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# Synthesis of SAPO-20 Using Isopropylamine as a Template from a SAPO-34 Precursor

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**Abstract.** SAPO-20 molecular sieve with the SOD framework was successfully synthesized using SAPO-34 as the precursor and isopropylamine (IPA) as the template by phase- transformation route. The influence of post-treatment time (in IPA, $H_2O$, and SAPO-34 system) and NaOH concentration (in IPA, NaOH, $H_2O$, and SAPO-34 system) on the products was investigated. The results showed that sheet debris SAPO-34 building the hollow-inside cubic morphologies which was padding with irregular SAPO-34. It was received for the as-synthesized spherical aggregation SAPO-20 with hexagonal shape when the ratio of n($OH^-$)/n ($H_2O$) is 0.12 and the ratio of n(IPA)/n ($H_2O$) is 0.07 in the synthesis gel. This method not only develops a new route for the synthesis of SAPO-20 molecular sieve, but also provides a way of using waste SAPO-34 catalyst, which can be used as a new exploration model for energy saving, consumption reduction and comprehensive utilization in SAPO-34 catalyst process.

**Keyword.** SAPO-34, SAPO-20, morphology; hollow-inside cubic, phase-transformation route

## 1. Introduction

Sodalite, AlPO-20 and SAPO-20 are analogs of the sodalith structure (SOD), that is, they have stacking sequence of ABC of 6-ring, cubic, $Im^3m$, a = 8.870Å. The syntheses of the very small pore SAPO-20 with the pore sizes of 0.3nm and the pore volumes of 0.40cm$^3$/g were described in the 1980s [1-4].

There are many methods for the synthesis of SAPO-20, such as: hydrothermal crystallization method [1, 4-10], $F^-$ system hydrothermal synthesis [11, 12], dry-gel conversion method [13], and liquid-phase crystallization [14]. The silicon source for the synthesis of SAPO-20 molecular sieves is silica sol [1, 5, 7, 10-13], white carbon black [5, 6] and fumed silica [8, 9] while aluminum source is involved in aluminum isopropoxide [5], activate alumina [5, 13], pseudoboehmite [1, 5-7, 9, 10, 12], bayerite [4], aluminum hydroxide [8], and aluminium chloride [11].

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The interzeolite conversion method is an alternative synthesis strategy for the hydrothermal conversion of one zeolite into another [15-19]. To the best of our knowledge, this is the first reported on the transformation of CHA-type zeolite into SOD-type zeolite. It is well to know that SAPO-34 molecular sieve is a catalyst for the industrialized production of olefin from methanol. However, there are two major problems for SAPO-34 molecular sieve catalysts in the process of methanol conversion to olefins. One is that SAPO-34 is rapidly inactivated for carbon deposition because of its small pore size (8-ring, 0.43 nm). Although improving the anti-coking of the nanosized SAPO-34 or hierarchical pore structure SAPO-34 catalyst by changing the synthesis conditions, it still can not fundamentally solve the problem of deactivation. The other is that SAPO-34 catalyst is easy to be worn out which recycled in fluidized bed reactor. The wear resistance of the catalyst can be improved to a certain extent by controlling the molding conditions or adding binders of the catalyst. After MTO industrialization, many cycles of regeneration and wear of the catalyst will result in a large amount of waste material containing silicon, aluminum and phosphorus. Reasonable and efficient use of the waste material can not only save resources, but also improve the economic benefits of MTO process [20].

This work is mainly focused on the two following respects: (1) the effects of post-treatment time of SAPO-34 molecular sieve in the presence of IPA and water on its structure, (2) the effect of NaOH concentration on the product selectivity. A novel method for low-cost synthesis of SAPO-20 molecular sieves using SAPO-34 molecular sieves and IPA as raw materials is presented.

## 2. Experimental Section

### *2.1. Reagents*

The following starting materials were used for the synthesis: pseudo boehmite (75% $Al_2O_3$), NaOH (Merc), phosphoric acid (85%), CAB-O-SILM-5, TMAOH (25 wt%), and isopropyl amine (IPA, Fluka). All chemicals were employed without further purification.

### *2.2. Synthesis*

### *2.2.1. Synthesis of SAPO-34*

Hydrothermal method was explored to prepare SAPO-34 which was reported in Ref. [21]. In a typical procedure for the synthesis of SAPO-34, 9.2 g of pseudoboehmite was slurried in 28 g of deionized water and 15.4 ml of orthophosphoric acid and stirred for 7 hours. Then 6.5 g M-5, 11.6 g morpholine and 39 g water mixed well and slowly added to before-mentioned solution. The hydrogel stirred for another 7 hours with the following molar composition: $1.0P_2O_5$:$1.0Al_2O_3$: $1.1SiO_2$: 1.3morpholine: $52H_2O$. Crystallization was conducted at 200 °C for 4 days. After crystallization the product was filtrated from the mother liquor, washed with deionized water and dried at 100 °C for 12 h. The as-synthesized product labeled as ST.

### *2.2.2. Synthesis of SAPO-20*

Hydrothermal method was explored to prepare SAPO-20 which was reported in Ref.

[2]. The molar ratio of the reaction mixture was 0.75TMAOH: $P_2O_5$: $Al_2O_3$: $SiO_2$: $50H_2O$. In a typical synthesis, 2.8 g of orthophosphoric acid was added to 6.5 g of deionized water. Then 1.7 g of pseudoboehmite was slowly added in the phosphoric acid solution. The obtained mixture is aged for half of hour. To this mixture 2.1 ml of silica sol was added and mixed well. 7.9 ml of TMAOH was added after this was stirred for another three hours. The final mixture pH was about 7. Crystallization was conducted at 150 °C for 3 days. After crystallization the product was filtrated from the mother liquor, washed with deionized water and dried at 100 °C for 12 h. The sample was labeled as SOD-R.

### *2.2.3. Post-treatment Time*

A typical procedure for the post-treatment was carried out as follows. 0.85 grams of as-synthesized SAPO-34 was added to a solution consisting of 12.6 g of IPA mixed with 55 g of water under stirring. The resulting mixture was then transferred into an autoclave, which was heated to 160 °C and kept at this temperature for 1, 2, 3, 4 and 8 days, and the samples are labeled as T-1, T-2, T-3, T-4 and T-5, respectively. After crystallization, the solid product was recovered by filtration, washed with deionized water, and dried at 100 °C for 12 h. As comparison, 7.9 g IPA was used, and the temperature was 160 °C and the post-treatment time was 4 d. The sample was labeled as T-6.

### *2.3.4. Phase-Transformation*

Synthesis of SAPO-20 from a SAPO-34 Precursor. A typical procedure for the phase-translation was carried out as follows. 0.85 g of as-synthesized SAPO-34 was added to a solution containing 12.6 g of IPA, x g sodium hydroxide and 55 g of water under stirring (x=0.5 g, 1.0 g and 1.5 g). The resulting mixture was then transferred into an autoclave, which was heated to 160 °C and kept at this temperature for 4 days, and the samples are denoted as C-1, C-2, and C-3, respectively. After crystallization, a series of operation, such as filtrating, washing with distilled water and drying in air, was carried out and finally the solid product was recovered. As comparison, 0.85 g of T-6, 12.6 g of IPA, 1.5 g sodium hydroxide and 55 g of water were used. The sample was labeled as C-4.

### *2.3. Characterization*

It was performed for X-ray diffraction (XRD) on a Rigaku D/max-2500-type powder diffractometer with Ni-filter (Cu Kα radiation $\lambda = 0.15418$ nm). The diffraction pattern was recorded within the angular range of $2\theta$ from 5 to 35° with an interval of 0.5 s and steps of 0.02° at 30 mA (tube current) and 40 kV (tube voltage). The morphology and size of the products were characterized by a Jeol 6300-F scanning electron microscope (SEM, Shimadzu Corporation) operated at 10-15 kV.

## 3. Results and Discussion

### *3.1. Effect of Post-treatment Time on SAPO-34 Structure*

The XRD pattern of as-synthesized ST (figure 1 ST) is in agreement with that of

SAPO-34 molecular sieve [2], and no other peaks were detected. This implies that pure SAPO-34 is obtained. The effect of time of IPA post-treatment SAPO-34 on its structure are shown in figure 1. We can see from figure 1, post-treatment time from T-1 to T-5, the products maintain the CHA structure. Prolonging the post-treatment time, the XRD diffraction peaks intensity decreases. Moreover, there are three weak peaks at 2θ=7.1, 19.5 and 21.4° in T-5, which indicating that some of SAPO-5 has been formed. For sample T-6, the post-treatment product is amorphous, which indicating that IPA is good for the stabilization of SAPO-34 structure.

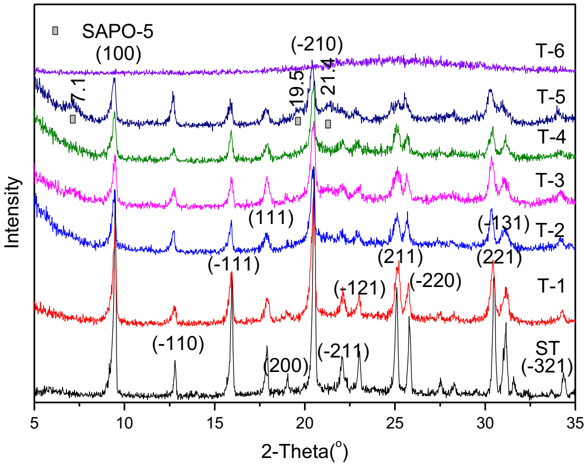

**Figure 1.** XRD pattern of ST, T-1, T-2, T-3, T-4, and T-5.

In addition, it was observed that post-treatment time strongly governs the morphology and the size of the crystals. Figure 2 shows the SEM images of sample ST–T-5. It is obvious that the above samples have completely different morphologies. Sample ST with pure phase CHA was observed the typical cubic morphology which is 6-10μm in size. Samples T-1 show different morphologies with sheet debris, irregularity, cubic, defective cubic, and defective hollow-inside cubic. Prolonged post-treatment time from T-2 to T-5, the cubic SAPO-34 disappears, the sheet debris SAPO-34 is depleted, and the size of irregularity materials are decreased. Moreover, for sample T-5, there are cylindrical or spherical products which is SAPO-5 by XRD.

In our previous study [20], we discovered that the $OH^-$ concentration had a great effect on the product selectivity fixed the post-treatment conditions. The evolution of products with increasing the $OH^-$ concentration were low crystallization SAPO-34, SAPO-34 and SAPO-40, and SAPO-25 (or AlPO-25) and SAPO-56.

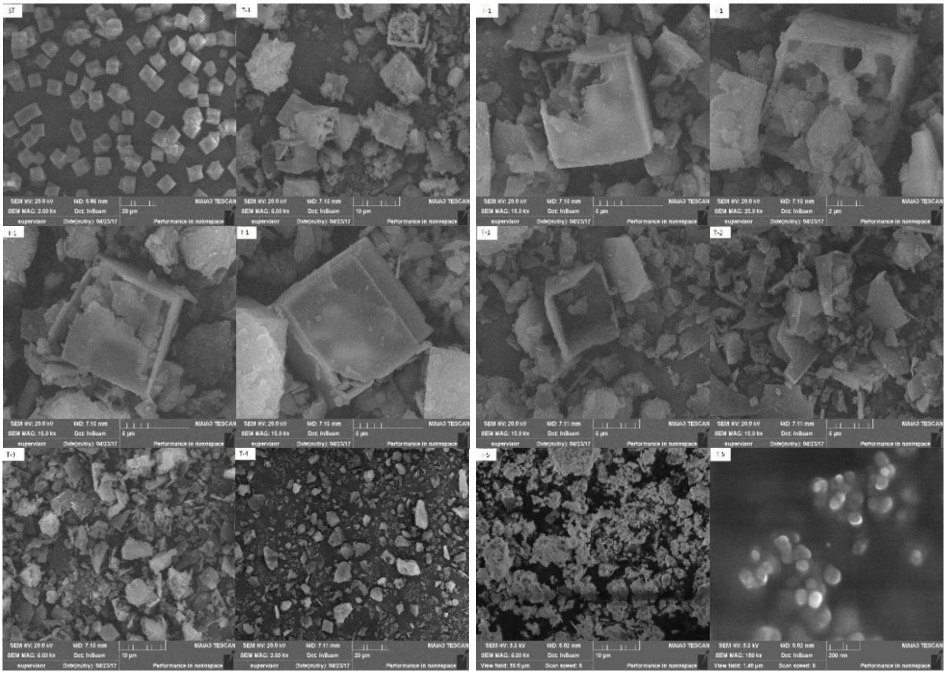

**Figure 2.** SEM images of ST, T-1, T-2, T-3, T-4, and T-5.

### *3.2. Effect of NaOH Concentration on the Product Selectivity*

The XRD pattern of SOD-R (figure 3) is in agreement with that of SAPO-20 [2], which the 2θ values at 13.9, 19.7, 22.0, 24.2, 27.9, 31.3 and 34.4°. The effect of NaOH concentration on the product of phase-transformation was investigated with the gel molar composition of xNaOH:21 IPA:350 $H_2O$ (and 0.85g SAPO-34 (ST) or 0.85g (T-6)). The XRD patterns of obtained samples are shown in figure 3. Without NaOH, the product is CHA with low crystallization (figure 1 T-4). At low concentrations of x=12.5 (C-1), the main product is SAPO-20 molecular sieve, but it co-crystallized with SAPO-21 corresponding the 2θ values at 15.7, 17.3, 18.2, 18.9, 20.6, 21.2, 21.6, 25.9, 26.3, 28.6, 30.6, and 32.6° [2]. However, when the NaOH amount was increased to x=25 (C-2), the SAPO-21 content was increased. At x=37.5 (C-3 and C-4) pure SAPO-20 crystal can be observed. Moreover, with increasing the amount of sodium hydroxide, the 2θ values of the characteristic peaks of SAPO-20 shift to a low angle.

Figure 4 shows the morphology of the products. SOD-R (SAPO-20 molecular sieves, illustrated in figure 4) has spherical morphology with particle size varying between 1 to 5μm. C-1 (a mixture of SAPO-20 and -21) display irregular shapes, while C-3 exhibits hexagonal shape (SAPO-20) and cylindrical morphology (SAPO-21). The morphology of C-4 with spherical aggregation consisted of hexagonal shape SAPO-20 is quite different from SOD-R.

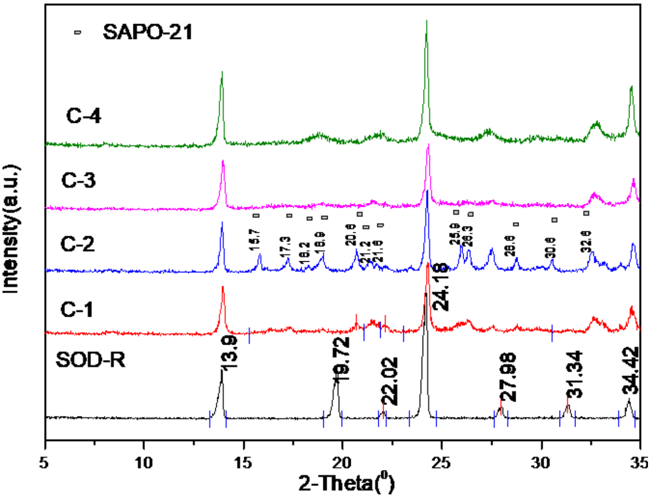

**Figure 3.** XRD pattern of SOD-R, C-1, C-2, C-3, and C-4.

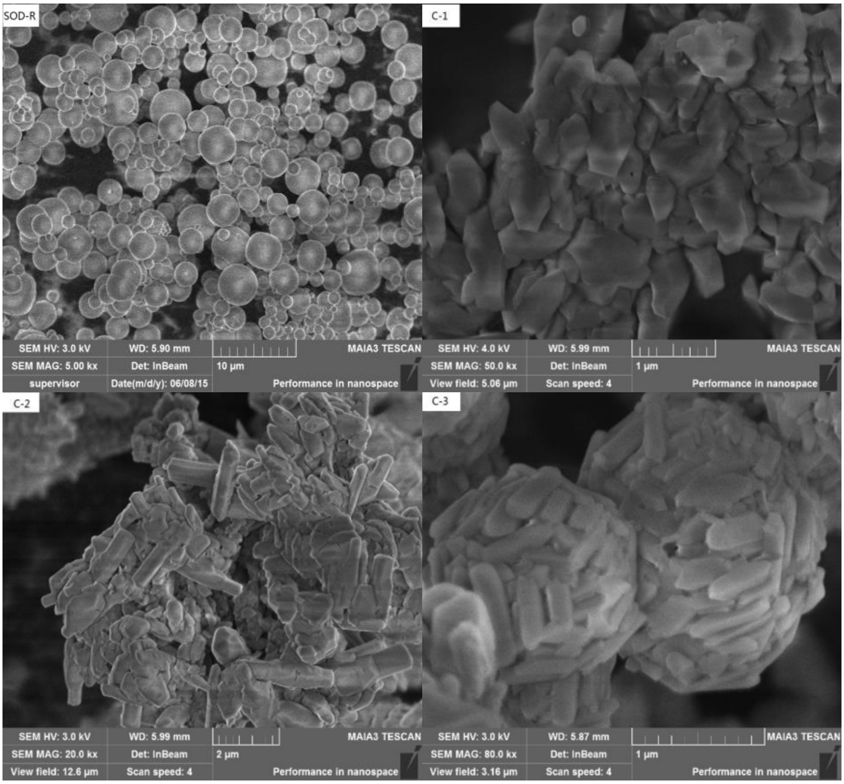

**Figure 4.** SEM images of SOD-R, C-1, C-2, C-3, and C-4.

## 4. Conclusion

A SAPO-20 silicoaluminophosphate molecular sieve with very small-pore has been synthesized using IPA template and spent SAPO-34 as starting materials in aqueous media without addition of any external silicon source and aluminum source. This work has certain reference significance for the generation of cubic morphology of SAPO-34 molecular sieves.

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