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Highly stable hierarchical ZSM-5 zeolite with intra- and inter-crystalline porous structures

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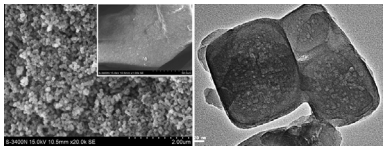
HIGHLIGHTS

- Hierarchical ZSM-5 nanocrystals with meso- and macropores are synthesized.
- Each ZSM-5 nanocrystal contains intra-crystalline mesopores generated by PEG.
- The aggregation of ZSM-5 nanocrystals produces inter-crystalline macropores.
- Hierarchical zeolites with high crystallinity are achieved in only 12 h at 160 °C.
- Hierarchical ZSM-5 shows higher catalytic activities than conventional ZSM-5.

GRAPHICAL ABSTRACT



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ABSTRACT

Highly stable hierarchical ZSM-5 zeolites with intra-crystalline mesopores and inter-crystalline macropores have been synthesized via a steam-assisted conversion in the presence of polyethylene glycol. XRD, SEM, TEM, N_2 sorption and mercury intrusion measurement revealed that the irregular intra-crystal mesopores (2–10 nm) in each zeolite nanocrystal were generated by the removal of encapsulated PEG, and the inter-crystalline macropores (50–90 nm) were formed by the aggregation of the well crystallized ZSM-5 nanocrystals with a small size (50–200 nm). The ZSM-5 zeolite nanocrystals were achieved by a dense-gel with high TPA^+/SiO_2, highly concentrated TPA^+ can induce a burst in nucleation rate during the first step of steam-assisted conversion, which makes the dry gel easy to convert into zeolite nanocrystals, PEG arrested in the gel can be easily encapsulated by zeolite crystals during the steam-assisted conversion. Finally, these nanocrystals containing intra-crystalline mesopores aggregate into the bulky materials with an inter-crystalline macroporous network. In addition, the mesopore volume and external surface areas of Hier-ZSM-5 can be easily adjusted by changing the amount of PEG. Catalytic tests showed that Hier-ZSM-5 had a similar activity to Nano-ZSM-5, which must be collected by high-speed centrifugation; while had a higher activity than Con-ZSM-5, especially for the reactions involving large molecules. The high catalytic activity and easy separation from liquid mixture of Hier-ZSM-5 would facilitate its practical applications in chemical industry.

1. Introduction

Zeolites are widely used as catalysts or catalyst supports in a variety of applications in the refining and (petro)chemical industries, due to their high surface area, high acidity and good (hydro)thermal stability [1–3]. Notwithstanding the positive effect of the presence of micropores (pore size <2 nm), such as shape selectivity [4–6], while an important drawback of these microporous zeolites is their small pores, which is hard to be accessed by bulky reactants, this hinders their application in fine-chemical and pharmaceutical industry. The quest for optimizing catalytic

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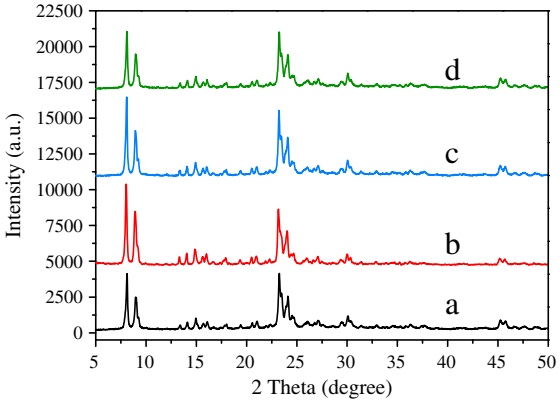

Fig. 1. XRD patterns of Hier-ZSM-5 synthesized with different amount of PEG, (a) Hier-ZSM-5-0, (b) Hier-ZSM-5-1, (c) Hier-ZSM-5-1.5, (d) Hier-ZSM-5-2.

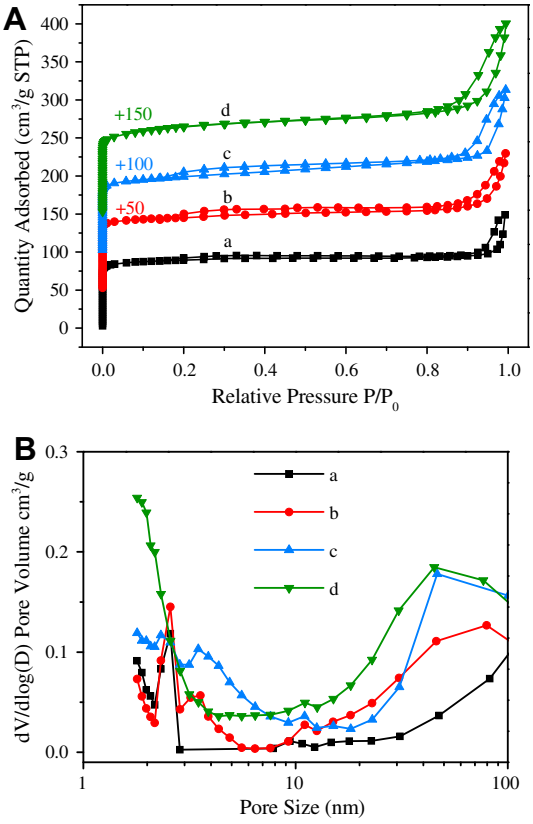

Fig. 2. N_2 sorption isotherms (A) and pore size distributions, (B) of Hier-ZSM-5 synthesized with different amount of PEG (a) Hier-ZSM-5-0, (b) Hier-ZSM-5-1, (c) Hier-ZSM-5-1.5, (d) Hier-ZSM-5-2.

conversion by facilitating diffusion of reactants and products and controlling coke formation has recently stimulated much research on hierarchical zeolitic materials. Generally, a second or even third pore system in zeolite crystals can be generated via either non-templating or templating synthesis procedure. The former approach intends to create a secondary pore system via post synthesis treatment, including acid/base leaching [7–10] and steaming [11], however, these treatments suffer from partial destruction of zeolite structures and loss of acidic sites. On the other hand, templating synthesis methods including soft templates (silylated polyethyleneimine [12] and cationic polymers [13]) and hard templates

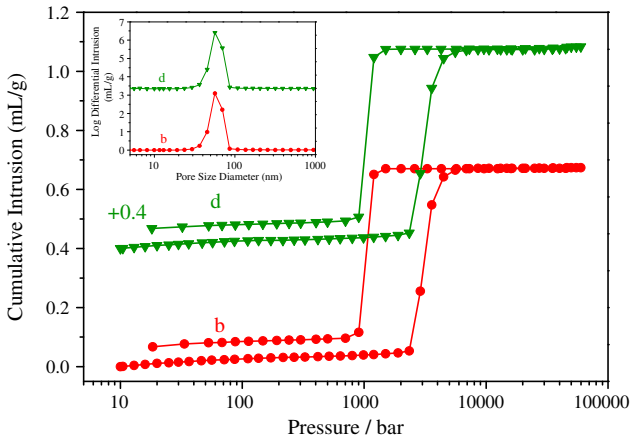

Fig. 3. Mercury intrusion porosimetry investigations of, (b) Hier-ZSM-5-1 and (d) Hier-ZSM-5-2.

Table 1
Textural parameters of various samples at different synthesis conditions.

Samples	S_{BET} ($m^2\ g^{-1}$)	S_{micro} ($m^2\ g^{-1}$)[a]	V_{total} ($cm^3\ g^{-1}$)	V_{meso} ($cm^3\ g^{-1}$)	V_{micro} ($cm^3\ g^{-1}$)[a]	V_{total} ($cm^3\ g^{-1}$)[b]
Hier-ZSM-5-0	324	283	0.19	0.07	0.12	–
Hier-ZSM-5-1	320	277	0.26	0.13	0.13	0.67
Hier-ZSM-5-1.5	336	250	0.31	0.19	0.12	–
Hier-ZSM-5-2	393	267	0.36	0.24	0.12	0.68
Nano-ZSM-5	313	279	0.20	0.07	0.13	–
Con-ZSM-5	300	278	0.17	0.03	0.14	–
Hier-ZSM-5-0 h	9	–	0.02	–	–	–
Hier-ZSM-5-3 h	159	105	0.09	0.04	0.05	–
Hier-ZSM-5-6 h	233	185	0.17	0.08	0.09	–
Hier-ZSM-5-9 h	306	265	0.19	0.07	0.12	–

[a] Determined by the t-plot method.
[b] Obtained by mercury porosimetry.

(carbon particles [14], carbon nanotubes [15], carbon aerogels [16,17], mesoporous carbon [18] and $CaCO_3$ [19]) offer the opportunity to generate controllable mesopore system based on the size and amount of the mesoporogen additive. Truly mesoporous sponge like MFI zeolites were obtained by adding specially designed amphiphilic organosilane surfactants into a conventional hydrothermal synthesis system [20]. Recently, Ryoo's group [21] successfully synthesized ordered mesoporous MFI-type zeolite and disordered Beta zeolite by using different Gemini-type templates.

Nanozeolites have been repeatedly suggested to be excellent candidates for enhancing mass transport in catalytic application due to intrinsically short diffusion paths. It is well known that the creation of mesoporosity can be obtained through the assembly of nanozeolite crystals. The assembly of nanozeolites into hierarchical zeolite materials is usually performed in a multistep approach; nanozeolites were first obtained, and subsequently assembled via an additional soft or hard surfactant [22–25]. Very few studies about the direct assembly of nanozeolites by using polymer or organosilanes during synthesis were reported