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Growth of ZSM-5 zeolite microparticles from crystal seeds for catalytic hydration of cyclohexene[†]

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The synthesis of ZSM-5 microparticles (MPs) possesses scientific and industrial importance due to the corresponding kinetic effects and operation issues. In this paper, a simple and scalable crystal seed growth approach was developed to synthesize ZSM-5 MPs, without an organic template, for the catalytic hydration of cyclohexene to cyclohexanol. As ZSM-5 sub-microparticles (SMPs) were used as the crystal seeds, the as-synthesized ZSM-5 MPs exhibit higher crystalline degrees and larger sizes, with an average diameter up to 8.78 μ m, than that of commercial ZSM-5 SMPs. The as-synthesized ZSM-5 MPs exhibit high catalytis in the hydration of cyclohexene to cyclohexanol, the ZSM-5 MPs exhibit high catalytic performances, in a long running experiment of up to 1000 h, and a superior sedimentation property compared to commercial ZSM-5 SMPs.

1. Introduction

The synthesis of morphology- and size-controllable molecular sieve materials possesses scientific and industrial importance due to the corresponding kinetic effects and operation issues.¹⁻³ It is an important general strategy to assemble nanoparticles (NPs) or submicroparticles (SMPs) for the morphology- and size-controllable construction of complex structures, and has been applied to the synthesis of a large number of inorganic materials.⁴⁻⁶ The crystal seed growth method can be employed to assemble NPs or SMPs and then to synthesize the morphology- and size-controllable complex crystal structures, including molecular sieve particles.⁷⁻¹² In the case of the syntheses of molecular sieves, organic templates are required for effective crystal seed growth methods and are often followed by complicated post-treatment to remove these organic templates.^{13,14} It is valuable therefore to synthesize morphology- and size-controllable molecular sieve materials through crystal seed growth methods without employing any organic templates.¹⁵ ZSM-5 molecular sieves have been regarded as an important solid acid catalyst for the hydration of cyclohexene to cyclohexanol, due to their excellent catalytic

performances, superior mechanical strength, and high thermal stability.¹⁶⁻¹⁸ ZSM-5 NPs can also be synthesized by a crystal seed growth method.¹⁵ The tunable diameters of the ZSM-5 particles are expected to influence the catalytic performances and sedimentation separation property. Because of the facile sedimentation property, ZSM-5 microparticles (MPs) are favorable in industrial processes.¹⁹⁻²² However, this is still a serious problem for ZSM-5 MPs as catalysts, with the contradiction between the negative effect of the MPs diameters on the catalytic activity and the positive effect of MPs diameters on the sedimentation separation performance, in this catalytic reaction system. The employment of organic templates should also be avoided for more facile and environmental benign synthesis processes.^{15,23,24} In this paper, we report a facile crystal seed growth strategy for the synthesis of ZSM-5 MPs under hydrothermal conditions with ZSM-5 SMPs as the crystal seeds. The as-synthesized ZSM-5 MPs possess typical micrometer diameters. As catalysts in the hydration of cyclohexene to cyclohexanol, the ZSM-5 MPs exhibit high catalytic performances, in a long running experiment of up to 1000 h, and a superior sedimentation property compared to commercial ZSM-5 SMPs.

2. Experimental section

2.1 Material synthesis

Na-ZSM-5 microparticles (MPs) were synthesized from industrial silica gel (SiO₂ content: 26.5 wt %), NaOH and alumina hydroxide (AR) without any template. The gel, with a complete composition of 11.5 Na₂O-100 SiO₂-3 Al₂O₃-2750 H₂O, was employed for the synthesis of the ZSM-5 MPs. The gel mixture was treated with the crystal seeds (H-ZSM-5 from Nankai University, 0.5 wt % of silica gel) in a Teflon lined stainless steel autoclave, under hydrothermal conditions, at 180 °C for 48 h after a designed aging time (0–24 h). The average sizes of the ZSM-5 MPs were controlled by adjusting the aging time. The Na-ZSM-5 MPs with the average diameter of 8.78, 4.08, 2.15, and 1.52 mm were obtained and denoted as ZSM-5-A, B, C, and D according to the aging time (ZSM-5-A: 0 h, ZSM-5-B: 5 h, ZSM-5-C: 20 h, and ZSM-5-D: 24 h), respectively. The solid was separated by filtration, dried at 110 °C for 8 h, calcined at 550 °C in air for 4 h and then exchanged in an aqueous solution of ammonium nitrate (0.5 mol L^{-1}) three times to obtain H-ZSM-5 MPs. The actual molar ratio of SiO₂/Al₂O₃ of the assynthesized H-ZSM-5 MPs was controlled in the range of 23 to 25.

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The H-ZSM-5 SMPs were obtained from commercial sources (NZ from Nankai University and JZ from Japan, respectively, Fig. S1 and S2, ESI†).

2.2 Material characterization

The phase structures of the ZSM-5 MPs were characterized by X-ray diffraction (XRD, PANalytical B.V., X'pert PRO) with Cu-K α (λ = 1.5418 Å) and a scanning rate of 1.2° min⁻¹. The morphology and size of the ZSM-5 particles were observed by scanning electron microscope and energy dispersive spectroscope (SEM-EDS, JEOL, JSM-6700F operating at 20 kV). The element distribution of the ZSM-5 particles was analyzed in Ar support gas by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Thermo Scientific iCAP6000, Thermo Fisher, USA). The average diameters of the ZSM-5 particles were analyzed on a Laser particle size distribution instrument (Rise-2002, Jinan, China). The N₂-sorption isotherms were obtained on a NOVAl000e (Quantanchrome, USA) at 77 K. From the adsorption branch of the isotherm curves, the total specific surface areas (A_{Total}) of the ZSM-5 particles were calculated by the multipoint Brunauer-Emmett-Teller (BET) method. The pore volume (V_{pore}) was calculated by a single point method with the Capillary condensation model. The micropore surface area (A_{micro}), external surface area (A_{ex}) , micropore volume (V_{micro}) and mesopore volume (V_{meso}) were calculated by a *t*-plot method. The NH₃ Temperature Programmed Desorption (NH₃-TPD) was obtained on a NH₃-TPD analyzer produced by the Zhejiang Fantai Corp. The acid sites and strength of the ZSM-5 particles were characterized by the Hammett indicator method and Pyridine Fourier Transform Infrared Spectroscopy (FT-IR).

2.3 Catalysis measurement

The catalytic hydration of cyclohexene was employed to examine the catalytic performances of the ZSM-5 catalysts. In a typical catalytic reaction, water (50 ml) and cyclohexene (50 ml) was treated in a high pressure agitated autoclave (250 ml), with the catalyst (3.9 g), at 399 K for 210 min. The initial pressure was controlled at 0.4 MPa and the rotate speed was controlled at 900 rpm. After being kept in a standing state for 12 h, the organic phase was analyzed using a gas chromatograph (GC-9790) equipped with a flame ionization detector and a 30 m capillary column (OV1701). The internal standard method was used to determine the composition of the organic phase. The transmittance of the aqueous phase was measured on a UV-VIS spectrophotometer (752 type, Shanghai Third Analysis Instrument Factory) to investigate the sedimentation of the catalysts.

3. Results and discussion

The key step of this synthesis route is the use of ZSM-5 SMPs as the crystal seeds. The synthesis of the ZSM-5 MPs is illustrated in Scheme 1. The industrial silica gel and alumina hydroxide were used as the raw materials to prepare the gel mixture. With the assistance of the ZSM-5 SMPs (Obtained from Nankai University, named as NZ) as the crystal seeds, the gel mixture was treated in a stainless steel autoclave under hydrothermal conditions at 180 °C for a period of time, without any organic templates. After being separated by filtration, dried at 110 °C, and calcined at 550 °C in



Scheme 1 Illustration of the synthesis process for the ZSM-5 MPs through a crystal seed growth method.

air for 4 h, Na-ZSM-5 was obtained. H-ZSM-5 was obtained by ion exchange of Na-ZSM-5 with an aqueous solution of HNO_3 three times.

The morphology of the ZSM-5 SMPs and MPs was observed by SEM (Fig. 1). The ZSM-5 MPs possess an olive-like shape in the micrometer scale from 2 to 10 μ m. The increase in aging time provides the decrease in size of the ZSM-5 MPs (Fig. 1 a–d). In this investigation, the olive-like shape can be obtained and the distribution of the particle sizes is also kept uniform. However, the ZSM-5 particles from the commercial sources possess submicrometer sizes (Fig. 1f, S1, ESI†). This distinctive structure characteristic is evidence that the ZSM-5 MPs have be synthesized from the ZSM-5 crystal seeds under hydrothermal conditions.

The phase structure of the ZSM-5 MPs was characterized by XRD patterns (Fig. 2). The clear diffraction peaks at $2\theta = 7.9^{\circ}$, 8.8°, 23.1°, 23.9°, and 24.4° provide evidence for the MFI zeolite topology of the ZSM-5 MPs.^{15,25} The average diameters of the ZSM-5 MPs were measured by a Laser particle size distribution instrument and are consistent with the results from the SEM images (Fig. 1 and Table S1, ESI†). The crystallite sizes in the range of 30–80 nm can be calculated by the Scherrer equation for



Fig. 1 SEM images of the ZSM-5 MPs synthesized at various aging times (a) 0, (b) 5, (c) 20, (d) 24 h, and the ZSM-5 SMPs (e) NZ and (f) JZ.



Fig. 2 XRD patterns of various ZSM-5 zeolites.

the various crystalline planes (112, 101, and 313) in the ZSM-5 MPs, which are smaller than the results from the SEM images. This disagreement between crystallite sizes indicates that the ZSM-5 MPs are multicrystal structures and composed of ZSM-5 NPs (Table S1, ESI†).

The surface areas and porosity of the ZSM-5 MPs were measured by N₂-sorption isotherms. The ZSM-5 MPs possess high surface areas (A_{Total}), from 206 to 320 m² g⁻¹, which are similar to their sub-microscale counterparts (NZ and JZ). The micropore surface areas are the main content of the total surface areas and exhibit the same changing tendency as the total surface areas (Table 1). These large surface areas will be propitious in forming more active sites for the catalytic reaction. This similar changing tendency can be found for the pore volumes of the ZSM-5 MPs (Table 1). The micropore volumes are the main content of the total pore volumes, which also provide evidence for the formation of the ZSM-5 MPs. The existence of these mesopore surface areas and mesopore volumes may be due to the substantial accumulation of the ZSM-5 SMPs domains in the ZSM-5 MPs, which will be able to facilitate the diffusion of the reactants in the pores of the catalyst and improve the catalytic performance.^{26,27}

To research the surface property of the ZSM-5 MPs, the acid strength distribution and total acid amounts of the ZSM-5 particles were measured through the Hammett indicator method with neutral red ($pK_a = + 6.8$), methyl red ($pK_a = + 4.8$), dimethyl yellow ($pK_a = + 3.3$), dicinnamalacetone ($pK_a = -3.0$) as the indicator, respectively, and n-butylamine as the titration agent

Table 1 Surface areas and porosity of the H-ZSM-5 zeolites

Sample	$\begin{array}{c} A_{\text{Total}}^{a} & A_{\text{micro}}^{b} \\ (\text{m}^2 \text{ g}^{-1}) \end{array}$		$A_{\rm ext}^{\ \ c}$	$V_{\text{pore}}^{d} V_{\text{micro}}^{e}$ (cm ³ g ⁻¹)		V _{meso} ^f
ZSM-5-A	206	153	51.8	0.130	0.084	0.046
ZSM-5-B	269	202	67.3	0.161	0.103	0.058
ZSM-5-C	306	231	74.8	0.193	0.126	0.067
ZSM-5-D	320	264	56.2	0.213	0.160	0.063
NZ	297	225	72.2	0.184	0.123	0.061
IZ	323	254	69.0	0.216	0.153	0.063

^{*a*} A_{total} : total surface area ^{*b*} A_{micro} : surface area of micropore ^{*c*} A_{ext} : external surface area ^{*d*} V_{pore} : total pore volume ^{*e*} V_{micro} : micropore volume ^{*f*} V_{meso} : mesopore volume. (Fig. 3).^{28,29} The ZSM-5 particles with different average diameters possess significant different total acid amounts. It can be observed that the increasing diameters in the ZSM-5 MPs provides the decreasing total acid amounts due to decreasing surface areas. The smaller ZSM-5 MPs possess greater surface areas and more acid sites. The smaller particles possess increasing high-energy surface active sites, which further increase the amount of acid centers.

The Brönsted acid sites (A_B) /Lewis acid sites (A_L) for the different ZSM-5 MPs sizes were measured by the NH₃-TPD method (Table S2, ESI[†]). The peak position of ZSM-5-C was shifted slightly to a higher temperature, which indicated that the acid strength of ZSM-5-C was slightly stronger than those of other samples. In addition, the Brönsted acid sites of the ZSM-5 MPs were less than those of NZ and JZ, which may be attributed to the lower surface area and pore volume of the ZSM-5 MPs. The total acid amount measured by the Hammett method was significantly greater than the NH₃-TPD method, which may be related to the lipophilicity of the high-silica zeolite surface and that the adsorption of organic amine (organic base) was stronger than that of ammonia (inorganic base).

The catalytic hydration of cyclohexene to cyclohexanol was employed to examine the catalytic performance of the ZSM-5 MPs and SMPs. The ZSM-5 MP catalysts provide similar catalytic performances to the commercial ZSM-5 SMP catalysts, including the conversion of cyclohexene and the selectivity of cyclohexanol (NZ and JZ, Fig. 4a). The conversion of cyclohexene can be obtained from 7.43% to 11.40%, which are also comparable to the commercial ZSM-5 SMPs.^{16,30} The activity and stability of the ZSM-5 MPs, including the conversion of cyclohexene and the selectivity of cyclohexanol were also investigated in a long running experiment and are shown in Fig. 4b. In the first 200 h, a high conversion from 8.8% to 9.6% was obtained with a high selectivity from 94% to 98%. In the second 200 h, the conversion decreased gradually to 3.5%, which could be attributed to the inactivation of the catalysts.^{31,32} After the regeneration treatment with H_2O_2 , the excellent catalytic performance of the ZSM-5 MPs was achieved again with a high initial conversion up to 9.5% and high initial selectivity up to 98.5%.33 After a running time of 300 h, the inactivation of the catalyst was observed for a second time. The regeneration of the catalysts was conducted three times in the long running experiment of 1000 h, and good conversion and selectivity were always observed. These excellent catalytic performances and the significant sedimentation separation property of the ZSM-5 MPs show that they may be a superior alternative for commercial ZSM-5 SMPs in wide industrial applications.^{34,35}



Fig. 3 The acid amounts and strength distribution of the ZSM-5 particles.



Fig. 4 (a) The catalytic performances of the ZSM-5 catalysts in the hydration of cyclohexene to cyclohexanol, (b) the stability properties in a long running time of up to 1000 h, (c) the transmittance of the reaction mixture with the ZSM-5 particles in the sedimentation process, and (d) the photo images of the sedimentation process in the reaction mixture with the ZSM-5 MPs and ZSM-5 SMPs.

It is noteworthy that the ZSM-5 MPs exhibit a distinctively improved sedimentation separation performance compared to the ZSM-5 SMPs (Fig. 4c, d). The clear difference in the transmittance of the aqueous reaction mixture shows that the ZSM-5 MPs can be more easily separated from the reaction mixtures than their sub-microscale counterparts, which can be observed from the photo images (Fig. 4c, d). This superior sedimentation performance of the ZSM-5 MPs will be of great benefit in industrial applications.

4. Conclusions

In conclusion, a simple and scalable crystal seed growth approach was developed to synthesize ZSM-5 MPs, without an organic template, for the catalytic hydration of cyclohexene to cyclohexanol. Due to the use of crystal seeds, the assynthesized ZSM-5 MPs exhibited a good crystalline degree and possess larger sizes, with an average diameter up to 8.78 µm, than that of commercial ZSM-5 SMPs. As catalysts for the hydration of cyclohexene, the catalytic performance of the ZSM-5 MPs has been investigated in a long running experiment of up to 1000 h, with a high conversion of cyclohexene, high selectivity of cyclohexanol, and excellent stability. The main advantage of the ZSM-5 MPs is the significantly improved sedimentation separation performance compared to that of the ZSM-5 SMPs. These improvements in the catalytic performance of the ZSM-5 MPs show its wide potential application as an alternative for ZSM-5 SMPs. Work in this direction is currently under way in our laboratory.

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