

Polycrystalline ZSM-5 Aggregates Induced by Seed and Catalytic Performance in Methanol to Hydrocarbon

WANG Xuchang¹, JIAO Chuyu¹, JI Zhuo¹, JIAO Qirui¹, QIN Bo², DU Yanze², ZHENG Jiajun¹, LI Ruifeng¹

(1. Key Laboratory of Coal Science and Technology MOE, Research Centre of Energy Chemical & Catalytic Technology, Taiyuan University of Technology, Taiyuan 030024, China; 2. SINOPEC Dalian Research Institute of Petroleum and Petrochemicals Co., Ltd. SINOPEC, Dalian 116045, China)

Abstract: Synthesis of ZSM-5 zeolite typically utilizes small molecule polyamines or quaternary ammonium salts as organic structure guiding agent (OSDA). By contrast, the OSDA-free hydrothermal synthesis system eliminates the use of organic templates and the subsequent calcination procedure. This not only reduces the cost of synthesis, but also prevents environmental pollution from the combustion of organic templates, representing an eco-friendly approach. Despite this, literature suggests that even so-called template-free synthesis systems often involve trace amount of organic substances like alcohol. In the present work, a calcined commercial ZSM-5 zeolite was served as seed, with sodium aluminate as aluminum source and silica sol as silicon source, ensuring an entirely template-free synthesis system. Polycrystalline ZSM-5 aggregates consisted of rod-like nanocrystals were successfully prepared in the completely OSDA-free system. Effects of the Si/Al ratio in ZSM-5 seed, dosage and crystallization conditions such as crystallization temperature and crystallization time on ZSM-5 synthesis were investigated. The results show that a highly crystallinity ZSM-5 aggregate consisting of primary nano-sized crystals less than 100 nm is produced from a gel precursor with 5.6% (in mass) seed after hydrothermal treatment for 48 h. Furthermore, the Si/Al ratio in ZSM-5 seed has little effect on the topological structure and pore structure of the synthesized samples. However, the seeds with a low Si/Al ratio facilitate faster crystallization of zeolite and enhance the acidity, especially the strong acid centers, of the catalyst. The catalytic performance of the synthesized polycrystalline ZSM-5 was evaluated during dehydration of methanol and compared with a commercial reference ZSM-5r. The results exhibit that as compared with the reference catalyst, the fabricated sample has a longer catalytic lifetime (16 h vs 8 h) attributed to its hierarchical pores derived from the loosely packed primary nanoparticles. Additionally, the prepared polycrystalline catalyst also exhibits a higher aromatics selectivity (28.1%–29.8% vs 26.5%).

Key words: ZSM-5; polycrystalline aggregate; crystal seed; structure guiding agent

ZSM-5 is a typical microporous zeolite with a three-dimensional ordered double-10-membered rings channel structure. Where, the diameter of “Z” shaped pore is about 0.53 nm×0.56 nm, and the diameter of the rectilinear elliptical pore perpendicular to “Z” shaped one is about 0.51 nm×0.55 nm. The two kinds of pore cross each other, and the size of aperture at intersection is about 0.9 nm. As a solid-acid catalyst, ZSM-5 zeolite has been widely used in petrochemical industry. For example,

in the field of fluid catalytic cracking (FCC) catalysis, ZSM-5, as an active component, can significantly elevate the olefin/oil ratio in products^[1]. Most syntheses require organic structure guiding agents (OSDAs) as templates to guide and stabilize the zeolite framework. As OSDA, the most representative one should be tetrapropylammonium (TPA) cation, either in the form of its hydroxide (TPAOH) or in the form of its salt, preferably bromide (TPABr), or a mixture of salt and hydroxide. The conventional

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Biography: WANG Xuchang (1997–), male, Master candidate. E-mail: wangxuchangxc@163.com

王旭昌(1997–), 男, 硕士研究生. E-mail: wangxuchangxc@163.com

Corresponding author: ZHENG Jiajun, professor. E-mail: zhengjiajun@tyut.edu.cn

郑家军, 教授. E-mail: zhengjiajun@tyut.edu.cn

synthesis of ZSM-5 zeolite typically relies on OSDA, which not only consumes resources but also leads to energy expenditure and environmental pollution^[2]. As a consequence, it has become extremely desired to develop an eco-friendly method for synthesizing ZSM-5 without organic templates.

Synthesis of zeolite crystals in an OSDA-free system has been an interesting alternative method because it avoids using organic templates and consequent calcination procedure. In general, OSDA often plays important roles in directing crystallization and filling micropores. In recent years, an OSDA-free synthesis strategy of zeolites with the help of zeolite seeds has been successfully developed, in which, the zeolite seed plays a similar role to the OSDA for guiding zeolite crystallization from the amorphous precursor. Consequently, researchers have devoted to synthesizing highly crystalline ZSM-5 in the absence of organic templates^[3-11]. For example, template-free systems have been reported to produce micro-, submicron-, and nano-scale ZSM-5 using an eco-friendly seed-assisted one-step method^[2]. Hierarchical ZSM-5 zeolites composed of nanocrystals was also synthesized by template-free seed-assisted technique in a gel precursor containing ethanol and using aluminum isopropoxide as Al-species and tetraethoxysilane (TEOS) as Si-species^[6]. MFI-SDS (SDS: seed-directed synthesis) crystals could be assembled from the rod-like nanocrystals with the same aligned direction in an OSDA-free synthesis system facilitated by the zeolite seeds^[7]. For another example, nanocrystalline ZSM-5 was synthesized with the help of a seed suspension liquid obtained by dispersing the calcined seed in ethanol. However, in the synthesis procedures mentioned above, some organic substances are more or less involved. For example, TEOS as silicon resource^[6-7], or Al(OiPr)₃ as aluminum resource^[6,11], or crystals containing OSDA as seeds^[2,8,10], or suspension seeds in ethanol^[9-10] will inevitably bring organics especially alcohols in the synthesis system. Organic substances like ethanol, whether added directly or produced from hydrolysis in the synthesis system, can act as structure-directing agent to constructing zeolite micropores^[12-17]. As a consequence, these so-called OSDA-free system are not entirely template-free because the alcohol indirectly or directly introduced into the synthetic system actually acts as a template to fill the zeolite micropores and stabilize the zeolite framework structure.

In the present work, a calcined commercial ZSM-5 zeolite was served as seed, with sodium aluminate as aluminum source and silica sol as silicon source, ensuring an organic template-free synthesis system. Polycrystalline ZSM-5 aggregates consisting of rod-like nanocrystals were successfully prepared in a completely

OSDA-free system. The effects of Si/Al ratio, dosage of seeds, crystallization temperature and crystallization time on the synthesis of ZSM-5 zeolite were investigated in detail.

1 Experimental

1.1 Synthesis of ZSM-5 polycrystalline aggregates

ZSM-5 was prepared with the molar ratio of $n(\text{SiO}_2) : n(\text{Al}_2\text{O}_3) : n(\text{H}_2\text{O}) : n(\text{Na}_2\text{O}) = 1 : 0.04 : 10 : 0.1$. Firstly, a certain volume of distilled water was measured, and then a certain mass of sodium aluminate (41% Al_2O_3 , 35% Na_2O , Sinopharm Group) and sodium hydroxide (96%, Sinopharm Group) were added into the distilled water and stirred until the solution was clarified. Then, colloidal silica (40% (in mass), Qingdao Ocean Chemical Co., Ltd.) was dropwisely added into the aforementioned solution followed by stirring at room temperature for about 5 min. Subsequently, crystal seed (NK-18, NK-27, and NK-200 (obtained from Nankai University) with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of 18, 27, and 200, respectively), which was calcined at 550 °C for 6 h in air, was added and stirred for 4 h. The obtained gel precursor was transferred into a hydrothermal reactor lined with polytetrafluoron and crystallized for a certain time at 160 °C. After crystallization, the zeolite was washed to neutral with deionized water, and the samples were named as Z5n-x-y. Here, the “n”, “x”, and “y” are the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of the crystal seed ($n=18, 27, 200$), added amount of seed ($x\% = (m_{\text{seed}}/m_{\text{gel}}) \times 100\%$), and crystallization time (h), respectively. Alternatively, the effect of crystallization temperature on the sample was further investigated, and the corresponding samples were denoted as Z5n-x(T), where “T” represents the crystallization temperature.

The as-synthesized Na-zeolite samples were calcined at 550 °C in muffle furnace with air for 6 h, and the ammonium-formed sample was then obtained by exchanging with 1 mol/L ammonium chloride solution at a solid-liquid ratio of 1 : 20 for three times, 60 °C, and each time for 2 h. After drying, the ammonium-formed zeolite samples were calcined at 550 °C in muffle furnace for 6 h so as to offer H-formed zeolite catalysts.

1.2 Characterization

X-ray powder diffraction (XRD) patterns were measured in the 2θ range from 5° to 50° at a scanning speed of 4 (°)/min by a Shimadzu XRD-6000 diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 40 kV and 30 mA. The relative crystallinity (RC) was calculated by comparing the peak areas of XRD diffraction between $2\theta = 22.5^\circ\text{--}25.0^\circ$ of the as-synthesized samples with those of Z518-5.6-48. The morphologies and elemental mappings of samples were obtained using a Hitachi

S4800 scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). Transmission electron microscope (TEM) images were recorded on a JEM-2100F microscope with an accelerating voltage of 200 kV. Fourier transform infrared (FT-IR) spectra of zeolite framework vibration were measured using a Shimadzu FTIR-8400 spectrometer in KBr pellets. N_2 adsorption/desorption isotherms at $-196\text{ }^{\circ}\text{C}$ were carried out on a NOVA 1200e sorption analyzer after the samples were activated at $300\text{ }^{\circ}\text{C}$ in vacuum for 3 h. The pore size distribution curves were determined based on the Barrett-Joyner-Halenda (BJH) mode with the adsorption branch of the isotherm. The microporous surface area (S_{mic}), microporous volume (V_{mic}), and external surface area (S_{ext}) were calculated from the t -plot method. Temperature-programmed desorption of ammonia (NH_3 -TPD) was carried out on an Autochem II 2920 apparatus equipped with a thermal conductivity detector (TCD). About 20 mg of catalyst was loaded in a U-model quartz tube and supported by quartz wool. Then, it was treated at $550\text{ }^{\circ}\text{C}$ for 3 h in a highly purified He (99.999%) flow. After cooling down to $120\text{ }^{\circ}\text{C}$, the sample was saturated with a NH_3 (15%)/He gas mixture, followed by purging with the highly purified He flow at $120\text{ }^{\circ}\text{C}$ for 1 h. Then, the temperature was increased at a rate of $10\text{ }^{\circ}\text{C}/\text{min}$ in a highly purified He flow ($30\text{ mL}/\text{min}$), and desorption of NH_3 was monitored. In this experiment, a water trap was set up between the sample and the TCD to avoid the influence of water.

1.3 Tested in Methanol dehydration

Methanol dehydration performance was evaluated using a fixed bed reactor. Firstly, the bottom of the stainless steel reaction tube was filled with an appropriate amount of 250–630 μm (40–60 mesh) quartz sand, and 0.2 g catalyst (187.5–630 μm (40–80 mesh)) was filled into the reaction tube, and then an appropriate amount of quartz sand was added. The zeolite catalyst was purged with N_2 ($30\text{ mL}/\text{min}$) at $550\text{ }^{\circ}\text{C}$ for 2 h. Under atmospheric pressure, the flow rate of carrier gas N_2 was $50\text{ mL}/\text{min}$, the mass space velocity was 2.4 h^{-1} , and the reaction performance of the catalyst was tested at $430\text{ }^{\circ}\text{C}$.

2 Results and discussion

2.1 Effect of seeds amount

Fig. 1 is XRD patterns of the as-synthesized samples with different dosages of the seeds. The diffraction peaks at $2\theta=7.88^{\circ}$, 8.76° , 23.00° , 23.84° , and 24.30° can be ascribed to the characteristic diffraction peaks of MFI topology (JCPDS 44-00033)^[2,3,5-10]. The amount of added crystal seed is crucial for the formation of ZSM-5 zeolite.

A gel precursor without seed only generates an amorphous phase in the sample Z518-0-48. With a seed mass fraction of 2.8%, the prepared sample Z518-2.8-48 exhibits characteristic MFI topological structure diffraction peaks, alongside noticeable MOR zeolite peaks at $2\theta=6.5^{\circ}$ and 9.8° (JCPDS 00-048-0512), indicating a predominantly MFI structure with minor MOR inclusions. It can be inferred from Fig. 1 that about 5.6% seed added in the gel precursor is enough to induce and guarantee the formation of a pure and high crystallization ZSM-5 zeolite. Fig. 1 shows that increasing seed amount from 5.6% to 11.2% makes the sample Z518-11.2-48 having the similar yet slightly intense characteristic diffraction peaks compared to the sample Z518-5.6-48. The above result also suggests that a further increase in seed amount has little effect on the topological structure of the as-synthesized sample.

As shown in Fig. S1(a1, a2), the SEM images of NK-18 suggest that the initial ZSM-5 serving as the seed is mono-dispersed crystal with a size of 1–2 μm . It can be seen from Fig. 2 and Fig. S1 that the crystal seed amount strongly affects the formation and the morphology

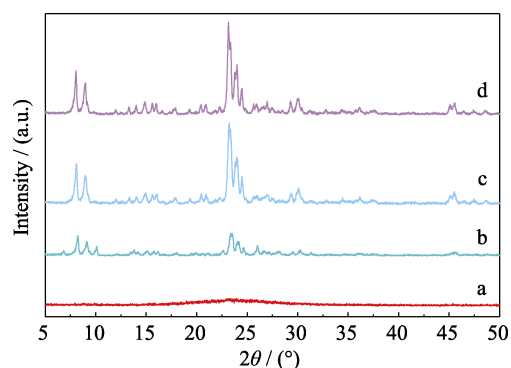


Fig. 1 XRD patterns of the as-synthesized samples added with different amounts of the seeds
(a) Z518-0-48; (b) Z518-2.8-48; (c) Z518-5.6-48; (d) Z518-11.2-48

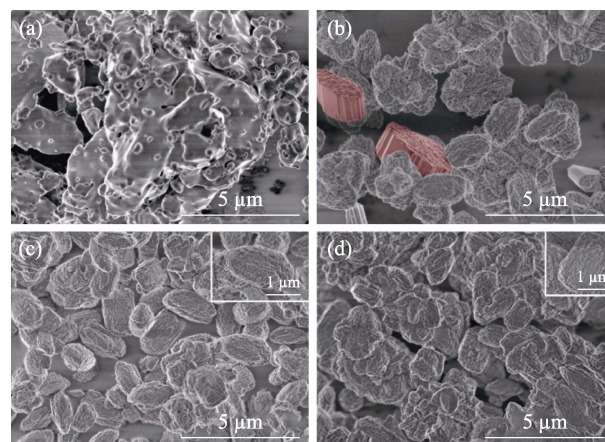


Fig. 2 SEM images of the samples prepared with different amounts of seeds
(a) Z518-0-48; (b) Z518-2.8-48; (c) Z518-5.6-48; (d) Z518-11.2-48
The part rendered in red may be MOR zeolite; Colorful figures are available on website

of the sample. The morphology of the sample is very different from that of the seed crystals. The sample Z518-0-48 yielded from a gel precursor without any seed displays a worm-like amorphous monolith (Fig. 2(a)), agreeing well with the results of XRD as shown in Fig. 1. An appropriate seed dosage in the precursor yields polycrystalline morphology in the sample. As shown in Fig. 2(b-d), all samples Z518-2.8-48, Z518-5.6-48, and Z518-11.2-48 display polycrystalline aggregates, which further consist of loosely aggregating primary nanocrystals with an estimated size less than 100 nm (Fig. S2). As shown in Fig. 2(b), some plate-like crystals (the part rendered in red) can be found, which may be the impure MOR zeolite. This is in agreement with the aforementioned XRD results. No amorphous form can be detected in Z518-2.8-48, Z518-5.6-48 and Z518-11.2-48 samples, indicating that the appropriately seed amount ensures high crystallinity and prevents the formation of amorphous and impure MOR phase. As shown in Fig. S3, both of the sample Z518-5.6-48 and Z518-11.2-48 have the similar N_2 adsorption-desorption isotherms with a combination of type-I and type-IV, indicating the coexistence of the micropore and mesopore. The corresponding BJH pore size distribution curves of samples show that a mesopore distribution ranging from 5 to 50 nm can be found in the two samples, which can be ascribed to the intercrystalline mesopore structure resulted from the loosely aggregating primary nanocrystals in the polycrystalline aggregates as shown in Fig. S2. The N_2 adsorption data as shown in Table S1 shows that the Z518-5.6-48, and Z518-11.2-48 samples have the similar porous and crystalline structure, confirming that the further increased amount of the seed from 5.6% to 11.2% has little effect on the porosity structure and elevating crystallinity of the as-synthesized samples.

2.2 Effect of crystallization time

XRD patterns of the samples yielded from the same

gel precursor with different crystallization time and corresponding crystallization kinetic curve are shown in Fig. 3. The characteristic diffraction peaks at $2\theta=7.9^\circ$, 8.8° and 23° in sample Z518-5.6-0 can be attributed to the influence of ZSM-5 seeds in the gel precursor, indicating that ZSM-5 crystal seeds can remain relatively stable during the preparation. The main reason is that the Si/Al ratio of seed NK-18 is relatively low, and the zeolite framework with negative charge has electron repulsion on OH^- . In the alkaline environment, the Al atom in the framework can protect the nearby Si atom from the nucleophilic attack of hydroxide ions, thus forming the protective barriers for Si species^[18-20]. When $0\text{ h} < t$ (crystallization time) $< 14\text{ h}$, the characteristic diffraction peaks attributed to MFI topological structure in the samples Z518-5.6-4, Z518-5.6-8, and Z518-5.6-12 gradually increase with the prolonged crystallization time (Fig. 3(a)), while the corresponding relative crystallinity of the samples such as Z518-5.6-12 is still low ($<20\%$, Fig. 3(b)), indicating that the synthesis gel system is still in the nucleation induction stage^[21]. When the crystallization time " t " $\geq 14\text{ h}$, the characteristic diffraction peaks of the samples increase sharply (Fig. 3(a)), and the relative crystallinity of corresponding sample Z518-5.6-14 reaches about 92% of the sample Z518-5.6-48 (Fig. 3(b)).

As shown in Fig. 4, all of the samples yielded from the same gel precursor with different crystallization time exhibit the characteristic vibration bands of MFI topological structure. For example, the absorption bands near 453 , 553 and 790 cm^{-1} belong to the internal framework vibration, the double five-member ring vibration and the asymmetric stretching of the AlO_4 and SiO_4 tetrahedron of MFI topological structure, respectively. It was reported that the ratio of the absorption band strength at 553 cm^{-1} to that at 453 cm^{-1} could be used to assess the degree of crystallization of the samples^[22]. It can be inferred from Fig. 4(a) that

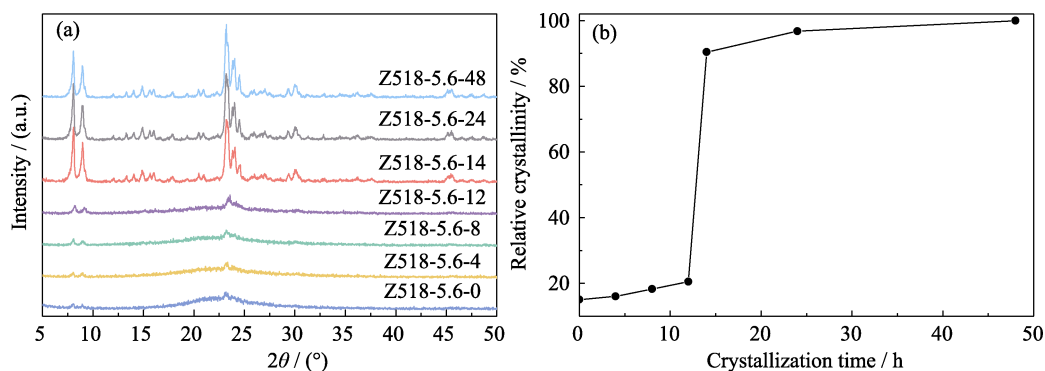


Fig. 3 XRD patterns of the samples with different crystallization time (a) and corresponding crystallization kinetic curve (b)

Relative crystallinity (RC) was calculated by comparing the peak areas of XRD patterns in the range of $2\theta=22.5^\circ\text{--}25^\circ$ of the samples with those of Z518-5.6-48

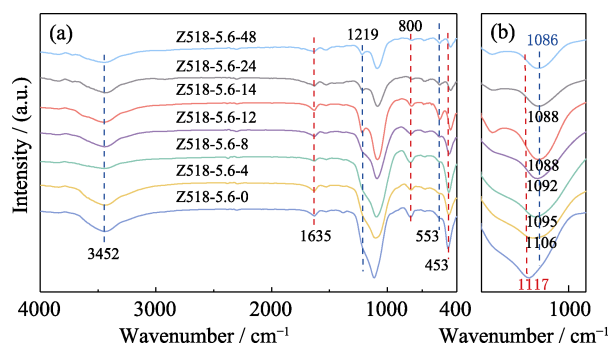


Fig. 4 FT-IR spectra of the samples prepared from the same gel precursor with different crystallization time

with the crystalline time increasing, the relative degree of crystallinity of the sample gradually increases. This is consistent with the results as shown in Fig. 3(b). In addition, the asymmetric stretching vibration of TO_4 ($\text{T}=\text{Si}$ or Al) at 1090 cm^{-1} is closely related to the Si/Al ratio of the zeolite framework, and the increased Si/Al ratio causes the vibration moving towards higher wavenumber. Fig. 4(b) suggests that the prolonged crystalline time causes the asymmetric stretching vibration of TO_4 shift to the low wavenumber, potentially indicating more Al species incorporation into the zeolite framework and reduced Si/Al ratios in the synthesized samples.

As shown in Fig. 5, with the crystallization time shorter than 8 h, the amorphous phase dominates in the samples. With the crystalline time at least 14 h, all crystals in the samples Z518-5.6-14, Z518-5.6-24 and Z518-5.6-48 have the similar polycrystalline aggregates, which are further composed of primary nanocrystals, and

no amorphous phase can be obviously observed. It can be seen from Fig. 5(i, j) that the crystals in the sample Z518-5.6-48 are exactly polycrystalline aggregates consisting of the rod-like nanocrystals with a diameter less than 100 nm. TEM image of sample Z518-5.6-48 also shows that some of the crystals have a core-shell structure: a monocrystal core warped by a polycrystalline shell, which makes the as-synthesized crystals seem more like a polycrystalline aggregate.

Fig. 6 is the N_2 adsorption-desorption isotherms and corresponding BJH pore size distribution curves. It can be seen from Fig. 6(a) that the N_2 adsorption isotherm curves exhibit a steep increase at a relative pressure $p/p_0 < 0.02$ and a hysteresis loop at a relative pressure p/p_0 in the range of 0.45–0.80, indicating the co-existence of intrinsic micropores and meso- or/and macropores in the samples. The hysteresis loops at a relative pressure $p/p_0 = 0.45\text{--}0.80$ can be attributed to the capillary condensation^[17] in open mesopores or macropores obtained by filling the interparticles spaces of primary MFI zeolite in the aggregates. Moreover, hysteresis loops at $p/p_0 > 0.80$ in the nitrogen isotherms are pronounced in samples, especially Z518-5.6-4 crystallized for shorter duration, likely due to macropores in the worm-like amorphous phase as shown in Fig. 5(b). The BJH pore structure distributions calculated from the adsorption branch of the isotherms are shown in Fig. 6(b). Samples Z518-5.6-14, Z518-5.6-24 and Z518-5.6-48 have an obvious mesopore distribution centered at about 15 nm, attributing to the intercrystalline mesopores between the primary MFI crystals in the aggregates^[6-8,11]. Larger pore distribution, centered

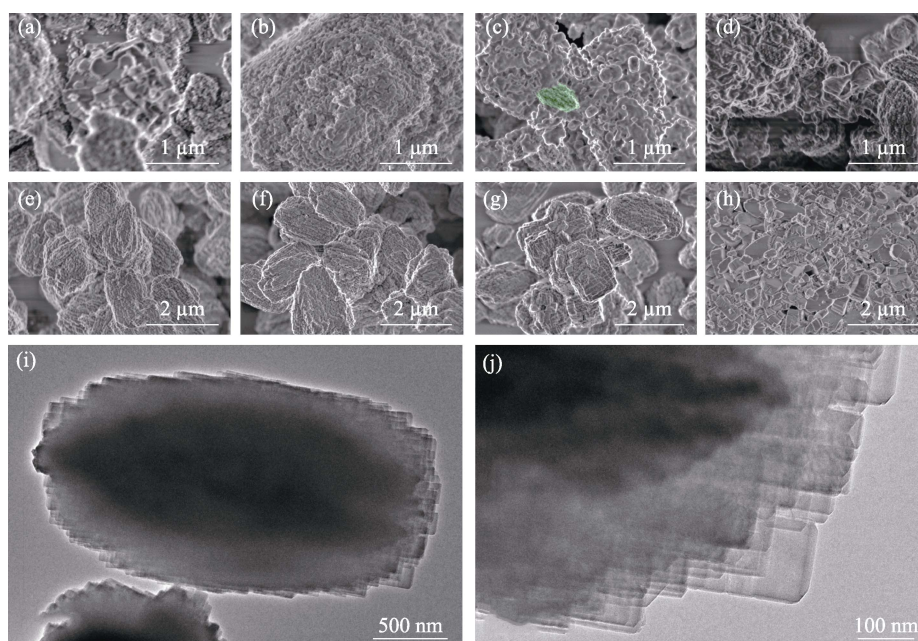


Fig. 5 SEM and TEM images of the as-synthesized samples with different crystallization time
SEM images of (a) Z518-5.6-0, (b) Z518-5.6-4, (c) Z518-5.6-8, (d) Z518-5.6-12, (e) Z518-5.6-14, (f) Z518-5.6-24, (g) Z518-5.6-48 and (h) NK-18; (i, j) TEM images of Z518-5.6-48

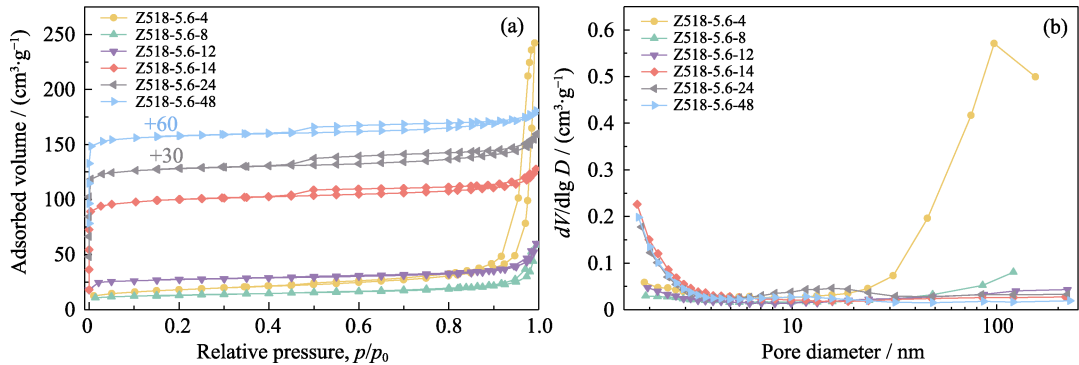


Fig. 6 N₂ adsorption-desorption isotherms (a) and corresponding BJH pore size distribution curves (b) of the samples prepared from the same gel precursor treated with different crystallization time

around 100 nm in samples Z518-5.6-4 and Z518-5.6-8, can be ascribed to the macropores in the worm-like amorphous phase (Fig. 5(b, c)). As shown in Table 1, with the prolonged hydrothermal treatment time, the microporous properties such as microporous areas (S_{mic}) and microporous volume (V_{mic}) display a continuously increased trend, suggesting a progressively increased relative crystallinity, which is in agreement with the

results as shown in Fig. 3(b).

2.3 Effect of crystallization temperature

Effect of crystallization temperature on the sample was also investigated. As shown in Fig. 7(f), crystallization temperature plays an important role in the formation of the ZSM-5 zeolite. When the crystallization temperature is not higher than 120 °C, the obtained samples are mainly amorphous (Fig. 7(a, b, f)). When the crystallization

Table 1 Textural properties of the as-synthesized samples with different crystallization time

Sample	$S_{\text{BET}}/(\text{cm}^2 \cdot \text{g}^{-1})$	$S_{\text{mic}}/(\text{cm}^2 \cdot \text{g}^{-1})$	$S_{\text{ext}}/(\text{cm}^2 \cdot \text{g}^{-1})$	$V_{\text{total}}/(\text{cm}^3 \cdot \text{g}^{-1})$	$V_{\text{mic}}/(\text{cm}^3 \cdot \text{g}^{-1})$	$V_{\text{ext}}/(\text{cm}^3 \cdot \text{g}^{-1})$	*RC/%
Z518-5.6-4	66	13	51	0.375	0.002	0.373	16.0
Z518-5.6-8	48	26	22	0.089	0.009	0.080	18.2
Z518-5.6-12	105	84	21	0.093	0.031	0.062	20.5
Z518-5.6-14	396	355	41	0.198	0.134	0.064	90.4
Z518-5.6-24	390	351	40	0.200	0.131	0.069	96.7
Z518-5.6-48	392	351	41	0.213	0.132	0.081	100

* Relative crystallinity (RC) is the crystallinity of the samples relative to that of the reference Z518-5.6-48, calculated by comparing the peak areas of XRD diffraction within $2\theta=22.5^\circ\text{--}25^\circ$ of the samples with those of sample Z518-5.6-48

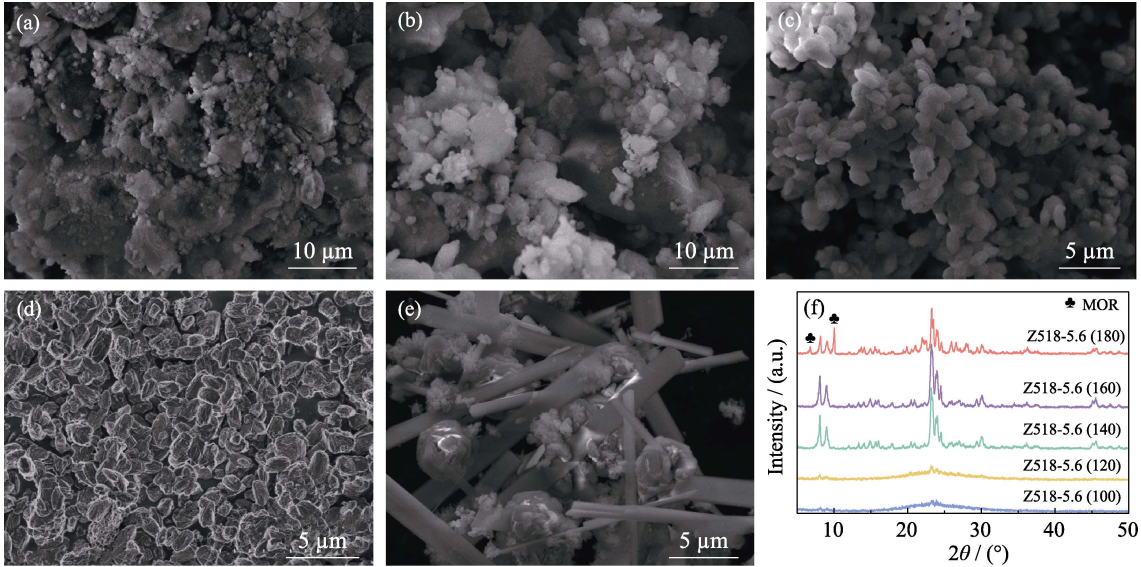


Fig. 7 SEM images and corresponding XRD patterns of the samples synthesized at different crystallization temperatures SEM images of (a) Z518-5.6(100), (b) Z518-5.6(120), (c) Z518-5.6(140), (d) Z518-5.6(160) and (e) Z518-5.6(180); (f) Corresponding XRD patterns of the samples synthesized at different crystallization temperatures All samples were obtained from the same gel precursor as the one yielded the sample Z518-5.6

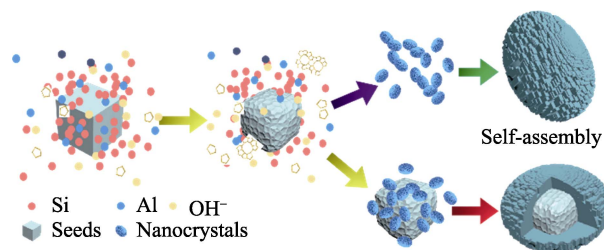
temperature is 140 and 160 °C, pure ZSM-5 zeolite is formed, and the relatively low temperature give the sample Z518-5.6(140) with a mono-crystal of approximately 500–1000 nm (Fig. 7(c)), and the elevated crystallization temperature offers the sample Z518-5.6(160) with a polycrystalline aggregate morphology (Fig. 7(d)). When the crystallization temperature arrives at 180 °C, the as-prepared sample is a mixed crystals composed of MOR and MFI topological structures (Fig. 7(e, f)). The higher temperature may accelerate dissolution of seed crystals, and then alters the Si/Al ratio of the gel precursor, which deviates from the gel component required for the formation of the targeted ZSM-5 zeolite.

2.4 Formation process of the polycrystalline aggregates

The formation process of the polycrystalline aggregates can be summarized as shown in Scheme 1. Despite having a low framework Si/Al ratio, the commercial ZSM-5 (NK-18) maintains relative stability as a crystal seed during the preparation of gel precursor^[19–20]. While, in the subsequent hydrothermal synthesis process, it is inevitable that the ZSM-5 crystal seeds are partially dissolved by the alkaline gel precursor. The dissolved seeds will release abundant primary/secondary structural units, which contributes to stimulating an explosive nucleation and results in the formation of a large number of nanocrystals^[23]. During the hydrothermal crystallization, zeolite seeds along with the primary/secondary structural units resulted from partially dissolved seeds play the similar role to OSDA for directing zeolite crystallization from the amorphous gel precursors. Due to the high surface energy, the nanocrystals caused by the explosive nucleation during a short time are extremely unstable. In order to decrease the surface energy, the nanocrystals interact and self-assemble into polycrystalline aggregates^[6–7,17], or they adsorb on the external surface of the reserved seed crystals, forming the polycrystalline aggregates with the reserved seed crystals as cores and rod-like nanocrystals as shell^[24].

2.5 Effect of Si/Al ratio of seeds

In order to investigate effect of Si/Al ratio of the seed on the synthesis of ZSM-5, seeds such as NK-18, NK-27,



Scheme 1 Formation process of the polycrystalline ZSM-5 aggregates induced by seeds

NK-200 with different Si/Al ratios were used to prepare ZSM-5 in the organic-templates-free system. It can be inferred from Fig. S4(a) that Si/Al ratio of the seeds has little effect on the synthesis of pure phase ZSM-5 zeolite. Samples Z518-5.6-48, Z527-5.6-48 and Z5200-5.6-48 exhibit similar characteristic diffraction peaks, indicative of MFI topological structure with a slightly weakened peak intensity corresponding to the increased Si/Al ratios of the used seeds (Fig. S4(a)). It can be seen from Fig. S4(b) that the samples induced by the different seeds have the similar N₂ adsorption-desorption isotherm, and the microporous properties of the as-synthesized samples display an expressively decreased trend with enhanced Si/Al ratios of the seeds (Table 2). The above result suggests that low Si/Al ratio seeds may facilitate and accelerate zeolite crystallization. Fig. S5 demonstrates that the samples Z527-5.6-48 and Z5200-5.6-48, induced by the seeds of NK-27 and NK-200 respectively, exhibit similar polycrystalline aggregate morphology to the Z518-5.6-48, rather different from their respective seeding crystals (Fig. S1), with no amorphous phase presenting in the samples. EDS analyses are displayed in Fig. S6. Combining with the results in Table 2, the different seeds have a little effect on the Si/Al ratio of the synthesized ZSM-5 samples, which have the similar Si/Al ratio of about 11.3–11.6, significantly lower than those of the used seeds. As shown in Fig. S7, the samples Z518-5.6-48, Z527-5.6-48 and Z5200-5.6-48 display similar NH₃-TPD curves. Table 2 reveals that the samples have the comparable acid density, except Z518-5.6-48 which was produced from the gel precursors with low Si/Al ratio seeds and possesses strong acid sites than the samples Z518-5.6-48 and Z527-5.6-48 induced by seeds with relatively high Si/Al ratios.

2.6 Catalytic test in methanol dehydration

Methanol to hydrocarbon (MTH) is chosen as a prob reaction and evaluated in a fixed bed microreactor, and the results are shown in Fig. 8, 9 and Fig. S8. A commercial purely microporous ZSM-5 zeolite with a similar Si/Al ratio comparable to the synthesized hierarchical ZSM-5 zeolite, served as a reference catalyst. Its porous structure, acidity and morphology are shown in Table 2 and Fig. S9. Fig. 8 illustrates the substantial variation in the catalytic lifetime. At the beginning of the reaction, all catalysts achieve a 100% conversion rate of methanol, indicating that the acidity in each is sufficient for the complete conversion of methanol. The stability of the catalysts follow an order as following: ZSM-5r<Z518-5.6-48≈Z527-5.6-48<Z5200-5.6-48. Generally, the catalytic life is closely related to the acid property and pore structure of zeolite catalysts^[25]. Table 2 reveals

Table 2 Physical and chemical properties of the samples yielded from the similar gel precursor induced by a crystal seed with different Si/Al ratios

Sample	$S_{\text{BET}}/(\text{cm}^2\cdot\text{g}^{-1})$	$S_{\text{mic}}/(\text{cm}^2\cdot\text{g}^{-1})$	$V_{\text{total}}/(\text{cm}^3\cdot\text{g}^{-1})$	$V_{\text{mic}}/(\text{cm}^3\cdot\text{g}^{-1})$	$V_{\text{meso}}/(\text{cm}^3\cdot\text{g}^{-1})$	*RC/%	**Si/Al	Acid density/ $(\mu\text{mol}\cdot\text{g}^{-1})$			
								Weak	Medium	Strong	Total
Z518-5.6-48	392	352	0.19	0.13	0.06	100	11.3	218	65	293	576
Z527-5.6-48	376	333	0.19	0.12	0.07	99	11.3	212	83	224	519
Z5200-5.6-48	356	314	0.19	0.12	0.07	99	11.6	205	79	221	505
ZSM-5r	377	343	0.14	0.14	0.03	100	17.4	168	53	236	457

* Relative crystallinity (RC) is the crystallinity of the samples relative to that of the reference Z518-5.6-48, calculated by comparing the peak areas of XRD diffraction within $2\theta = 22.5^\circ\text{--}25^\circ$ of the samples with those of sample Z518-5.6-48

** Determined by EDS analysis

that Z518-5.6-48 possesses the highest acid density among the synthesized polycrystalline aggregates catalysts, which is likely the primary cause of its relatively shorter catalytic life. The decrease in acid density helps to inhibit secondary reactions of olefins formed during the MTO reaction process, such as oligomerization and hydrogen transfer reactions. Acid site with a mild acid strength (Table 2) is propitious to decrease coke deposition^[26]. As compared with the reference ZSM-5r catalyst, the extended catalytic life of the polycrystalline aggregate catalysts can also be ascribed to the introduced hierarchical pore resulted from the loose aggregation of nanosized primary crystals. The introduction of mesoporous system can significantly shorten the length of micropore channels, reduce the secondary reaction of the formed olefins, promote the rapid escape of products, and therefore bate the formation of carbon deposition. Therefore, the varying stability of different

catalysts (Fig. 8) may reflect the synergistic effect combining with different acids and pore structures of catalysts.

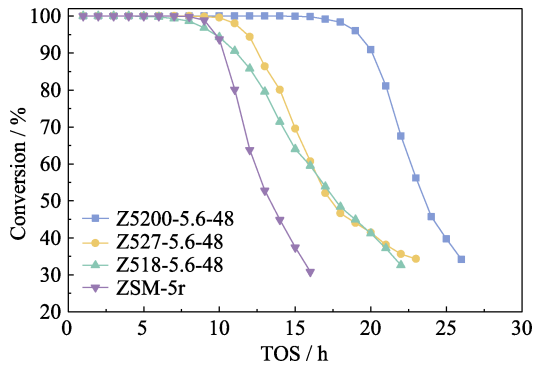


Fig. 8 MTH reaction performance of the samples using crystal seeds with different Si/Al ratios

Reaction conditions: $T=430^\circ\text{C}$, $p_{\text{total}}=1\text{ atm}$, $\text{WHSV}=2.4\text{ h}^{-1}$, catalysts weight=200 mg

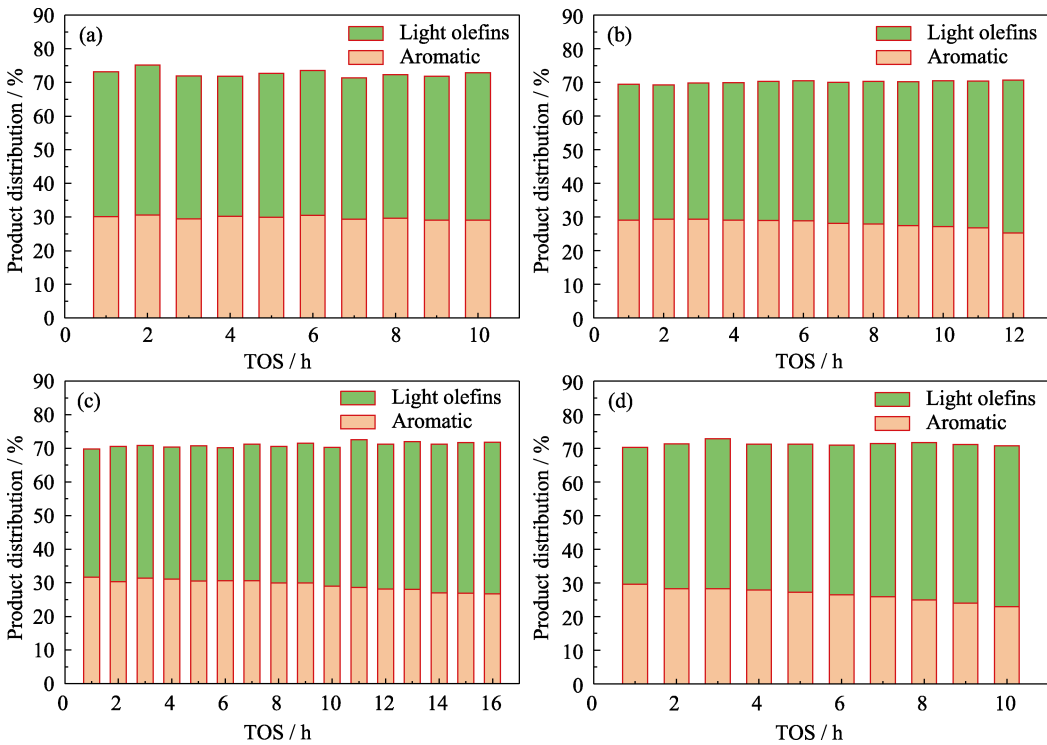


Fig. 9 Selectivity of light olefins over the catalysts with time on stream

(a) Z518-5.6-48; (b) Z527-5.6-48; (c) Z5200-5.6-48; (d) ZSM-5r

Reaction conditions: $T=430^\circ\text{C}$, $p_{\text{total}}=1\text{ atm}$, $\text{WHSV}=2.4\text{ h}^{-1}$, catalysts weight=200 mg

It can be inferred from Fig. 9 that as compared with the purely microporous ZSM-5r, the hierarchical Z518-5.6-48, Z527-5.6-48 and Z5200-5.6-48 catalysts have a slightly increased selectivity towards aromatic hydrocarbon. For example, the average selectivity for the total aromatic hydrocarbon over time is 29.8%, 28.1% and 29.4% on Z518-5.6-48, Z527-5.6-48 and Z5200-5.6-48 catalysts, respectively, all exceeding the 26.5% of the reference ZSM-5r. However, higher light olefins including ethylene, propylene and butene were found on the reference ZSM-5r catalysts. The average selectivity of the light olefins on ZSM-5r is 44.8%, which is obviously higher than the 42.3%, 42.0% and 41.7% observed on Z518-5.6-48, Z527-5.6-48 and Z5200-5.6-48 catalysts, respectively. Higher selectivity of light olefins on the reference catalysts can be attributed to its low acid density resulted from the high Si/Al ratio (Table 2). Obviously, reducing acid density of catalyst can effectively suppress oligomerization and hydrogen transfer reaction, thereby improving the selectivity of light olefin^[27]. Introducing hierarchical pores also aids in the rapid escape of olefin intermediate products, avoiding the secondary olefin reaction. However, the increased acid density in the Z518-5.6-48, Z527-5.6-48 and Z5200-5.6-48 catalysts may elevate the secondary reactions of the olefin intermediate, potentially undermining the positive effect of the introduced hierarchical pore system on the light olefins selectivity.

3 Conclusions

Polycrystalline ZSM-5 aggregates were synthesized by a Sol-Gel system without any OSDA. The seeds played a crucial role in directing zeolite crystallization from the amorphous precursor and accelerating the nucleation and crystallization. Adding approximately 5.6% calcined seed to the gel precursor is sufficient to promote the formation of a pure and high crystallization ZSM-5 zeolite, whereas an excessively low amount of seed leads to an amorphous phase or a sample represented by ZSM-5 mingled with a little MOR phase. The Si/Al ratio of the seeds has a slight effect on synthesizing pure ZSM-5 zeolite, whereas low Si/Al ratio seed facilitate the formation and crystallization of ZSM-5 zeolite with a relatively higher degree of crystallinity and more abundant acid sites. In dehydration of methanol, the hierarchical Z5200-5.6-48 exhibits a catalytic life of 16 h, rather longer than the 8 h of the reference ZSM-5r because of the introduced hierarchical pore structure derived from the loosely aggregated ZSM-5 primary nanoparticles. Due to the high acid density, the prepared

hierarchical pore catalysts exhibit higher aromatics selectivity (28.1%–29.8%) than the ZSM-5r catalyst (26.5%), but lower light olefin selectivity (41.7%–42.3%) compared to the reference catalyst (44.8%).

Supporting Materials

Supporting materials related to this article can be found at <https://doi.org/10.15541/jim20240016>.

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晶种诱导合成 ZSM-5 多晶聚集体及其在 甲醇制碳氢化合物中的催化性能

王旭昌¹, 焦楚钰¹, 季卓¹, 焦其瑞¹, 秦波²,
杜艳泽², 郑家军¹, 李瑞丰¹

(1. 太原理工大学 能源化工与催化研究中心, 太原 030024; 2. 中国石油化工集团 大连石油化工研究院, 大连 116045)

摘要: 合成 ZSM-5 沸石通常以小分子多元胺或季铵盐作为有机结构导向剂(OSDA)。无 OSDA 的水热合成体系避免了使用有机模板和随后的煅烧步骤, 这不仅可以降低合成成本, 而且避免因有机模板燃烧造成环境污染, 是一种环境友善的合成方法。然而, 已有的研究显示, 某些有机物如乙醇, 会或多或少地参与所谓的无模板合成系统。为确保合成体系中不带有有机模板, 本研究以煅烧的商用 ZSM-5 沸石为晶种, 铝酸钠为铝源, 硅溶胶为硅源, 在无 OSDA 的体系中成功制备了一种由棒状纳米晶组成的多晶 ZSM-5 聚集体。详细研究了 ZSM-5 晶种的硅/铝比、加入量和晶化条件(如晶化温度以及晶化时间)等对 ZSM-5 沸石合成的影响。研究结果表明: 以含质量分数 5.6% MFI 拓扑结构晶种的凝胶前驱体为原料, 经水热处理 48 h, 可制得由尺寸小于 100 nm 的初级纳米晶粒组成的高结晶度 ZSM-5 多晶聚集体; ZSM-5 晶种的硅/铝比不影响样品的拓扑结构、孔结构, 但低硅/铝比的晶种更有利于目标沸石快速结晶, 并更有利于获得高酸量尤其是较强酸量的 ZSM-5。采用甲醇脱水考察合成的多晶 ZSM-5 的催化性能, 并与商用参比 ZSM-5r 催化剂进行比较。结果表明, 与参比催化剂相比, 合成的样品因疏松聚集的纳米初级晶粒堆积形成多级孔而具有较长的催化寿命(16 h vs 8 h), 且合成的多晶聚集体催化剂具有较高的芳烃选择性(28.1%~29.8% vs 26.5%)。

关键词: ZSM-5; 多晶聚集体; 晶种; 结构导向剂

中图分类号: TQ174 文献标志码: A 文章编号: 1000-324X(2024)08-0945-10

Supporting materials:

Polycrystalline ZSM-5 Aggregates Induced by Seed and Catalytic Performance in Methanol to Hydrocarbon

WANG Xuchang¹, JIAO Chuyu¹, JI Zhuo¹, JIAO Qirui¹, QIN Bo², DU Yanze², ZHENG Jiajun¹, LI Ruifeng¹

(1. Key Laboratory of Coal Science and Technology MOE, Research Centre of Energy Chemical & Catalytic Technology, Taiyuan University of Technology, Taiyuan 030024, China; 2. SINOPEC Dalian Research Institute of Petroleum and Petrochemicals Co., Ltd. SINOPEC, Dalian 116045, China)

Table S1 Pore structure parameter and relative crystallinity of the as-synthesized samples

Sample	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	$S_{\text{mic}}/(\text{m}^2 \cdot \text{g}^{-1})$	$S_{\text{ext}}/(\text{m}^2 \cdot \text{g}^{-1})$	$V_{\text{total}}/(\text{cm}^3 \cdot \text{g}^{-1})$	$V_{\text{mic}}/(\text{cm}^3 \cdot \text{g}^{-1})$	RC/%
Z518-5.6-48	392	351	41	0.213	0.132	100
Z518-11.2-48	388	346	42	0.199	0.128	99

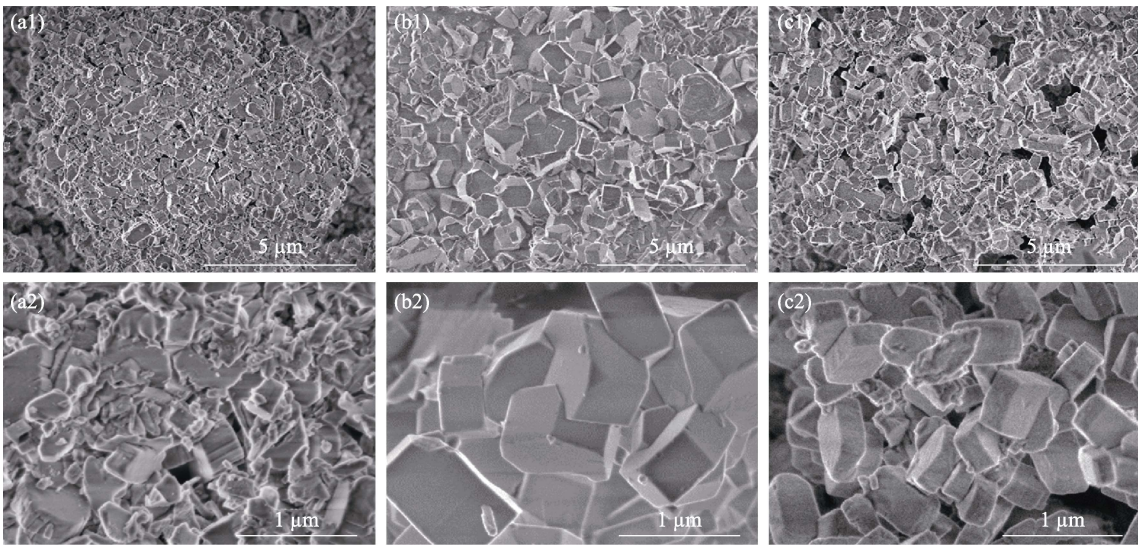


Fig. S1 SEM images of the crystal seeds (a1, a2) NK-18; (b1, b2) NK-27; (c1, c2) NK-200

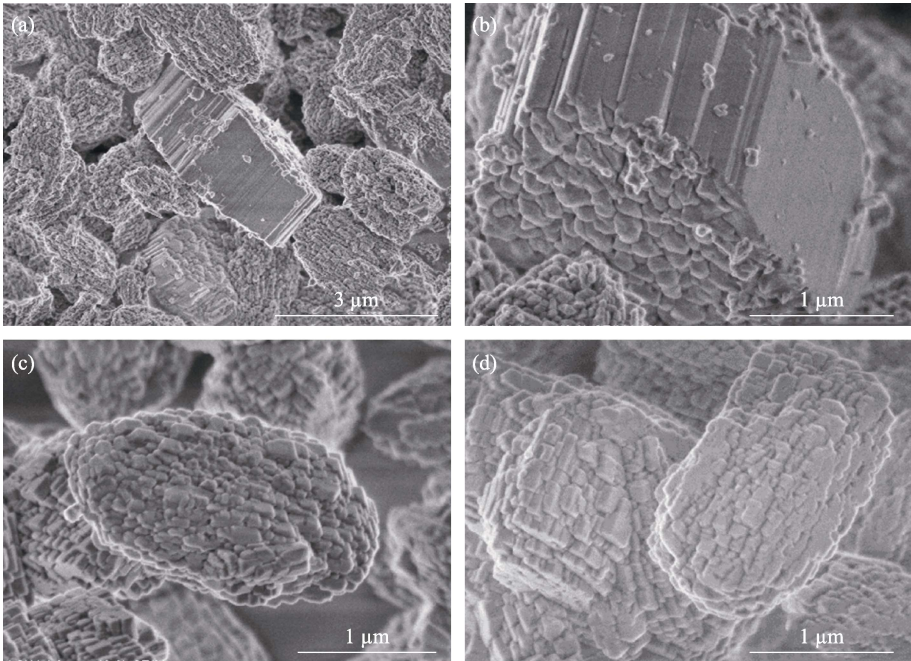


Fig. S2 SEM images of (a, b) Z518-2.8-48, (c) Z518-5.6-48, and (d) Z518-11.2-48

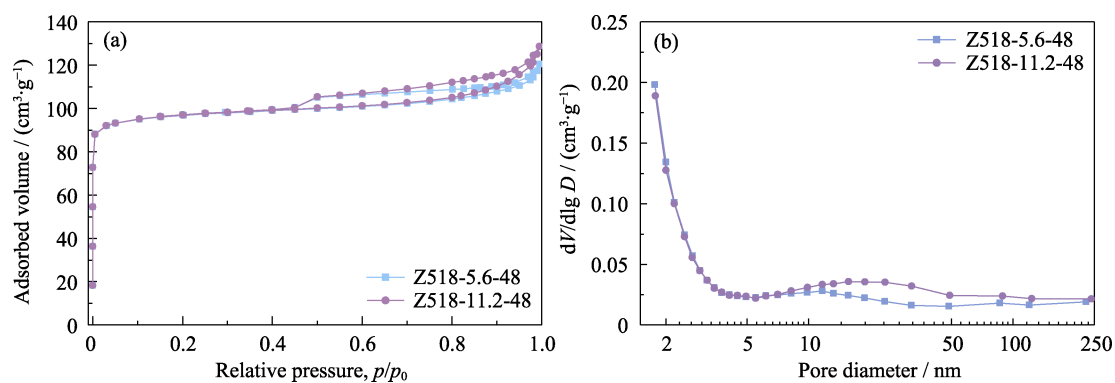


Fig. S3 N_2 adsorption-desorption isotherms (a) and corresponding BJH pore size distribution curves (b) of the as-synthesized samples

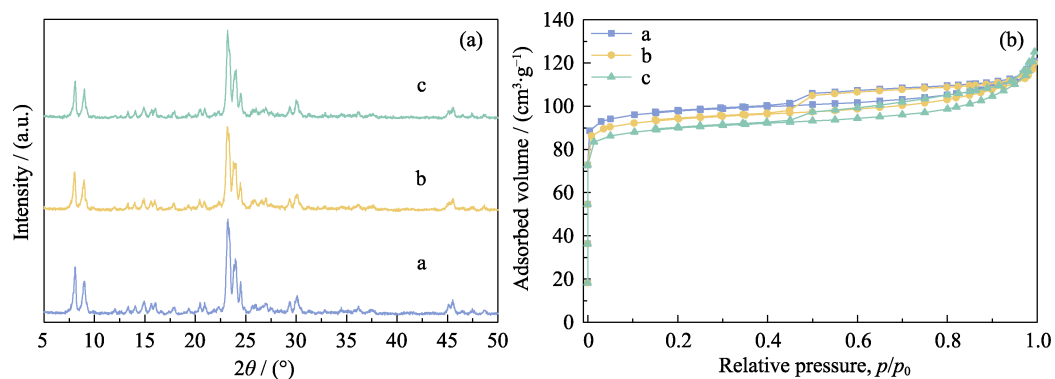


Fig. S4 XRD patterns (a) and N_2 adsorption-desorption isotherms (b) of the samples prepared in an OSDA-free system induced by seeds with different Si/Al ratios
(a) Z518-5.6-48; (b) Z527-5.6-48; (c) Z5200-5.6-48

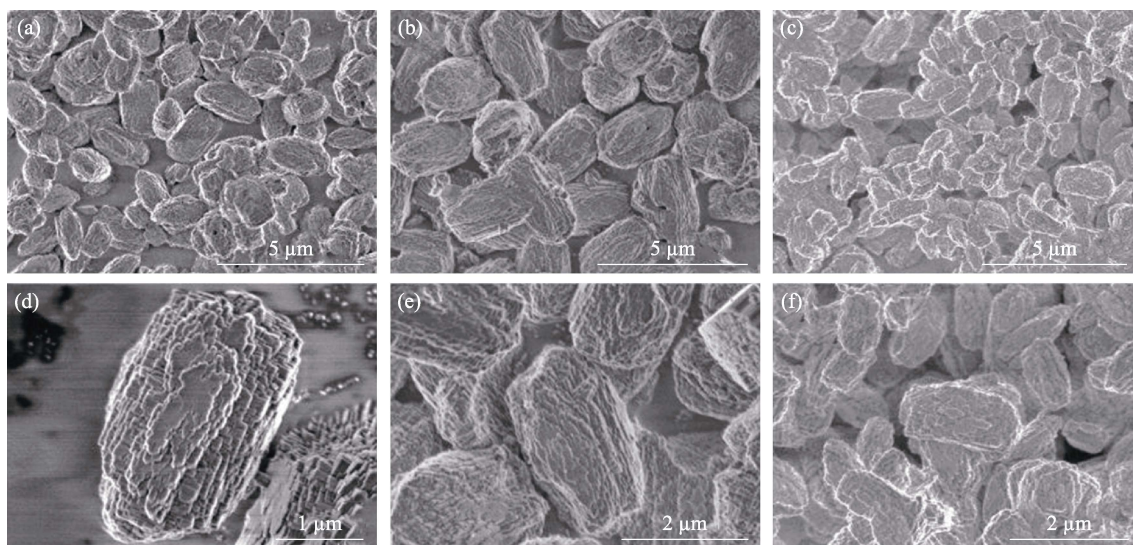


Fig. S5 SEM images of the samples yielded from a similar gel precursor induced by seeds with different Si/Al ratios
(a, d) Z518-5.6-48; (b, e) Z527-5.6-48; (c, f) Z5200-5.6-48

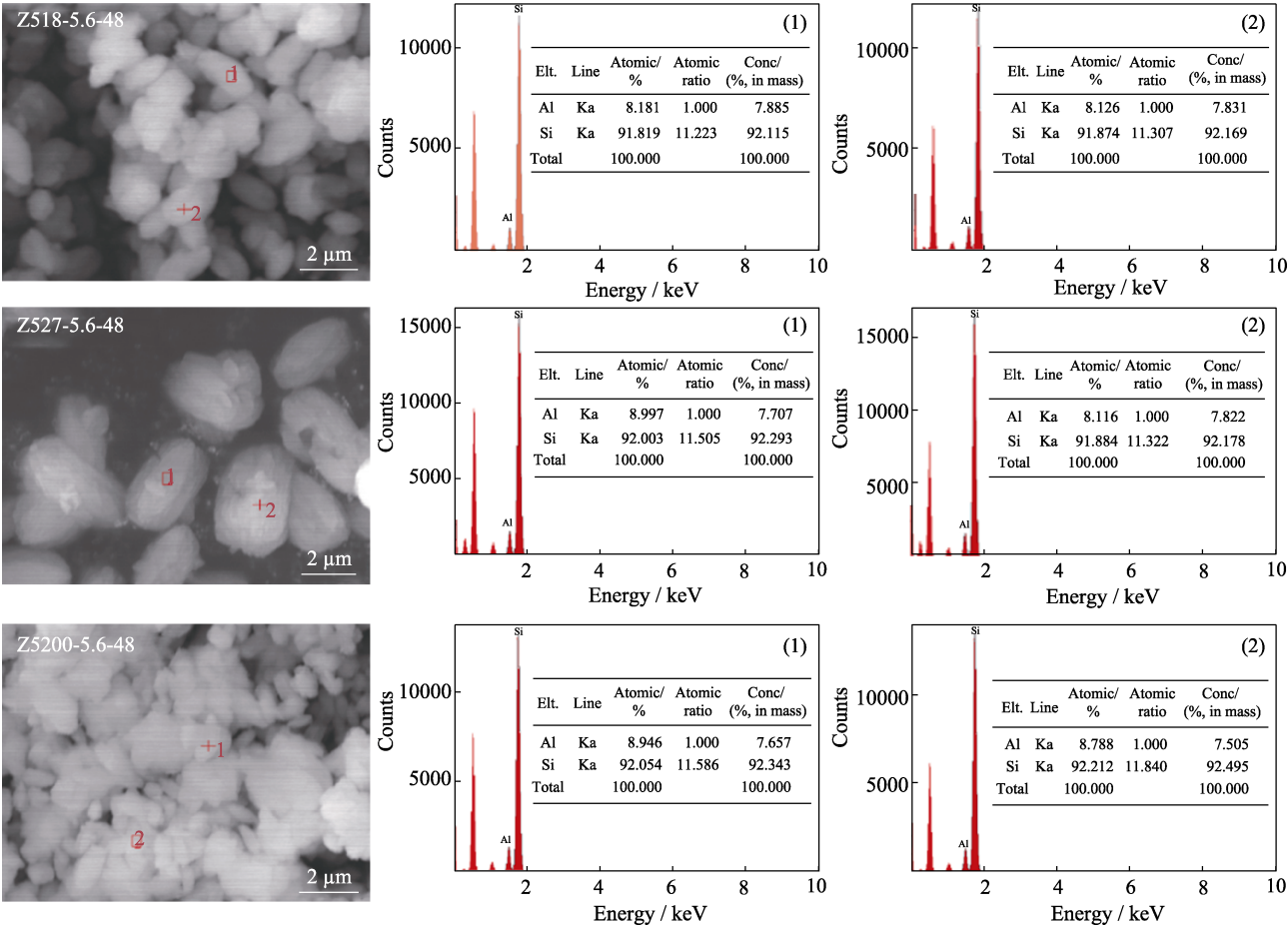


Fig. S6 EDS analyses of the samples induced by the seeds with different Si/Al ratios

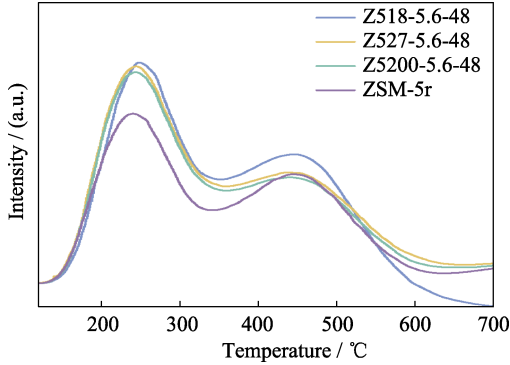


Fig. S7 NH_3 -TPD profiles of samples Z518-5.6-48, Z527-5.6-48, and Z5200-5.6-48 induced by seeds with different Si/Al ratios and the reference ZSM-5r

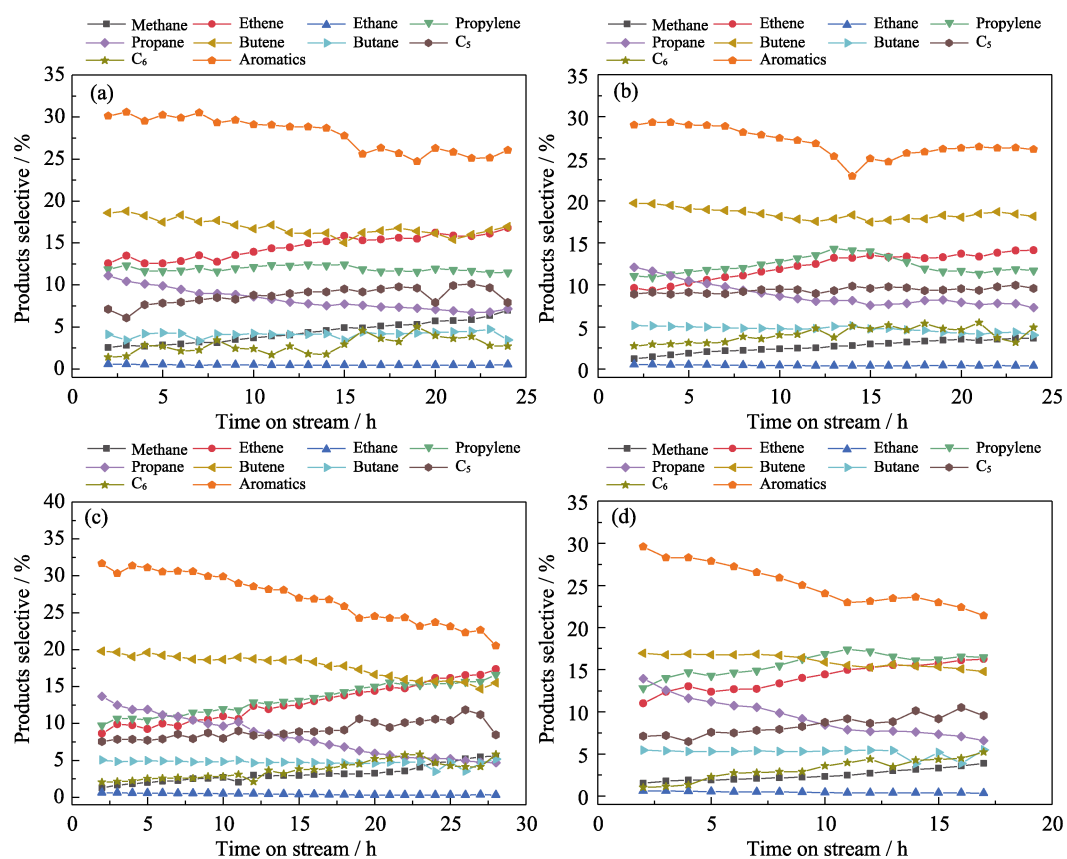


Fig. S8 Selectivity of final products over ZSM-5-x catalysts with time on stream
(a) Z518-5.6-48; (b) Z527-5.6-48; (c) Z5200-5.6-48; (d) ZSM-5r. Reaction conditions: $T=430\text{ }^{\circ}\text{C}$,
 $p_{\text{total}}=1\text{ atm}$, $\text{WHSV}=2.4\text{ h}^{-1}$, catalysts weight=200 mg

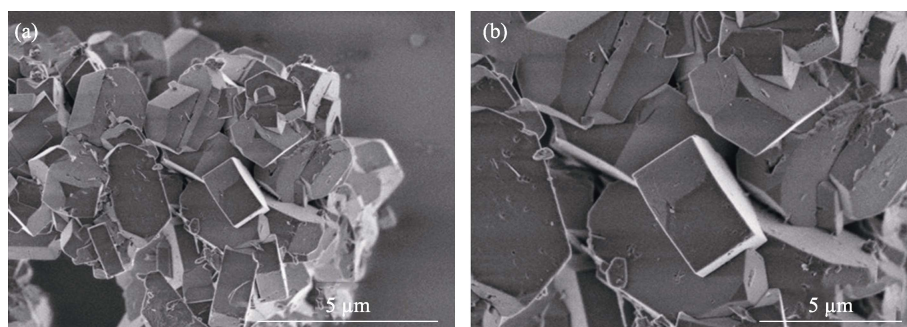


Fig. S9 SEM images of the commercial reference ZSM-5r