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Multimodal Zr-Silicalite-1 zeolite nanocrystal aggregates with interconnected hierarchically micro-meso-macroporous architecture and enhanced mass transport property

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ABSTRACT

Hierarchical porous architecture with interconnected trimodal micro-meso-macroporous systems constructed from uniform zeolite Zr-doped silicalite-1 nanocrystals has been prepared. The synthesis has been made by using glycerin as a reaction medium via a quasi-solid-state crystallization of hierarchically meso-macroporous zirconosilicate precursor under the effect of the structure directing agent TPAOH. The presence of glycerin is crucial in the synthesis systems to maintain the porous hierarchy. The pores interconnectivity, Zr location in the framework, the acidity and the catalytic activity have been studied by laser-hyperpolarized ^{129}Xe NMR spectroscopy, UV–visible spectroscopy, temperature-programmed desorption of ammonia and the catalytic isopropylbenzene cracking probe reaction, respectively. The products possess well-defined macrochannels interconnected with mesopores located in the macropore walls, which in turn have been constructed from microporous MFI-type zeolite units. ^{129}Xe NMR study indicated that the hierarchically micro-, meso-, macro-pore systems are homogeneously distributed throughout the final materials and well interconnected, which is important for molecular diffusion. The TPD-NH$_3$ investigation revealed that the hierarchically micro-meso-macroporous materials constructed from zeolite Zr-Silicalite-1 nanocrystals present strong acidity.

1. Introduction

MFI-type zeolite is one of crystalline microporous catalysts and is widely used in various hydrocarbon processing (such as ZSM-5) and oxidation catalysis (such as TS-1) owing to their strong catalytic performance, excellent thermal, hydrothermal and chemical stabilities [1–7]. However, one disadvantage of these zeolitic catalysts is that their pores (about 0.55 nm) are too small to be accessed by bulky reactants hindering their use in the fine chemical and petroleum processing industries [8,9]. Preparation of nanosized particles is a good option to obtain fast diffusion rate of reactants and high conversion of bulky molecules [10–13]. However, the reduction in crystal size of zeolites from the micrometer to the nanometer scale leads to the decrease in the crystalline degree, the thermal stability, and substantial changes in the properties. Zeolites with hierarchical porosity are mostly preferred, which can possess a great superiority in practical catalysis applications compared with conventional zeolites featuring only micropores due to their significantly improved accessibility and molecular transport, and higher surface area [14,15]. There have been many successful approaches to hierarchical MFI-type zeolites [16]. The synthetic techniques involve (i) chemical and/or physical post-treatment, such as the steaming or acid leaching methods [17–19]; (ii) hard templating synthesis, such as carbon and colloid templating [20–22]; (iii) soft templating synthesis, such as the use of amphiphilic organosilanes [23,24]. However, for increased efficiency within industrial processes, hierarchically porous zeolitic catalysts displaying both micro-meso-macroporosity and strongly active sites are more desirable. As an ideal hierarchically porous zeolite structure, such a MFI-type zeolite, should contain a well-defined macropore system to enhance matter transport, interconnected mesopores for increased selectivity and highly crystalline zeolite to provide molecular-sieving and shape selective effect, all of which are evenly distributed throughout one single material.

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More importantly, desired metal doping can provide strongly catalytically active sites, yielding a greater range of potential applications in catalysis.

In general, one metal doping only provides single functionality, for example, Al heteroatom in the silicalite framework being acid site, and Ti heteroatom in the silicalite framework being oxidation active site. Preparation of hierarchically micro-meso-macroporous materials constructed from zeolite units including ZSM-5, Beta, and TS-1 nanocrystals, which presented high catalytic activities, have been described in our very recent works [25–27]. These catalysts exhibited single functionality. Zr-doped zeolites gather an increasing interest in catalysis due to their unique multifunction alities of Zr heteroatom, which can be not only acid site but also oxidation sites. Herein, we developed a novel crystallization system to prepare hierarchically MFI-type zeolites with significant micro-meso-macroporous structure (defined as MMM), which was constructed from Zr-doped silicalite-1 nanocrystals via the structure directed crystallization of an amorphous meso-macroporous zirconosilicate precursor under glycerin medium. The final products present very good interconnectivity between the micropores, mesopores, and macropores, which will greatly improve its accessibility and enhance the mass transport property in catalytic application. Moreover, the resultant hierarchical micro-meso-macroporous materials constructed from Zr-doped silicalite-1 nanocrystals show very strong acidity, which is very important for their application as solid acid catalysts.

2. Experiment

2.1. Materials

Zirconium-butoxide (80 wt.% solution in butoxide), tetramethyl orthosilicate (TMOS, 99%), tetraethyl orthosilicate (TEOS, 99%), Tetrapropylammonium oxide (TPAOH, 25% in water), and glycerin were purchased from Aldrich.

2.2. Preparation of hierarchical zeolite Zr-Silicalite-1

A typical synthesis procedure was as follows:

Step 1: A meso-macroporous zirconosilicate with an amorphous structure was synthesized by dropping a mixture of 10 g zirconium-butoxide (80 wt.% solution in butoxide) and 10 g tetramethyl orthosilicate (TMOS) into 300 g distilled water as described in Refs. [28–30]. The solid products were collected and dried at 60 °C. Then, the products were used as the precursor in step 2.

Step 2: The precursor (1 g) was impregnated with 10 g Tetrapropylammonium hydroxide (TPAOH, 25% in water), 10 g tetraethyl orthosilicate (TEOS) and 15 g H_2O, and stirred for 3 h at room temperature. The dry gel was obtained after removing the water from the mixture under vacuum at 70 °C. Then, the gel was mixed with 5 ml glycerin and transferred into a Teflon-lined autoclave and aged at 130 °C for 2 days. The products were washed with distilled water, dried at 60 °C, and calcined at 550 °C for 4 h to remove the organic residues.

2.3. Characterization

X-ray diffraction (XRD) patterns were obtained with a Panalytical X'Pert diffractometer using Cu Kα radiation (λ = 1.54178 Å). Scanning electron microscopy (SEM) experiments were performed on a JSM-7500F electron microscope (JEOL, Japan). Transmission electron microscopy (TEM) experiments were performed on a Philips CM20 with an acceleration voltage of 200 kV. The nitrogen adsorption and desorption isotherms at the temperature of liquid nitrogen were measured using a Micromeritics ASAP 2010 M system. Solid-state ^{29}Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE500 spectrometer, and chemical shifts were referenced to tetramethylsilane for ^{29}Si. Ultraviolet–visible (UV–vis) spectra were measured in diffuse reflectance mode on a Perkin–Elmer Lambda 35 spectrometer, with $BaSO_4$ as a reference. Temperature-programmed desorption of ammonia (TPD-NH_3) curves were obtained in the range 120–800 °C at a rate of 15 °C/min. Continuous-flow laser-hyperpolarized (HP) ^{129}Xe NMR experiments [31,32] were carried out at 110.6 MHz on the Varian Infinity-plus 400 spectrometer using a 7.5 mm probe head.

The catalytic probe reaction of isopropylbenzene cracking was performed at 300 °C by pulse injections. In each run, 50 mg of catalyst was used, the pulse injection of the reactant was 0.4 ml, and the reaction flow rate was 53.7 ml/min.

3. Results and discussion

Fig. 1 shows the meso-macroporous zirconosilicate precursor and representative hierarchically micro-meso-macro porous Zr-Silicalite-1 (MMM-ZrS-1) by SEM and TEM characterizations. SEM images showed that precursor had well-defined macropores with a large pore size distribution (300 nm to 1.5 μm), which were constructed from amorphous zirconosilicates nanoparticles (Fig. 1a and b). It is worth noting that well-defined macropores were preserved in the product after the quasi-solid-state crystallization process -(Fig. 1c). Moreover, in the product the interconnected mesopores in the walls of macropores were constructed entirely from uniform nanocrystals with MFI-type zeolite morphology (Fig. 1d). TEM revealed that the product that was subjected to 2 days treatment under the effect of structure directing agent TPAOH, MMM-ZrS-1, was fully constructed from zeolite nanocrystals with high crystallinity (Fig. 1e and f). This means that the amorphous domains of the initial precursors have been completely transformed into highly crystalline zeolitic phases in the final product MMM-ZrS-1 after a crystallization transformation process for 2 days at 130 °C. In addition, the high magnification TEM image (Fig. 1f) and the circular streaking in the electron diffraction pattern (inset of Fig. 1e) further indicated the generation of an randomly orientated zeolite MFI-type structure in MMM-ZrS-1 with a highly crystallinity, which was further proved by XRD characterization (Fig. 2). Generally, under the effect of structure directing agent, the MFI-type zeolite nanocrystals were easily formed by the conventional hydrothermal condition [3]. However, this rapid growth and the strong interaction between the growing zeolite Zr-Silicalite-1 nanocrystals during the crystallization process would lead to the collapse of the macropores constructed from the aggregation of nanoparticles in the hydrothermal condition. Notably, meso-macroporous structure had been successfully retained over a long range in the product MMM-ZrS-1 as observed (Fig. 1). This implies that the crystallization transformation condition and glycerin medium used in this reaction system had really played roles in preserving the meso-macroporous framework during the crystallization process. The zirconium atoms were fully incorporated into the final zeolite structure, as evidenced by energy dispersive X-ray spectroscopy (EDS) (see Fig. S1), Inductively Coupled Plasma (ICP) and in particular by UV–visible spectroscopy, which will be discussed in the following section, and the ratio of Si/Zr was 68.5.

The powder X-ray diffraction (XRD) patterns of meso-macroporous zirconosilicate precursor and MMM-ZrS-1 are shown in Fig. 2. The meso-macroporous zirconosilicate precursor had an amorphous structure as evidenced by a broad peak around $2\theta = 23°$ in the XRD pattern (Fig. 2a). It is worth mentioning that a highly crystalline zeolite MFI-type structure, as evidenced by the peaks with high intensity at 8° and 23°, which are associated with a zeolite

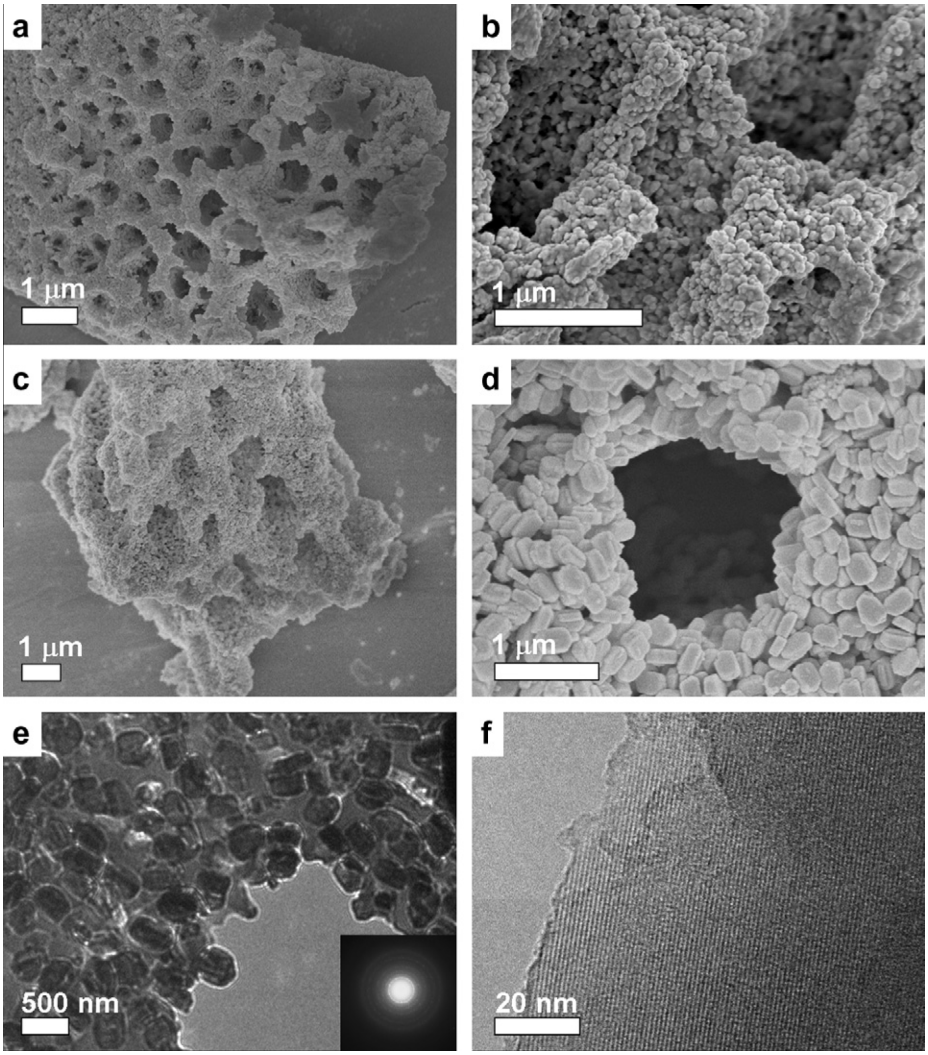

Fig. 1. SEM (a and b) images of meso-macroporous zirconosilicate precursor. SEM (c and d) and TEM (e and f) images of MMM-ZrS-1. The inset of e is the corresponding selected area electron diffraction (SAED) pattern taken from many particles.

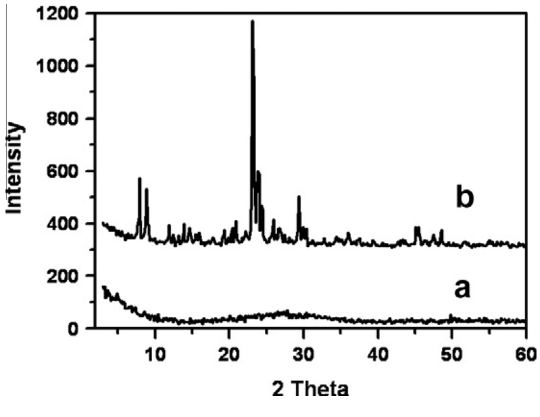

Fig. 2. XRD patterns of meso-macroporous zirconosilicate precursor (a) and MMM-ZrS-1 (b).

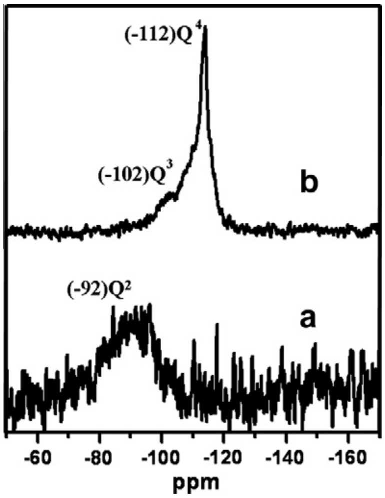

Fig. 3. ^{29}Si MAS NMR spectra of meso-macroporous zirconosilicate precursor (a) and MMM-ZrS-1 (b).

MFI-type crystal symmetry, had been obtained in the product MMM-ZrS-1 (Fig. 2b). These results confirmed that the structure directed crystallization process had successfully occurred under the effect of microporous structure directing agent TPA$^+$ by employing the crystallization system in glycerin medium at 130 °C, which was further confirmed by ^{29}Si MAS NMR spectroscopy (Fig. 3). The meso-macroporous zirconosilicate precursor was mainly made up of cross-linked Q^2 silica units [−92 ppm, $Si(O-Si)_2(OH)_2$] (Fig. 3a), which indicated the presence of immense amounts of amorphous zirconosilicate or oxides in the framework of the precursor. After crystallization transformation process for 2 days at 130 °C, the resonance at −92 ppm (Q^2) disappeared, and a highly intense resonance at −112 ppm [Q^4, $Si(OSi)_4$] and a shoulder peak at −102 ppm [Q^3, $Si(OSi)_3(OH)$ or $Si(OSi)_3(OZr)$] were observed (Fig. 3b), indicating that the coordination states of the Si and Zr species were transformed from an amorphous to a crystalline framework and micro-meso-macroporous product consists primarily of cross-linked Q^4 silica units and Q^3 units as deduced from a very high Q^4/Q^3 ratio. These studies confirmed that MMM-ZrS-1 with a highly crystalline zeolite framework was obtained in 2 days at 130 °C via a chemical crystallization transformation process in glycerin medium.

N_2 adsorption–desorption isotherms and pore size distributions of precursor and MMM-ZrS-1 are displayed in Fig. 4. The precursors exhibited a type IV isotherm with a very small hysteresis loop at $p/p_0 = 0.45–0.55$ (Fig. 4a), indicating the existence of mesopores. The pore size distribution determined by the BJH method was centered at 3.4 nm (Fig. 4b). Meanwhile, it can be observed a large hysteresis loop, a well-defined step occurring at high $p/p_0 = 0.8–1.0$, which should be attributed to the presence of interspace between amorphous nanoparticles. It is worth mentioning that MMM-ZrS-1 exhibited a type IV isotherm with a steep uptake below $p/p_0 = 0.2$ (Fig. 4c), and a hysteresis loop was located at a high p/p_0 range (0.8–0.95), indicating the presence of microporosity and large interparticles mesoporosity in the product, respectively. The BET surface area was 438 m^2/g containing a micropore surface area of 149 m^2/g (see Table 1). The micropore size distribution calculated by the HK method was 0.5 nm, which is in good agreement with the pore size of zeolite MFI (see Table 1). The BJH pore size distribution of MMM-ZrS-1 was centered at 15 nm (Fig. 4d), which might be attributed to the uniform void resulted from the aggregation of uniform zeolite Zr-doped silicalite-1 nanocrystals. It can be concluded that the final product, MMM-ZrS-1, possessed a well-defined macroporosity with uniform interconnected mesopores constructed from microporous zeolite nanocrystals.

Zirconium is increasingly used in catalysis due to its moderate acidity and oxidation properties. The incorporation of zirconium as tetrahedral coordination state into zeolite allows these properties to be manifested in a solid acid catalyst and shape selective catalyst [33,34]. The UV–visible spectrum showed that there were a considerable amount of octahedral Zr species in the initial meso-macroporous zirconosilicate precursor as evidenced by the presence of a reflectance band around 260 nm (Fig. 5a). It can be found that the coordination states of Zr species changed from octahedral to tetrahedral species which was evidenced by the change in the reflectance bands from 260 to 220 nm (Fig. 5). Notably, Zr species in MMM-ZrS-1 were mainly located in tetrahedral coordination state by the intense band at 220 nm (Fig. 5b), which is very important to selective oxidation catalysis. These results suggested that most of amorphous Zr species had been transformed into a tetrahedral coordination state and incorporated into the final micro-meso-macropore framework.

^{129}Xe NMR spectroscopy is a useful tool to characterize porous materials. The use of optical pumping techniques for the production of hyperpolarized (HP) xenon can increase sensitivity of several orders of magnitude ($\times 10^4$) [35,36] and laser-hyperpolarized (HP) ^{129}Xe NMR is proved to be powerful technique in studying the porosity of porous materials [31,37], or even reaction processes and kinetics [32,38]. The observed ^{129}Xe chemical shift could reflect mainly interactions between xenon atoms and the surface. Xe is also very sensitive to the geometry and may represent the connectivity and uniformity of the pores. Fig. 6 shows the variable-temperature laser-hyperpolarized ^{129}Xe NMR spectra of MMM-ZrS-1. The peaks at 0 ppm in the spectra are from xenon in the gas phase. All signals at lower field are originated from the adsorbed xenon in the zeolites. From the range of chemical shift, the signal at 104 ppm originates from Xe adsorbed in the microporous channels

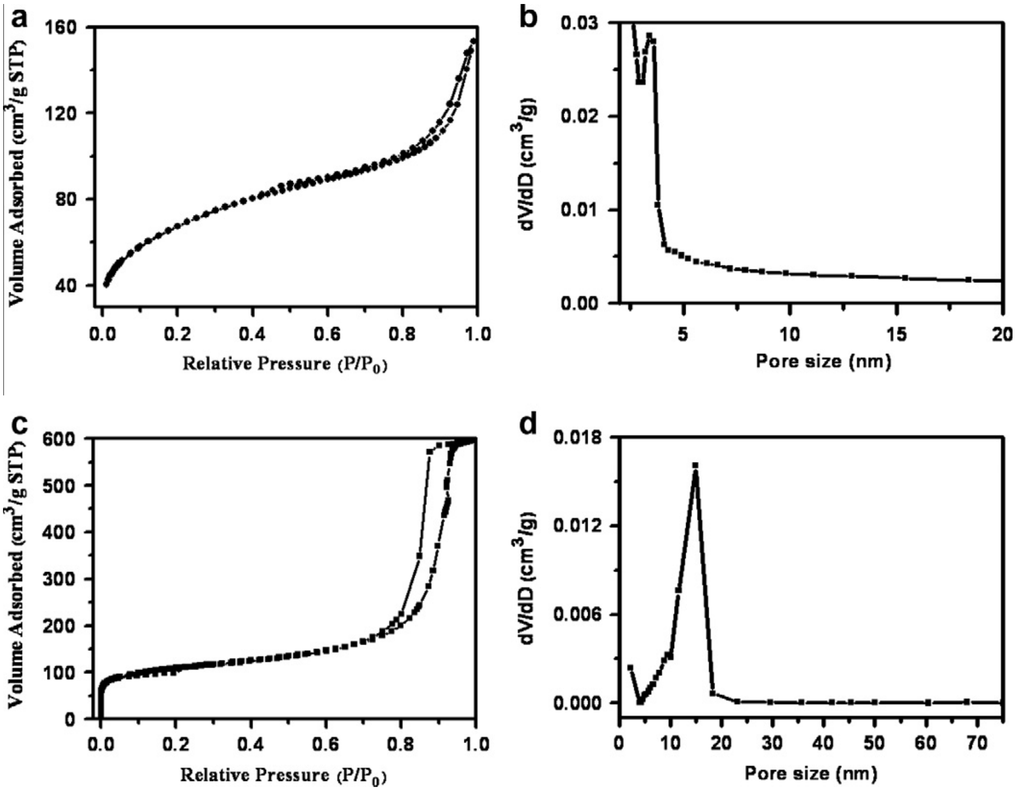

Fig. 4. N_2 adsorption–desorption isotherms and pore size distributions: (a and b) meso-macroporous zirconosilicate precursor; (c and d) MMM-ZrS-1.

Table 1
Textural property and desorption temperature of ammonia of zirconosilicate precursor and MMM-ZrS-1.

Samples	S_{BET}[a] ($m^2 g^{-1}$)	S_{micro}[b] ($m^2 g^{-1}$)	D_{meso}[c] (nm)	V_{BJH}[c] ($cm^3 g^{-1}$)	V_{micro}[b] ($cm^3 g^{-1}$)	T_{NH3} (°C)
Precursor	238	74	3.4	0.246	0.032	450
MMM-ZrS-1	438	149	15	0.92	0.071	670

T_{NH3} is desorption temperature of ammonia.
[a] Calculate by BET method.
[b] Calculate by *t*-plot method.
[c] Calculate by BJH method.

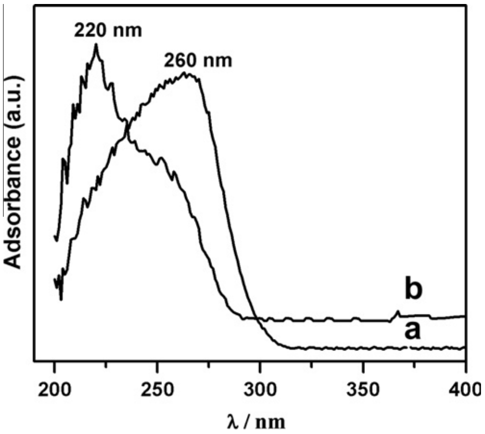

Fig. 5. UV–visible spectra of meso-macroporous zirconosilicate precursor (a) and MMM-ZrS-1 (b).

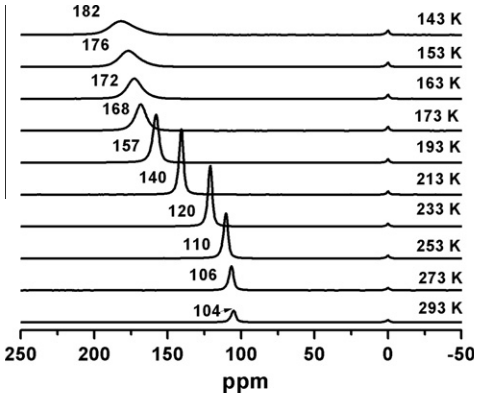

Fig. 6. Laser-hyperpolarized ^{129}Xe NMR spectra of Xe adsorbed in MMM-ZrS-1. The temperature is varied from 143 to 293 K.

of MMM-ZrS-1 at room temperature, which further indicates the microporous structure of product MMM-ZrS-1. Moreover, the chemical shift of this signal increases as the temperature decreases. This shift is due to the enhanced Xe–zeolite surface and Xe–Xe interactions at lowered temperature. It is worth mentioning that it is hard to observe the signal of adsorbed Xe in mesopores from the ^{129}Xe NMR spectrum even at extremely low temperature of 143 K. The absence of the signal of adsorbed Xe in mesopores implies that the exchange rate of Xe among the mesopores and micropores is very fast, which further means that product MMM-ZrS-1 presents a very good interconnectivity between the micropores and mesopores which highly facilitates the molecular diffusion from large pores to microporous nanoreactor where deep reactions can occur. Consequently, combining with the SEM, TEM and N_2 sorption results, multimodal Zr-Silicalite-1 zeolite nanocrystal aggregates with hierarchically micro-meso-macropore system having an enhanced mass transport property have been obtained via a quasi-solid-state crystallization process.

The acidities of the samples (zirconosilicate precursor and MMM-ZrS-1) were characterized by temperature-programmed desorption of ammonia (NH_3-TPD) (Fig. 7). It can be seen that two NH_3 desorption peaks for both of precursor and MMM-ZrS-1 were detected, indicating the desorption of weak and strong acid sites [39,40]. The fact that the desorption temperature of NH_3 from the strong acid sites on the MMM-ZrS-1 (670 °C) was much higher than that of zirconosilicate precursor (450 °C) with an amorphous framework and nanosized zeolite ZSM-5 (Al-doped silicalite, around 500 °C), might be attributed to the corresponding highly crystallinity of the framework and the introduction of Zr heteroatom in MMM-ZrS-1. The strong acidity would guarantee a good catalytic performance of the hierarchically structured Zr-doped silicalite-1 materials. The catalytic property of final product MMM-ZrS-1 was tested by the well-known probe reaction of the cracking of isopropylbenzene. The conversion with calcined MMM-ZrS-1 catalyst can yield 25%. More important, the MMM-ZrS-1 catalyst shows a high selectivity and only the products C_{6-8} were obtained, which might be attributed to the improved diffusion and uniform mesopore system resulted from the hierarchical trimodal porous structure aggregated from uniform Zr-doped silicalite-1 nanocrystals.

The first key to synthesize hierarchically porous materials with micro-meso-macroporous structure constructed from zeolite Zr-Silicalite-1 nanocrystals is to find an efficient strategy that not only transform the amorphous phases of meso-macroporous precursor into Zr-Silicalite-1 zeolitic structure but also retain the meso-macroporous structure. The general synthesis procedure of hierarchically micro-meso-macroporous materials with zeolite Zr-Silicalite-1 architecture and the corresponding high resolution TEM images are as illustrated in Fig. 8. In general, zeolitic silicalite-1 structure can be formed with the effect of structure directing agent TPA^+ under conventional hydrothermal conditions in water. However, the meso-macroporous structure of the precursor would be completely destroyed during a hydrothermal crystallization condition in water (see Fig. S2). The amorphous zirconosilicate precursors were impregnated with a mixture of TPAOH and an additional silica source, thoroughly mixed and eventually the aqueous phase was removed via evaporation, and then glycerin was added to this solid forming a quasi-solid-state system (Fig. 8a). Glycerin, a viscous fluid with low volatility, is used as the reaction medium, thus the diffusion performance of reactants in the framework of meso-macroporous precursor will be greatly decreased as opposed to fully conventional hydrothermal condition, which will reduce the reaction activity of zeolite structure directing agents, thus slow down the crystallization transformation speed. Meanwhile, low vapor pressure reaction condition resulted from the low volatility property and high boiling point of glycerin liquid is also beneficial to decrease the crystallization speed. In this reaction system, zeolite structure directing agent TPAOH could still strongly interact with the growing crystal domains, meaning that the amorphous zirconosilicate particles could be converted to silicalite-1 type zeolite nanocrystals with incorporated zirconium. The amorphous nanoparticles can be gradually transformed into zeolitic structure at a

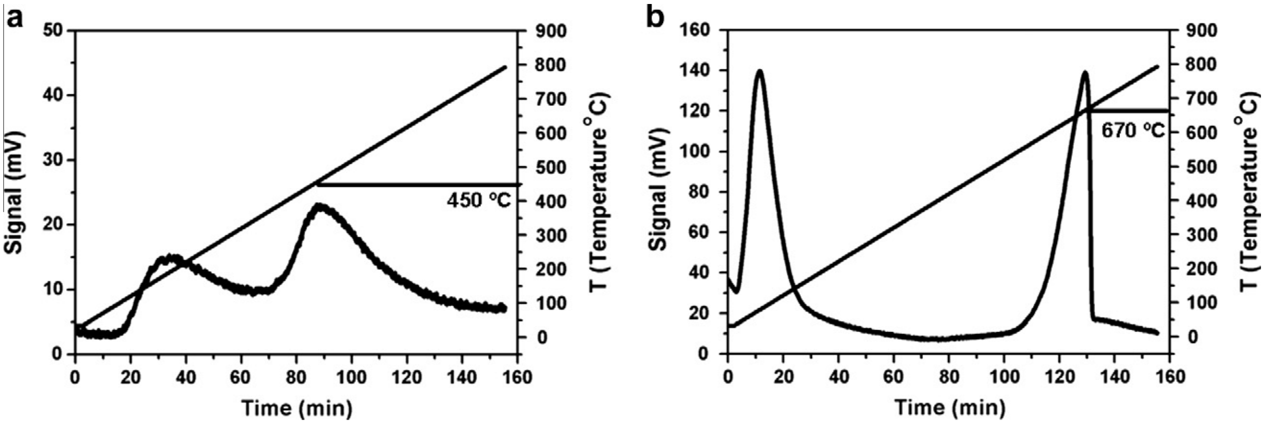

Fig. 7. Temperature-programmed desorption of ammonia (NH_3-TPD) curves: (a) zirconosilicate precursor; (b) MMM-ZrS-1.

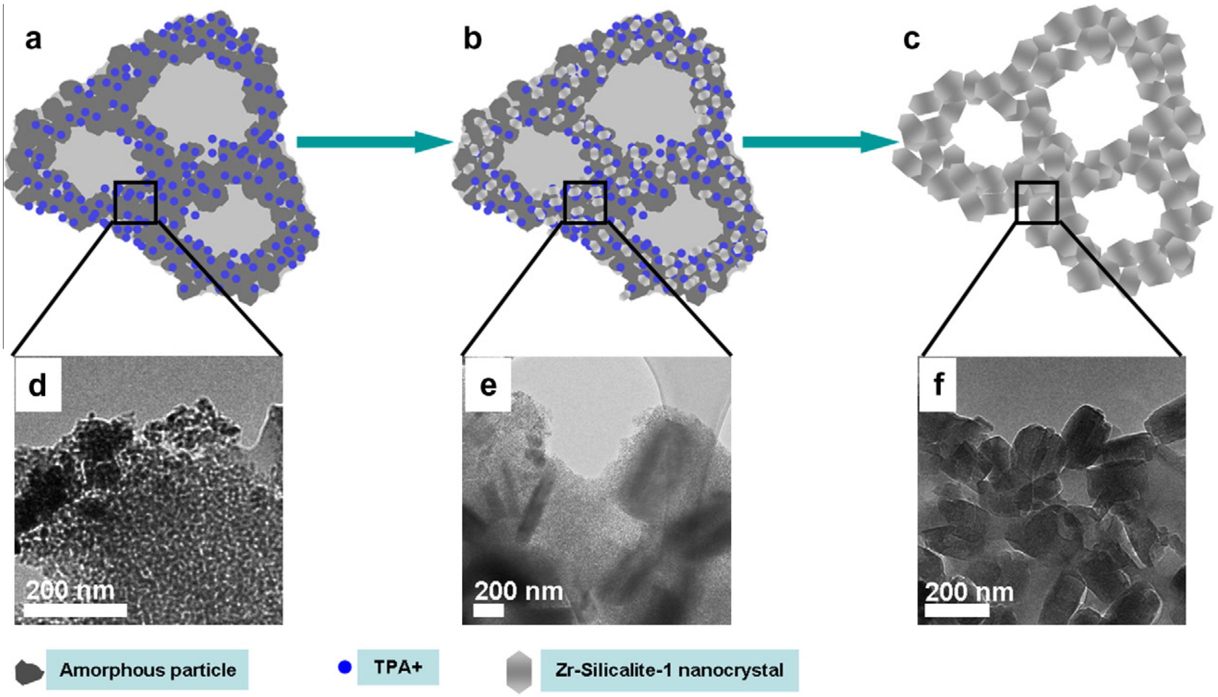

Fig. 8. (a–c) Schematic representation of the synthesis of hierarchically micro-meso-macroporous materials constructed from zeolite Zr-Silicalite-1 nanocrystals via a quasi-solid-state crystallization transformation process in glycerin medium; High resolution TEM images of products over different reaction time: (d) zirconosilicate precursor; (e) product obtained over 1 day reaction time; (f) MMM-ZrS-1.

relatively slow speed on the effect of structure directing agent, which is an important factor to avoid the collapse of the walls of macropores owing to the weak interaction between these nanoparticles. In this case, some zeolite Zr-Silicalite-1 nanocrystals were gradually formed within the continuous amorphous inorganic matrix as they had embedded themselves in the macropore walls under the effect of structure directing agent TPAOH via the quasi-solid-state crystallization process at 130 °C (Fig. 8b). High resolution TEM image proved that some small zeolite MFI-type nanocrystals formed in the walls of macropores in the product obtained via this quasi solid crystallization process in glycerin medium at 130 °C for 1 day (Fig. 8e). Furthermore, glycerin would play a role as a supporter to hold the macropores because of its viscosity at high temperature, which is unfavorable for the solid nanoparticulate mobility. As the process proceeded, meso-macroporous structure in the product can be well retained and amorphous nanoparticles can be transformed into Zr-doped zeolite silicalite-1 nanocrystal at pre-defined temperatures and reaction times on the effect of structure directing agent in this quasi solid crystallization process using glycerin medium (Fig. 8c). Electron microscopy image showed that the final product MMM-ZrS-1 presented a well-defined macroporous structure (Fig. 1c) and interconnected mesopore system which fully constructed from highly crystalline zeolite Zr-Silicalite-1 nanocrystals (Figs. 1 and 8f). The synthesis of hierarchically structured MMM-ZrS-1 with highly crystalline and uniform nanocrystals, which provided strong acidity and tetrahedral coordination oxidation species, should be attributed directly to the quasi solid-state crystallization process, because this system using the glycerin as a carrier medium, not full hydrothermal conditions, can preserve the meso-macroporosity of the amorphous phase during crystallization as limiting the water concentration minimizes re-hydrolysis of the zirconosilicate. Another advantage of this chemical crystallization transformation process under glycerin medium is easy to form MFI-type zeolite with uniform particle size because of the slow crystallization process. In fact, some successful attempts were previously demonstrated using glycerin as a reaction medium to directly synthesize silicalite-1 nanocrystals [41], and MFI-type zeolite-coated mesoporous aluminosilicates [42,43], recrystalize mesoporous SBA-15 into microporous ZSM-5 [44] and secondary crystallization of mesoporous walls into microporous materials with MFI structure [45,46], respectively. It is very remarkable that the zeolite nanocrystals in the final products exhibited a uniform particle size of around 500 nm in length and 300 nm in width (Figs. 1e and 8f), resulting in relatively uniform mesovoids (15 nm) as evidenced by the mesopore size distribution obtained through N_2 adsorption desorption measurements (Fig. 4).

4. Conclusion

The quasi-solid-state system is efficient for the synthesis of hierarchically zeolite Zr-doped silicalite-1 materials constructed from highly crystalline and uniform nanocrystals. Glycerin instead of water as a reaction medium plays a key role to preserve the meso-macroporous hierarchy. ^{129}Xe NMR study showed the very good inter-connectivity of the porous hierarchy. The final product presents strong acidity and tetrahedral coordination oxidation species, which will exhibit not only great accessibility from the macropores, but also plentiful acid sites and/or oxidation sites for used in catalytic reactions. Although many hierarchical zeolites have been developed, the quasi-solid-state system that uses a glycerin medium to synthesize micro-meso-macroporous materials with highly crystalline zeolite Zr-Silicalite-1 architecture, in particular, is reported rarely.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2012.03.018.

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