# Synthesis of Pure SAPO-31 with Di-*n*-hexylamine as a Novel Structure Directing Agent

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Di-*n*-hexylamine was originally used to synthesize pure SAPO-31 as a structure directing agent (SDA) and the synthesized SAPO-31 crystals have some novel features. After loaded with Pt, it exhibits higher selectivity to isomerization compared with the results of SAPO-31 prepared by the regular method.

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Since the first report on the synthesis of Silicoaluminophosphate molecular sieves (SAPOs), there has been a steady growth of interest in medium pore SAPOs because of their application to shape-selective catalysis. Although SAPO-31 (ATO-structure type) has 12-membered ring channels in the structure, the nearly circular opening with an effective diameter of 0.54 nm brings it under the medium-pore category.[1] Some studies revealed the potential and future utilization of SAPO-31 in catalysis in the field of alkylation, amination and isomerization.

The synthesis of the SAPO-31 was first reported by Lok et al.[2] in a patent in 1983. The synthesis was carried out by hydrothermal crystallization at 473 K with di-*n*-propylamine as template. Although the synthesis has been regarded as the most effective method until quite recently, the preparation of SAPO-31 is shown to be difficult to be reproduced and the product being often coexists with other microporous phases.[2–6] Much effort has been devoted to overcome this problem. In 1990, Zubowa et al.[7] reported the synthesis of pure SAPO-31, but Abbad et al. failed in attempts to reproduce it. In order to synthesize pure SAPO-31, Abbad et al.[8] developed a route with di-*n*-propylamine as template using a fluoride medium. In this study, we report a novel, effective synthesis method by which pure SAPO-31 is synthesized with di-*n*-hexylamine as SDA.

A typical synthesis of SAPO-31 with di-n-hexylamine as a SDA is as follows: 30.0 g of 85% $H_3PO_4$ were added to 75.0 g of distilled $H_2O$ in a Teflon beaker, 51.0 g of aluminium isopropoxide and 7.5 g of fumed silica were slowly added with stirring in turn. Next 21.0 g of di-*n*-hexylamine were added. The mixture was placed in a stainless-steel autoclave lined with PTFE, heated at 443 K and kept with no stirring under autogenous pressure until crystallization was completed. After the autoclave was quenched, crystalline products were filtered, washed with deionized water and dried at 363 K overnight. For comparison, SAPO-31-R was also synthesized with di-*n*-propylamine as template according to regular synthesis method.[6]

In Figure 1, the XRD pattern of the as-synthesized SAPO-31 is compared with the XRD pattern corresponding to as-synthesized SAPO-31-R. The XRD pattern of the latter is in good agreement with the result of the literature.[2–4,6] As presented in Figure 1, the peaks marked with star symbol and circle symbol are respectively attributed to SAPO-11 (AEL-structure type) phase and tridymite phase in terms of *d* values (interplanar spacing) in the previous literature.[9,10] The use of di-*n*-propylamine as template in the synthesis of SAPOs leads to a variety of structure types.[8] Medium pore molecular sieves, i.e., SAPO-11, SAPO-31, SAPO-41, have been prepared in the presence of the secondary amine.[3,4] Specificity of organic additive to a specific structure type has not been observed for di-*n*-propylamine. Although the conditions of crystallization were exactly controlled, other phases (such as SAPO-11) were of frequent occurrence at final products. By comparison with di-*n*-propylamine, di-*n*-hexylamine is highly specific SDA of SAPO-31. Under a wide range of synthesis factors, di-*n*-hexylamine promotes the crystallization of high purity SAPO-31. As far as we know, there has been little information about the SDA role of di-*n*-hexylamine in the synthesis of SAPOs.

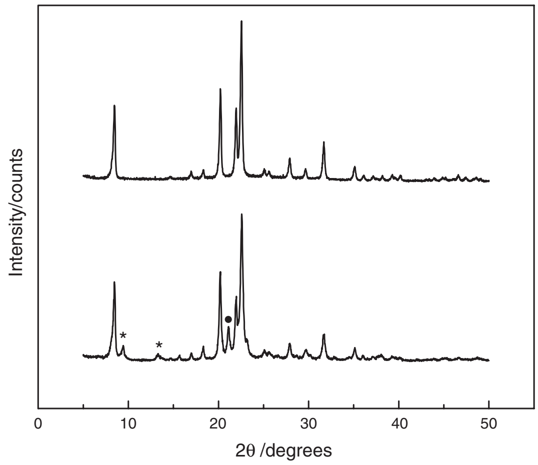

**Figure 1.** XRD patterns of SAPO-31 (top) and SAPO-31-R (bottom).

The spectra of $^{29}$Si CP/MAS NMR are shown in Figure 2, a broad band in the scope of −85 to −120 ppm is typical for multiple tetrahedral environments of silicon.[3] This indicates a combination of the substitution of a single Si for a single P (SM2 mode) and two Si for one Al and one P (SM3 mode). In the sample of SAPO-31-R, main $^{29}$Si resonance is positioned at −94 ppm, indicative of Si (4Al). But the sample of SAPO-31 shows maximum intensity in the chemical shift range from −94 ppm to −98 ppm. The Si signal at −98 ppm is due to Si (nAl(4−n)Si, $n \leq 3$), suggesting that SM3 mode of Si incorporation is more in the SAPO-31 than in the SAPO-31-R. For the given amount of Si in framework, SM3 substitution should lead to decrease of the amount of Brønsted acid.

In Figure 3, the SEM images of samples provide information concerning the morphology of the crystalline phases. Individual rod-like crystals of about 1 μm in length are observed in the SAPO-31, this crystal morphology is similar to hexagonal prismatic crystals obtained by Abbad et al.[8] However, crystal morphology of SAPO-31-R is close to 5–15 μm spherical agglomer-

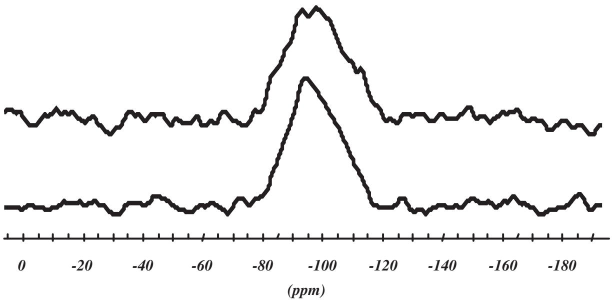

**Figure 2.** $^{29}$Si CP/MAS NMR spetra of SAPO-31 (top) and SAPO-31-R (bottom).

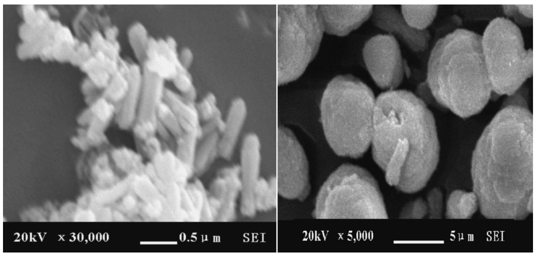

**Figure 3.** SEM images of SAPO-31 (left) and SAPO-31-R (right).

ate of crystals described by Zubowa et al.[7] In addition to the influence on the purity of the final products, di-*n*-hexylamine also leads to the changes in the morphology of the final products.

So research on the conversion of linear alkanes over the pure SAPO-31 loaded with noble metal is a subject of current interest. The hydroisomerization of long-chain alkanes is of considerable interest and plays an important role in the petroleum industry. Properties of oil such as pour point, freezing point, and viscosity index are significantly improved by introducing side chain along the linear carbon chains in petroleum.

The Pt/SAPO-31 catalysts were prepared by means of impregnation method. After calcined at 853 K for 8 h, these molecular sieves were impregnated with 0.5% Pt, dried and calcined in air, then pressed into wafer ($\delta = 2.54$ mm). The conversion of *n*-octane was carried out in a continuous flow fixed-bed reactor. The Reaction conditions were as follows: $p = 1.0$ MPa, $n(H_2)/n(n\text{-}C_8{}^0) = 2$, WHSV($h^{-1}$) $= 2.0$, $m$(catalysts loaded) $=$ 2 g. Before activity measurements, the catalyst was activated at 683 K for 1 h in hydrogen flow (27.2 mL/min). Gas products were analyzed on-line by a gas chromatograph equipped with sebaconitrile/PAW packed column, and liquid products by a gas chromatograph equipped with an OV-101 capillary column. Catalytic performance of conversion of *n*-octane over Pt/SAPO-31 is shown in the Table 1.

**Table 1.** *n*-Octane hydroisomerization results of Pt/SAPO-31

| Reaction Temperature/K | *n*-Octane Conversion/wt % | Hydroisomer Selectivity/wt % |
|---|---|---|
| 603 | 14.19 | 97.11 |
| 620 | 30.87 | 97.12 |
| 633 | 52.00 | 96.56 |
| 643 | 66.81 | 95.19 |
| 658 | 81.30 | 90.91 |
| 668 | 86.02 | 84.41 |
| Pt/SAPO-31-R[a] | 81.05 | 86.25 |

[a] Reaction temperature = 658 K, WHSV = 5.9.

Table 1 shows that selectivity to isomerization over Pt/SAPO-31is still high under high *n*-octane conversion. The medium pore system of SAPO-31 suppress the formation of multibranched alkylcarbenium ions which is susceptible to cracking.[3] Hydrocracking become important with increase of *n*-octane conversion, so $C_8$ isomer yield goes through a maximum. The highest $C_8$ isomer yield is obtained under 658 K, approximately 73.9%. By compared with selectivity over Pt/SAPO-31-R, Pt/SAPO-31 has higher selectivity to isomerization under a similar conversion and the same temperature, i.e., 81.30% and 658 K. We think that other microporous phases of SAPO-31-R shown in XRD pattern bring about more hydrocracking. In addition, higher the reaction temperature over Pt/SAPO-31 is explained by the lower acidity of SAPO-31 according to the result of $NH_3$–TPD. $NH_3$–TPD acid amount of SAPO-31 and SAPO-31-R was 0.69 and 0.81 mmol/g respectively, and the lower acidity of SAPO-31 has close relation to SM3 substitution of Si in SAPO-31.

For synthesis of pure SAPO-31, it is a novel and effective method to use di-*n*-hexylamine as SDA. The novel route changes purity, morphology, location of Si, acidity of the SAPO-31. It is more interesting for the pure SAPO-31 that higher selectivity to isomerization can be obtained on the conversion of *n*-octane by avoiding of hydrocracking which other phases bring about.

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