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Three-stage crystallization: an effective way to reduce the crystal size and improves the catalytic performance of SAPO-34 for MTO

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SAPO-34 crystals were prepared via a high-low-high temperature crystallization procedure with triethylamine (TEA) as template. Three-stage crystalization benefits the nucleation while inhibits the growth of grains, which favors the formation of small size crystals. The lifetime of three-stage samples were prolonged in the MTO process.

Due to its unique CHA structure and moderate acidity, SAPO-34 zeolite exhibits good performance in catalytic conversion of methanol to light olefins (MTO). SAPO-34 based catalyst has been successfully applied in the commercialized MTO unit since 2010.^[1] However, the conversion of methanol and formation of olefins is accompanied with the rapid formation of confined aromatics in SAPO-34 cages. These aromatics, especially the large scale phenanthrene and pyrene, reduce the diffusion of methanol and olefins and even fully block the channels which leads the deactivation of the catalyst. ^[2] Catalyst has to be regenerated continuously in circulating fluidized bed to maintain its reactivity. The continuous burning of coke increases the costs and reduces the economic benefits of MTO process. ^[1, 3]

Analysis reveals that the coke compounds, especially phenanthrene and pyrene, tend to locate at the near-surface region of SAPO-34 crystal. ^[2c, 2d, 4] The near-core region of SAPO-34 crystal, though still active for methanol conversion, is inaccessible for reactant. Preparation of small size or hierarchical SAPO-34 has been proved to be effective way to increase the accessibility of near-core cages and to prolong the catalytic lifetime. Many methods, such as optimizing the raw material, microwave assisted,^[5] ultrasonic assisted,^[6] seed assisted,^[7] the using of crystal growth inhibitor,^[8] and two-stage crystallization,^[9] have been proposed to reduce the crystal size of SAPO-34. These methods are effective on the synthesis of small or nano-scale SAPO-34. However, these methods lead the crystallization apparatus more complex, extend the length of synthetic route or increase the use of additional reagent. Moreover, most of these methods employ the costly tetraethylammonium hydroxide (TEAOH) as template agent. The development of simple, convenient and low cost method for small size SAPO-34 synthesis is still of great significance.

Triethylamine and morpholine (MOR) are much cheaper than TEAOH. However, gels with them as template have higher crystal growth speed than ones with TEAOH do, which leads to the formation of large scale SAPO-34 crystal.^[10] In order to overcome the rapid crystal growth and increase the amount of initial crystalline grain, we lower the crystallization temperature

Provincial Key Laboratory of Oil & Gas Chemical Technology, College of Chemistry & Chemical Engineering Northeast Petroleum University Daqing 163318, Heilongjiang, P.R. China E-mail: luomingjian@nepu.edu.cn after short high temperature duration, then raise the crystallization temperature again for the further nucleation and crystal growth. This simple high-low-high temperature crystallization procedure is proved to be effectively in reducing the size of SAPO-34 crystals. Contrast to samples obtained from conventional one-stage or two-stage methods, three-stage SAPO-34s show longer catalytic lifetime in MTO process.

A series of SAPO-34 samples were prepared with gel of a same composition $1Al_2O_3$: $1.1 P_2O5$: 0.6 SiO2: 4.0 TEA: 60 H2O. The one-stage sample was crystallized at 200 °C for 24 h and labelled as S-200. The two-stage one was first crystallized at 100 °C for 2 h, then 200 °C for 24 h. This sample was labelled as S-100/200. Three-stage samples were first crystallized at 200 °C for 0.5, 1, or 2 h, then 40, 70, 100 or 130 °C for 2 h, and at last 200 °C for 24 h. Three-stage samples were labelled as S-200-x/y/200, where x indicated the first stage time and y indicated the second stage temperature.



Figure 1. XRD patterns of samples. Symbol * indicates the AFI type SAPO-5.

Powder XRD patterns of samples and index lines for SAPO-34 are showed in Figure 1. Typical diffraction peaks of CHA structure SAPO-34 at 9.6° , 13.2° , 16.2° , 20.8° , 26.0° and 31.1° were observed on all samples. Very weak peaks for AFI-type SAPO-5 at 7.7°, 19.9° , and 22.6° were observed on the sample S-200-2/100/200. Crystallinities of samples were listed in Table

1. Except for the low value of S-200-1/40/200, crystallinities of other samples were similar.

The yields, prosities, sizes and framwork (P(Si)/Al of samples are listed in Table 1. All samples had similar yields except S-200. All samples had type I isotherms typically for pure microporous material (Figure S1). Although there were no remarkable differences, the specific surface areas and micro pore volumes of three-stage samples were a little higher than those of S-100/200 and S-200 (Table 1). EDX results (Table 1) indicated

Table 1. Yield, porosity, crystallinity, size and framework P(Si)/Al of samples

that the one-stage S-200 had the lowest P/AI and the highest Si/AI, while the two-stage S-100/200 was the opposite. Values of three-stage samples were similar and between those of S-200 and S-100/200. High initial temperature (one- and three-stage samples), especially the persistent high crystallization temperature (S-200), favored the substitution of Si for P and AI in the framework. Conversely, low initial temperature (two-stage, S-100/200) inhibited the reactivity of Si.

Complee	Yield ^a	S _{BET} ^D	S _{micro} ^c	S _{ext} ^a	V _{micro} ^c	Crystallinity	Average size ^e	D/AL f	C:/AL	
Samples	%	m²/g	m²/g	m²/g	m³/g	%	μm	P/AI	5I/AI	(SI+P)/AI
S-200	45	495	484	11	0.23	89	10.7	0.807	0.284	1.091
S-100/200	65	512	500	12	0.24	94	4.6	0.840	0.229	1.069
S-200-0.5/100/200	69	581	571	10	0.27	93	3.5	0.827	0.258	1.085
S-200-1/100/200	66	525	508	17	0.24	90	3.1	0.828	0.251	1.079
S-200-2/100/200	67	565	550	15	0.26	94	4.3	0.822	0.251	1.073
S-200-1/40/200	61	531	515	16	0.25	80	4.5	0.830	0.263	1.093
S-200-1/70/200	65	559	544	15	0.26	92	2.9	0.835	0.243	1.079
S-200-1/130/200	67	557	544	13	0.26	92	3.9	0.815	0.247	1.062

^a Product yield is calculated by the mass ratio of calcined solid product to SiO₂, Al₂O₃ and P₂O₅ in the synthesis gel; ^b S_{BET} (total surface area), calculated by BET equation with data 0.05<P/P₀<0.30; ^c S_{micro} (Micropore area) and V_{micro} (Micropore surface volume) calculated by *t*-plot method; ^d S_{ext} (external surface area) calculated by S_{BET} -S_{micro}; ^e number average size; and ^f Measured by EDX.



Figure 2. SEM image of samples. A: S-200; B: S-100/200; C: S-200-0.5/100/200; D: S-200-1/100/200; E: S-200-2/100/200; F: S-200-1/40/200; G: S-200-1/70/200; H: S-200-1/130/200.

SEM images of samples are showed in Figure 2 and S2. Crystal size distributions are showed in Figure S3. The crystal size of S-200 (Figure 2 A) distributed in 6~20 µm range with a average value 10.7 µm, which was much larger than other samples. The crystal size of S-100/200 (Figure 2 B) distributed in 2~9 µm, mainly 3~6 µm with a average value 4.6 μ m. Three-stage samples had small crystal sizes. Particles were mostly in 2~5 µm range. A relative short first stage (200 °C) time (Figure 2 C) favored the formation of small size crystal. Prolonging the first stage time to 2 h (Figure 2 E) led to dual-scale distribution: ones were in 8~12 μ m, which were similar to one-stage product; the others were about 2~3 µm, the same as other threestage samples. The temperature of second stage also affected crystal size. Low temperature sample was relative large (40 °C, Figure 2 F, average 4.5 μm), moderate temperatures favored small size products (70 °C, Figure 2 G, average 2.9 μm), and grain size increased again at a relative high temperature (100 and 130 °C, Figure 2 D and H, 3.1 and 3.9 µm, respectively).

All SAPO-34 samples show similar NH₃-TPD profiles (Figure 3). Two peaks at about 175 and 400 °C are corresponded to weak and strong acidic sites.^[7a, 11] Amount of acidic sites are summarized in Table S1. Except S-200-2/100/200, other three-stage samples had some more strong acidic sites than S-200 and S-100/200. Perhaps the first two hour at 200 °C is the decisive factor of the acidity of S-200-2/100/200. Though remarkable difference in silicon content (Table 1), no apparent correlation between Si content and amount or strength of acidic site was observed. Therefore, rather than the amount of Si, how Si cooperated with Al and P should be the main factor that affected the acidity of sample.

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Figure 3. NH₃-TPD profiles of samples.



Scheme 1. Mechanism of one-stage and three-stage crystallization procedure.

The crystallization of microporous aluminophosphates was supposed to compose of four general steps: ^[12] (1) the initial formation of a reactant gel, comprising (Me)AlO_{3/5}-O-PO₃ type nanometer-sized primary species, (2) the growth of such species into secondary larger macromolecularly disordered aggregates containing interdispersed template cations, (3) the onset of crystallization (nucleation), and (4) crystallite growth. Accordingly, a probable mechanism of three-stage crystallization of SAPO-34 is illustrated in scheme 1. Primary species and disordered aggregates participated in both nucleation and the growth of grain. The nucleation and the grain growth competed with each other. A persistent high temperature (one-stage) favored the growth of grain which led to large scale crystal. For example, the average crystal size of S-200 was about 10.7 μ m. And the S-200-2/100/200, which was first hold on 200 °C for two hours, had certain amount of big crystals. On the contrary, nucleation dominated the crystallization procedure if the temperature was lowered down after a short high duration. The increase in nucleus led to more small size crystal, as it was observed in all three stage samples. Additionally, EDX results indicated one-stage high temperature sample had the highest silicon content, the two-stage low-high temperature sample had the lowest silicon content, while the silicon contents of three-stage high-low-high temperature samples were between one- and two- stage ones. It is supposed that AI-O-Si participates in the formation of aggregates (nucleus) and the growth of crystal. High crystallization temperature promotes the formation AI-O-Si which favors the formation of large aggregates (nucleus) and the growth of crystal. Therefore, crystals obtained under high temperature condition (S-200) tended to big size and high Si content. Conversely, low temperature reduces the formation of Al-O-Si. Aggregates grow in a low speed but also less amount. As a result, crystals obtained under low-high temperature condition (S-100/200) tended to relative small size and high Si content. The high-low-high temperature process, however, favors the formation of massive Al-O-Si at high temperature, then temperature is low down to prevent the formation of large aggregates and favors the formation of massive small ones, at last these small aggregates are grow into SAPO-34 crystal at high temperature. Therefore, three-stage samples were small size with moderate Si contents. However, more evidences are needed for confirming and further revealing the role of silicon.



Figure 4. Conversion of methanol and selectivity of ethene + propene at 425 $^{\circ}$ C and 2 h⁻¹.

The catalytic performances of samples on methanol to olefin reaction are showed in Figure 4. All three stage samples, except the S-200-1/40/200, had longer life time and high ethene + propene selectivity than the one- and two-stage samples. Since samples were similar in crystalline phase (XRD), porosities (N₂ adsorption/ desorption) and acidity (NH₃-TPD), this improvement should

10.1002/ejic.201800393

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be mainly ascribed to the size-performance effect that the smaller particle size, the better catalytic performance. However, though the two-stage S-100/200 sample had much smaller size than that of one-stage S-200, it showed a shorter life time than the latter. This anti size-performance result might be caused by the low silicon content, or the difference in silicon cooperation manner in the frame work. The duration of the first high temperature stage and the temperature of the secondary stage also affected the performance of three-stage samples. The suitable first stage duration and secondary stage temperature were roughly one hour and 100 °C, respectively.

In summary, we have demonstrated a high-low-high temperature three-stage crystallization process for reducing the crystal size of SAPO-34. Lowering the crystallization temperature after short high temperature duration benefited the nucleation while inhibited the growth of grains, and consequently favored the formation of small size SAPO-34. Crystallization process also affected Si content in final product. The crystallization process had little effect on crystalline phase, porosities and acidity of samples. The lifetime of three-stage samples were prolonged in the MTO process, which was mainly ascribed to the decrease in crystal size.

Supporting information

process. Additional details experiments on N₂desorption/adsorption isotherms. SEM images, and amounts of acidic sites are given in the electronic supporting information.

Acknowledgements

We thank the financially supported from Heilongjiang Youth Science Foundation (QC2015013) and NEPU cultivate Science Foundation (2017PYZL-03). We also thank the support of Analysis and Test Center of Northeast Petroleum University for XRD and SEM analysis.

Keywords: three-stage crystallization; small size; SAPO-34; methanol to olefin; triethylamine

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10.1002/ejic.201800393