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Mesoporogen-free synthesis of high-silica hierarchically structured ZSM-5 zeolites and their superior performance for methanol-to-propylene reaction

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Abstract: A series of hierarchically structured ZSM-5 zeolites (ZSM-5 HSZs) with a Si/Al ratio of about 200 have been successfully synthesized in the absence of additional mesoporous agents. XRD, N2 sorption isotherms, SEM, TEM and NH3-TPD results showed that the obtained HSZs materials possess high crystallinity, interconnected micro/mesoporous structures and similar total acid amounts. Meanwhile, in the methanol-to-propylene (MTP) reaction, compared to the microporous counterpart, all synthesized ZSM-5 HSZs demonstrated superior performance benefitting from their hierarchical porous structures. Interestingly, ²⁷AI MAS NMR and Py-FTIR results confirmed the inter-transformation of framework and extra-framework AI species with the extension of materials crystallization duration and consequently the variation of materials surface acidity. As a result, the optimized catalyst achieved the highest initial propylene selectivity of 54.4% and the longest catalyst lifetime (t_{90}) of 175 h under the weight hourly space velocity (WHSV) of 1.0 g g⁻¹ h⁻¹. Moreover, a new "in situ alkali etching-hydrothermal restoring" mechanism has been proposed to elucidate the structural evolution of here reported high-silica ZSM-5 HSZs during the synthesis.

Introduction

The catalytic conversion of methanol-to-olefins (MTO) over acidic zeolites, as an alternative to the traditional petrochemical route, not only alleviates the contradiction between the growing demand of olefins and the limited petroleum reservoirs, but also agrees with the concept of green and sustainable chemistry strategy, because the process for methanol production is diverse from coal, natural gas, renewable biomass, and even CO₂. ^[1] Up to now, although dispute still exists about the detailed course in MTO reaction, a dual-cycle hydrocarbon pool mechanism is

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commonly accepted, in which the relative propagation extent of the aromatic-based cycle and the olefins-based one determines the product distributions in the effluent. ^[2] When propylene is the main target product, known as methanol-to-propylene (MTP) reaction, ZSM-5 zeolites with MFI-type topology structure are the most promising candidates due to their adjustable surface acidity, high stability, 3D-connected and suitable microporous system. ^[3] In recent years, aiming at the improvement of selectivity of target propylene and catalyst lifetime in MTP reaction, researches on the newly structured ZSM-5-based catalyst have been attracting increasing concerns from both industry and academia. ^[4]

The acid sites in ZSM-5 zeolites are the active centers for MTP reaction, but also catalyze the undesired secondary reactions, i.e. hydrogen transfer, cyclization and aromatization reactions.^[5] Especially for high-alumina ZSM-5, the high-density acid sites would induce the serious secondary reactions, which leads to the decrease of target propylene selectivity and the rapid deactivation of catalysts. Therefore, high-silica ZSM-5 is the preferred catalyst for MTP. For instance, Mei et al. found that when the Si/Al ratio of ZSM-5 catalysts increased from ca. 10 to 110, the catalyst lifetime would be increased by more than 5 times and the propylene selectivity increased by about 10%. [3a] On the other hand, elemental modification and/or post-synthesis treatment are also adopted for the surface acidity adjustment of ZSM-5 to suppress the possible side reactions. Hu et al. even modified the acidity of ZSM-5 zeolites by boron incorporation. The followed tests showed that, compared to unmodified ZSM-5 zeolites, the stability of boron incorporated ZSM-5 zeolites were significantly improved. [3c] Yarulina et al. found that Ca2+-modified ZSM-5 had a twofold increase of propylene selectivity and a nine times longer catalyst lifetime in MTO reaction. Possible reasons lie in the transformation of Brønsted acid sites (BAS) to Lewis acid ones (LAS) and the decrease of acid strength resulting from the calcium modification. [6]

Besides surface acidity, the textural property is another critical parameter influencing the catalyst performance in MTP. For conventional ZSM-5 zeolites, the sole presence of microporous channels hinders the diffusion of reactants and products in them and consequently increases the residence time of product propylene, which increase the probability of side reactions even with high-silica materials. More importantly, once a channel is blocked by coke species, the nearby zones may become less connected with the outside, which makes it difficult for the reactants to approach the active sites in reality and thus lead to the catalyst gradual deactivation. [7] To enhance the mass diffusion in the zeolite catalysts, hierarchically structured zeolites (HSZs) have made great progress recently through top-down process^[8] or bottom-up synthesis.^[4b, 9] Zhang et al. used a spent zeolite catalyst as part of silica/alumina raw materials and the attached coke species as the template to synthesize mesopore-

containing ZSM-5 zeolites. Interestingly, compared to the parent zeolite, the catalytic lifetime of the refabricated ZSM-5 catalyst increased by two times and the propylene selectivity increased [4b] bv 7%. Kim et al. designed 3-[(trimethoxysilyl)propyl]hexadecyldimethylammonium chloride (TPHAC) organosilanes as the mesopore-directing surfactants to synthesize mesoporous ZSM-5 zeolites. Catalytic results showed that the resultant materials have the stronger resistance to deactivation than microporous zeolites. [4a] Unfortunately, template synthesis of HSZs is not a cost-effective and highly efficient method and the post-synthesis elimination of templates would emit a large amounts of greenhouse gases. From the point of view of potential applications, synthesis of HSZs in the absence of additional mesoporogens is desired. [10]

Very recently, based on the dry-gel crystallization (DGC) conversion course, a mesoporogen-free method for synthesis of ZSM-5 HSZs have been developed in our group. [11] Here, this method have been extended for synthesis of high-silica ZSM-5 HSZs with a Si/Al ratio of as high as around 200 and their potential applications in MTP reaction have been explored. As expected, all synthesized HSZs catalysts showed the superior performance in MTP reaction, which means high initial propylene selectivity (52.0+%) and long catalyst lifetime (t_{90} , 66+ h) under the WHSV of 1.0 g g⁻¹ h⁻¹. In contrast, the microporous ZSM-5 counterpart showed an initial propylene selectivity of only 47.8% and a catalyst lifetime of as short as 13 h. More interestingly, the inter-transformation between BAS and LAS during DGC synthesis was reported with the extension of crystallization duration. As a result, the optimized catalyst achieved the highest initial propylene selectivity of 54.4% and the longest catalyst lifetime of 175 h in MTP reaction. Moreover, a new "in situ alkali etching-hydrothermal restoring" mechanism has been proposed to demonstrate the structural evolution of here reported high-silica ZSM-5 HSZs during DGC synthesis.

Results and Discussion

Physicochemical properties of synthesized HSZs-*t* and ZSM-5(200)

XRD patterns of the synthesized HSZs-t (hierarchically structured ZSM-5 zeolites synthesized by steam-assisted crystallization, in which t refers to the crystallization duration (h)) and ZSM-5(200) (microporous zeolites with a Si/Al ratio of about 200) are shown in Figure 1a and Figure S1a, and the corresponding RCs (relative crystallinity) are listed in Table 1 and Table S1. For sample HSZs-1 and HSZs-3, only weak diffraction peaks are observed, indicating the amorphous nature or incomplete crystallization of synthesized materials. When the crystallization duration extended to 5 h, the resultant HSZs-5 exhibits the typical diffraction spectrum associated with MFI-type topology zeolites and the calculated RC is ~92%, demonstrating its high crystallinity. Further extension of the crystallization duration, the similar diffraction patterns are obtained as that of HSZs-5 and the RC change is unobvious, which imply that for sample HSZs with Si/Al ratio of about 200, as short as 5 h is enough for the complete conversion of amorphous precursors to crystallized materials. Because only highly crystallized zeolites shows apparent catalytic activities in MTP, the following characterizations are mainly focused on HSZs-*5*, HSZs-*10* and HSZs-*4*8.

N₂ sorption isotherms of synthesized HSZs-t and conventional ZSM-5(200) are shown in Figure 1b and Figure S1b, and their textural properties are summarized in Table 1 and Table S1. As expected, the isotherm of ZSM-5(200) exhibits the typical type I profile with a sharp uptake in the range of $P/P_0 < 0.1$ and a plateau at $0.4 < P/P_0 < 1.0$, which belongs to the microporous materials. The specific surface area (S_{BET}) and the total pore volume (V_{total}) of ZSM-5(200) are 367 m² g⁻¹ and 0.21 cm³ g⁻¹, respectively. In contrast, HSZs-5, HSZs-10 and HSZs-48 exhibit the typical type IV isotherms with a hysteresis loop and an uptake at high relative pressures ($0.4 < P/P_0 < 1.0$). Moreover, compared with microporous ZSM-5(200), HSZs materials (entry 1-3 in Table 1) shows larger specific surface areas and pore volumes. The corresponding pore size distributions (PSDs) are shown in Figure S2. Although the difference is small among them, in the range of 2.0~10.0 nm the three synthesized HSZs materials demonstrate a slightly higher PSDs compared to ZSM-5(200). On the other hand, it is noted that the effect of prolonging crystallization duration on HSZs textural properties is insignificant, although HSZs-48 shows a slightly lower external surface area. It is consistent with above XRD conclusion that under the here synthesis conditions, high-silica HSZs could achieve high crystallinity in a short crystallization duration. Both of them proves that the successful synthesis of high-silica HSZs has been realized in the absence of additional mesopore agents through the DGC procedure.



Figure 1. (a) XRD patterns and (b) N_2 sorption isotherms of synthesized HSZs- t and ZSM-5(200).

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Table	1.	Textural	properties,	compositions	and	RCs	of	synthesized	HSZs-t
and ZS	SM	-5(200)							

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Entry	Sample	S _{BET} (m ² /g)	V _{total} (cm ³ /g)	Si/Al _{ICP}	RC (%)	
1	HSZs-5	491	0.30	179	92	
2	HSZs-10	479	0.30	179	94	
3	HSZs-48	486	0.29	179	91	
4	ZSM-5(200)	367	0.21	187	100	

SEM and TEM images of synthesized HSZs and conventional ZSM-5(200) are shown in Figure 2, Figure 3 and Figure S3. Different from the irregular shape of amorphous gel precursors (Figure S3), HSZs materials (Figure 2a-c) exhibit similar uniform globular particles of 400~500 nm with rough and porous surfaces irrespective of the crystallization duration. As a comparison, the SEM image of ZSM-5(200) in Figure 2d reveals the classical coffin-shape morphology with smooth surfaces. In Figure 3, the TEM images of HSZs materials indicate that the additional mesopores are present inside the zeolite particle. The parallel lattice fringes throughout the entire particles in high resolution TEM (HRTEM) image and the corresponding electron diffraction (ED) pattern (inset) confirm the single-crystalline nature of synthesized HSZs. In order to further clarify the internal structure of synthesized HSZs, the SEM image of crosssection polished HSZs-10 is shown in Figure 4. Disordered mesoporous channels (e.g. the areas pointed by arrow) are obvious, which provide large external surface areas and mesopore volume.



Figure 2. SEM images of (a) HSZs-5, (b) HSZs-10, (c) HSZs-48 and (d) ZSM-5(200).

The aluminum contents of all materials were determined by ICP-OES and their Si/Al ratios were listed in Table 1. All synthesized HSZs materials have similar Si/Al ratio of about 180 that is close to the designed Al content. Further, Figure 5 depicts



Figure 3. TEM and HRTEM images of (a, d) HSZs-5, (b, e) HSZs-10 and (c, f) HSZs-48. The insets in (d-f) are the corresponding electron diffraction patterns.



Figure 4. SEM image of cross-section polished HSZs-10.



Figure 5. NH₃-TPD profiles of synthesized HSZs-*t* and ZSM-5(200).

the NH₃-TPD profiles of HSZs materials and ZSM-5(200) and Table 2 summarizes the quantitative results. As expected, all samples exhibit two desorption peaks at about 150 °C and 350 °C, respectively, in which the former is usually assigned to the weak acid sites, while the latter is ascribed to the strong acid sites and always considered as the active sites in MTP reactions.

^[12] Specifically, the quantitative results indicate that all materials possess the approximate strong acid amount of $32\sim42 \ \mu mol \ g^{-1}$.

Overall, high-silica ZSM-5 HSZs have been successfully synthesized in the absence of additional mesoporogens. The characterization results show that the synthesized HSZs have high crystallinities, interconnected micro/mesoporous structures, uniform particle size and approximate total acid amount.

Table 2. Acidic properties of synthesized HSZs-t and ZSM-5(200)							
Sample	By NH ₃ -TPD (µmol/g)			By Py-FTIR (µmol/g)			
	Weak	Strong	Total	BAS	LAS	B+L	
HSZs-5	47	37	84	17	2	19	_
HSZs-10	38	34	72	15	5	20	
HSZs-48	42	42	84	18	2	20	
ZSM-5(200)	80	32	112	-	-	-	

Catalytic performance of synthesized HSZs and ZSM-5(200) in MTP

The catalytic results over synthesized HSZs materials and ZSM-5(200) are shown in Figure 6 and methanol conversions and product selectivities after 2 h time on stream are summarized in Table S2. In general, at the initial stage of reaction, for all catalysts, the methanol conversions are ~100% (Figure 6a) and the selectivities to target propylene are larger than 45.0% (Figure 6b), which reflects the high intrinsic activity of MFI-type aluminosilicate zeolites in MTP. Afterwards, suffering from the coke formation, all of them gradually deactivate with time on stream. Nevertheless, their specific performances are significantly different. For example, the catalyst lifetimes of HSZs-5, HSZs-10, HSZs-48 and ZSM-5(200) are about 136 h, 175 h, 66 h and 13 h, respectively, while their initial propylene selectivities are 53.1%, 54.4%, 52.0% and 47.8%. To address these differences, the effect of catalyst pore structures and acidic properties would be discussed separately in the following section. For comparison, literature reports about MTP performance over various ZSM-5-based catalysts, especially mesostructured materials synthesized with or without mesoporous agents, have been listed in Table S4. [3c, 4b, 4e, 13] Irrespective of detailed reaction conditions, here synthesized HSZs-10 shows better results in most cases. Moreover, considering the superiority of here reported mesoporogen-free method for production of HSZs, its potential applications is expectable.

Compared to microporous ZSM-5(200), the synthesized HSZs materials exhibit better performances in the MTP reaction, that is, longer catalyst lifetimes (Figure 6a, 66+ h vs 13 h), higher selectivity to propylene (Figure 6b, 52.0+% vs 47.8%), and lower selectivity to C₁-C₃ alkanes and C₅₊ compounds in the testing period (Figure 6c&d). The latters are often referred to the undesired by-products and/or coke precursors resulted from the secondary reactions, i.e., hydrogen transfer, cyclization and aromatization reactions, which lead to the decrease of target



Figure 6. (a) Methanol conversions and (b-d) product selectivities of the MTP reactions over synthesized HSZs-*t* and ZSM-5(200). Reaction conditions: WHSV = 1.0 g g⁻¹ h⁻¹, T = 460 °C, P_{total} = 1.0 atm.

propylene and deactivation of catalysts. ^[14] Since both HSZs materials and ZSM-5(200) have the similar Si/AI ratios and consequently the similar acid amounts, as shown in above ICP (Table 1) and NH₃-TPD results (Figure 5 and Table 2), it is believed that the hierarchically micro/mesoporous system in the HSZs, confirmed by their relatively large specific surface area (entry 1-3 in Table 1) and interconnected micro/mesoporous

structures (Figure 4), is favorable for the enhancement of materials catalytic performance. Additionally, we even synthesized ZSM-5 HSZs with Si/Al ratio of about 400, denoted as HSZs(400). For the same reason, although its acid amount is much lower compared with that of ZSM-5(200), its catalyst lifetime is about 102 h and the initial propylene selectivity is 54.1%, which are also superior to those of the latter (Table S2&3 and Figure S4).

For HSZs catalysts, the auxiliary mesoporous structures breaks the connectivity of the original microporous structures of zeolites, which brings three kinds of benefits to the MTP reaction. Firstly, the target propylene could diffuse from the acid sites in a timely manner through the shortened diffusion length in microporous channels, which inhibits the occurrence of secondary reactions. As a result, HSZs catalysts get high selectivity to propylene and low production of C1-C3 alkanes and C_{5+} compounds, as shown in Figure 6b-d. Also, it offers a quick path for the diffusion of bulky coke precursors out of micropore system, e.g. aromatic species, which delays the accumulation of coke precursors and decrease the coke formation rate in catalysts. [4a, 4e, 15] To verify this hypothesis, the TG analysis of spent catalysts were conducted, as shown in Figure 7. Specifically, the spent microporous ZSM-5(200) exhibits a weight loss of 4.06% between 300 °C and 800 °C. Considering its lifetime of about 13 h, the corresponding average coke formation rate is 3.1*10⁻³ h⁻¹. In contrast, for HSZs-5, HSZs-10 and HSZs-48, these rates are 5.2*10-4 h-1, 4.3*10-4 h-1 and 8.0*10⁻⁴ h⁻¹, respectively, which are decreased by 74~87% in comparison with that of ZSM-5(200). Therefore, HSZs series catalysts achieve long lifetime (Figure 6a). Secondly, due to the small pore size, the available active sites for conventional zeolites are often limited to the near pore-mouth area. The accumulation of coke or coke precursors in this area leads to the rapid deactivation of ZSM-5(200). However, for HSZs catalysts, introduction of mesoporous structures provides more open micropore mouth and more accessible active sites are thus obtained. Consequently, under the identical MTP reaction conditions, HSZs catalysts would demonstrate a long duration of 100% methanol conversion and the prolonged lifetime before apparent deactivation appears. Lastly, large external surface area and pore volume with HSZs catalysts increase their coke tolerance capacity. [3c, 16] When the methanol conversion decreased to 90%, the total coke contents for four spent





catalysts follow the order of HSZs-10(7.50%) > HSZs-5(7.04%) > HSZs-48(5.31%) > ZSM-5(200)(4.06%).

For the tested HSZs materials, although they have the similar textural properties (entry 1-3 in Table 1) and the approximate total acid amount (Figure 5 and Table 2), their difference on MTP catalytic performance is also remarkable. In order to clarify these differences, the analysis of ²⁷AI MAS NMR and Py-FTIR had been conducted. As shown in Figure 8a, HSZs-5 and HSZs-48 exhibit a main peak centered at ca. 55 ppm, attributed to the tetrahedrally coordinated framework AI species (FAL), while the resonances at ca. 0 ppm are very weak, which is usually assigned to the octahedrally coordinated extra-framework AI species (EFAL).^[17] These results demonstrate that almost all AI atoms in HSZs-5 and HSZs-48 are isomorphous substituted for Si atoms in Silicalite-1 frameworks. In contrast, HSZs-10 shows a slight decrease in peak intensity at ca. 55 ppm and an apparent peak appears at ca. 0 ppm indicating the formation of EFAL. All these results imply that accompanying with the extension of crystallization duration, a portion of FAL in preformed HSZs materials (HSZs-5) would be removed from the zeolite frameworks (HSZs-10) and then re-incorporated again (HSZs-48).

Figure 8b shows the Py-FTIR spectra of HSZs-5, HSZs-10 and HSZs-48, in which the bands at 1546 cm⁻¹ and 1455 cm⁻¹ are assigned to the pyridine chemisorbed at BAS and LAS, respectively, while the band at 1490 cm⁻¹ corresponds to the adsorption of pyridine on both the BAS and LAS. ^[5b. 6] The calculated BAS and LAS amounts are summarized in Table 2. The total amounts of BAS and LAS are almost the same among



Figure 8. (a) ²⁷AI MAS NMR spectra and (b) Py-FTIR spectra after evacuation at 200 °C of synthesized HSZs-*t*.

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HSZs-5, HSZs-10 and HSZs-48. However, as the crystallization duration is extended, the concentration of BAS decreases first and then restores, while the concentration of LAS increases first and then declines, being consistent with the above ²⁷Al MAS NMR results. It is worth noting that a difference between the quantitative results of NH₃-TPD and Py-FTIR for synthesized HSZs is observed, which may be due to their relatively low acidic amount and the actual pyridine pre-desorption temperature. Similar results could be found from the recent work of Liang et al., in which the difference between the quantitative results of NH₃-TPD and Py-FTIR increases gradually with the decrease of zeolite acidic amount. ^[12]

The relatively low BAS concentration with sample HSZs-10 contributes to the inhibition of side reactions such as hydrogen transfer for propylene, and may therefore suppress the propagation of aromatic-based cycle. Moreover, a lower BAS density may delay the further reactions of polymethylbenzenes to form polycyclic aromatic compounds (i.e., coke precursor). ^[18] In addition, from the "in situ alkali etching-hydrothermal restoring" mechanism proposed in this work (discussed in the following part), the presence of alkaline "water pool" will lead to the demetallization effect in the pre-formed zeolite particles, that is, the acid sites on the external surface, i.e., non-selective acid sites, may be effectively removed. As a result, the undesirable consecutive reactions such as isomerization, alkylation and oligomerization occur on the external surface acid sites are largely suppressed. ^[19] Interesting results could be found in a recent publication by Gascon et al, in which a subtle interplay between BAS and LAS sites is confirmed, from both experimental and theoretical calculation results, to obtain an optimally ZSM-5-based MTP catalysts. [20] Similar phenomena occurred to here synthesized HSZs catalyst. Although the total acid amounts almost kept constant for all HSZs materials, sample HSZs-10 exhibits the best MTP catalytic performance, i.e the highest initial propylene selectivity of 54.4%, the lowest average coke formation rate of 4.3*10⁻⁴ h⁻¹ and the longest lifetime of 175 h.

Materials synthesis mechanism

In one of our primary reports about mesoporogen-free synthesis of ZSM-5 HSZs with a Si/Al ratio of 50, a kinetically controlled nucleation-growth mechanism has been proposed, in which the dynamic balance between the microscopic and localized water pools and the steam plays a key role. [11a] Subsequently, a modified surface hydrophilicity/hydrophobicityregulation mechanism has been suggested to elucidate the difference on the structural evolution of titanosilicate and aluminosilicate zeolites. [21] However, in this study, when highsilica ZSM-5 HSZs with a Si/Al ratio of about 200 have been synthesized under the identical conditions, only sub-micron particles with relatively lower mesopore volume, but neither zeolite nanocrystals [21] nor HSZs with abundant mesoporous structures, [11a] could be obtained, as shown in Figure 2&3 and Table 1. Figure S5 are the typical digital photos of assynthesized HSZs materials. Apparently, with the extension of crystallization duration, the resultant material has experienced a transition from "dry powders" of sample HSZs-5 to "damp powders" of sample HSZs-10, and to "precipitates" of sample HSZs-48. Additionally, above ²⁷AI MAS NMR and Py-FTIR results demonstrate the (re)doping/demetallation course of aluminum species into/from the zeolite frameworks during the extended crystallization duration. Based on these results, here a new "*in situ* alkali etching-hydrothermal restoring" mechanism is proposed for synthesis of high-silica HSZs by DGC conversion, as shown in Scheme 1.



Scheme 1. Illustration of steam-assisted crystallization process of HSZs-*t.* (a) Steam-assisted crystallization system. (b) Transition state. (c) Hydrothermal system.

In the first stage of Scheme 1a, e.g. for synthesis of HSZs-5, kinetically controlled nucleation-growth mechanism the dominates, similar to the preparation of HSZs with Si/Al ratio of 50. [11a] Due to the low content of aluminum doping, the assynthesized zeolite particles are highly crystallized in a short time of 5 h and keeps at the dry state as the dry-gel precursors. Importantly, nearly all AI atoms are tetrahedrally coordinated in the zeolite framework. Meanwhile, the increased zeolite crystallinity also leads to the enhancement of framework hydrophobicity.^[21] Therefore, when the crystallization duration is further extended (Scheme 1b), e.g., in synthesis of HSZs-10, the water affinity of zeolite internal/external surfaces becomes weaker and consequently the microscopic and localized water pools would gradually integrate with each other. As a result, the as-synthesized materials is damp but no longer dry. Moreover, because these integrated water pools are strongly alkaline, the demetallation, i.e., desilication accompanying dealumination, would happen in the pre-formed zeolite particles, similar to the conventional post-alkaline etching [8c, 22] and in situ etching course ^[23] for preparation of HSZs. Then, EFAL will appear in the resultant materials, as shown in above ²⁷AI MAS NMR and Py-FTIR results. It should be noted that although the course of highsilica HSZs is artificially divided into three stages, in practice, it is impossible to definitely separate them from each other, and they may occur simultaneously. Lastly, when the crystallization duration is long enough (Scheme 1c), e.g., in the synthesis of HSZs-48, the macroscopic "water pools" is apparent and the material crystallization conversion turns into a direct hydrothermal system. Since the usage of alkaline source is fixed, compared to the solution alkalinity of stage b, the relatively lower alkalinity in stage c of direct hydrothermal system would weaken the alkali etching effect and the EFAL would probably reincorporate into the defect sites of zeolite frameworks again, as confirmed by above ²⁷AI MAS NMR and Py-FTIR results.

Conclusions

A series of hierarchically structured ZSM-5 zeolite catalysts (Si/Al~200) have been successfully synthesized by a facile and eco-friendly mesoporogen-free steam-assisted crystallization (SAC) strategy. XRD, N₂ sorption isotherms, SEM and TEM results show that the obtained HSZs materials exhibit similar uniform globular particulate morphology (ca. 400~500 nm in diameter) with high crystallinity, interconnected micro/mesoporous structure and large specific surface area. Importantly, all synthesized HSZs catalysts show excellent catalytic performance in MTP reaction with the WHSV of 1.0 g g ¹ h⁻¹, i.e., high initial propylene selectivity (52.0+%) and long catalyst lifetime (t_{90} , 66+ h). As a comparison, the initial propylene selectivity over microporous ZSM-5 counterpart is as low as 47.8%, and the catalytic lifetime is only 13 h, mainly due to the huge diffusion barrier caused by its sole microporous system. More interestingly, it is found that with the extension of the crystallization duration. Al dopants experienced a process of isomorphous substitution of framework Si, dealumination from crystallized zeolite frameworks and then re-doping into the frameworks again, which led to the inter-transformation of materials BAS and LAS and consequently the varied MTP performance. Over the optimized sample HSZs-10, the highest initial propylene selectivity of 54.4% and the longest catalyst lifetime of 175 h are thus achieved. Accordingly, a new "in situ alkali etching-hydrothermal restoring" mechanism has been proposed to illustrate the microscopic and macroscopic structural evolutions of here reported high-silica ZSM-5 HSZs during DGC synthesis.

Experimental Section

Reagents

Tetraethyl orthosilicate (TEOS) and methanol (\geq 99.5 wt%) were purchased from Shanghai Lingfeng Chemical Co., Ltd (China). Aluminum isopropoxide (Al(*I*PrO)₃) was obtained from Aladdin Reagent Co., Ltd (China). Tetrapropylammonium hydroxide (TPAOH, 25 wt%) was purchased from Yixing Dahua Chemical Co., Ltd (China). Ammonium chloride (NH₄Cl) was obtained from Sinopharm Chemical Reagent Co., Ltd (China). All reactants were used as received without further purification.

Materials preparation

High-silica ZSM-5 HSZs with Si/AI ratio of 200 were prepared according to the previous reports. ^[11] In a typical process, 10.42 g of TEOS and 0.051 g of Al(*i*PrO)₃ were mixed at room temperature for 0.5 h. Then, 18.00 g of deionized water was added and stirring was continued for another 0.5 h. Subsequently, 4.067 g of TPAOH (25 wt% aqueous solution) was added dropwise into the mixture. The molar ratio of the resultant sol was 1.0 SiO₂: 0.0025 Al₂O₃: 0.1 TPAOH: 23.38 H₂O. The mixture was stirred at 40 °C in water bath to get the transparent precursor gel which was dried at the same temperature for the next 48 h. The aged precursor gel was crushed and then transferred into an Al₂O₃ crucible and put into an 80 mL Teflon container. 0.7 g of deionized water was added into the bottom of the Teflon container avoiding contacting

with the precursor gel. Then, the Teflon container was fitted into a stainless steel autoclave and the autoclave was heated in a preheated oven at 150 °C for a given period of time (*t*). The obtained products were dried at 80 °C overnight and then calcined at 550 °C in static air for 6 h to remove the organic components. To obtain the H-form zeolites, assynthesized HSZs materials were ion-exchanged with 1 M NH₄Cl solution three times at 80 °C for 4 h and then dried at 80 °C for 6 h. Finally, all the NH₄-form materials were calcined at 550 °C in static air for 6 h. The resultant materials were denoted as HSZs-*t*, in which *t* refers to the crystallization duration (h). In this work, the values of *t* were 1, 3, 5, 10 and 48, respectively.

Characterization

The powder X-ray diffraction (XRD) patterns of samples were recorded on a Rigaku Ultima IV X-ray diffractometer at 40 kV and 40 mA, using Cu Ka radiation source, with a scanning rate of 5 ° min⁻¹ and an angular step size of 0.02 °. The integrated peak areas of synthesized samples in the 20 range of 22.5-25 degrees were compared with that of commercial ZSM-5(200) zeolite for obtaining the relative crystallinity (RC). [16a] N2 adsorption-desorption experiments were performed on a Micromeritics Tristar 3000 porosimeter at 77 K. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area (S_{BET}) and the adsorbed nitrogen volume at about P/Po of 0.990 was used to determine the total volume (Vtotal). In addition, the t-plot method was used to calculate the micropore surface area (Smicro) and the micropore volume (Vmicro). The external surface area (Sext) and mesopore volume (Vmeso) were obtained by the total data minus the corresponding micropore data. The field-emission scanning electron microscopy (FE-SEM) images were obtained on a HITACHI SU8220 and FEI-Magellan 400L under an operating voltage of 1 kV. In order to observe the interior of zeolite particles, the synthesized materials and graphite were mixed and then processed with argon jons on an E-3500 jon milling system to conduct the cross-section polish. Transmission electron microscopy (TEM) images were obtained on a JEM-2100F electron microscope. The aluminum content of samples were determined on the Agilent Technologies 725 inductively coupled plasma optical emission spectrometry (ICP-OES). The solid-state ²⁷Al Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectra were recorded on a Varian VNMRS 400WB spectrometer. The ammonia temperatureprogrammed-desorption (NH₃-TPD) of samples were analyzed on a Micromeritics AutoChem II 2920 instrument equipped with a thermal conductivity detector (TCD). The materials (ca. 200 mg) were pretreated in an He flow (30 mL min-1) at 600 °C for 2 h at a heating rate of 10 °C min-1 to remove adsorbed impurities, then cooled down to 100 °C, and saturated adsorption with NH₃ for 1 h. Then, the He flow (30 mL min⁻¹) was used to remove the physical adsorbed ammonia at 100 °C for 1 h. Subsequently, the NH3-TPD profiles were recorded from 100 °C to 500 °C at a heating rate of 10 °C min⁻¹. Fourier transform infrared spectra of adsorbed pyridine (Py-FTIR) were recorded on a Perkin-Elmer Frontier FTIR instrument. The materials were ground and pressed into selfsupporting wafers, which were activated at 500 °C for 2 h in vacuum and then cooled down to room temperature. Subsequently, the spectra of zeolite frameworks were recorded. Next, the materials were saturated with pyridine vapor for 0.5 h and then evacuated at 200 °C for 0.5 h. After cooling to room temperature, the spectra were recorded in 1350-1750 cm⁻¹ range. According to the previous literature, the extinction coefficients used for quantification are 1.67 and 2.22, respectively. Assuming that an acid site can adsorb a pyridine molecule, the concentrations of Brønsted acid sites (BAS) and Lewis acid sites (LAS) can be calculated by Eq. (1) and (2), respectively,

 $c_{BAS} = 1.88IA(B) R^2/W$

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 $c_{LAS} = 1.42IA(L) R^2/W$

where IA(B) and IA(L) correspond to the integrated absorbance of BAS and LAS band (cm⁻¹), respectively, R corresponds to the radius of catalyst disk (cm) and W corresponds to the weight of disk (mg). ^[24] Thermogravimetric analysis (TGA) of used catalysts were carried out on a Netzsch STA 494 C Jupiter TG/DSC instrument. The weight loss of deactivated catalysts between 300 °C and 800 °C were taken as the total coke content. Correspondingly, the catalyst average coke formation rate was calculated by dividing the total coke content by the catalyst lifetime (t_{90}).

(2)

Catalytic tests

The MTP reactions were performed in a quartz tubular fixed-bed reactor (i.d., 8 mm) at atmospheric pressure and a K-type thermocouple was placed near the catalyst bed for the detection and control of the reaction temperature. Prior to reaction, 0.2 g of sieved catalyst particles (40-60 mesh) were loaded between two quartz wool plugs and activated at 550 °C in the nitrogen flow of 50 ml min-1 for 2 h. Then, the catalyst bed temperature was decreased to 460 °C for MTP reaction. A high performance liquid chromatography (HPLC) pump was used to feed methanol into the reactor system with the weight hourly space velocity (WHSV) of 1.0 g g $^{\text{-1}}$ h $^{\text{-1}}$ and the nitrogen flow was maintained at 50 ml min⁻¹. The product effluent was analyzed by an online gas chromatograph of GC/2010 plus (Shimadzu, HP-PLOT/Q capillary column) with a flame ionization detector (FID). The transfer line between the reactor and the gas chromatograph was maintained at 250 °C to avoid the possible condensation of organic moieties. Dimethyl ether (DME) was treated as an unconverted reactant, so the methanol conversion (X_{MeOH}) and product selectivity (S_{CxHy}) were calculated according to Eq. (3) and (4), respectively,

$$X_{MeOH} = \frac{N_{MeOH}^{i} - (N_{MeOH}^{0} + 2N_{DME}^{0})}{N_{MeOH}^{i}} \times 100\%$$
(3)

$$S_{C_x H_y} = \frac{x \times N_{C_x H_y}^o}{N_{MeOH}^i - (N_{MeOH}^o + 2N_{DME}^o)} \times 100\%$$
(4)

where N is the number of moles and x is the number of carbon atoms, superscript *i* and *o* refer to the components at the inlet and outlet of reactor, respectively.

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Mesoporous Materials*

Hangle Guo, Tongguang Ge, Jian Lv, Changlin Du, Jian Zhou,* Zhicheng Liu, Zile Hua*

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