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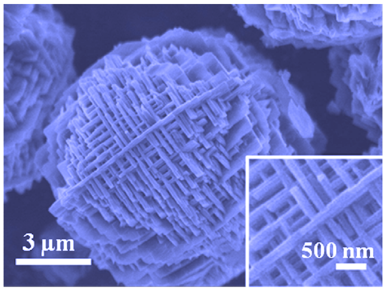

This work presents a facile, economic and green synthesis of highly active house-of-cards-like ZSM-5 by the addition of N-methyl-2-pyrrolidone (NMP) into template-free zeolite synthesis system.

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N-methyl-2-pyrrolidone assisted synthesis of hierarchical ZSM-5 with house-of-cards-like structure†

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Development of facile, economic and green routes towards the synthesis of hierarchical zeolites with high catalytic activity still remains a challenge in modern industrial catalysis. In this paper, we report on a novel synthesis of house-of-cards-like ZSM-5 (HCL-ZSM-5) via the introduction of N-methyl-2-pyrrolidone into template-free zeolite synthesis system. Importantly, the HCL-ZSM-5 presents much better catalytic performances in cracking of cumene and 1, 3, 5-triisopropylbenzene (TIPB) than conventional porous catalysts (ZSM-5, Y zeolite and Al-MCM-41).

Zeolites (crystalline microporous aluminosilicates) are the most important heterogeneous acid catalysts in modern industrial procedures (e. g. oil refinery, fine chemistry and environmental catalysis) in virtue of their strong acidity, shape selectivity and high hydrothermal stability.[1] However, the intrinsic minor micropores may in some cases become a major restriction for their further applications in bulky molecules-involved processes because the mass transport is negative, especially when the catalysis is diffusion-controlled.[2] More severely, the frequent blocking of microporous channels, caused by the strong adsorption of guest molecules, could even account for the rapid deactivation of catalysts.[3] Down-sizing strategy is admittedly effective for solving the problem. In comparison with conventional bulk zeolites, nano zeolites have richer external surface and shorter micropore canals, which can offer the reactants more active sites to contact with, and thereby leads to a remarkable catalytic activity and coking-tolerant ability.[4] Undersized zeolites, as we know, are not appropriate for practical applications owing to the poor maneuverability (difficulties of separation and shaping), meanwhile the pressure drop in packed-bed reactors is much higher.[5] The emergence of aluminum-containing mesoporous materials (e. g. Al-MCM-41, Al-MCM-48, and Al-SBA-15) may afford an opportunity for the effective conversion of bulky molecules.[6] Unfortunately, these materials suffer from weak acidity and poor hydrothermal stability.[7] Recently, hierarchical zeolites have attracted much attention both in fundamental researches and industrial applications depending on their dual advantages of microporous zeolites (strong acidity, high thermal and hydrothermal stability) and mesoporous materials (large surface area and fast mass transfer).[8] Several strategies such as polymers,[9] organosilanes,[10] inorganic nanoparticles[11] and post-treatments[12] have been proved available for producing zeolites with hierarchical architectures, but still some challenges including procedural complexity, economic feasibility and environmental issues remain to be broken through for commercial requirements. For instance, house-of-cards-like (HCL) zeolites could be successfully synthesized applying complex organic quaternary ammonium salts.[13] Apart from the expensiveness, the generation of poisonous residues is far from environmental benefits. Herein, we present our detailed work on a simple and green synthesis of house-of-cards-like ZSM-5 (HCL-ZSM-5) assisted with low-cost N-methyl-2-pyrrolidone (NMP).

Fig. 1 shows the characterizations (phase, morphology and textural parameters) of the powder product crystallized at 140 °C for 72 h. As shown in Fig. 1A, the entire X-ray diffraction (XRD) pattern confirms well with the typical MFI structures. Corresponding scanning electron microscopy (SEM) images (Fig. 1C and 1D) indicate that the ZSM-5 sample presents a regular house-of-cards-like morphology (~10 μm), which consists of some orthogonal sheet-like crystals. Seen from the high-resolution SEM, the typical thickness of crystal sheets is about 100 nm (inset in Fig. 1D). To the best of our knowledge, this is the first observation of such a complex morphology for the ZSM-5 zeolites synthesized without the presence of quaternary ammonium salts. N_2 adsorption-desorption isotherms of HCL-ZSM-5 is shown in Fig. 1B. The steep uptake at low relative pressures together with large hysteresis loop (moderate relative pressures) and a slight uptake at higher relative pressures indicate a micro-meso-macro hierarchical porous characteristic. On the basis of non-local density functional theory (NLDFT), a broad distribution of meso-macropores around 16 nm (5-80 nm) is clearly observed (inset in Fig. 1B). The result is seemingly contradictory to the SEM images. We think, here, the internal constitution of HCL- ZSM-5 is different from that of outside, which becomes a little occlusive with the gradual thickening of primary crystal sheets.

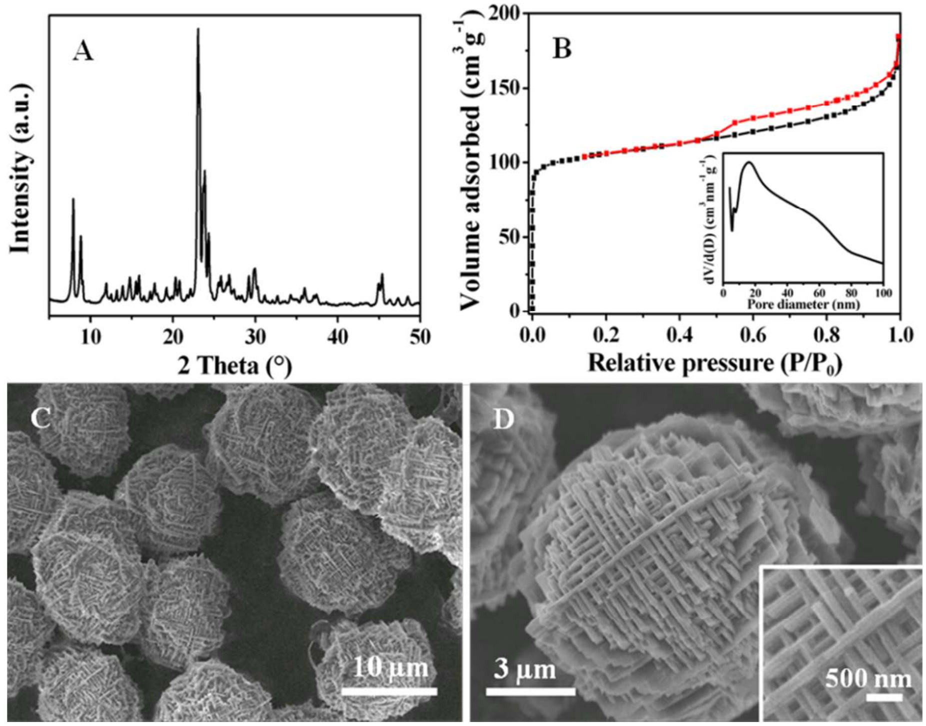

Fig. 1 (A) XRD pattern, (B) N_2 adsorption-desorption isotherms and corresponding NLDFT pore size distribution (inset), and (C, D) SEM images of HCL-ZSM-5. Inset in (D) shows high-resolution SEM image of HCL-ZSM-5.

Even so, the presence of such secondary pores would also offer additional benefits in catalysis. Calculated from the curve, Brunauer–Emmett–Teller (BET) surface is 413 m^2 g^{-1}, among which, external surface area is about 182 m^2 g^{-1} estimated by the t-plot method.

To get further insights into the formation procedure of the HCL-ZSM-5, time-consumed experiments were conducted. Before the onset of crystallization (6 h), the precursor presented a cross-linked coralline morphology, as shown in Fig. 3A. After crystallization for 18 h, weak diffraction peaks associated with MFI structure started to appear (Fig. 2), but still no crystal-like substance came into sight from the SEM image (Fig. 3B). TEM shows that there existed some foliated crystals inside the micron-sized disk gel (Fig. 3E**)**. Here, the foliated crystals, we think, should have a hydrophilic surface, which likely interact with the surrounding aluminosilicate and promote their further growth. As time went on (24 h), the diffraction peaks became obvious, and ZSM-5 polycrystal with simple intersecting structure was clearly visible (Fig. 3C). Corresponding TEM indicated that the ZSM-5 polycrystal had a sheet-like mother crystal, on which intergrown crystals nucleated (patch-like parts) and vertically grew (Fig. 3F). Further extending the reaction time to 48 h, intersecting crystals with more open structure

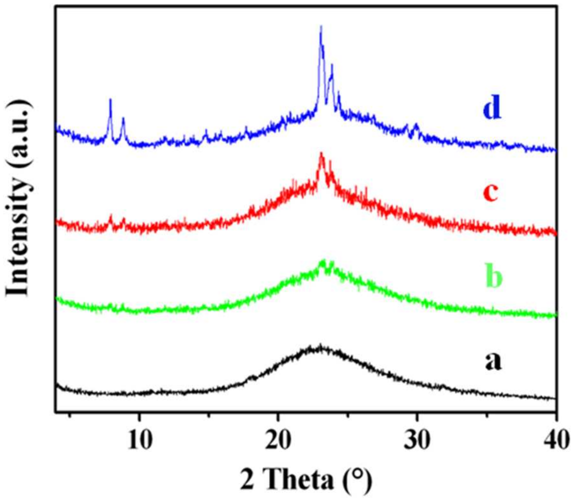

Fig. 2 XRD patterns of the products prepared at 140 °C for (a) 6 h (b) 18 h (c) 24 h and (d) 48 h.

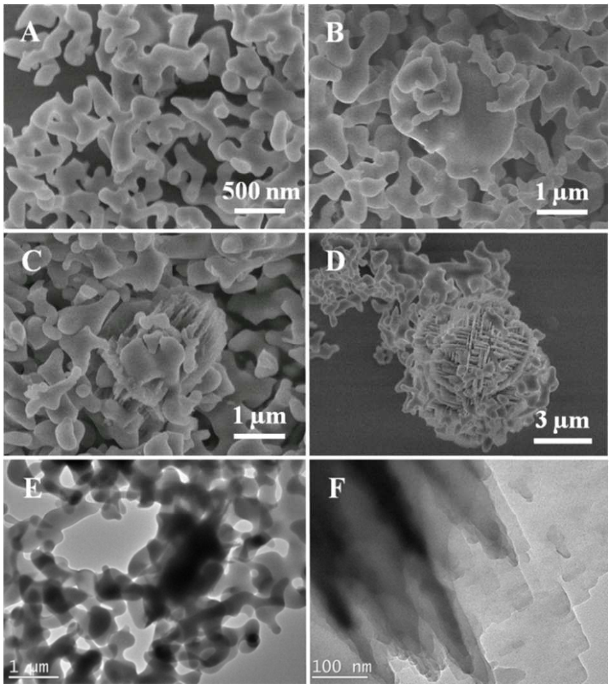

Fig. 3 SEM images of the products synthesized at 140 °C for (A) 6 h (B) 18 h (C) 24 h and (D) 48 h. (E, F) TEM images of the products prepared at 140 °C for 18 h and 24 h, respectively.

were gradually developed (Fig. 3D). Finally (72 h), pure ZSM-5 with intriguing HCL morphology was fully formed.

The liquid-state ^{13}C NMR spectrum of the supernatant obtained at 140 °C for 72 h is shown in Fig. 4A. In addition to NMP, trace quantity of N-Methyl-4-aminobutyric acid is detected, which arises from ring-opening decomposition of NMP, confirming that NMP is relatively stable in our highly alkaline synthesis condition. It should be noting that HCL morphology cannot be obtained if NMP is absent in the starting aluminosilicate gel (Fig. S1 and S2, ESI†). Clearly, NMP plays a critical role in the control of the special morphology. Although the detailed mechanism of action is still unclear, the HCL structure may be formed by defect intergrowth mechanism,[14] epitaxial intergrowth of two structures (e. g. MFI and MEL),[13a, 13b] or other else.[13c]

The chemical activity of crystalline aluminosilicate zeolite is generally correlated to the coordination environment of aluminium atoms, which can be identified by ^{27}Al MAS-NMR. As shown in Fig. 4B, the calcined HCL-ZSM-5 sample exhibits just one single resonance peak at about 54 ppm, assigned to tetrahedrally coordinated framework aluminium species, suggesting that all the Al atoms are located at intra-framework. Moreover, the acidity of H form HCL-ZSM-5 was performed by temperature-programmed desorption of ammonia (TPD-NH_3) experiment (shown in Fig. 4C). The peaks centred around 225 °C and 470 °C are assigned to weak and strong acidic sites, respectively, in good agreement with conventional H form ZSM-5. The above results suggest that the acidity of HCL-ZSM-5 is similar to that of conventional ZSM-5, and all the Al

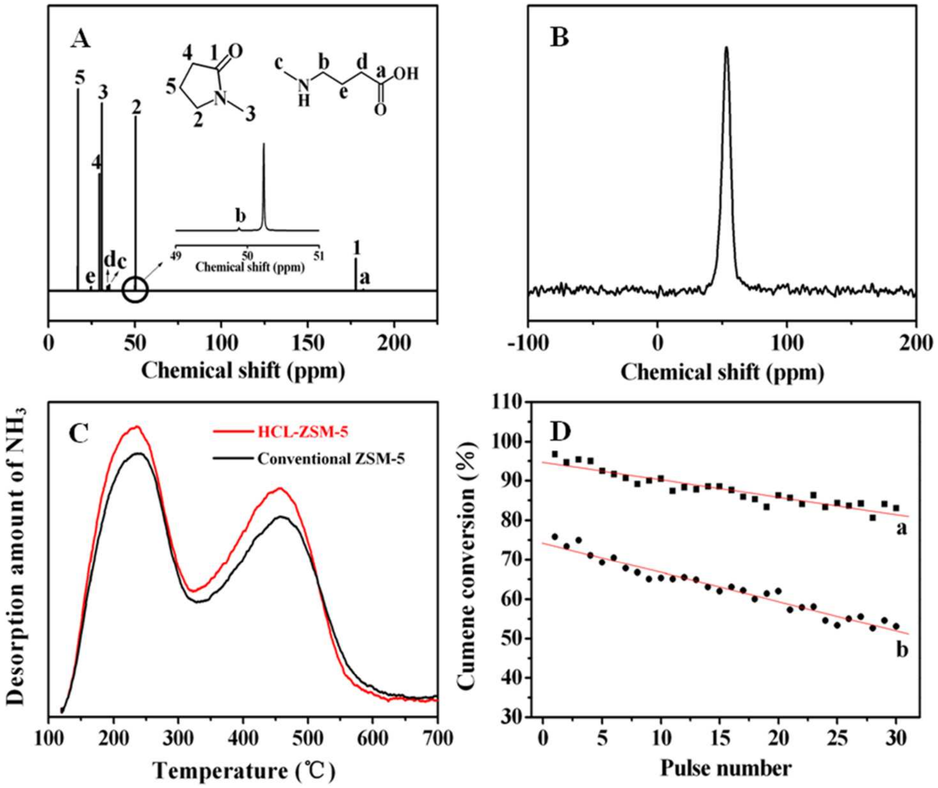

Fig. 4 (A) Liquid-state ^{13}C NMR spectrum of supernatant obtained at 140 °C for 72 h. (B) Solid-state ^{27}Al NMR spectrum of calcined HCL-ZSM-5. (C) TPD-NH_3 curves of H form (red) HCL-ZSM-5 and (black) conventional ZSM-5. (D) Cumene cracking of (a) HCL-ZSM-5 and (b) conventional ZSM-5.

Table 1 Textural parameters and catalytic activities in cracking of cumene and 1, 3, 5-triisopropylbenzene (TIPB) for various catalysts.

Sample	Si/Al (-)	S_{BET} ($m^2 g^{-1}$)	S_{ext} [a] ($m^2 g^{-1}$)	d_{meso} [b] (nm)	Cumene cracking (%)	TIPB cracking (%)
ZSM-5	17.1	325	31	—	75.8	15.7
Y	7.2	494	43	—	78	21.3
Al-MCM-41	50	495	495	2.8	16.3	41.8
HCL-ZSM-5	19.3	413	182	16	96.7	90.5

[a] S_{ext}, external surface area; [b] d_{meso}, mean mesopore size.

species in HCL-ZSM-5 framework are stable.

Catalytic activities of HCL-ZSM-5 and various conventional porous catalysts (ZSM-5, Y zeolite and Al-MCM-41) in the cracking of cumene are shown in Fig. 4D and Table 1. Notably, HCL-ZSM-5 is more active than the three conventional porous catalysts, and also exhibits a lower trend of deactivation with comparison to the conventional ZSM-5. The results, we think, are in close connection with the presence of strong acidity coupled with special HCL morphology of our HCL-ZSM-5.[13] Furthermore, catalytic activity of HCL-ZSM-5 has been checked in cracking of 1, 3, 5-triisopropylbenzene (TIPB), as shown in Table 1. Conventional ZSM-5 and Y zeolites presented initially low TIPB conversions of 15.7 % and 21.3 %, respectively, whereas our HCL-ZSM-5 afforded a better result about 90.5 %, which was also higher than Al-MCM-41 (41.8 %). The striking disparity between HCL-ZSM-5 and conventional microporous catalysts should boil down to the large dynamic diameter of TIPB molecules, which cannot diffuse through the inner pore of microporous zeolites. Therefore, cracking reaction only occurs on their small external surfaces. As for Al-MCM-41, the relatively weak acidity as well as poor hydrothermal stability, originating from its amorphous nature of the pore walls, is considered as the major cause of lower conversion.[7] It is believed that the existence of large amounts of strong acid sites on the abundant external surface of our HCL-ZSM-5 could offer the bulky TIPB molecules more highly active sites to react with, and naturally results in a higher conversion.[15]

Conclusions

In summary, hierarchical ZSM-5 with house-of-cards-like structure has been successfully prepared by the addition of NMP into the template-free zeolite synthesis system. With the large external surface and strong acidity, house-of-cards-like ZSM-5 exhibits much better catalytic performances than conventional porous catalysts (ZSM-5, Y zeolite and Al-MCM-41). We think that this work would provide a novel feasible strategy for the industrial production of highly active ZSM-5 catalysts on a large scale.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental and characterization details, XRD pattern, SEM image. See DOI: 10.1039/c000000x/

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