Recent advances in hierarchically structured zeolites: synthesis and material performances

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Hierarchically structured zeolites (HSZs) have attracted increasing attention in the last few years, thanks to their unique hierarchical porous structures combining micro- and mesoporosity and superior material performances, especially in the bulky molecules-involved catalysis and adsorption applications. In this Feature Article, the recent advances in the HSZs synthetic methodologies and material performances in catalysis are overviewed. Further, some perspectives for the future development of HSZs are discussed.

1. Introduction

Zeolites are an important class of crystalline porous materials with cage- or channel-like structures. Due to their well-defined micropore sizes for molecular shape selectivity, large specific surface areas, intrinsic acidity, and high (hydro)thermal and chemical stability, they have shown great (or potential) applications in many modern industrial processes related to catalysis, adsorption, and separation. However, the small sizes (typically \(< 1.2\) nm) of the inherent intracrystalline micropore channels or windows of pure zeolites are becoming a more and more significant obstacle for their applications in bulky molecules-involved processes. The diffusion limitation of relatively large molecules in the micropore channels would result in a poor access of reactants to the zeolite active sites, and more severely, the frequent blocking of the diffusion path and the fast deactivation of the zeolites.

To solve the diffusion problems of guest species in zeolites, ordered mesoporous materials (OMMs) with adjustable larger pore sizes (2–30 nm), such as M41s, SBA-n, and MSU-x, have been successively invented since the 1990s. However, until now, their practical applications are still far from the extensive success, especially in the petrochemical processes, owing to their amorphous frameworks and the resultant low stability and lack of (strong) acidity. Around 2001, some progress in the templating synthesis of highly stable and acidic mesostructured materials was made through the incorporation of zeolite secondary building units (SBU) in the mesoporous frameworks, whose precursors could be the aged zeolite...
synthesis sols or the destructive products of pre-synthesized zeolites. Unfortunately, no typical X-ray diffraction peaks assigned to the specific zeolite structures appeared in their wide-angle XRD patterns, and strictly speaking, these synthesized products were still amorphous materials. Thus, a novel class of hierarchically structured zeolites (HSZs) or so-called mesoporous zeolites is highly desired, which should have additional intra- or inter-crystalline mesoporosity in addition to the inherent microporosity of zeolites. These HSZs would integrate the characters of mesoporosity and the microporous crystalline structure of zeolites, viz., improved mass transportability of guest species through the interconnected micropore-to-mesopore and mesopore-to-mesopore networks and zeolitic stability and activity. When ordinary mesoporous surfactant templates and small molecule organic ammonium agents for microporous zeolites were directly used for the preparation of HSZs, earlier attempts achieved little success, because there was no expected synergistic or consecutive structure-directing effect occurring between those two size-scale templates. Actually, the obtained products were either microporous zeolite crystals or amorphous mesoporous materials or phase-separated mixtures of them, rather than the desired single-crystal-like HSZs. In the following years, many new kinds of organic and inorganic mesoporogens, classified as “soft” or “hard” templates, including some specially designed and/or synthesized bifunctional agents, have been introduced in this templating synthesis of HSZs. Among them, the typical ones include amphiphilic organosilanes, polymers, carbon materials, and nanosized organic/inorganic particles. Specifically, single-crystal-like HSZs micropores, evidenced by the continuous and well-crystallized lattice structure coexisting with the mesoporous network in the HRTEM image, were synthesized in our laboratory. In this report, poly(methyl methacrylate) (PMMA) nanospheres were found to be a dual-functional template for the generation of mesoporosity and spherical HSZs particles, and an average mesopore size of 13 nm was obtained, thanks to the great volume shrinkage of PMMA nanospheres during the heat treatment. Very interestingly, by a twice hard-templating approach, HSZs with ordered mesoporosity were reported for the first time by Tsapatsis et al. in 2008. In this report, three-dimensionally ordered mesoporous (3DOM) colloidal crystals composed of monodisperse silica nanoparticles (10–40 nm) were used as templates for replicating mesoporous carbons at first, then zeolite precursors were introduced into the resultant carbon replicas with large enough mesopore sizes, and a subsequent steam-assisted crystallization (SAC) treatment led to the formation of uniform and isolatable nanocrystals and single-crystal zeolites with ordered imprinted mesoporosity (HSZs).

Alternatively, different from above mentioned “bottom-up” synthesis for HSZs, starting from the pre-synthesized microporous zeolites, a post-demetallation process by steaming or acid/base selective leaching is another effective strategy to fabricate HSZs with additional intracrystalline mesoporosity. In fact, by this post-synthesis demetallation process, HSZs or so-called modified zeolites have been extensively studied for a long time and some of them have been actually used in the petrochemical industry, such as the well-known ultrastable Y (USY) catalysts. Better catalytic performances (activity, selectivity, durability, and recyclability) were achieved compared with their parent zeolites. Possible modifications induced by the post-synthesis demetallation treatment were not limited only to micro/mesoporous structures, but also to material compositions and active site distributions, all of which would cooperatively contribute to the improvement of material performances.

In a word, whether by template synthesis or by the post-synthetic demetallation process, a common target for HSZs preparation is that the resultant products should be the single-crystal-like materials with well-controlled and penetrating mesoporous structures, and maximally preserved native characters of pure zeolites (microporosity, acidity, and stability). In the past decade, significant progress has been made in the development of HSZs synthetic methodologies and material performances, such as catalytic properties, and a number of excellent reviews about HSZs have also been published in the last few years. Interestingly, a very recent review, which was given by Chal et al., outlined HSZs’ industrial perspectives, however, no detailed information on the catalytic performance of HSZs was addressed. Here, in this Feature Article, combined with our new results on HSZs synthesis with the ordinary cationic or copolymer surfactants as the mesoporogens, the most recent advances in this rapidly growing research field will be reviewed, mainly focusing on the publications in the last three or four years. To concentrate our reviewing and also limited by the article length, mainly the direct synthesis of HSZs by using soft templates and post-synthesis demetallation/desilication will be concerned in this article.

2. Templating synthesis of HSZs

2.1 HSZs synthesized with specially designed templates

Direct synthesis of HSZs with multi-length scale templates is a straightforward idea originated from the successful preparation of OMMs via supramolecular micelles. However, as mentioned
above, these preliminary attempts were unsuccessful due to the strong phase-separation tendency between the employed mesoscale templates and the rapidly growing zeolite crystals. To get the single-crystal-like HSZs with this direct synthesis method, mesoscale templates and/or synthesis processing should be well designed to control the interactions between these templates and zeolitic species during crystallization. In this respect, a great progress has been made by Ryoo et al. in 2006. Through the specially designed and synthesized amphiphilic organosilanes, [3-(trimethoxysilyl)propyl]hexadecyldimethylammonium chloride ([CH₃O]₃SiC₈H₁₇N(CH₃)₂,C₁₆H₃1), TPHAC), and their structural analogues, the covalent linkages between the growing crystal domains and mesostructure directing agents were formed, which were stable in the basic synthesis solutions and effectively suppressed the exclusion of mesoscale templates from the growing zeolite crystal phases. Consequently, mesoporous zeolites built with randomly oriented zeolite nanocrystals were obtained.

In recent years, using these amphiphilic organosilanes as mesoscale templates, this methodology has been applied to HSZs synthesis with different framework structures and compositions, such as (Me)-ZSM-5, LTA zeolite, TS-1, microporous aluminophosphate, and even basic sodalite. Their mesopore diameters could be finely tuned depending on the chain lengths of the organosilanes and/or the hydrothermal synthesis parameters (temperature, time, etc.). Moreover, as reported in LTA HSZs synthesis, the mesopore diameters could even be expanded up to 24 nm when the excessive organosilane surfactants or the auxiliary pore-expanding agents, such as EO₂₀PO₇₀EO₂₀ triblock copolymers, were introduced. NH₃·TPD or CO₂·TPD characterization results confirmed that the synthesized HSZs possessed the similar acidic or basic properties to those of corresponding OMMS counterparts. However, for small molecular reactions, the catalytic activities of the dealuminated HSZs were lost almost completely, though the as-synthesized HSZs were stable in the basic synthesis solutions and effectively suppressed the exclusion of mesoscale templates from the growing zeolite crystal phases. Consequently, mesoporous zeolites built with randomly oriented zeolite nanocrystals were obtained.

Fig. 1 The three-dimensional molecular structure of ‘bifunctional’ cationic surfactant (C₂₂₋₄₆₋₄). Reproduced with permission from ref. 32 Copyright 2009, Macmillan Publishers Limited.

Very recently, a bifunctional diquaternary ammonium-type surfactant (as shown in Fig. 1) was designed by the same group, in which the diammonium head group acts as an effective structure-directing agent for the MFI zeolite, while the hydrophobic interaction between the long-chain tails induced the formation of a mesoscale micellar structure. The resultant materials were mesostructured, which were composed of three-dimensionally intergrown multilamellar or even unilamellar zeolite nanosheets depending on Na⁺ concentrations and pH values of the synthesis mixtures. More interestingly, through pillaring post-treatment, a widely used process for the pore-generation or pore-expansion upon the layered materials, the template-containing MFI multilamellar nanosheets could be transformed into the pillared zeolite nanosheets, as shown in Fig. 2. An almost ideal micro-/mesoporous HSZ was successfully prepared, which possesses long-range structural ordering in both micro- and mesopore regimes. Compared with those of purely microporous zeolites, greatly enhanced catalytic activities and increased catalyst lifetimes were achieved in the typical reactions of bulky molecules-involved cracking of branched polyethylene, protection of benzaldehyde with pentaerythritol, condensation of 2-hydroxyacetophenone with benzaldehyde, or methanol-to-gasoline conversions, due to their significantly enhanced external surface areas, and consequently the increased number of easily accessible surface acid sites of the zeolite nanosheets. Also, in a very recent report, surfactant-modified MFI-zeolite nanosheets were used as highly efficient anion-exchangers for the removal of nitrate ions from the aqueous effluents.

On the other hand, in Xiao’s recent report, a cationic polymer, polydiallyldimethylammonium chloride (PDADMAC), was used as the mesoscale template. The electrostatic interaction between cationic polymer templates and negatively charged beta nanocrystals (30–80 nm) induced the formation of micrometre-sized (2–20 μm) and mechanically stable HSZs microspheres. In addition to a relatively large mesopore volume, similar pore characters and more importantly, similar catalytic performances were obtained between the synthesized HSZs microspheres and the corresponding zeolite nanocrystals. When large-scale industrial applications were considered, easier catalyst separation, whether in material preparation or in catalyst recycling via a filtration route, would be the major advantage of HSZs microspheres compared with zeolite nanocrystals. Similarly, micrometre-sized HSZ particles composed of nanosized zeolite crystals could also be prepared with Pluronic triblock copolymer F127 or even without the additional mesoscale templates. As one of the most important oxidation catalysts, TS-1 HSZs could also be synthesized using the amphiphilic organosilanes as the soft templates. However, although the resultant
products possessed the expected interconnecting micro-/mesopore systems and better performances in the catalytic oxidations of bulky substrates in the hydrophobic media, lower activity or even complete ineffectiveness in phenol hydroxylation was observed when aqueous H$_2$O$_2$ was used as the oxidant. Different from the hydrophobicity of pure TS-1 zeolite, the presence of a large number of surface defects and consequently the hydrophilicity of these synthesized TS-1 HSZs should be the main reason.

Fortunately, an interesting result was recently reported by Li et al.$^{40}$ Using nanosized carbon black as the mesoporous hard template, TS-1 HSZ was prepared via the SAC process, whose particles were composed of many nanosized zeolite crystals. Its mesoporosity was confirmed with variable-temperature $^{129}$Xe NMR spectroscopy and the Ti species has almost the same coordination environment as those in purely microporous TS-1 zeolite. Importantly, in the following model reaction of phenol hydroxylation, TS-1 HSZs showed similar product selectivity but significantly higher catalytic activity (phenol conversion up to 33% in 4 hours, a maximum based on a phenol-to-H$_2$O$_2$ ratio of 3) than TS-1 zeolite (19.3% under identical reaction conditions). Similarly, enhanced catalytic activity for phenol hydroxylation was also obtained for the alkaline-treated TS-1 catalyst.$^{41}$ The penetrable mesopores were thought to be the main reason for the enhanced activity of TS-1 HSZs. However, both of them did not give any catalytic properties about bulky molecules involved reactions.

2.2 HSZs synthesized with conventional soft templates

It is well-known that the ordinary surfactant templates for OMMs synthesis, e.g. cetyltrimethylammonium bromide (CTAB) and triblock copolymer P123, are not the suitable agents for HSZs synthesis, because of their limited charge densities and consequently weak interactions with zeolitic species. However, our recent results showed that under the controlled synthesis conditions, HSZs could also be synthesized with these ordinary mesoscale templates, especially via a steam-assisted crystallization (SAC) process.$^{42-45}$ As an extension of our previous work,$^{46}$ when CTAB was used as the mesoporous template, HSZs hollow spheres with an average mesopore size of around 3.0 nm were synthesized through carefully controlling the synthetic procedure.$^{42}$ More specifically, the key parameters for the successful synthesis of HSZs by this process have been identified to be the pre-hydrolysis temperature of sol precursors and the following hydrothermal treatment. TEM images gave the direct evidence for the coexistence of the mesoporous structure and the zeolite crystal lattice structure.

The SAC process is also called vapor-phase transport (VPT) or dry gel conversion (DGC), which is one of the effective routes to synthesize conventional zeolites, e.g. Silicalite-1, ZSM-5 and beta zeolite.$^{47,48}$ Unlike in the conventional hydrothermal synthesis where zeolite crystallization occurs in a large-scale solid–liquid system, in the SAC process, dried gel precursors contact only with water and/or microporous template steam. Since mass transport during this framework crystallization transformation is greatly suppressed due to the absence of a continuous liquid phase, this crystallization process is considered to be nearly an in situ course. Therefore, if the precursors possess mesoporous structures and cautious control is made, phase separation tendency between the zeolite precursors and the template molecules within the dried gel precursors can be inhibited during the SAC process, and a hierarchical micro/mesoporous structure could be achieved by this strategy. A few years ago, using dried zeolitic species/CTAB hybrids$^{49}$ or AlMCM-41/TPAOH as precursors,$^{50}$ the
DGC route was usually adopted for the synthesis of mesoporous zeolites (or composites). The resultant products exhibited higher adsorption capacities than microporous zeolite and amorphous mesoporous counterparts. Recently, a new type of hierarchically structured composites of ZSM-5 nanocrystals embedded in a well-connected mesoporous matrix was also synthesized by the DGC method, in which TPAOH simultaneously worked as the microporous template and the mesoporous scaffolding agent. Though the resultant TUD-C or TUD-M materials do not have a fully crystalline structure, they showed an improved hydrothermal stability. More importantly, by varying the crystallization conditions, the zeolite crystal size and the mesopore size can be tuned systematically.

Based on the SAC process, very recently, ε-TUD-1, one kind of HSZs with zeolitic mesoporous frameworks, has been prepared by our group by employing Al-doped TUD-1 mesoporous silica as precursors. In this synthesis, triethanolamine (TEA) and its polymer derivative poly-TEA work not only as the mesoscale templates, but also as the scaffolds to keep the intactness of the mesostructures during the SAC process. As shown in Fig. 3, the obtained HSZs particles showed the penetrable mesoporosity and, more importantly, the single crystalline features as revealed by the HRTEM image and the electron diffraction pattern on a large area (Fig. 3C). As a result, a greatly improved hydrothermal stability was observed with the resultant HSZs, which showed only ~10% loss of specific surface areas even after 200 h hydrothermal treatment. As a comparison, an ~40% specific surface area loss was found after 50 h hydrothermal treatment for the corresponding amorphous mesoporous precursors.

Applicability of such a SAC approach has also been verified in the preparation of TS-1 HSZ, which exhibits high catalytic activity and a strongly prolonged lifetime in the selective oxidation of 2,3,6-trimethylphenol (TMP) to trimethyl-p-benzoquinone (TMBQ). This excellent catalytic performance is closely related to its hierarchical micro/meso-structures, and high stability against mesostructure collapse and Ti leaching during the catalytic applications. Further, this process could be extended with other conventional surfactant templates, such as F127, P123, and Brij series, which are highly commercialized low-cost products and now widely used for the synthesis of mesoporous materials. Similar to using TEA agent, the resultant HSZs displayed the disordered but well-defined mesoporosity. Also, the synthesized materials demonstrated high catalytic activity and remarkably improved anti-deactivation performance in the cracking of TIPB and also esterification reactions. In a word, the key to the successful synthesis of HSZs by the SAC process using these conventional soft templates is believed to be the suppression of phase separation between the mesoporous templates and the silica species during the crystallization transformation, where extensive liquid phase should not be present.

Based on the similar considerations as the above mentioned SAC process to suppress the mobility of silicates and/or templates during crystallization, direct hydrothermal synthesis of BEA HSZs is also feasible when one type of cyclic diammonium (CD) was used as a structure-directing agent. The highly crystallized BEA HSZs product was composed of...
interconnected zeolite nanocrystals of 10-15 nm in diameter. More interestingly, the synthesized HSZs inherited the morphology and meso- and/or macroporous characters of the precursor gels or diatomaceous earth sources (pseudomorphic crystallization). A possible explanation lies in the strong interactions between CD and silicates and the rigidity of the CD molecule, which prevented phase separation during hydrothermal treatments. Due to the enhanced molecular diffusion through mesopores in the HSZs catalyst, in a model reaction of the isopropylation of naphthalene, the BEA HSZ still retained 74% of its initial catalytic activity after 5 h of employment, while the conventional zeolite lost its catalytic activity completely.

3. HSZs synthesis by a demetallation route

HSZs synthesis via a demetallation route starts from a pre-synthesized zeolite precursor. Through selective leaching of framework atoms (Al$^{3+}$, Si$^{4+}$, Ti$^{4+}$, etc.), intracrystalline mesopores can be introduced within the zeolite precursor particles. Possible leaching processes include steam or acid treatment for dealumination, base treatment for desilicification, and H$_2$O$_2$ treatment under microwave irradiation for detitaniaion. Among them, the best known way to create mesopores in zeolite is dealumination. Although this treatment improves the catalytic performance of zeolites, recent 3D-TEM and PFG-NMR analyses indicated that the mesopores introduced by dealumination do not yield an interconnected pore network and therefore contribute little to molecular diffusion. Desilication is now considered to be a more effective strategy than dealumination for introducing mesopores in zeolites. Up to dates, beside NaOH solution, generally used alkaline treating solutions include inorganic (LiOH, KOH, Na$_2$CO$_3$) and organic (TMAOH, TPAOH, and TBAOH) compounds. Some multi-constituent leaching agents or multistep treating processes were also adopted recently. For example, a two-step route comprising treatment in sodium aluminate followed by acid extraction had been successfully developed to introduce secondary mesoporosity in ZSM-5. Compared with ordinary desilication by NaOH solution, this two-step route led to equivalent mesopore surface areas. However, a higher solid yield is attained due to the one order of magnitude lower dissolution rate of silicon. Consequently, the resultant HSZs have much smaller mesopores (5 nm) and the Si/Al ratio is very similar to that of the starting precursor.

3.1 HSZs synthesis by desilication: effect of micro-/mesoporous templates and treating conditions

To modulate the desilication process for HSZs synthesis, partial detemplation (microporous structure directing templates) of zeolites followed by desilication in alkaline medium has been attempted. This process is based on the fact that the template-containing zeolite is virtually inert to Si leaching upon treatment in aqueous NaOH solutions. Depending on the pre-desilication calcination temperature, the microporous template was partially removed and these template-free portions would be susceptible to the subsequent alkaline leaching. Thus, under typical desilication conditions, mesopore surface areas of the resultant HSZs could be controlled in the range of 20-230 m$^2$/g$^{-1}$. In the catalytic pyrolysis of low-density polyethylene, the progressively enhanced activity was obtained with the increasing amount of mesopores. More interestingly, even for ZSM-5 zeolite with the template being completely removed, bulkier quaternary ammonium cations (TPA$^+$ or TBA$^+$ ions) could also work as efficient pore-growth moderators, which were introduced by impregnating the parent zeolites with the corresponding salts prior to NaOH treatment, or in the form of hydroxide compounds as one part of alkaline sources. The quaternary ammonium cation moderates the pore growth by buffering the OH$^-$ attack and prevents the over-fast Si extraction (leaching rate and leaching degree). This unique feature leads to the resultant HSZs with smaller mesopores and better preserved microporosity. Compared with parent zeolites and solely NaOH-treated samples, faster molecular diffusion and higher catalytic performances in the benzene alkylation with ethylene were observed in (NaOH + TPAOH)-treated zeolite. Optimal ZSM-5 HSZ was obtained upon the desilication process with the mixed (NaOH + TPAOH) alkaline solution.

Surfactant CTAB, a commonly used template for the preparation of M41s materials, was found to be helpful for the pseudomorphic transformation of pre-synthesized zeolite Y to HSZs, though the detailed mechanism is not clear yet. TEM images of parent and alkaline-treated zeolites indicated that the resultant product maintained the typical crystalline morphology of the precursor zeolite Y and possessed an interconnected network of micro- and mesopores. Another different feature from classical desilication processes is that the presence of CTAB ensured no preferential silica extraction under the reported treating conditions and the Si/Al molar ratios before and after alkaline leaching kept almost constant. However, the N$_2$ adsorption-desorption isotherm and NH$_3$-TPD results showed obvious decreases in microporosity and the strength and intensity of the strong acid sites in the synthesized HSZs.

Although attempts to modify the porous characteristics of ferrierite by dealumination were unsuccessful, desilication, with aqueous NaOH solutions or with a sequential treatment in aqueous NaAlO$_2$, HCl, and NaOH solutions, has been proven to be feasible under relatively harsher conditions than for other frameworks (MFI, MTW, and MOR) with a similar Si/Al ratio. As shown in Fig. 4A, under optimal conditions (0.2 M NaOH solution, 353 K, 9 h), the N$_2$ uptake of sample AT-16 at lower relative pressures is similar to that of the parent (P) material, which evidences the preservation of microporosity. The increased uptake at middle-to-high relative pressures and a hysteresis loop present in the mesopore region indicate the appearance of mesoporosity in the alkaline-treated ferrierite samples. Further, as shown in Fig. 4B, the NH$_3$-TPD results confirm the similarity of acid strength and acid intensity between sample P and sample AT-16. However, for the over-treated sample AT-11 (0.5 M NaOH solution, 353 K, 3 h), serious damage of the intrinsic microporous crystallinity led to the decrease of the strong acid intensity. In the following model reaction, the pyrolysis of low-density polyethylene (LDPE), the introduction of mesoporosity in the optimally alkaline-treated sample AT-16 promoted the LDPE degradation with respect to the parent zeolite, and what appeared to be
more interesting was the possibility of tuning the product
distribution, though this required further verification.

3.2 HSZs synthesis by the combined dealumination and
desilication

For the post-synthetic desilication process, in some cases, a
sequential treatment of first acid-leaching dealumination and
then alkaline-leaching desilication became necessary, since
there exists an optimal Si/Al molar ratio in the range of
25–50 for the desilication process and some zeolite precursors
have lower Si/Al ratios. As reported by van Bokhoven et al.,
the synthesized mordenite HSZs showed near 100% conversion in
3 h in the alkylation of benzene with benzyl alcohol, but the
conversions with other catalysts (conventional mordenite,
mordenite HSZs synthesized with amphiphilic organosilanes
or carbon templates) were less than 3%. However, in some
other cases, the multi-step treating sequence should be
optimized, i.e. first alkaline-leaching desilication (introduction
of mesoporosity) and then acid washing (surface acidity
modification), as reported in ZSM-5 HSZs synthesis for
shape-selective xylene isomerization. In addition to the
development of secondary mesoporosity, the alkaline-leaching
desilication treatment also induced substantial aluminium
redistribution, increasing the density of Lewis acid sites
located at the external surface and the concentration of
Bronsted centers at the pore mouths. As a consequence,
for just one-step alkaline-treated zeolite, although a higher
ω-xylene conversion was obtained compared to the purely
microporous counterpart, the selectivity to p-xylene decreased
and fast deactivation occurred. A subsequent mild HCl washing
became necessary, which could selectively eliminate the
deactivated sites and lead to an approximately twofold increase
in p-xylene yield and a reduced deactivation rate. From these
results, it is clear that for the HSZs preparation with a
post-synthetic desilication process, the detailed processing
parameters (treating sequence, alkaline/acid sources, compositions,
temperature, etc.) should be carefully selected, which heavily
depends on the zeolite precursor frameworks, active site
characters and the specific requirements of the catalytic
process under investigation.

4. HSZs performances and characterizations

4.1 Molecular adsorption and diffusion characteristics in
HSZs

With the development of HSZs synthesis methodology, attention
should also be paid to their structural characters and perfor-
mances in the practical applications. Actually, although
in the reported (model) reactions the improved material
performances of HSZs have often been attributed to the
enhanced diffusion capability of reactants and/or products in
the highly developed micro-/mesopore systems, little direct
evidence of the diffusion characteristics had ever been given.
To answer these questions, some newly published results could
be most helpful.

In Groen’s research, the taper element oscillating micro-
balance (TEOM) technique has been adopted to get an
accurate assessment of the diffusion characteristics of large
and gradient-free ZSM-5 zeolite and the corresponding
ZSM-5 HSZs obtained from post-synthetic desilication. Neopentane was used as a probe molecule to exclude the effect
of coke formation during tests. Since the intrinsic diffusivity of
neopentane in the micropores should be the same in both
samples, they concluded that the characteristic diffusion path
length in HSZs is dramatically reduced due to the presence of
an accessible interconnected network of micro/mesopores.
Consequently, compared with that of purely microporous
zeolite, a two orders of magnitude faster diffusion of neopentane
in the HSZs was found. This was the first time that the
enhanced diffusion capability of HSZs was evidenced directly.

Similar conclusions could be found in other reports about
the diffusivity characterization of toluene in template-synthesized
mordenite HSZs and of cumene in NaOH-treated ZSM-5

Fig. 4 (A) N2 isotherms of the parent (P) and alkaline-treated
ferrierite samples (AT-11 and -16). Inset: adsorption BJH pore size
distribution. (B) NH3-TPD profiles of the parent and alkaline-treated
ferrierite samples. Reproduced with permission from ref. 66.
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4.2 Effect of surface acidity and mesoporosity of HSZs on material performances

To evaluate the possible differences in type, concentration, strength of acidic sites and their locations between purely microporous zeolites and HSZs (carbon template synthesis), pyridine, d$_3$-acetonitrile and 2,6-di-tert-butyl pyridine were used as probe molecules for FT-IR characterization. Results showed that no substantial difference could be observed when smaller sized pyridine and d$_3$-acetonitrile were used. In contrast, for larger 2,6-di-tert-butyl pyridine molecules, due to the steric limitation effect, high concentrations of Brønsted sites at the mesopore surface of HSZs were identified. Moreover, through model reactions of toluene disproportionation, toluene alkylation with isopropyl alcohol, and p-xylene alkylation with isopropyl alcohol, the impact of the additional mesopores on material performances was clarified. For the diffusion-controlled reactions (toluene disproportionation or p-xylene alkylation with isopropyl alcohol), reactant conversion increased with increasing mesopore volume. Comparatively, reactant conversion would not increase significantly with increasing mesopore volume for the product-desorption-controlled reactions (toluene alkylation with isopropyl alcohol). On the other hand, when para-selectivity was concerned in products, the presence of mesopores might show a negative effect, since the shortened diffusion length is detrimental for their selectivity.

Very recently, the positive impact of mesoporosity on MFI zeolite catalyst lifetime has been confirmed for practical methanol-to-hydrocarbon (MTH) reactions through control experiments. As shown in Fig. 5, a roughly linear correlation between the mesoporosity and the catalytic lifetime was illustrated. For HSZs, higher external surface area means longer catalyst lifetime, which is not sensitive to the adopted synthesis methodology, whether by post-synthetic desilication or by hard-template synthesis with nanocarbon materials or by soft-template synthesis with amphiphilic organosilanes. Since the coke deposition in the micropores is highly detrimental to the catalytic activity and stability, it has been evidenced that the enlarged external surface area and shortened diffusion path length would facilitate the mass transfer of coke precursors from the micropores to the external surfaces and consequently prevent the catalysts from quick deactivation. Similar phenomena were observed in aromatization and isomerization of 1-hexene over alkali-treated HZSM-5 zeolite. As a simplified consideration, Fig. 6 gives a scheme of the reduced channel blockage of the alkali-treated HZSM-5 zeolite by the micro-/mesoporosity. In HSZs, due to the interconnection between micropores and mesopores, the diffusion path in micropores is greatly shortened. As a result, the aromatization and isomerization products or even coke deposition would be accelerated. In contrast, the aromatization and isomerization of 1-hexene over the micron-sized micropores of the as-synthesized HZSM-5 zeolite would be more difficult due to the shorter diffusion path in micropores.
precursors formed in the micropores can diffuse out of the pores on time, while coke deposition tends to occur in the mesopores of HSZs. Thus, the improved catalytic stabilities in aromatization and isomerization can be achieved due to the reduced coke formation/diffusion path blockage in the micropore network.

Using silylated polymers as mesoporogens, Pinnavaia et al. reported MSU-MFI HSZs with adjustable mesopore size.\textsuperscript{75} Very recently, these HSZs have been evaluated as the gas-oil cracking catalysts.\textsuperscript{76} Results showed that compared with the purely microporous ZSM-5 counterpart, MSU-MFI HSZs possessed not only higher catalytic activity and longer lifetime, but more importantly, the prior selectivity for desired products. Since ZSM-5 is currently used as a commercial fluid catalytic cracking (FCC) additive to boost octane ratings and liquefied petroleum gases yields, the application of MSU-MFI HSZs is expected.

### 4.3 HSZs as catalytic supports

In conventional zeolites, the small sized micropore network can be seldom employed to load active guest species due to the resulting pore narrowing or even blockage of the micropore channels by the guests. The HSZs, possessing an interconnected micropore–mesopore network, are not only the channels by the guests. The HSZs, possessing an interconnected micropore–mesopore network, are not only the active catalysts by themselves, but also the ideal supports for the other functional species, like the commonly used (porous) carbon, OMMs, and γ-Al₂O₃, etc. Compared with amorphous OMMs and purely microporous zeolite supports, positive effects of HSZs lie in the enhanced mass transport capability. The HSZs, possessing an interconnected micropore–mesopore network, are not only the active catalysts by themselves, but also the ideal supports for the other functional species, like the commonly used (porous) carbon, OMMs, and γ-Al₂O₃, etc. Compared with amorphous OMMs and purely microporous zeolite supports, positive effects of HSZs lie in the enhanced mass transport capability. Thus, the improved catalytic performance of noble metals incorporated HSZs (ZSM-5 or β-zeolite) for the hydrodesulfurization (HDS) of bulky 4,6-dimethyl-dibenzothiophene (4,6-DMDBT), though their selected HSZs varied in the synthesis methodology and the resultant micro- and mesoporous structures. In addition to the favored fast diffusion of bulky 4,6-DMDBT molecules in larger mesopore sizes of HSZs, more importantly, the strong acidity of HSZs made great and also key contributions to the improved catalytic performance. First, the strong acidity within HSZs is favorable for demethylation and scission of a C–C bond connecting the two rings of a 4,6-DMDBT molecule, which may transform the refractory component into more reactive species and thus accelerate HDS. Second, since partial electron transfer can occur from the supported metal particles to acidic sites of HSZs, the resultant electron-deficient metal particles have, no doubt, higher sulfur resistance and better hydrogenation properties.

### 4.4 Quantitative indexing for the micro-/mesoporosity of HSZs

Although a number of methodologies of HSZs syntheses have been developed and their catalytic performances been investigated extensively, reports on quantitative indexing for the micro-/mesoporosity are still rare. Very recently, two kinds of indexes have been proposed for the quantitative assessment of the micro-/mesoporosity of HSZs. One is an accessibility index (ACI)\textsuperscript{81} and the other is the hierarchy factor (HF).\textsuperscript{64} ACI is derived from infrared spectroscopy of probe molecules over HSZs or other porous solids. For ZSM-5 zeolite, the selected probe molecules could be pyridine (0.57 nm), 2,6-lutidine (0.67 nm), and 2,4,6-collidine (0.74 nm). Since probe molecules could be adsorbed on specific surface sites determined by their physical sizes and chemical properties, ACI would reflect the (relative) amount of the accessible specific surface sites (e.g., the accessible number of Bronsted acid sites among the total ones). As shown in Fig. 7, it gives the ACI of substituted alkylpyridines as a function of the mesopore surface area of ZSM-5 zeolite parent (P) and three ZSM-5 HSZs derivatives (H1/H2/H3) synthesized from a post-synthetic desilication treatment. Apparently, with the increase of material mesopore surface area or so-called the extent of mesoporosity, ACI of the largest probe molecule (ACI(Coll)), 2,4,6-collidine, increases from 0.06 for sample P, to 0.11, 0.15 and 0.38 for sample H1, H2, and H3, respectively. For bulky molecules involved reactions, higher ACI value means higher accessibility of surface Bronsted acid sites and consequently possible superior material performances.

On the other hand, based on the hypothesis that the catalytically functional centers are located in the micropores (active sites) and the guest accessibility is contributed by the auxiliary mesopores, HF is defined as the product of the relative micropore volume (V\textsubscript{mic} / V\textsubscript{total}) and the relative mesopore surface area (S\textsubscript{meso} / S\textsubscript{BET}). Its effectiveness has been confirmed by the above alkylation reaction of benzene with alkaline-treated ZSM-5 under the presence of pore-growth moderator organic ammonium cations, in which a perfect linear dependence of ethylbenzene (EB) productivity on sample's HF was obtained (Fig. 8).\textsuperscript{64} The maximization of HF should be the target for the newly structured HSZs design and the novel synthesis methodology.
development, which reflects a favorable balance between the enhanced mass transport contributed by auxiliary mesoporous structures and the native microporosity/acidity of zeolites in HSZs for an overall catalytic performance. Generally, Fig. 9 shows the hierarchy factor plotted in a contour plot as functions of the relative mesoporous surface area and relative microporous volume from the available all four textural parameters in the published references. As expected, the enhanced catalytic performances can be found clearly along with the increased HF value from zeolite nanocrystals, to desilicated and some template-synthesized HSZs. Comparatively, purely microporous zeolites or OMMs, suffering from the absence of wide enough and effective fast diffusion pathways or of intrinsic strong acidity, showed much decreased HF values and consequently lower catalytic activity or performance than HSZs. Nevertheless, it should be noted that since the HF index is still based on a simplified hypothesis and only several specific examples were verified, further work is necessary to confirm its generality and to upgrade it or re-build a new general index for the characterization of the structural features and material performances of HSZs and their essential correlations.

5. Summary and outlook

To diminish the diffusion limitations present in purely microporous zeolites during applications, hierarchically structured zeolites (HSZs) have attracted ever-increasing attention in recent years. Up to now, either through direct synthesis or a post-synthetic demetallation (desilication) process, various kinds of HSZs of multiple framework structures and compositions have been prepared, all of which possess auxiliary inter- or intracrystalline mesoporous structures in addition to the native microporosities. As a consequence, improved material performances, i.e. high (hydro)thermal stability, superior activity, and increased catalytic performance and lifetime, have been achieved in above summarized model and/or practical catalysis applications.

Among those two synthetic methodologies, direct synthesis is actually a “bottom-up” pathway and always associated with soft or hard templates as mesoporogens and/or mesoporous structure directing agents. The resultant products could possess the well-controlled mesoporous characters (mesopore sizes, size distributions, mesopore surface areas, and mesopore volumes, etc.). However, because of the strong exclusion effect by the growing zeolitic species, HSZs would be the kinetically controlled intermediate phases. Thus, sol (or dry gel) preparation and following crystallization parameters should be carefully tuned to get the uniform and single-crystal(-like) HSZs products, especially when the ordinary mesoscale templates, such as CTAB, TEA, and F127, were used as in our recent reports.42–45,56 The key to the direct “bottom-up” HSZs synthesis by using mesoscale templates is to prevent the phase separation between the templates and the growing zeolitic species, e.g. by covalent bonding between the mesopores and the silicon precursors through specially designed templates such as amphiphilic organosilanes,8 or by excluding the presence of a continuous liquid phase during crystallization when those ordinary mesoscale templates were used. Importantly, the synthesized HSZs particles with these ordinary templates showed a single crystalline feature as evidenced by TEM and electron diffraction characterizations and the mesopores are

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Fig. 8 Correlation between ethylbenzene (EB) productivity and the hierarchy factor (HF) (P and QA, for the parent and alkaline-treated zeolites, respectively). Reproduced with permission from ref. 64. Copyright 2009, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Fig. 9 The hierarchy factor (HF) plotted in a contour plot as a function of the relative mesoporous surface area and the relative microporous volume of different zeolite types prepared by different methods. Reproduced with permission from ref. 64. Copyright 2009, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
the penetrating intracrystal ones. Such a structure feature ensures the high performance and stability of the resultant materials. On the other hand, for the “top-down” post-synthetic desilication process, the post-synthesized zeolite precursors could endow the resultant HSZs with a high degree of microporous crystallization as in purely microporous zeolites. Although it is well accepted now that the post-synthetic desilication process is superior compared with that of dealumination, the mesoporous characters of the resultant HSZs are still less-controlled and the material compositions and surface states may be changed during this selective leaching process. Sequentially multistep treatments and/or some additional moderating agents are required to get HSZs materials with balanced performances.

In general, whether by direct synthesis or by the post-synthetic desilication process, a suitable balance between microporosity and mesoporosity in the resultant HSZs is very important. In this respect, the hierarchy factor (HF) is a simplified and effective index in evaluating the HSZs properties or designing newly structured HSZs, in which both the native functions of micropores and the enhanced diffusion capability of reactants/products in mesopores are considered. Further research of HSZs should include not only the new processes/methodologies to realize the simultaneous and accurate controlling over the compositions and structures on micro- and mesoporous scales, catalytic performance such as activity, product selectivity, coke formation and lifetime, but also a general index to characterize and to correlate the structural features and material performances of HSZs.

In addition to the further investigation on HSZs themselves, the synthesis of HSZs-based composites will be another focus in future. The loading of heterogeneous active species such as metallic nanoparticles on zeolites, or the introduction of active guests in the pore channels of conventional mesoporous silica, has been proved to be effective in enhancing the material performances of zeolites or conventional mesoporous materials. One can expect that the loading of active species in the hierarchical pore channels of HSZs should be equally effective as in conventional mesoporous materials. Little work has been reported in this direction but the results have been very encouraging.77–80 Such a composite combines the advantages of zeolite crystals of native catalytic activity, mesoporous structures benefiting the fast diffusion of reactants/products, and the additional functions of introduced guests and their possible synergistic effect with the HSZs supports.

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Notes and references

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