Direct Synthetic Strategy of Mesoporous ZSM-5 Zeolites by Using Conventional Block Copolymer Templates and the Improved Catalytic Properties
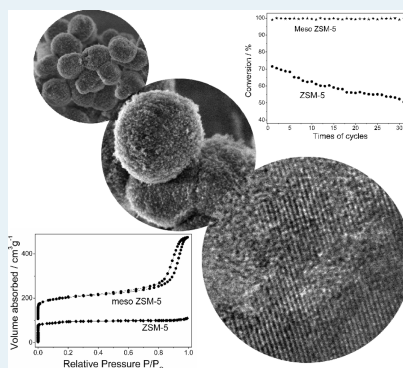
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S *Supporting Information*

ABSTRACT:

Employing conventional block copolymers as scaffold, a direct synthetic route of mesoporous zeolites has been developed with the assistance of post-steaming treatment. Such hierarchical micro/mesostructure demonstrated the greatly enhanced catalytic activity for probe reactions, such as cracking of triisopropylbenzene and esterification reactions involving bulky molecules, because of the increased external surface, and the diminished coke formation by the greatly shortened diffusion length in microporous networks.

KEYWORDS: heterogeneous catalysis, hierarchical structure, mesoporous materials, templating methods, zeolites

INTRODUCTION

Zeolites are a series of crystalline microporous aluminosilicates which have found wide applications in catalysis, the separation field, and the environmental field because of their inherent unique structure.[1,2] Unfortunately, zeolite catalysts often suffer from slow diffusions of bulky reactants/products in their channel systems, particularly in the upgrading of crude oil and the field of fine chemicals, as a result of their small pore size (<1.5 nm).[3−6] High expectations to conquer such problems have placed on mesoporous materials, which possess pores with larger size,[7−9] since early in their invention; later, however, they have been found apparently incompetent in serious circumstances for their inherent amorphous frameworks, and consequent low hydrothermal stability and the absence of catalytic activity.

In recent years, successful synthesis of so-called mesoporous zeolites by constructing mesopores in zeolites or by making mesoporous frameworks crystallized into zeolites without destroying the mesostructure is increasingly thought as the most effective solution to overcome the above drawbacks of either pure zeolites or amorphous mesoporous aluminosilicates. Up to date, a number of routes have been developed to synthesize such

a hierarchical structure, which can be mainly divided into non-templating and templating approaches.[10−23] Dealumination or sequential desilication-dealumination,[10−15] as a representative non-templating method, involves post-etching of intact zeolites to achieve mesoporosity, and the properties of the products need further investigation.[24,25] Among the templating methods, hard templating[16−20] has been first employed to create mesopores inside zeolites with various categories, but complicated multi-steps were usually involved in the hard templating approaches because of the incompatibility between hard substrates and precursor species. In recent years, a soft templating method,[21−23] including cationic or silylated polymer and amphiphilic organosilane as the templates, has been drawing increasing attention for its ease of use and high efficiency to create mesoporosity. Unfortunately, efforts must be paid to specially design and synthesize such supramolecular templates which are mostly unavailable on the market to date. It is therefore greatly desired to develop a general direct synthetic strategy of mesoporous
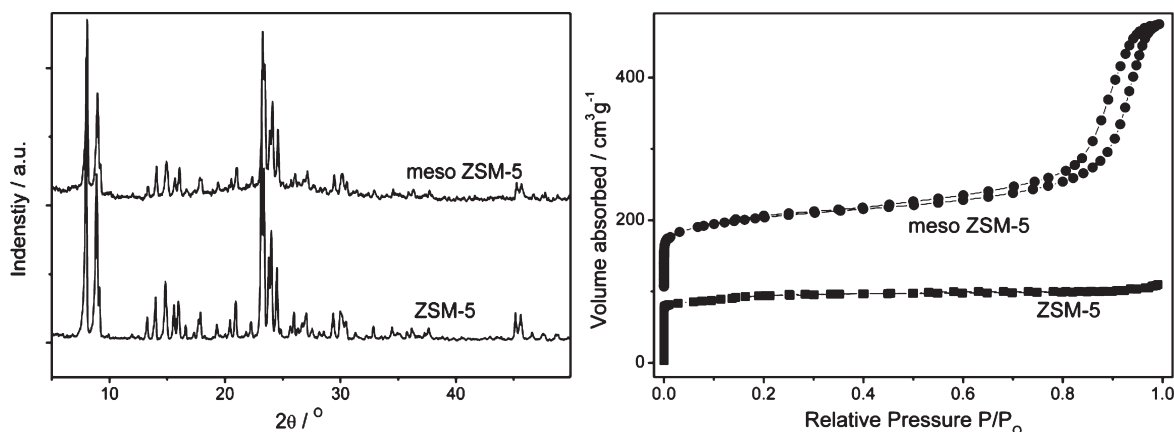
Figure 1. XRD patterns (left) and N_2 sorption isotherms (right) of (■) ZSM-5 and (●) meso ZSM-5. For comparison purpose, the isotherm of meso ZSM-5 was offset by 100 cm^3 g^{-1}.

Table 1. Chemical and Textural Properties of Conventional ZSM-5 and Meso ZSM-5

sample	mole ratio of Si/Al[a]	S_{BET}[b]/m^2 g^{-1}	S_{micro}[c]/m^2 g^{-1}	$S_{external}$[c]/m^2 g^{-1}	V_{micro}[c]/cm^3 g^{-1}	V_{pore}[d]/cm^3 g^{-1}	D_{pore}[d]/nm
meso ZSM-5	68	467	190	277	0.09	0.65	9.8
ZSM-5	66	311	214	97	0.11	0.17	

[a] Determined by ICP-AES method. [b] Surface area by Brunauer−Emmett−Teller (BET) method. [c] Micropore and external surface areas and micropore volumes by t-plot method. [d] Total pore volumes of P/P_0 = 0.97 and average diameters were calculated by Barrett−Joyner−Hallenda (BJH) method.

zeolites by using a conventional surfactant template, such as block copolymers for their low cost and high market availability, as the mesopore porogen. However, such a synthesis strategy still remains a great challenge in the field of mesoporous zeolites to date. The failure in the direct synthesis of mesoporous zeolite using conventional soft templates has been mainly attributed to the weak combining force between these soft templates and the silicate species;[3−6] as a result, during the crystallization and growth process of zeolite particles, phase separation between surfactant and zeolite crystals would inevitably took place, and consequently, no mesoporous zeolites, but a mixture of separate amorphous mesoporous materials and pure zeolite crystals, could be obtained. Therefore, the "confined synthesis" of mesoporous zeolites by using conventional surfactant molecules, which can easily dissolve and assemble in water, has been believed to be almost impossible except for producing the strong interaction between mesoporous templates and precursor species in solution such as using the amphiphilic organosilane[6,23] as meso-template or alternatively, performing the crystallization process apart from the solution condition.

In the present work, employing conventional block copolymers, such as F127, P123 or Brij series as soft templates, which are highly commercialized products and now widely used for the synthesis of mesoporous materials, a direct synthetic route of hierarchical mesoporous zeolites has been developed with the assistance of post-steaming, and the mesopore size and pore volume can be tuned by changing the amount of meso templates. The precursors of zeolites and mesoporous templates were first transformed into homogeneous gels and then, such gels were dried and subsequently, crystallized under the steam condition.[26−31] In this strategy, block copolymer molecules are not employed as meso-templates to self-organize with silica sources into ordered mesoporous matrixes in solution, but act as a kind of scaffold to keep their confined space during the transformation of gels to zeolites instead. Moreover, the steam treatment was performed on dried gels, and the phase separation between the template and the solid silica phase was successfully avoided thanks to the absence of liquid water phase in the system. Therefore, the steam treatment technique on the template-containing solid gel, which makes the aluminosilicate framework crystallize into zeolite, is believed to be the key in avoiding phase separation between the templates and the silica matrix, which has puzzled researchers for a long time in the synthesis of mesoporous zeolites by conventional hydrothermal method. Moreover, as the temperature for steam treatment is the same as or very close to that used in conventional hydrothermal synthesis, which is much lower than the temperature needed for dealumination, dealumination of zeolites[23] will not take place in the present study.

■ RESULTS AND DISCUSSION

The X-ray diffraction (XRD) pattern (Figure 1) clearly shows the characteristic peaks of MFI type zeolite in spite of weak intensity, indicating clear crystallization of the ZSM-5-type zeolite (named as meso ZSM-5) synthesized by using F127 as the soft template. The N_2 sorption isotherm of the synthesized materials (Figure 1) possesses a typical type-IV isotherm with the capillary condensation at the high relative pressure between about 0.7 and 0.9, suggesting a relatively large mesopore size (Table 1). Comparatively, the neglectable uptake in the isotherm of conventional ZSM-5 zeolite at P/P_0 > 0.1 reveals the absence of mesoporosity in it. Both isotherms of meso ZSM-5 and conventional ZSM-5 exhibit a sharp uptake at P/P_0 < 0.02 indicating the similar microporosity. The mesoporosity of meso ZSM-5 was further confirmed by obvious increases of both pore volume (V_{pore}) and external surface area ($S_{external}$) (Table 1). Moreover, the pore volume and average diameter can be tuned to a large extent by changing the mass of templates used (Supporting Infortmation, Table S1). The SEM images of meso ZSM-5 (Figure 2) show a representative particle possessing a
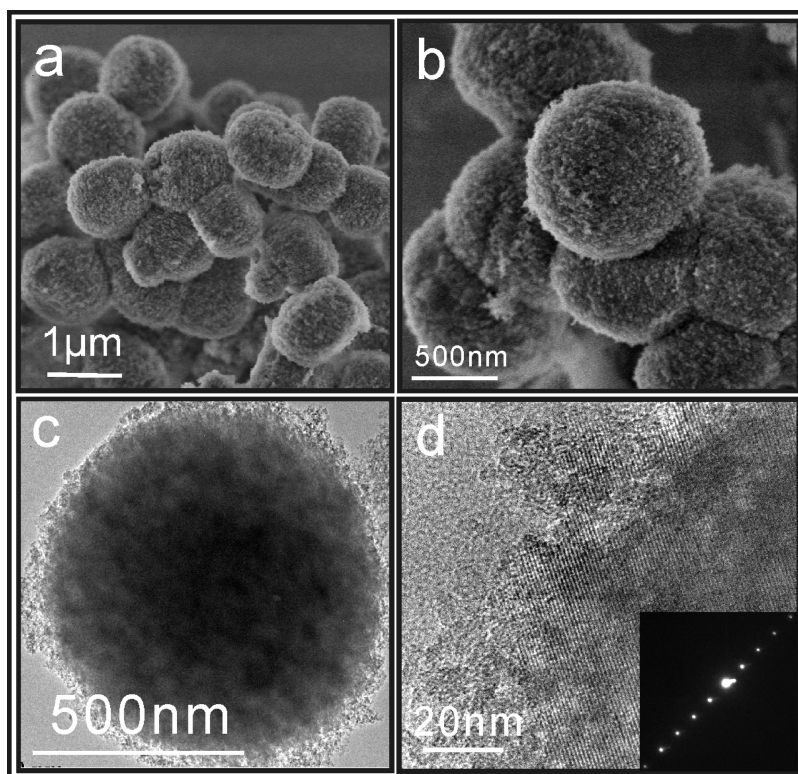
Figure 2. SEM and TEM images of meso ZSM-5: (a) and (b) SEM images at different magnifications; (c) TEM image of a single particle at a higher magnification; (d) HR-TEM image at the edge of the particle in (c) exhibiting the continuous lattice stripes with an ED pattern in the inset.
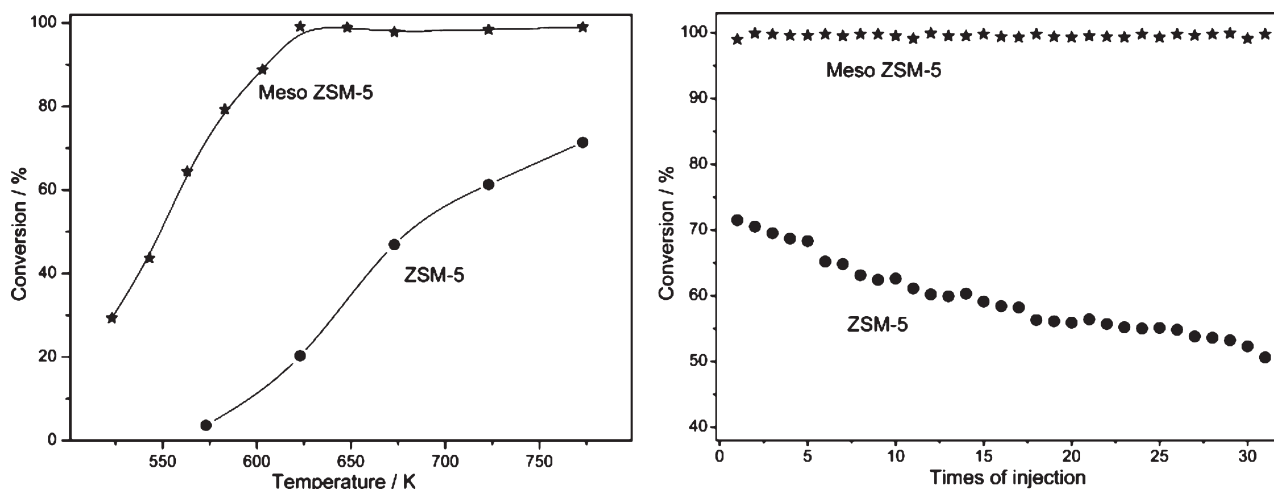
Figure 3. Catalytic properties of conventional ZSM-5 (●) and meso ZSM-5 (★) employed in the cracking of TIPB as a probe reaction: (a) catalytic activities (conversions) at different temperatures, and (b) deactivation behavior at 773 K.

spherical morphology with non-smooth surface and relatively uniform diameter of around 1 μm. The TEM image (Figure 2) directly reveals the significant mesoporosity development, and in the meantime demonstrates the similar morphology obtained when special organosilane was used as the mesopore porogen.[23] Furthermore, the lattice fringe can be clearly seen in the framework of the present meso ZSM-5 using F127 as the mesopore template. Such single crystalline pattern reveals that the part or the whole framework can be regarded as a single crystal with penetrating mesoporous network inside, and moreover, such patterns can be found in the whole sample (Supporting

Information, Figure S1). As a result, high thermal/hydrothermal stability can be expected. Moreover, the present direct synthetic strategy can be well extended to the cases when other block copolymers were used. Similar products have been obtained (Supporting Information, Figures S2 and S3) with almost identical efficiency when P123 and Brij-series copolymers were employed as templates, indicating the universality of the present strategy. Encouraged by such unique hierarchically porous structure with a crystallized framework, outstanding catalytic properties are expected especially when the large molecular reactants/products are involved.

As the oil becomes heavier, the catalyst deactivation caused by coking in oil refining led to frequent process interruptions caused by the need to allow zeolite catalyst recovery and consequently, the marked cost-up, which is gradually becoming a serious problem in the petrochemistry field. Mesoporous zeolites, believed as the upgrade of conventional zeolites for their abundant external surface and "exposed" catalytic active sites by the creation of mesopores, have been tried as catalysts for reactions involving bulky molecules, and their promoted activities have been confirmed by various reports.[23−25,31−34] In the present work, the cracking of 1,3,5-triisopropylbenzene (TIPB), a typical probe reaction for the cracking of bulky aromatic hydrocarbons, was chosen to investigate the catalytic activity and anti-deactivation properties of as-synthesized mesoporous zeolites. The catalytic results show that meso ZSM-5 performed remarkably with enhanced catalytic activity over conventional ZSM-5 zeolites in all temperature points tested (Figure 3). In details, the conversion of TIPB was only 3.6% at 573 K and gradually increased to 71.4% with the temperature increased to 773 K when using ZSM-5 as catalyst. Comparatively, the TIPB conversion using meso ZSM-5 as catalyst increased rapidly with the rise of temperature from 523 to 623 K and then, a complete conversion of about 100% was obtained and kept at above 623 K, indicating improved catalytic activity in TIPB cracking as compared to conventional ZSM-5. In addition, conventional ZSM-5 suffered from a definite deactivation in which about 30% of activity was lost after 30 times of injection at 773 K whereas no significant activity loss was detected in the case of meso ZSM-5 in the given 30 injections (Figure 3), indicating the excellent anti-deactivation property of meso ZSM-5. The improved catalytic performances can also be illuminated by the hierarchy factor (HF) theory which was developed by Perez-Ramirez et al.[35] In this report, the HF of meso ZSM-5 is about 0.09, similar to that of the desilicated sample, and the values of S_{meso}/S_{total} and V_{micro}/V_{total} (0.6 and 0.15, respectively) indicate the high relative mesoporosity which favors diffusion of TIPB.

It is believed that diisopropylbenzene (DIPB), isopropylbenzene (IPB), and benzene are the products in the cracking of TIPB in the sequence of isopropyl separation from the benzene ring one by one respectively in three steps. Among them, there are two kinds of DIPB, p-DIPB and m-DIPB, as a result of isomerization. The contents and evolution of product distributions (Supporting Information, Figure S4) in the 30 injections provided more information about catalytic properties. The main products by using ZSM-5 as catalyst are DIPB and propylene, and lean contents of IPB and benzene were detected, indicating the low cracking degree because of the larger size of reactants than the micropore diameter of ZSM-5. In more detail, p-DIPB became the main component (ca. 90%) of DIPB (Supporting Information, Figure S5) after isomerization of m-DIPB, which is known as shape-selective effect due to the more effective diffusion of p-DIPB in microporous networks of ZSM-5. Almost in contrast, no DIPB could be detected in the products by using meso ZSM-5 as catalyst, and instead, benzene and propylene became the main products indicating the much deeper cracking degree. Generally, the surface character, concentration, or strength of surface acid sites and porosity are believed to be the main factors affecting the catalytic property. As only insignificant differences in the concentration and strength of surface acidic sites and surface character between ZSM-5 and meso ZSM-5 can be found, as indicated by the NH_3-TPD (Supporting Information, Figure S6) and NMR results (Supporting

Information, Figure S7), respectively, it is reasonable that the high performance of meso ZSM-5 in the cracking of TIPB should be mostly attributed to its abundant external surface and "exposed" catalytic active sites by the creation of mesostructure in meso ZSM-5 which made acidic sites accessible to bulky reactants and subsequently, the greatly deepened cracking of TIPB.

The deactivation of conventional ZSM-5 as catalyst is also clear as can be found from the gradually increased DIPB contents from 50% to 60% and correspondingly decreased contents of benzene and IPB in the given injections during the evolution of products (Supporting Information, Figure S4). Comparatively, the contents of IPB increased from 7% to 10% by using meso ZSM-5 as catalyst (Supporting Information, Figure S4), meanwhile the conversion of TIPB remained at a high level of about 100%, indicating insignificant deactivation of meso ZSM-5 catalyst. In addition, the ZSM-5 catalyst used in cracking for 30 injections showed remarkably higher mass loss than meso ZSM-5 catalyst, as revealed by TG measurement (Supporting Information, Figure S8), suggesting more apparent coke formation of the former, in good agreement with deactivation results. It is commonly believed that the coke formation is associated with the diffusion length of reactants/products in the internal networks of microporous zeolites; longer diffusion length would lead to more severe coke formation.[36,37] By constructing the mesoporous networks in ZSM-5 crystals, the maximum diffusion length of reactants/products in the micropores networks can be shortened from the zeolite crystal diameter in conventional ZSM-5, which is usually in micrometer size, to the nanosized framework thickness of meso ZSM-5: nearly 100 times reduction of diffusion length was achieved by creating mesostructure in ZSM-5. In summary, the hierarchical micro/mesostructure of mesoporous zeolite demonstrated the greatly enhanced catalytic activity for reactions involving bulky molecules because of the increased external surface, and even more importantly, the greatly diminished coke formation by the shortened reactant/product diffusion length in microporous networks of mesoporous zeolites.

The improved catalytic property was also demonstrated by the esterification reactions of benzyl alcohol with different aliphatic acids (Supporting Information, Figures S9 and S10) in which large molecular species were involved. It is noteworthy that meso ZSM-5 and ZSM-5 possess similar catalytic activities in the esterification of benzyl alcohol with methanoic and acetic acids because of the facile diffusion of reactants/products in microporous networks; however, with the increase of carbon atom number in aliphatic acid to four or above, meso ZSM-5 exhibited significantly improved catalytic properties above conventional ZSM-5 with the Turnover Number (TON) value of meso ZSM-5 being three times of that of conventional ZSM-5 at the carbon atom number of 8. Apparently, the presence of the mesostructure in meso ZSM-5 should be responsible for the catalytic activity enhancement because of the high accessibility of large reactant molecules in mesopores.

■ CONCLUSION

The persistent existence of the templates within the dry gel during steaming plays a role of mesopore generation in the framework crystallization process. The present steam-assisted strategy has been identified equally efficient for using F127, P123, and Brij-series and therefore can be regarded as a general

approach when using block copolymer surfactants as soft templates, taking advantage of their low cost and high market availability. Moreover, the hierarchical micro/mesoporous structure of the mesoporous zeolite, namely, meso ZSM-5, showed much increased external surface and shortened diffusion length in microporous networks as compared to conventional zeolites, which demonstrated high catalytic activity and remarkably improved anti-deactivation performance in the cracking of TIPB and also esterification reactions. Such a facile and direct synthesis of mesoporous zeolites and their excellent catalytic properties suggest the significant application possibilities in oil refining and fine chemical synthesis involving bulky molecules. Further work would be necessary for the generalization of this method to other kinds of zeolites and the anti-deactivation properties to other catalytic reactions.

■ ASSOCIATED CONTENT

ⓈSupporting Information. Experimental details, Figures S1−S10 and Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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