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REVIEW ARTICLE

Mesoporous zeolites as efficient catalysts for oil refining and natural gas conversion

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Abstract Zeolites have been regarded as one of the most important catalysts in petrochemical industry due to their excellent catalytic performance. However, the sole micropores in zeolites severely limit their applications in oil refining and natural gas conversion. To solve the problem, mesoporous zeolites have been prepared by introducing mesopores into the zeolite crystals in recent years, and thus have the advantages of both mesostructured materials (fast diffusion and accessible for bulky molecules) and microporous zeolite crystals (strong acidity and high hydrothermal stability). In this review, after giving a brief introduction to preparation, structure, and characterization of mesoporous zeolites, we systematically summarize catalytic applications of these mesoporous zeolites as efficient catalysts in oil refining and natural gas conversion including catalytic cracking of heavy oil, alkylation, isomerization, hydrogenation, hydrodesulfurization, methane dehydroaromatization, methanol dehydration to dimethyl ether, methanol to olefins, and methanol to hydrocarbons.

Keywords mesoporous zeolite, catalysis, oil refining, natural gas conversion

1 Introduction

Microporous crystalline aluminosilicate zeolites are widely used in petrochemistry and fine-chemical industry because of their large surface area, high adsorption capacity, high thermal and hydrothermal stabilities, strong acid sites within their defined micropores, and shape-selectivity in catalysis [1–3]. However, zeolites with sole micropores are imposed by severe mass-transfer constraints, which results in poor catalytic performance (such as lifetime and convention) in bulky substrate catalytic reactions [2–5]. Ordered mesoporous materials such as MCM-41 [6,7] and SBA-15 [8,9] with good mass transfer have once been expected to solve this problem. Unfortunately, compared with zeolites crystals, poor hydrothermal stability and weak acidity of these mesostructured materials hinder their catalytic applications in petrochemical chemistry [1,2,10] due to the amorphous nature of the mesoporous walls. The strategies for improving hydrothermal stability of ordered mesoporous materials have been developed by partly crystallization of mesoporous walls *via* the addition of as-synthesized zeolitic seeds solution in the synthesis procedure [11–14] or employing "high-temperature synthesis" routes [15,16]. However, the thus obtained materials are still insufficient for the catalytic application in industrial processes [17,18]. To solve these problems, many efforts have been devoted to synthesize nanosized zeolites [19,20], ultralarge pore zeolites, and hierarchical mesoporous zeolites. Nanosized zeolites can offer more active sites in catalysis compared with conventional zeolites due to their larger external surface area, but they are difficult to be separated from the reaction mixture or catalysis system [19,20]. Ultralarge pore zeolites (such as UTD-1 [21], VPI-5 [22], ITQ-33 [23], JDF-20 [24], ITQ-37 [25], and ITQ-43 [26]) have been regarded as ideal candidates for improving the mass transfer and catalytic conversion of bulky molecules, but special and high-cost organotemplates hinder their catalytic applications in industry. Recently, great efforts have been put forth to prepare mesoporous zeolites by creating mesopores into the zeolite crystals [17,27–31], which combines the advantages of mesostructured materials (fast diffusion and accessible for bulky molecules) and microporous zeolites (strong acidity and high hydrothermal stability) instead of upgrading their individual performances in catalytic reactions [32]. In this review, we briefly summarize the preparation, characterization and catalytic

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applications of mesoporous zeolites as efficient catalysts in oil refining and natural gas conversion.

2 Synthesis

2.1 Post-synthesis treatments

Mesoporosity can be introduced into the zeolite crystals through post-synthesis treatments including steaming [33] and leaching methods with acidic or basic media [34,35]. However, post-synthesis treatments always result in a significant reduction of zeolite crystallinity and the formation of amorphous aluminosilicate fragments in disordered and uncontrolled mesopores, which could negatively affect catalytic performance [27].

2.2 Templating strategies

Mesoporous zeolites with good crystallinity can be prepared employing mesoscale templates, which could be achieved by "hard" or "soft" templating strategies [27,29,30]. In hard-templating strategies, mesopores can be "duplicated" into zeolite crystals directly by using the secondary mesoscale templates such as carbon nanoparticles [36–38], carbon nanotubes [39,40], carbon nanofibers [41], carbon aerogels [42–45], and mesoporous carbons [46–53]. In addtion, some inorganic nanoparticles such as nano-sized $CaCO_3$ can also be used as hard templates for synthesizing mesoporous zeolites [54]. Many mesoporous zeolites including FAU, MFI, BEA, LTA, LTL, MEL and MTW framework types can be successfully synthesized by using these hard templates. Notably, most mesopores in these cases are disordered and unopened. Recently, Tsapatsis' group [49–51] prepared a series of ordered mesoporous zeolites (3Dom-i zeolite) such as Silicalite-1, ZSM-5, beta, Y, A and L by using three dimensional ordered mesoporous carbons (3Dom carbon) as mesoscale templates (Fig. 1).

In soft templating strategies, mesopores could be successfully introduced into zeolite crystals directly because there are an interaction between the mesoscale soft templates and the aluminosilicate species. In 2006, Xiao et al. [55] firstly reported the synthesis of mesoporous beta zeolite by using the cationic polymers as mesopore-directing agents. Subsequently, Choi and Srivastava et al. [56–58] synthesized mesoporous ZSM-5 and A zeolites by using an amphiphilic organosilicate as mesopore-directing agent. Later in the same year, mesoporous ZSM-5 zeolite was also prepared by using a silylated polyethylenimine as mesopore-directing agent [59]. After then, mesoporous zeolites have been widely investigated and the most used templates are polymers, long chain organosilicates, and amphiphilic surfactants. For example, mesoporous ZSM-11 templated by polyvinyl butyral [60], mesoporous Y templated by long chain organosilicates [61], and mesoporous ZSM-5 templated by CTAB or F127 or P123 [62,63] have been reported. More recently, there are a breakthrough progress in the synthesis of mesoporous zeolites with ordered mesopores by using soft template strategy. Ryoo' group [64–66] designed a kind of bifunctional surfactants, such as $C_{22}H_{45}–N^+(CH_3)_2–C_6H_{12}–N^+(CH_3)_2–C_6H_{13}$ ($C_{22–6–6}$) and $C_{18}H_{37}–N^+(CH_3)_2–C_6H_{12}–N^+(CH_3)_2–C_6H_{12}–N^+(CH_3)_2–C_{18}H_{37}$ ($C_{18–6–6–18}$), which can direct the formation of zeolite structures on the mesoporous and microporous length scales simultaneously, yielding ZSM-5 zeolite nanosheets with a thickness (2 nm) of only a single unit cell (Fig. 2) or ordered mesoporous zeolites with hexagonal mesophase and MFI-like zeolite framwork, respectively. Xiao's group [67] recently designed a new type of polymer polystyrene-4-vinyl pyridine (PSt-co-P4VP), which can be used as the new polymer template for successfully synthesizing mesoporous ZSM-5 zeolite with *b*-axis-aligned mesoporous channels.

3 Catalysis

Mesoporous zeolites can be widely used as catalysts or supports in petrochemistry and fine-chemical synthesis such as cracking, alkylation, isomerization, hydrogenation

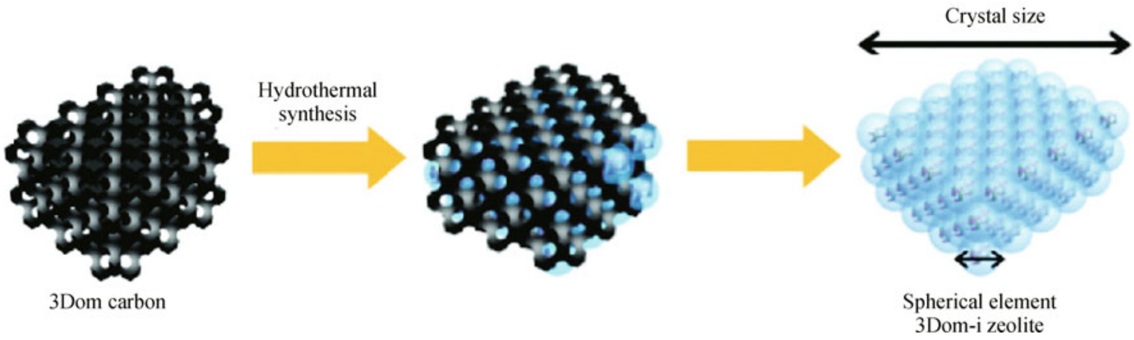


Fig. 1 Schematic illustration of 3Dom-i zeolite templating from 3Dom carbon. Reproduced by permission of Ref [51]. Copyright 2011 American Chemical Society

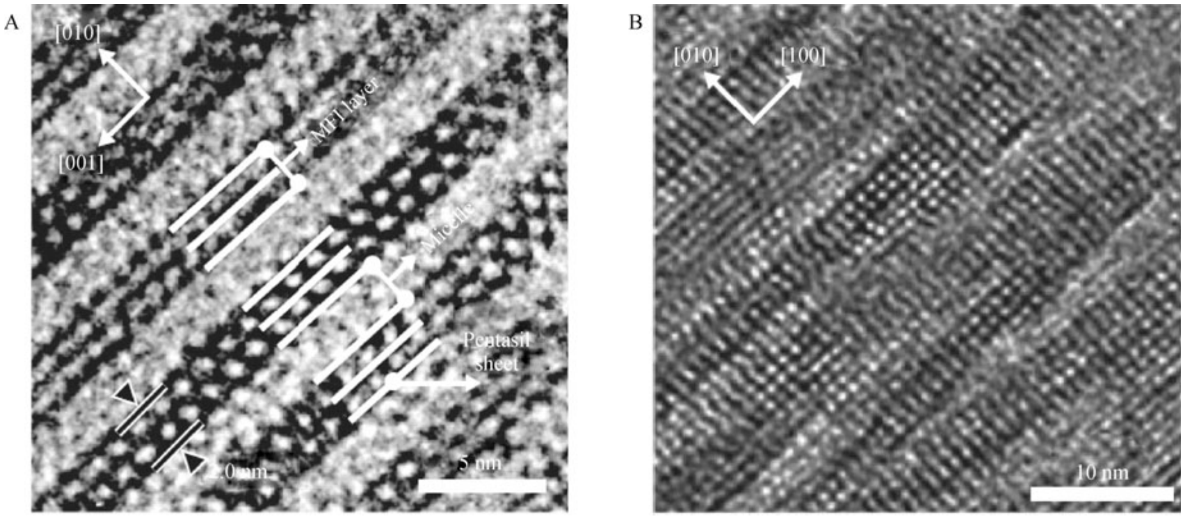


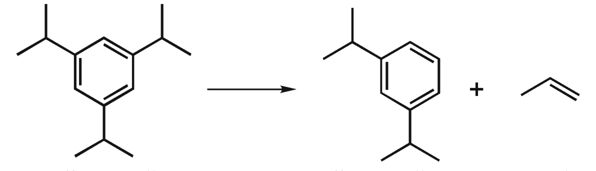
Fig. 2 HRTEM of as-synthesized (a) and calcined (b) MFI nanosheet templated from C_{22-6-6} surfanctant. Reproduced by permission of Ref. [64]. (Copyright 2009 Nature Publishing Group)

and hydrodesulfurization, methane dehydroaromatization, methanol dehydration to dimethyl ether, methanol to olefins (MTO), and methanol to hydrocarbons (MTH).

3.1 Cracking reactions

Fluid catalytic cracking (FCC) process is very important in industry because a huge amount of heavy hydrocarbon feedstocks can be further cracked into more valuable light oils. In these processes, USY with mesoporosity is widely used as the active component of the FCC catalysts. The introduction of mesoporosity in Y-zeolite by steaming and acid or base leaching can enhance the cracking activity of zeolite Y despite the acidic properties are modified by dealumination [1,28]. Kung et al. [68] concluded that minimizing diffusion restraints by the introduction of mesoporosity could be very important to increase rates of dimeric and oligomeric cracking reactions, which serve as an alternative explanation to highly active single sites. This explanation can be supported by that smaller ZSM-5 crystallites reduced the diffusion restraints and showed better catalytic activity than the parent samples for the cracking of linear or branched paraffins [69]. In a recent report by Garcia-Martinez et al. [70], mesostructured Y zeolites with well-controlled mesoporosity and high hydrothermal stability were prepared by a surfactant-assisted method and used in the FCC process. These mesostructured Y-zeolites produced significantly more gasoline and light cycle oil (LCO) as well as less bottoms and coke, because the presence of mesopores allows larger molecules in the vacuum gas oil (VGO) to access the active sites within the zeolite crystals. Tan et al. [71] synthesized a bimodal micro-mesoporous aluminosilicate by assembling preformed zeolite Y nanoclusters using a triblock polymer as template. This micro-mesoporous material produced light oil fraction in higher yield (53%) than the conventional Y catalyst (40% yield) in catalytic cracking of heavy oil.

In addition, mesoporous zeolites such as ZSM-5 and beta can be used as additives in a commercial USY FCC catalyst for imporving the catalytic activity and selectivity toward light olefins. For example, the higher propylene yield of 12.2 wt-% was achieved over E-USY/Meso-Z compared with 9.0 wt-% over E-USY/ZSM-5 [72], despite these additives did not affect the cracking activity of E-USY/additives at similar gas-oil yield. Mesopores in Meso-Z was stated as a key factor to the enhanced production of propylene, which suppressed secondary and hydrogen transfer reactions and offered easier transport and accessibility to active sites. Recently, ZSM-5 zeolites with small intracrystal mesopores (2.2 and 5.2 nm) templated by organosilane polymer templates were also investigated in selective petroleum refining [73]. Compared with conventional ZSM-5, the two mesoporous zeolites display much higher reactivity and selectivity toward light olefins (gasoline) in cracking of VGO. The gasoline yield increased from 12% to 19% when using the mesoporous zeolites at the temperature of 823 K, while the VGO conversion increased from 33% to 48%, which was attributed to the olefin precursor formation in small intracrystal mesopores and subsequent olefin formation



Scheme 1 Proposed reaction of 1,3,5-triisopropylbenzene cracking

in micropores. These examples showed that mesoporous ZSM-5 zeolites as FCC catalysts have higher catalytic cracking performance than parent ZSM-5 zeolites.

The bulky 1,3,5-triisopropylbenzene (TIPB) is usually chosen as a typical substrate (Scheme 1) for the cracking of bulky aromatic hydrocarbons over mesoporous zeolites [74]. For example, mesoporous ZSM-5 prepared by a steaming-assisted conversion method shows a much higher initial conversion (98%) than the conventional ZSM-5 (14%) in cracking of TIPB [75]. Similarly, Zhou et al. [63] synthesized mesoporous ZSM-5 by using block copolymer surfactants as template in the steaming-assisted strategy, which showed much higher catalytic activity and remarkably imporved anti-deactivation performance in the cracking of TIPB (Fig. 3) compared to the conventional ZSM-5, due to the much increased external surface and shortened diffusion length in microporous networks provided by the mesoporous zeolites. Mesoporous ZSM-11 zeolite shows a similar trend in the cracking of 1,2,4-trimethylbenzene, giving a higher conversion (67%) compared with 43% for conventional ZSM-11 at a relatively low temperature of 350°C [60]. Mesopores in ZSM-11 zeolite crystals also leads to a higher activity of mesitylene isomerisation due to the fast diffusion of the bulky mesitylenes in the mesoporous, which reduced retention times and chance of cracking to form smaller products, but increased chance of mesitylene isomerisation.

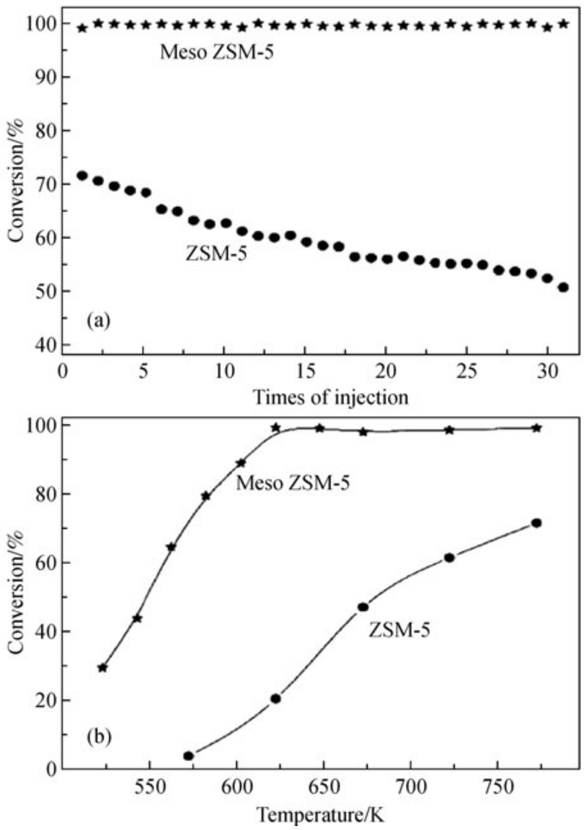


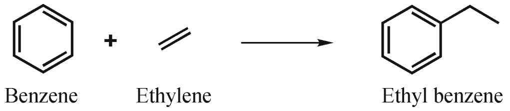
Fig. 3 Catalytic properties of conventional ZSM-5 and meso ZSM-5 employed in the cracking of TIPB (1,3,5-triisopropylbenzene) as a probe reaction: (a) deactivation behavior at 500°C, and (b) catalytic activities (conversions) at different temperatures. Reproduced by permission of Ref [63]. (Copyright 2011 American Chemical Society)

Cracking of heavy linear alkanes such as *n*-hexadecane catalyzed by mesoporous zeolites has also received much attention. Zeolites with strong acidity, such as ZSM-5, ZSM-12, and ZSM-11 have been investigated in these reactions. For example, mesoporous ZSM-5 zeolite templated by carbons shows a significantly increased activity in heavy *n*-hexadecane cracking, and a much higher *n*-hexadecane conversion (52%) than that of conventional ZSM-5 (17%) [76]. After the zeolites were impregnated with platinum, their cracking activity increased significantly and the mesoporous ZSM-5 still displayed higher activity. Notably, there was a four fold increase in *n*-hexadecane isomerisation over mesoporous ZSM-5, which was explained by that the shorter retention time of the substrates in zeolite crystals with mesoporosity leads to less carcking and more isomerisation activity. Similarly, mesoporous ZSM-12 also showed higher activity compared with conventional ZSM-12 in *n*-hexadecane cracking [77]. Mesoporous ZSM-12 also exhibited higher coke-resistance performance, because mesopores increase the number of entry points to the microporous system as well as the overall surface area, and thereby increase the amount of coking needed to restrict its accessibility. In a different study, mesoporous zeolites with MEL structure type, such as silicalite-2 and ZSM-11, and conventional ZSM-5 were investigated and compared in *n*-hexadecane cracking [78].

In addition, the cracking of the polymers such as polyethylene or polypropylene are often tested over mesoporous zeolites to produce light olefins, and it is found that mesoporous zeolites are good catalysts for these reactions [64,79].

3.2 Alkylation reactions

Alkylations of benzene and its derivatives are important reactions in oil refining and natural gas conversion. Mesoporous zeolites are more active in these alkylations reactions than conventional zeolites, due to the shorter diffusion path length in mesoporous zeolites. For example, mesoporous ZSM-5 prepared by carbon-templating showed higher conversion and ethylbenzene selectivity (18% and 81%, respectively) than the parent ZSM-5 (15% and 73%, respectively) (Scheme 2) [80,81]. Higher selectivity can be explained by the predominant level of monoalkylated product over mesoporous ZSM-5 resulting from a shorter diffusion path length in mesoporous zeolite crystal, while ethyl-benzene is difficult to diffuse in microporous zeolites leading to more polyalkylated products than those desired. Perez-Ramirez et al. [82] investigated the catalytic performance over mesoporous ZSM-5 obtained by desilication in liquid phase alkylation of benzene with ethylene, and highlighted a direct correlation between the catalytic activity in benzene alkylation and the hierarchy factor of ZSM-5, which was determined as the product ($V_{\text{micro}}/V_{\text{pore}}$) × ($S_{\text{meso}}/S_{\text{BET}}$). The productivity of ethylbenzene during benzene alkylation over selected zeolites shows a linear dependence on the hierarchy factor. These results show that a sample only having a pronounced mesoporosity as well as a relatively preserved microporosity performed well in this reaction.



Scheme 2 Proposed reaction of benzene alkylation with ethylene

Xiao et al. [55] synthesized a mesoporous zeolite beta by using mesoscale cationic polymers as soft template, which was used as catalyst in alkylation of benzene with 2-propanol. Mesoporous beta sample exhibited much higher activity and isopropylbenzene selectivity (both close to 100%) than the conventional beta, and more importantly, a remarkably slow deactivation over the mesoporous sample could be also observed (Fig. 4). de Jong et al. [83,84] reported the catalytic performance over a seriers of mordenite zeolites by dealumination or/and desilication used as catalysts in liquid alkylation of benzene with propylene. Various catalytic effects such as Al-content, inter- and intracrystalline porosity, acid strength and the presence of extra-framework aluminum were investigated. The mordenite samples by dealumination showed a slightly improved activity and a selectivity towards cumene/di-isopropylbenzene, compared with the parent mordenite sample. However, a subsequent optimized desilication treatment resulted in a mesoporous catalyst displaying a significantly higher activity (up to 27-fold increase) and an increased selectivity towards di- and tri-isopropylbenzene. The mordenite sample by desilication also displayed an excellent combined cumene/di-isopropylen benzene selectivity of >99% arising from suppressed propylene oligomerization.

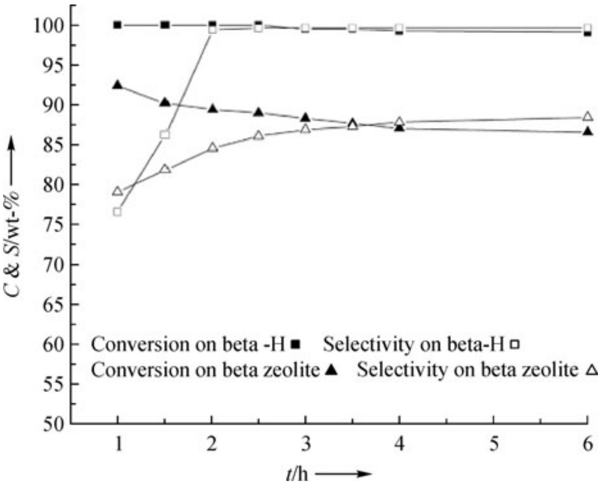


Fig. 4 Catalytic conversions (*C*. Wt-%) and selectivities (*S*. wt-%) in the alkylation of benzene with 2-propanol with various zeolites samples as a function of reaction time (Reaction temperature: 200°C; 4 : 1 benzene/2-propanol; reaction pressure: 2.0 MP, weight hourly spare velocity (WHSV): 10 h^{-1}). Reproduced by permission of Ref. [55]. (Copyright 2006 Wiley)

3.3 Isomerization reactions

3.3.1 Conversion of *n*-butene to isobutene

Isomerization of *n*-butene to isobutene catalyzed by zeolites is very valuable for producing low pollution gasoline additive of methyl tert-butyl ether (MTBE). Introduction of mesopores in zeolite crystals could improve the catalyst performance. An example is the use of fresh and steamed ferrierite (FER) catalysts in the isomerization of *n*-butene to isobutene [85]. The steamed FER catalyst with mesoporosity exhibited lower initial *n*-butene conversion but much higher selectivity of isobutene compared with the fresh catalyst. In a different report [86], mesoporous ferrierite zeolite prepared by recrystallization from alkaline solution in the presence of cetyltrimethylammonium bromide (CTAB) showed improved catalytic activity and selectivity in the isomerization of *n*-butene with respect to the parent ferrierite. The parent ferrierite gave 1-butene with 52% conversion while mesoporous ferrierite increased the conversion up to 67% and the isobutene selectivity from 48% to 61%. Similarly, mesoporous TON zeolites prepared by desilication using NaOH also showed a significant increase of activity in *n*-butene isomerization [87]. The creation of mesopores in zeolite crystals improved the diffusion of butene molecules within the zeolite crystal and thereby increased the turn over frequency (TOF) of the protonic sites. The catalytic activities in isomerization of linear paraffins over mesoporous zeolite catalysts were listed in Table 1.

3.3.2 Linear paraffins

Hydroisomerization of linear paraffins towards highly branched products is an important reaction in upgrading of oils. Mesoporous zeolites were used as catalyst in hydroisomerization of various linear paraffins, usually showing much better catalytic performance compared with the parent sample [88–95]. These linear paraffins commonly include *n*-hexane, *n*-heptane, *n*-octane, *n*-

Table 1 Catalytic activities in isomerization of linear paraffins over mesoporous zeolite catalysts

Substrates	Mesoporous zeolites	Synthesis strategies	Conversion/%	Isomer selectivity/%	Ref.
n-Hexane	ZSM-5/MCM-41	Recrystallization in base solution	22 (22)*	90 (81)	[89]
n-Hexane	ZSM-5 beta	Desilication	68 (59) 73 (53)	97 (96) 98 (91)	[90]
n-Heptane	ZSM-12 beta	Hard template	38 (10) 55 (23)	– –	[91]
n-Octane	ZSM-22	Desilication	78 (67)	75 (< 65)	[92]
n-Octane	SAPO-11	Soft template	43 (43)	98 (88)	[93]
n-Octane	Y-β	Recrystallization	52 (14)	76 (54)	[94]
n-Hexadecane	ITQ-6	Delamination	80 (30)	62 (42)	[95]

*The catalytic data in brackets correspond to the activities or isomer selectivities over parent samples

hexadecane (Table 1). Typically, in *n*-octane hydroisomerisation, mesoporous zeolites with one dimensional framework type used as catalysts attracted much attention. For example, the mesoporous bi-functional Pt/ZSM-22 catalyst prepared by base treatment clearly showed better performance than its microporous parent, giving a higher monobranched isomer yield [92]. This superior activity is attributed to an increased number of accessible micropores in the mesoporous zeolite. Fan et al. [93] prepared a mesoporous SAPO-11 zeolite by using a tetradecylphosphoric acid (TDPA) template to create mesopores. Compared with the conventional SAPO-11, this mesoporous SAPO-11 had much higher external surface (165–64 $m^2 \cdot g^{-1}$), mesoporous volume (0.31–0.06 $cm^3 \cdot g^{-1}$) with the intracrystal mesopores of 4–7 nm and more medium and strong Bronsted acid sites (165–76 $\mu mol \cdot g^{-1}$). In the hydroisomerization of *n*-octane, this mesoporous SAPO-11-based catalyst showed superior isomerization activity, enhanced selectivity to dibranched products, and decreased cracking selectivity (Fig. 5). These results indicate that mesopores in zeolite catalyst enhance the catalytic performance in *n*-octane hydroisomerization. Similarly, the Y-β zeolite composite with mesoporosity synthesized by using high silica Y zeolite as the precursor also showed an excellent hydrocracking activity and good hydroisomerization performance of *n*-octane [94]. Additionally, in the isomerizations of large hydrocarbons, such as *n*-hexadecane, mesoporous Pt/ITQ-6 was more active than Pt/FER, giving a higher ratio (2.1) of isomerisation to cracking products than Pt/FER (1.2) [95].

3.3.3 Xylene

The isomerization of *o*-xylene to *p*-xylene, a typical example of shape-selective catalysis by zeolites, is of great importance in petrochmical industry. *O*-xylene isomerization over mesoporous ZSM-5 prepared by desilication [96] showed higher conversion than the parent ZSM-5, owing to the reduced diffusion limitations. However, the selectivity of *p*-xylene decreased, more *m*-xylene formed, and the catalyst was rapidly deactivated, due to the deleterious effect of acidity on the external surface as a consequence of coking. These disadvantages could be reduced by washing the desilicated zeolite with acid to remove extra-framework aluminum (EFAl) species on the external surface for inhibiting the non-shape selective isomerization reaction [97]. The acid washed mesoporous ZSM-5 was more stable than parent ZSM-5 and untreated mesoporous ZSM-5, increasing the selectivity of *p*-xylene and the yield of *p*-xylene by two fold compared to parent ZSM-5.

3.4 Hydrogenation and hydrodesulfurization

Hydrogenation and hydrodesulfurization (HDS) are very important for removal of sulfur in gasoline and diesel fuels. Despite conventional zeolites show their advantages in these process, their pore size limitation inhibits their application in deep hydrogenation and hydrodesulfurization of diesel fuels. Mesoporous zeolite supported noble metal catalysts have been reported as good catalysts for hydrogenation of bulky aromatics and hydrodesulfurization of bulky 4,6-dimethyldibenzothiophene (4,6-DMDBT) [98–100]. These catalysts showed excellent catalytic performance, giving much better activities than Pd loaded other supports such as γ-Al_2O_3, conventional zeolites (Hbeta and HZSM-5), and ordered mesoporous meterials (Al-MCM-41), which is attributed to the unique factor that these mesoporous zeolites combined the advantages of strong acidity and large external surface area in the samples.

Recently, Fu et al. [61] prepared a mesoporous Y zeolite (Y-M) by using a long chain organosilane surfactant as a soft tempate, followed by Pd loading (Pd/Y-M). Very importantly, Pd/Y-M displays excellent catalytic performance in HDS of 4,6-DMDBT. Compared with mesoporous beta (80.0%) and ZSM-5 supported Pd catalysts (73.4%) as well as commercial catalyst of γ-Al_2O_3 supported Pd catalyst (31.4%), Pd/HY-M catalyst exhibited very high activity (97.3%) in HDS of 4,6-DMDBT

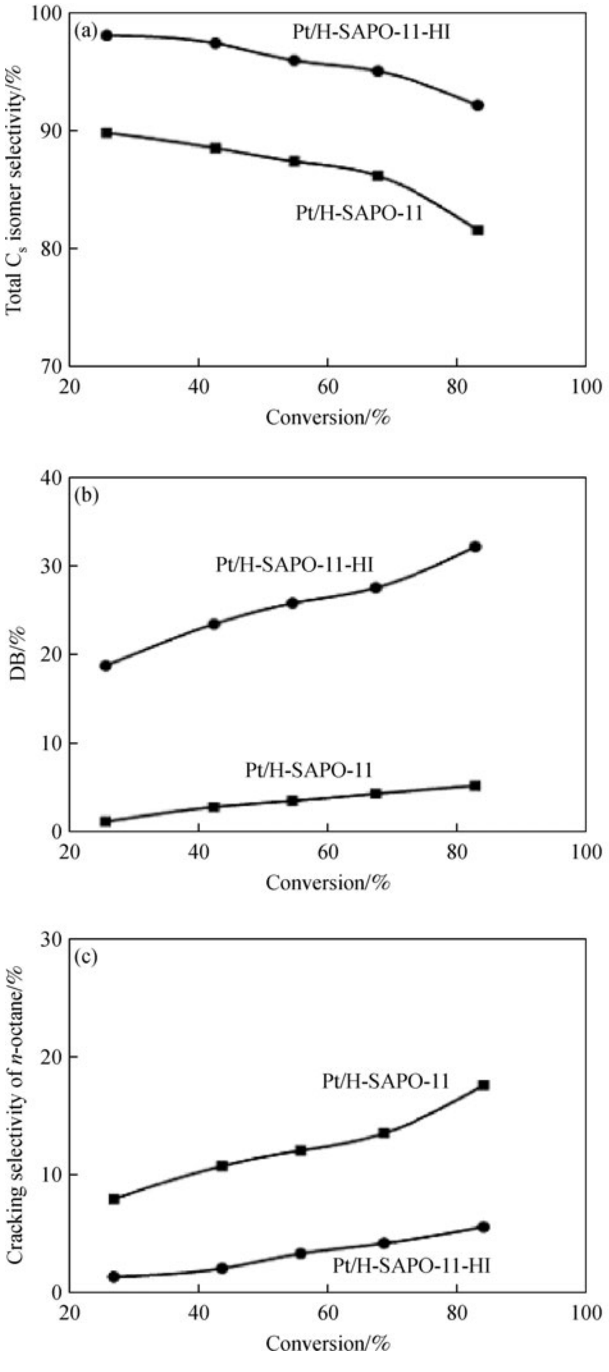


Fig. 5 Dependence of (a) the isomer selectivity, (b) the percentage of di-branched C_8 isomers in total C_8 isomers (denoted as DB), and (c) the cracking selectivity of *n*-octane in *n*-octane-hydroisomerization system on *n*-octane conversion over conventional Pt/H-SAPO-11 and mesoporous Pt/H-SAPO-11-HI catalysts. Reproduced by permission of Ref. [93]. (Copyright 2012 Elsevier)

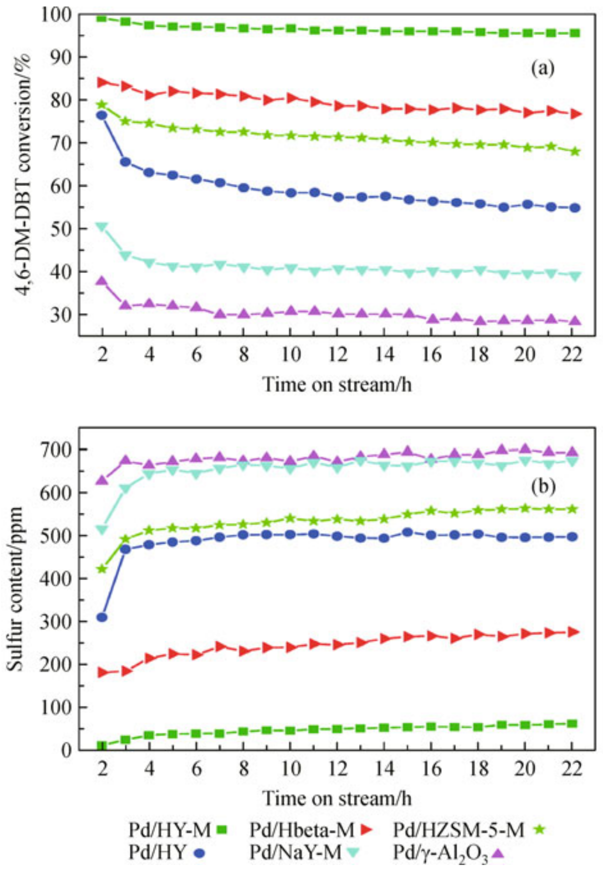


Fig. 6 Dependence of (a) the 4,6-DMDBT conversion and (b) the remaining sulfur content in 4,6-DMDBT-hydrogenation system on reaction time over Pd/HY-M, Pd/Hbeta-M, Pd/HZSM-5-M, Pd/HY, Pd/NaY-M and Pd/γ-Al_2O_3 catalysts. Reproduced by permission of Ref. [61]. (Copyright 2011 American Chemical Society)

(Fig. 6). The presence of mesoporosity in the zeolites play an important role for the contribution of catalytic activities.

In addition, even in the liquid-phase hydrogenation of benzene, a hierarchical mesoporous zeolite composite possessing beta-zeolite cores and Y-zeolite polycrystalline shells (denoted as BFZ) also showed excellent catalytic performance [101]. The benzene conversion over H-BFZ supported Ru (3 wt-%) is much higher than those over parent H-Y or H-*β*-zeolites supported Ru catalysts, which is ascribed to the improved diffusion and acid accessibility as well as the enhanced Ru dispersion because of the introduction of hierarchical mesopores.

3.5 Methane dehydroaromatization

In natural gas conversion research, the non-oxidative methane dehydroaromatization (MDA) is one of valuable and challenging topics in both academia and industry. Mo-based zeolite catalysts, e.g., Mo-ZSM-5 [102] have been often used as catalysts in this reaction. Su et al. [103] created mesopores in ZSM-5 zeolite by alkali treatment and found that the catalytic performance of mesoporous Mo-HZSM-5 catalyst in MDA had been enhanced. Recently, novel hierarchical mesoporous ZSM-5 was synthesized by using SBA-15 as the silica source, and showed good catalytic performance in the MDA reaction

[104]. The mesopores reasonably assigned to intercrystalline voids between the French fries-like crystals provide easier access to the active sites in micropores, resulting in the higher CH_4 conversion and the stronger coking-resistant performance. In one study reported by Martinez et al. [105], a bifunctional Mo/HZSM-5-BP catalyst for MDA was prepared by using a mesoporous HZSM-5 sample synthesized in the presence of carbon nanoparticles, and showed enhanced stability with time-on-stream compared with a Mo/HZSM-5, resulting in a higher and stable aromatics yield. This better tolerance to carbonaceous deposits of Mo/HZSM-5-BP could be attributed to the presence of the intracrystalline mesopores, allowing more coke to be formed while keeping a larger fraction of acid sites in the 10-ring channels active for aromatization. A similar result has also been confirmed by Kan et al. [106].

In addition, a nestlike hollow hierarchical mesoporous MCM-22 microspheres (MCM-22-HS) were synthesized by using carbon black as hard template and tested in the MDA reaction [107]. The Mo/HMCM-22-HS significantly improved methane conversion, benzene yield, and catalyst life (Fig. 7). The exceptional catalytic performance was attributed to the hollow and hierarchical mesoporous structure, which is favorable for the diffusion of larger molecular products, probably leading to significant improvement of the catalyst life.

All above these examples showed the presence of mesopores in zeolite catalysts in MDA reaction enhanced benzene yield and catalyst life.

3.6 Methanol dehydration to dimethyl ether

Dimethyl ether (DME) as a new synthetic fuel has attracted much attention due to its potential use as a substitute of diesel and liquefied petroleum gas. Generally, DME can be produced in a fixed bed reactor by methanol dehydration over porous solid acid catalysts such as zeolites. However, DME does not diffuse quickly enough in the sole micropore in zeolite, causing the catalyst to lose catalytic activity and selectivity quickly. Mesoporous zeolites, combining the strong acidity and hydrothermal stability of microporous zeolite with the fast mass transfer performance of mesoporous material, are also expected to be used for dehydration of methanol to DME to obtain

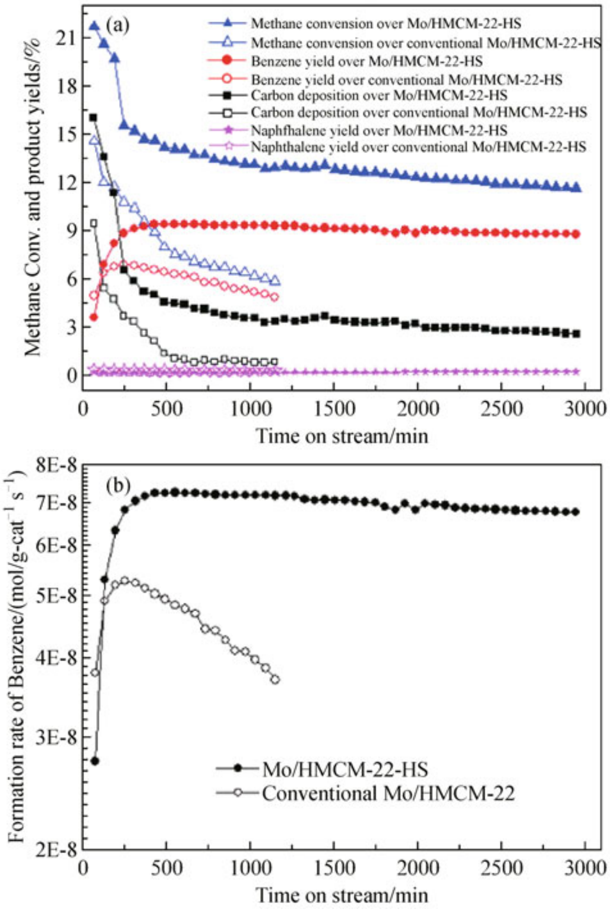


Fig. 7 (a) Catalytic performances of mesoporous Mo/HMCM-22-HS and conventional Mo/HMCM-22 catalysts in methane dehydroaromatization; (b) formation rates of benzene at 700°C on these two catalysts under space velocity of 1500 mL/(g·h). Reproduced by permission of Ref. [107]. (Copyright 2010 American Chemical Society)

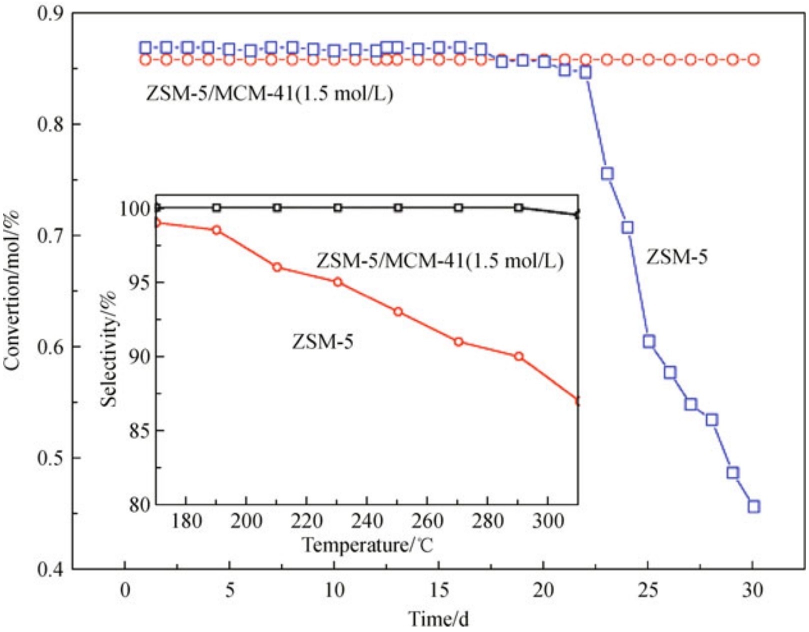


Fig. 8 Stability and selectivity in methanol dehydration over ZSM-5 and ZSM-5/MCM-41 composite alkali-treated by NaOH solution 1.5 mol/L. Reproduced by permission of Ref. [108]. (Copyright 2012 Elsevier)

an improved catalytic performance. For example, Tang et al. [108] reported that micro-mesoporous ZSM-5/MCM-41 composites prepared by combining a microporous zeolite silica source with nano self-assembly methods showed an optimum activity (X_{MeOH} = 86.6%), 100% DME selectivity and long catalyst life at 210°C in methanol dehydration to DME, much better than the parent ZSM-5 (Fig. 8).

Cho et al. [109] synthesized a mesoporous LTA zeolite by using organosilane surfactant as a mesopore-generating agent and ion-exchanged by Ca^{2+}. The mesoporous CaA catalyst showed higher conversion of methanol, lower selectivity to hydrocarbons, and slower deactivation compared to the conventional CaA zeolite sample (Fig. 9) in methanol dehydration to DME. For example, the mesoporous CaA gave a 34% methanol conversion at 1 h, and the selectivity of hydrocarbons was almost zero. However, under the same condition, the methanol conversion and hydrocarbon selectivity over the conventional CaA was 25% and 34% in methanol dehydration to DME, respectively.

3.7 Methanol to olefins

Methanol to olefins (MTO) is greatly important for solving the demand for light olefins. In the MTO process, Mei et al. [110] introduced the mesoporosity in high silica HZSM-5 by alkaline desilication and used the thus obtained zeolites as catalyst in methanol-to-propylene (MTP) reaction. The mesoporous HZSM-5 catalyst gave very high propylene selectivity (42.2%) and propylene/ethylene ratio (10/1) (Fig. 10). Characterizations by various techniques show that these open mesopores are very helpful for enhancing the diffusion of the primary olefin products, in particular to propylene and butylene, thus inhibiting undesirable secondary reactions.

Hierarchical mesoporous SAPO-34 zeolite with high crystallinity and excellent hydrothermal stability was synthesized in the nanoscale confined environment provided by the natural layered material kaolin (Fig. 11) [111]. The mesoporous SAPO-34 catalyst showed significant enhancement of catalytic activity and selectivity in the MTO reaction. Interestingly, a supported SAPO-34 catalyst with an average size of 60 μm was synthesized by a hydrothermal method on fully calcined kaolin microspheres pretreated with 4 wt-% NaOH solution [112]. This new SAPO-34 catalyst remained the pretreated CKMs structure and had high microporous volume ($0.27\ m^3 \cdot g^{-1}$) and mesoporous volume ($0.30\ cm^3 \cdot g^{-1}$) with mesopores of 15.8 nm, and thereby exhibited excellent catalytic performance with 100% methanol conversion, 90% light olefins selectivity, a long catalyst life, and strong mechanical stability at 450°C.

3.8 Methanol to hydrocarbons and methanol to gasoline

Methanol to hydrocarbons (MTH) reaction plays an important role in the conversion of biomass, coal, natural gas, and CO_2 to liquid hydrocarbon fuels, which can be tuned into production of gasoline-rich (methanol to

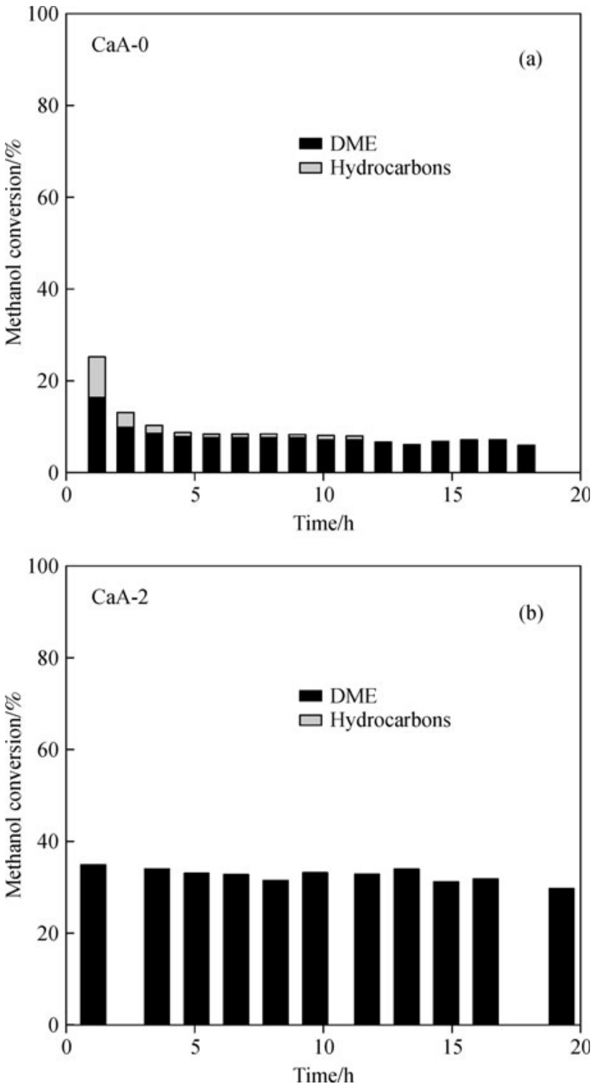


Fig. 9 Catalytic conversion of methanol to dimethyl ether (DME) over conventional CaA-0 (a) and mesoporous CaA-2 (b) zeolites at 400°C. Methanol conversion was calculated by considering DME and hydrocarbons as converted products. Reproduced by permission of Ref. [109]. (Copyright 2009 American Chemical Society)

gasoline, MTG) or olefin-rich (methanol to olefins, MTO) product mixtures by proper choice of catalyst and reaction conditions [113]. Very importantly, mesoporous zeolites showed an increased catalyst life in MTH or MTG reactions than conventional zeolites catalyst.

Mesoporous ZSM-5 synthesized from various routes showed an improved catalyst life in MTG and MTH, compared to conventional ZSM-5 [64,114–121]. As a typical example, Choi et al. [64] reported that ZSM-5 nanosheet showed equivalent initial activity, but a significant increase in catalyst life (Fig. 12), compared to parent ZSM-5. Recent works confirm that there are strong correlations between the catalyst life and the external surface area of mesoporous zeolites in MTH and MTG reactions [116,119].

4 Summary

The strategies for creating mesoporosity in zeolite crystals are briefly summarized. Very importantly, compared with conventional zeolites, the mesoporous zeolites exhibit excellent performance in oil refining and natural gas conversion such as cracking, hydrogenation and hydrodesulfurization of heavy oil, benzene alkylation, hydroisomerization, methane dehydroaromatization, methanol dehydration to dimethyl ether, methanol to olefins, and methanol to hydrocarbons. These phenomena are reasonably attributed to a fast diffusion and accessibility for reactants and products. These features are potentially important for applications of mesoporous zeolites in the future.

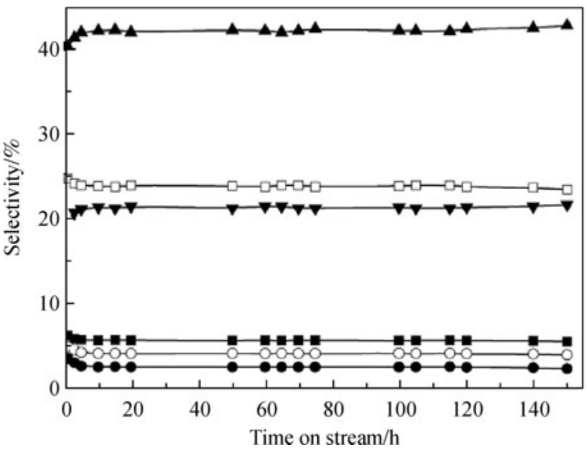


Fig. 10 Product selectivity of mesoporous HZSM-5 by alkaline treatment as a representative catalyst for MTP reaction as a function of time: C_3H_6, C_2H_4, C_4H_8, aromatics, C1–C4 saturated hydrocarbons, C5 and higher hydrocarbons excluding aromatics. Reaction conditions: $T = 470°C$, WHSV = 1 h^{-1}, $P_{CH_3OH} = 0.5$ atm, H_2O: CH_3OH = 1 ∶ 1. Reproduced by permission of Ref. [110]. (Copyright 2008 Elsevier)

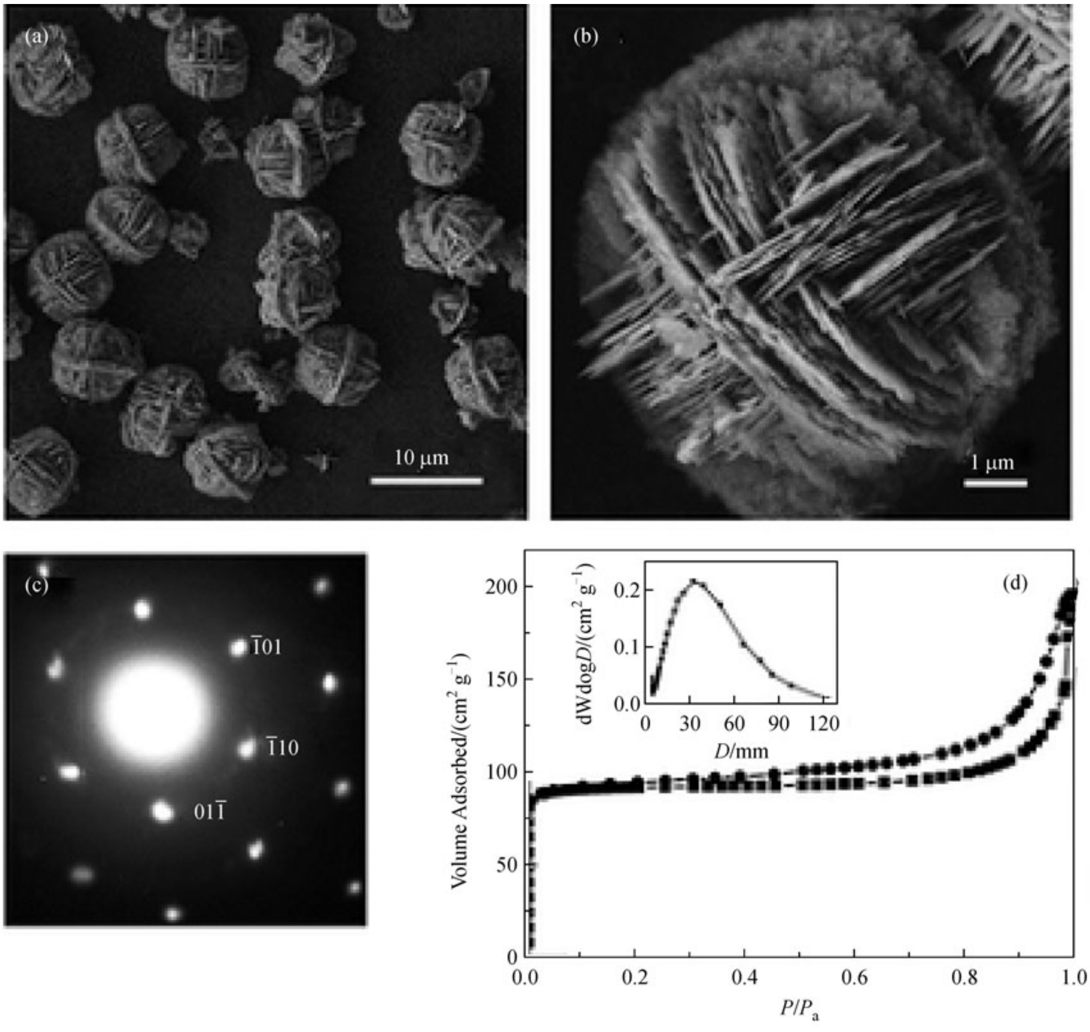


Fig. 11 (a) and (b) SEM images of the hierarchical mesoporous SAPO-34 zeolite at different magnifications; (c) SAED pattern of a horizontal mesoporous zeolite slice; (d) Nitrogen sorption isotherms and BJH pore size distribution (inset). Reproduced by permission of Ref. [111]. (Copyright 2009 Royal Soc Chemistry)

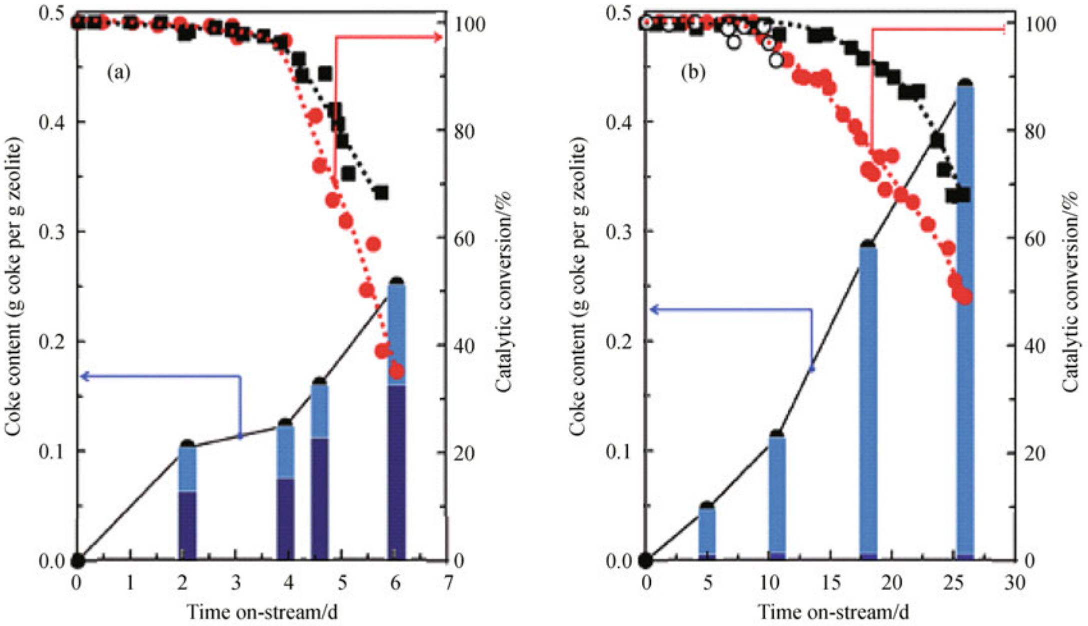


Fig. 12 Coke deposition over (a) conventional MFI zeolite and (b) unilamellar MFI zeolite catalysts during MTG conversion. Catalytic conversion over the unilamellar MFI was repeatedly investigated using three different synthesis batches (red circles, black squares, open circles, respectively). The catalytic measurement for conventional zeolite was repeated twice using the same sample (red circles and black squares). The solid black lines and the dotted red and black lines are guides to the eye. Dark blue bars indicate internal (inside the micropores of the zeolite) coke content, and light blue bars indicate external coke content. Reproduced by permission of [64]. (Copyright 2009 Nature)

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