{micro} from S_{BET}. The total pore volume (V_{total}) was calculated at $p/p_0 = 0.99$. The micropore volume (V_{micro}) was also derived from the t-plot method, and mesopore volume (V_{meso})

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was calculated by subtracting V_{micro} from V_{total} . The mesopore size distributions were estimated by using the Barrett-Joyner-Halenda (BJH) method from the desorption branch of the isotherms.

Fourier transform infrared (FT-IR) spectra of the samples were recorded in a Bruker Vertex 7.0 spectrometer, using the KBr wafer technique. The infrared absorbance spectra were recorded from 2000 to 400 cm^{-1} with a resolution of 4 cm⁻¹.

Temperature-programmed desorption of ammonia (NH₃-TPD) measurements were recorded using a Micromeritics 2910 chemical adsorption instrument. The samples were pretreated in a nitrogen flow at 400 °C for 1 h, and then cooled down to 100 °C, and ammonia was introduced with nitrogen as the carrier gas. After 60 min, the flow was switched to nitrogen, and the sample was heated to 700 °C at a rate of 10 °C min⁻¹. The desorbed ammonia was monitored by a thermal conductivity detector.

Solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) was used to investigate the coordination of Al and Si atoms in the ZSM-5 framework. The measurements were performed on a Varian infinityplus 300MHz NMR spectrometer equipped with two radio frequency channels at a field strength of 7.0 T. ²⁷Al MAS NMR spectra were recorded at 104.2 MHz at a spinning frequency of 5 kHz and 2.05 s intervals between successive accumulations. ²⁹Si MAS NMR spectra were recorded at 79.4 MHz at a spinning frequency of 5 kHz and 6.05 s intervals between successive accumulations.

Elemental analyses were carried out on an inductively coupled plasma optical emission spectroscope (ICP-OES) using a Varian Vista-MPX emission spectrometer.

Thermogravimetric (TG) analysis was evaluated by Shimadzu TGA-50 apparatus using a temperature ramp from 30 to 800 °C with a heating rate of 10 °C min⁻¹ in oxygen atmosphere.

2.5. Catalytic tests

The MTP reaction was tested in a continuous flow fixed bed reactor at 470 °C under atmospheric pressure and the weight hourly space velocity (WHSV) was kept constant at 8 h⁻¹. The catalyst loading was 0.5 g (mesh size: 20 - 40), and it was loaded into the middle section of a quartz tubular reactor with a 20 mm internal diameter and a total length of 400 mm. A thermocouple was positioned in the center of the catalyst bed in order to monitor the temperature. The catalyst was first activated at 470 °C for 1 h under high purity N₂ at a flow rate of 60 ml min⁻¹, prior to the start of the MTP reaction. HPLC infusion pump fed a liquid solution of methanol in water (50 mol.%) at a flow rate of 0.12 ml/min. After catalyst activation, high purity nitrogen at a flow rate of 60 ml min⁻¹ controlled using a mass flow controller carried the vaporized methanol into the reactor. To avoid possible condensation of hydrocarbons, the temperature of the effluent line was constantly maintained at 180 °C. An on-line gas chromatograph (GC-SP-3420) equipped with a flame ionization detector (FID) and a 50 m capillary column (HP-PLOT-Q) analyzed the products. The reaction performance results, including methanol conversion and product selectivity, were subsequently calculated by Eqs. (1) and (2).

Methanol conversion (%) =
$$\frac{N_{\text{MeOH}}^{i} - (N_{\text{MeOH}}^{o} + 2N_{DME}^{o})}{N_{\text{MeOH}}^{i}} \times 100$$
(1)

Selectivity (%) =
$$\frac{x \times N_{C_x H_y}^i}{N_{\text{MeOH}}^i - (N_{\text{MeOH}}^o + 2N_{DME}^o)} \times 100$$
 (2)

Where, N is the number of moles. Superscript i and o are to the components at the inlet and outlet of reactor, respectively, x is the number of carbon atoms. Dimethyl ether (DME) is considered as reactant.⁴⁰

3. Results and discussion

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3.1. Characterization of nano-sized ZSM-5 zeolites aggregates

SEM images (Fig. 1a-c) clearly shows a uniformly globular morphology of N-ZSM-5 with particle sizes of 400-600 nm homogeneously aggregated with 20-50 nm nano-crystallites. The aggregation due to the in situ self-assembly of these crystallites during the hydrothermal synthesis may give rise to abundant inter-crystallite mesopores. The N₂ adsorption-desorption isotherm (Fig. 1d) shows that there is a large hysteresis loop at p/p_0 of 0.45-0.95 in N-ZSM-5, which indicates the presence of mesoporous structure, formed in aggregates, and the hysteresis loop is a type-H4 isotherm, suggesting that both the micropores and mesopores exist. BJH pore size distribution of N-ZSM-5 sample shown in Fig. 1d inset exhibits a narrow peak at 3.6 nm and a relatively broad peak at 52.9 nm, revealing that N-ZSM-5 contains abundant mesopores. The texture properties of N-ZSM-5 are listed in Table 1. N-ZSM-5 exhibits a high specific surface area (414 m² g⁻¹) and a large mesoporous volume (0.23 cm³ g⁻¹). TEM image (Fig. 1e) shows that N-ZSM-5 particles are loosened texture, containing abundant mesopores open at the external surface, which is agreement with the results of SEM and N₂ adsorption-desorption isotherm. Under high magnification (Fig. 1f), clear lattice fringes are observed, confirming that nano-crystallites are highly crystalline.

XRD patterns (Fig. 2a) show that N-ZSM-5 has a typical MFI structure (peaks at 2θ of 7.9°, 8.7°, 23.1°, 23.9° and 24.4°).³⁹ FT-IR spectra (Fig. 2b) of N-ZSM-5 show intensive absorption bands at 1150-1050 cm⁻¹, 795 cm⁻¹ and 455 cm⁻¹, associated with internal asymmetric stretch, external symmetric stretch and T-O bend respectively.⁷ The optical density ratios of the absorption bands at 550 cm⁻¹ and 455 cm⁻¹ for N-ZSM-5 is 0.71, which is near to 0.7 for pure pentasil samples with high crystallinity of ZSM-5⁷, indicating that N-ZSM-5 has a good MFI frame structure.

²⁷Al and ²⁹Si MAS NMR was used to further reveal the coordination of Al and Si atoms in N-ZSM-5. One distinctive resonance peak at a chemical shift of 53 ppm in the ²⁷Al MAS NMR spectrum (Fig. 2c) which corresponds to tetrahedrally coordinated Al in the zeolite framework is

observed. Moreover, no resonance at 0 ppm, typically associated with the octahedrally coordinated Al in the extra-framework positions,⁴¹ confirms that the Al atoms are totally incorporated into the crystal frameworks of the N-ZSM-5. Fig. 2d shows the ²⁹Si MAS NMR spectra of N-ZSM-5. The intensive resonances at 114.5 ppm and 111.0 ppm are associated to the Si (4Si, 0Al) sites, and the peak at 104.2 ppm corresponds to Si (3Si, 1Al) sites.⁴² Resonances representing Si (2Si, 2Al) with chemical shift below 100 ppm sites are not observed, indicating that [Al-O-Si-O-Al] sequences are not present in the highly siliceous N-ZSM-5.⁴³ The resonance at 100.7 ppm of N-ZSM-5 belongs to the Si (3Si, 1OH) sites, which can be attributed to the hydroxyl groups on the large external surface of N-ZSM-5.²⁸

3.2. Effect of CTAB/SiO₂ ratio on the properties of ZSM-5

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The synthetic conditions of five samples with different CTAB/SiO₂ ratios (0.005, 0.015, 0.02, 0.03 and 0.05, respectively) and Con-ZSM-5 are summarized in Table 1. Here, N-ZSM-5 (CTAB/SiO₂=0.02) was re-synthesized in order to prove the reliability of this synthesis method. The SiO₂/Al₂O₃ molar ratios and texture properties of all samples are also summarized in Table 1. All the ZSM-5 samples have similar SiO₂/Al₂O₃ ratio, however, it is obvious that the CTAB/SiO₂ ratio has a significant impact on the textural properties of the ZSM-5 zeolites. At the relatively low CTAB/SiO₂ ratio, increasing the addition amounts of CTAB gives rise to the increase of total specific surface area (S_{BET}), external surface area (S_{ext}), pore volume (V_{total}) and mesoporous volume (V_{meso}). As the CTAB/SiO₂ is increased to 0.02, the sample (N-ZSM-5) exhibits the most excellent textural properties, It is noteworthy that S_{BET}, S_{ext}, V_{total} and 0.23 cm³ g⁻¹, significantly higher than those of Con-ZSM-5 (342 m² g⁻¹, 161 m² g⁻¹, 0.21 cm³ g⁻¹ and 0.09 cm³ g⁻¹, respectively). Further increasing the CTAB/SiO₂ ratio from 0.02 to 0.05, S_{BET}, S_{ext}, V_{total} and V_{meso} rapidly decrease.

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The XRD patterns (Fig. 3) of all the synthesized samples show typical diffraction characteristics for ZSM-5 structure, and no amorphous phase is detected, suggesting that they are successfully synthesized. The corresponding SEM images of the samples with different CTAB/SiO₂ ratios are shown in Fig. 4. Though all the samples have similar particle sizes, their morphologies are distinctly different. Con-ZSM-5 (Fig. 4a) has irregular block-like morphology aggregated with nanocrystals above 100 nm sizes. After the addition of CTAB, the morphologies of the samples (Fig. 4b-f) show significant change compared to that of Con-ZSM-5. At the relatively low CTAB/SiO₂ ratio from 0.005 to 0.02, the particles of ZSM-5 zeolites comprise the globular agglomerates of nano-crystallites, and the average sizes of the nano-crystallites gradually decrease to 30 nm, which is much smaller than that of Con-ZSM-5. The results indicate that CTAB may interact with the crystal nucleus and inhibit the crystal growth. The SEM image (Fig. 4d) of the sample with CTAB/SiO₂ ratio of 0.02 is in good accordance with that of the N-ZSM-5 (Fig. 1b), confirming the repeatability of this method to synthesize nano-sized ZSM-5 aggregates with mesopores. While the samples with CTAB/SiO₂ ratio of 0.03 and 0.05 (Fig.4e and f) show less rough surface, indicating that excessive amounts of CTAB results in the growth of crystal again.

To clarify the behaviour of CTA⁺ in the synthesis, it is useful to evaluate the amount of CTA⁺ incorporated in the as-synthesized samples by TG analysis. Fig. 5a presents the TG curves of Con-ZSM-5 and N-ZSM-5 synthesized with different CTA⁺/SiO₂ ratio before calcination. All samples show two regions of weight loss. The first region below 300 °C is assigned to desorption of water. Both Con-ZSM-5 and the sample with CTAB/SiO₂ ratio of 0.005 have a weight loss of 1.3%. Increasing the CTAB/SiO₂ ratio to 0.5, the weight loss increases greatly to 6.8%. This may be ascribed to hydrophilicity of the surface with more CTAB, which adsorbs more water. The second region of 300 °C-500 °C is ascribed to the combustion of the organic template.⁴⁴ For Con-ZSM-5,

the organic template of TPAOH is introduced in trace amount $(TPA^+/SiO_2=0.018)$ with the S-1 seeds, but the weight loss is 7.4%, which is much larger than the mass percentage of TPA^+ in the total mass (2.2%). Therefore, it is believed that the more weight loss is attributed to the condensation water from the elimination of the surface hydroxyl groups or removal of chemically bound water.⁴⁵ For N-ZSM-5 with CTAB/SiO₂ of 0.005, the weight loss increases by 1.8% in comparison with that of Con-ZSM-5, proving that most of CTA⁺ is occluded into the as-synthesized sample. However, when more CTAB is added, i.e., with CTAB/SiO₂ of 0.02 and 0.05, the weight loss only increases slightly, indicating that the excessive amounts of CTAB cannot be occluded into the as-synthesis samples. Fig. 5b further shows the amount of CTA⁺ incorporated into the samples and the variation of mesopore volumes as a function of CTA^+/SiO_2 ratios. With the addition of CTAB at low level, the mesopore volume increases due to the incorporation of CTA⁺ into the samples and/or the interaction of CTA⁺ with the crystal nucleus to restrain the growth of crystals and form nano-sized aggregates. However, the addition of excessive amounts of CTAB is not needed and has a negative effect with the mesopore volume being decreased.

3.3. Effect of S-1/SiO₂ ratio on the properties of ZSM-5

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Seed also plays an important role in the synthesis of zeolites and tunes the properties of the final products.¹² Four samples with different S-1/SiO₂ ratios (0.005, 0.02, 0.04 and 0.06, respectively) were synthesized with the same synthesis method of N-ZSM-5. Their SiO₂/Al₂O₃ ratios and texture properties are also listed in Table 1. The four samples all have similar SiO₂/Al₂O₃ ratios. With the increase of S-1/SiO₂ ratio from 0.005 to 0.06, the S_{BET} increases from 323 m² g⁻¹ to 381 m² g⁻¹, and the corresponding S_{ext}, V_{total} and V_{meso} of the samples increases to 213 m² g⁻¹, 0.26 cm³ g⁻¹ and 0.19 cm³ g⁻¹, respectively. This means the textural property especially external surface area and

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mesoporosity can be tuned, to a certain extent, by changing the using amount of the S-1 seeds in the preparation of nano-sized ZSM-5 zeolites.

XRD patterns in Fig. 6 show that all the synthesized samples with high crystallinity are obtained. SEM images of ZSM-5 zeolites synthesized with different S-1/SiO₂ ratios are shown in Fig. 7. All the ZSM-5 zeolites are the aggregated spheres of nano-crystallites. Although the average particle sizes of ZSM-5 zeolites have a reduction from 800 nm to 500 nm with increasing the S-1/SiO₂ ratio of 0.005 to 0.02, all the ZSM-5 zeolites show almost same average particle sizes around 500 nm further increasing the S-1/SiO₂ ratio up to 0.06. It should be pointed out that the average sizes of primary nano-crystallites gradually decrease from 100 nm to 40 nm with the increase of the S-1/SiO₂ ratio, which conduces to the increase of S_{BET}, S_{ext}, V_{total} and V_{meso}, as shown in Table 1. Similar results are also reported by Teng et al., who believed that more nuclei and surface were provided with the increase of seeds, and accordingly the primary particle became smaller.³⁵ The result of SEM images reveals that the employed amount of seeds has an important effect not only on the size of the ZSM-5 zeolites particles but also on the primary nano-crystallites.

3.4. Form mechanism of nano-sized ZSM-5 with mespores

According to seed surface crystallization mechanism suggested by Tang and co-workers,⁴⁶ the crystallization of ZSM-5 zeolites only occurs on the surface of seeds and accordingly the primary particle becomes larger than the seed crystals, but the primary crystals of the N-ZSM-5 aggregates are obviously smaller than the S-1 seeds with the sizes of 180 nm (Fig. 8a) in our syntheses. Therefore, a different process of the zeolite growth may be followed. Based on the above research by varying the CTAB/SiO₂ and S-1/SiO₂ ratios of synthesis precursor, a possible formation mechanism of N-ZSM-5 is proposed in this paper. Firstly, the S-1 seeds are dissolved into small fragmentations to provide more nuclei and surface of crystal growth, as reported in literatures.⁴⁷

Then these fragmentations induce the precursor aluminosilicates into ZSM-5 phase. Nevertheless, it is difficult for the growth of single isolated crystals because of abundant intergrowth and secondary growth, such as the Con-ZSM-5 (Fig. 4a). When the amphiphilic surfactants CTAB added into the precursor, each crystal nucleus interacts with CTAB and is dispersed, accordingly the intergrowth and secondary growth are inhibited. Meanwhile, large amounts of nanocrystals are formed, and further self-assemble into aggregates. Increasing the added amounts of seeds, the more crystal nuclei are provided, and the sizes of primary crystals of ZSM-5 aggregates are smaller. Based on the study above, the possible mechanism of the nano-sized ZSM-5 aggregates synthesized by modified seed-induced method with CTAB is proposed as Fig. 8b.

3.5. Catalytic performance on MTP reaction

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To investigate the catalytic properties of nano-sized ZSM-5 aggregates synthesized in this paper, both representative N-ZSM-5 Con-ZSM-5 catalysts characterized and were by temperature-programmed desorption of ammonia (NH₃-TPD). Fig. 9 displays that the curves of both catalysts with two peaks attributed to the desorption of NH₃ on the weak acidic sites and strong acidic sites are similar-shaped, respectively. Distinctly, the amounts of weak acid and strong acid of N-ZSM-5 are higher than those of Con-ZSM-5 (Table 2). Besides, the peak of weak acid displays a slight shift to lower temperature. It is probably due to that there are more accessible acid sites in N-ZSM-5 because of abundant mesopores and larger external surface area. Considering the excellent textural properties and modified acidity, N-ZSM-5 catalyst is expected to show better catalytic performances in the MTP reaction, compared with Con-ZSM-5.

To quickly evaluate the catalytic activities, MTP reactions over N-ZSM-5, Con-ZSM-5 and commercial ZSM-5 were carried out with WHSV of 8 h^{-1} . The conversion of methanol is presented as a function of time on stream (TOS) for the three catalysts in Fig. 10a. Methanol conversions over

N-ZSM-5, Con-ZSM-5 and commercial ZSM-5 are approximately 100% during the initial 37 h, 11 h and 20 h TOS, respectively, indicating the high initial stability of all catalysts. If the catalyst deactivation is defined as methanol conversions decreasing to around 95%, the catalytic lifetime of N-ZSM-5 (40 h) is much longer than that of Con-ZSM-5 (15 h) and commercial ZSM-5 (25 h). Therefore, compared with Con-ZSM-5 and commercial ZSM-5, N-ZSM-5 exhibits a pronounced improvement of the stability.

Fig. 10b displays the selectivity of propylene over N-ZSM-5, Con-ZSM-5 and commercial ZSM-5 catalysts as a function of TOS. At the initial stage (0.3 h), the selectivity towards propylene is amount to 38.6% for N-ZSM-5, remarkably higher than that of Con-ZSM-5 (32.2%) and commercial ZSM-5 (37.4%). The steady state with the stable propylene selectivity of the reaction is observed after about 2 h TOS for N-ZSM-5, 5 h for Con-ZSM-5 and 8 h for commercial ZSM-5. The steady period of reaction for N-ZSM-5 reaches more than 30 h, much longer than Con-ZSM-5 (13 h) and commercial ZSM-5 (18 h). The selectivity of ethylene and light olefin ($C_2^{=}-C_4^{=}$) for N-ZSM-5, Con-ZSM-5 and commercial ZSM-5 are shown in Fig. 10c and d. The average values of selectivity towards propylene, ethylene and $C_2^{=}-C_4^{=}$ for N-ZSM-5 at steady state are 39.5%, 12.2% and 71.7%, respectively, higher than Con-ZSM-5 (35.7%, 10.6% and 62.3%, respectively) and commercial ZSM-5 (37.9%, 11.5% and 67.9%, respectively), leading to a similar propylene/ethylene ratio (3.23, 3.36 and 3.29 respectively). With prolonged TOS, the deactivation stage occurs, and the propylene selectivity for all catalysts decreases slowly.

Fig. 11 further shows the coke deposition on the deactivated N-ZSM-5 and Con-ZSM-5 catalysts measured by TG analysis. N-ZSM-5 contains 2.43 wt.% coke deposit after 41 h TOS, while for Con-ZSM-5 the coke deposit is 2.11 wt.% after 16 h. The average coking rate on N-ZSM-5 is 0.06% per hour, much lower than that of 0.13% on Con-ZSM-5 catalyst. N-ZSM-5

exhibits a strong capability for coke tolerance, and retardation of catalyst deactivation. The excellently catalytic performance of N-ZSM-5 catalyst owes to that the nano sizes, large external surface area, and abundant mesopores of N-ZSM-5 can improve the diffusivity of methanol and products, and restrain the coke deposition,⁴⁸ thereby leading to the pronounced improvement of catalytic stability and propylene selectivity in MTP reaction.

4. Conclusions

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Highly crystalline nano-sized ZSM-5 zeolite aggregates (N-ZSM-5) with abundant inter-crystal mesopores are directly synthesized by a modified seed-induced method in the presence of CTAB. The addition of a small amount of CTAB can restrain the intergrowth and secondary growth of the primary nano-crystallites, therefore the nano-sized ZSM-5 aggregates are facilely obtained by the self-assembly of the nano-crystallites. Increasing the amounts of S-1 seeds gives rise to the gradual decrease of the primary crystallites sizes. N-ZSM-5 has a remarkable improvement on the stability and propylene selectivity in the methanol to propylene reaction compared with the conventional ZSM-5 and the commercial ZSM-5. This difference is due to the large external surface area and mesopore volume, which improve the diffusion rate and enhance the catalytic efficiency. In particular, the synthetic strategy provides a facile and economical method for the synthesis of N-ZSM-5 because of the low consumption of seeds and CTAB. The synthetic zeolites are expected to be widely usable in chemical industry as catalysts or adsorbents.

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Table captions

Table 1 List of synthesis conditions and derived parameters obtained from the N_2 adsorption-desorption isotherms of all ZSM-5 zeolites.

Table 2 Acid properties of the N-ZSM-5 and Con-ZSM-5 catalysts.

Figure captions

Figure 1 The morphology and textural property of N-ZSM-5: (a-c) SEM images under different magnification, (d) N₂ adsorption/desorption isotherm and BJH pore size distribution, (e) low magnification of TEM image and (f) high magnification of TEM image.

Figure 2 XRD patterns (a), FT-IR spectra (b), ²⁷Al MAS NMR spectra (c) and ²⁹Si MAS NMR spectra (d) of N-ZSM-5.

Figure 3 XRD patterns of Con-ZSM-5 and ZSM-5 zeolites synthesized with different CTAB/SiO₂ ratios: 0.005, 0.015, 0.02, 0.03 and 0.05.

Figure 4 SEM images of Con-ZSM-5 (a), and ZSM-5 zeolites synthesized with different CTAB/SiO₂ ratios: (b) 0.005, (c) 0.015, (d) 0.02, (e) 0.03 and (f) 0.05. All scale bars are 1 μ m. **Figure 5** (a) TG curves of Con-ZSM-5 and N-ZSM-5 synthesized with different CTA⁺/SiO₂ ratios before calcination; (b) The amount of CTA⁺ incorporated in the samples and variation of mesopore volumes as a function of increasing CTA⁺/SiO₂ molar ratios.

Figure 6 XRD patterns of ZSM-5 zeolites synthesized with different S-1/SiO₂ ratios: 0.005, 0.02, 0.04 and 0.06.

Figure 7 SEM images of ZSM-5 zeolites synthesized with different S-1/SiO₂ ratios: (a) 0.005, (b) 0.02, (c) 0.04 and (d) 0.06. All scale bars are 1 μ m.

Figure 8 SEM image of S-1 seed (a) and proposed mechanism for the synthesis of nano-sized ZSM-5 aggregates by modified seed-induced method with CTAB (b).

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Figure 9 NH₃-TPD profiles of N-ZSM-5 and Con-ZSM-5 catalysts.

Figure 10 Methanol conversion (a), propylene selectivity (b), ethylene selectivity (c) and light

olefin selectivity (d) of MTP reaction with time on stream over N-ZSM-5, Con-ZSM-5 and

commercial ZSM-5. Reaction conditions: 470 °C; 0.1 MPa; zeolite 0.5g; methanol WHSV = 8

 h^{-1} ; molar ratio of methanol and water = 1:1; carrier gas: high purity N₂, 60 ml min⁻¹. Testing was stopped at ~93% conversion.

Figure 11 TG curves of the N-ZSM-5 and Con-ZSM-5 catalysts after deactivation.

Samples	CTAB/SiO ₂ ratio	S-1/SiO ₂ ratio	SiO_2/Al_2O_3 ratio ^{<i>a</i>}	S_{BET}^{b} (m ² g ⁻¹)	S_{micro}^{c} (m ² g ⁻¹)	$\frac{S_{ext}^{c}}{(m^2 g^{-1})}$	V_{total}^{d} (cm ³ g ⁻¹)	V_{micro}^{e} (cm ³ g ⁻¹)	V_{meso}^{e} (cm ³ g ⁻¹)
N-ZSM-5	0.02	0.08	157	414	141	273	0.31	0.08	0.23
Con-ZSM-5	0	0.08	155	342	181	161	0.21	0.12	0.09
Z-0.005C-0.08S	0.005	0.08	146	366	174	192	0.22	0.10	0.12
Z-0.015C-0.08S	0.015	0.08	152	388	169	219	0.24	0.08	0.16
Z-0.02C-0.08S	0.02	0.08	158	416	145	271	0.30	0.07	0.23
Z-0.03C-0.08S	0.03	0.08	151	358	154	204	0.22	0.07	0.15
Z-0.05C-0.08S	0.05	0.08	157	318	169	149	0.17	0.10	0.07
Z-0.02C-0.005S	0.02	0.005	152	323	171	152	0.19	0.07	0.12
Z-0.02C-0.02S	0.02	0.02	147	369	192	177	0.23	0.09	0.14
Z-0.02C-0.04S	0.02	0.04	155	373	173	200	0.26	0.09	0.17
Z-0.02C-0.06S	0.02	0.06	159	381	168	213	0.26	0.07	0.19

^{*a*} Determined by ICP-OES. ^{*b*} Derived from the BET equation. ^{*c*} Micropore surface area (S_{micro}) was derived from the t-plot method, S_{ext} was calculated by subtracting S_{micro} from S_{BET}. ^{*d*} Calculated at $p/p_0 = 0.99$. ^{*e*} Micropore volume (V_{micro}) was evaluated by the t-plot method, V_{meso} was calculated by subtracting V_{micro} from V_{total}.

Table	2
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Catalvata	Total acidity	Strong acidity	Weak acidity	
Catalysis	$/(\text{mmol g}^{-1})$	$/(\text{mmol } g^{-1})$	$/(\text{mmol } g^{-1})$	
N-ZSM-5	0.314	0.149	0.165	
Con-ZSM-5	0.290	0.140	0.150	

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Figure 1



Figure 2











Figure 5

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Figure 8



Figure 9



Figure 10



Figure 11



80x67mm (300 x 300 DPI)