Synthesis of High Si-containing SAPO-11 by Post-Si Method

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High Si-containing SAPO-11 molecular sieve with enhanced SAPO domain has been successfully synthesized with diethylamine template by modified hydrothermal method. The sample was characterized with XRD, EDX, N_2 adsorption, SEM, ^{29}Si MAS NMR, NH_3-TPD. Bifunctional hydroconversion of *n*-dodecane on Pd/SAPO-11 catalyst showed high hydroisomer conversion and selectivity compared with the results of catalyst prepared by the normal method. The enhanced SAPO domain improves the catalytic results.

Since the discovery of the family of crystalline microporous aluminophosphates in 1982,[1] many research works have been devoted to this new type of molecular sieve materials. The acidity of Silicoaluminophosphates (SAPO) is strongly depended on the Si content, sitting and ordering in the lattice. When Si atoms are introduced into the framework of a hypothetical $AlPO_4$ at the phosphorous sites (mechanism SM2), a potential Brönsted site per Si atom would be generated. Simultaneous replacement of a pair of Al + P atoms by two Si atoms (mechanism SM3) in combination with mechanism SM2, according to the model 3 + 2(SM3 + SM2) advanced by Dwyer et al,[2] also yields potential Brönsted acidity. Although the latter substitution mechanism would lead to less than one acid site per framework Si atom, the resulting strength should be higher than the one arising from the SM2 substitution.[3]

Much effort has been devoted to modifying the gel composition and crystallization conditions to favor the Si substitution for P atoms in higher Si-containing SAPO-11. Some authors have employed a two-liquid phase synthetic medium or surfactant.[4,5] Conditions of 473 K and 24 h with dipropylamine template are applied in the usual synthetic method for SAPO-11. In this study, diethylamine, a much cheaper template, was applied as template instead of dipropylamine. Comparing with dipropylamine, diethylamine was more suitable for the higher Si-containing SAPO-11 by energetic analysis.[6] But unfortunately, under the normal synthetic conditions impurities of other structures appeared in our experiments. A novel procedure must be developed to synthesize high Si-containing SAPO-11. Post-Si synthesis method is employed in this study.

The post-Si synthesis of silicon-rich SAPO-11 was as follows: (1) pseudoboehmite was mixed with orthophosphoric acid and deionized water and the mixture was stirred at room temperature for 1 h. Diethylamine was added slowly and stirred for another 1 h, then this microemulsion was transferred into a stainless-steel autoclave and heated at 473 K for 15 h to form an amorphous precursor of $AlPO_4$ noted as sample 1. (2) Sample 1 was cooled down and silica gel was added with stirring, then transferred to a preheated oven at 573 K for 2 h to get sample 2. The resultant slurry was filtered, the product was washed with distilled water and dried at 393 K for 12 h and subsequently calcined at 823 K for 24 h. The chemical composition of the synthetic gel is given: $Al_2O_3 \cdot 1.1P_2O_5 \cdot 0.66SiO_2 \cdot 1.6Et_2NH \cdot 40H_2O$, where Et_2NH is diethylamine.

Products were characterized by powder X-ray diffraction (Rigaku D/MAX-II) fitted with Cu Kα radiation, Scanning electron microscopy SEM (Philip XL-30) and MAS NMR spectroscopy (Brucker MSL-300). The chemical compositions of the samples were determined by EDX. The acidity of the samples was characterized using temperature programme desorption of ammonia (NH_3-TPD).

XRD patterns of sample 1 and sample 2 are shown in Figure 1. It is observed that sample 1 did not fully crystallize when it was only heated at 473 K for 15 h. Most $AlPO_4$ atoms of sample were still in the state of disorder in sample 1, then silica gel was added and further heated at 573 K for 2 h, which led to well crystallization of SAPO-11 noted as sample 2. The SEM image of sample 2 is shown in Figure 2. Sample 2 crystallized well with quadrate layers about 2 μm in length, 1 μm in width, and 0.2 μm in thickness. EDX result of sample 2 showed that Si/Al was 0.42, which was higher than the ratio of 0.33 in the synthetic gel, indicating that Si was rich in external surface of SAPO-11.

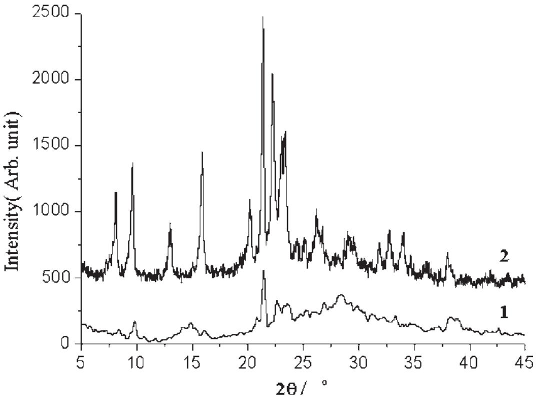

Figure 1. X-ray diffraction patterns of samples. Sample 1, Heated at 473 K for 15 h; Sample 2, Si-added sample 1 further heated at 573 K for 2 h, calcined at 823 K for 24 h.

BET surface of the calcined sample 2 was 199 m^2/g, which shows the SAPO-11 channels are not blocked up by amorphous materials. And NH_3-TPD acid amount was 0.71 mmol/g, most of them being weak acid. Py-IR acid amount was 0.76 mmol/g, Brönsted acid amount being 2.4 times than Lewis acidic amount. ^{29}Si MAS NMR spectrum is shown in Figure 3, line around -90 ppm which stands for SAPO domain is very strong, while line around -110 ppm which stands for Silica-rich domain is very weak.[5,7] It can be speculated that most Si atoms are incorporated in framework with SM2. It is assumed that in step one, synthetic

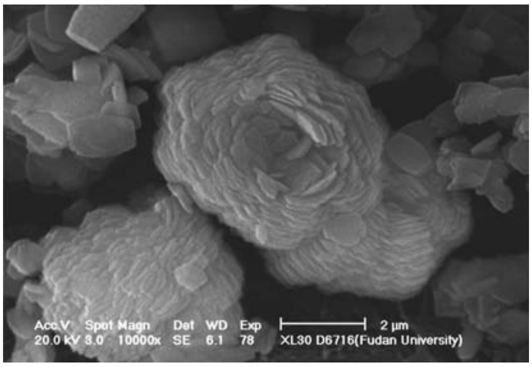

Figure 2. SEM image of SAPO-11.

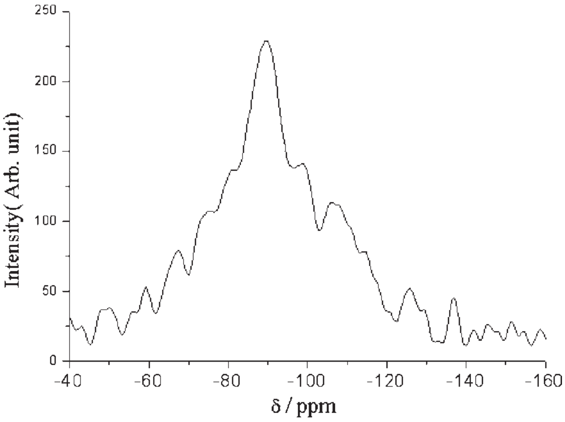

Figure 3. ^{29}Si MAS NMR spectum of SAPO-11.

gel being heated at 473 K for 15 h, form lots of small centers of P-Al-Et_2NH. After the silica gel is added and the mixture is heated up to 573 K for 2 h, the acidic P-Al-Si-Et_2NH framework is more stable than neutral in this high temperature. Si atoms are incorporated with SM2 other than SM3 to form more acidic centers for stabilizing the SAPO-11 framework.

Bifunctional hydroconversions of *n*-dodecane was applied to investigate the catalytic properties of the Pd/SAPO-11(Pd 1 wt%) sample. The catalytic conversions of *n*-dodecane were carried out in pulse microreactor at a pressure of 2.2 bar and a hydrogen flow rate of 40 mL/min. The catalyst (40 mg) with the particle size between 0.28 and 0.45 mm loaded in a fix-bed reactor was pretreated in situ by heating at 673 K for 2 h in hydrogen followed by the injection of 1 μL of reactant into the catalyst bed. Reactants and products were analyzed on line with a gas chromatograph, equipped with a flame-ionization detector and a capillary OV-101 column (50 m length, 0.25 mm i.d.). The reaction results are shown in Table 1.

Table 1. *n*-Dodecane hydroconversion results of Pd/SAPO-11

Reaction temperature/K	Hydroisomer conversion/wt%	Hydroisomer selectivity/wt%
523	20.9	100
548	41.2	98.3
563	64.3	86.3
573	78.1	82.6
598	66.1	73.0
623	30.2	30.8
Regular synthesis method[a]	40.1	67.2

[a]Reaction temperature is 573 K.

It can be seen from Table 1 that hydroisomer conversion reaches maxim at 573 K, while hydroisomer selectivity decrease with reaction temperature rises. The maximal hydroisomer conversion and hydroisomer selectivity are 78.1% and 82.6% respectively. Compared with the corresponding results of 40.1% and 67.2% Pd/SAPO-11 synthesized with normal method,[7] there is great advantage of the SAPO-11 sample synthesized with new method by diethylamine template. Et_2NH is of about 0.66 ~ 0.85 nm in length, which fits to the *c* axis length 0.837 nm of $AlPO_4$-11.[8] *n*-Pr_2NH is of about 0.70 ~ 1.04 nm in length, somewhat longer than *c* axis. When Si atoms are incorporated, the regular framework will be destroyed, and smaller template of Et_2NH can allow more great changes within framework which is made by higher Si atoms incorporated.

High Si-containing SAPO-11 samples have been synthesized by modified hydrothermal method and its structure and acidity have been investigated. SAPO-11 sample with high BET surface, high acid amount and enhanced SAPO domain was formed. After impregnated with Pd, it exhibits good hydroisomer conversion and selectivity compared with the results of catalyst prepared by the normal method. Diethylamine template size and post-Si synthesis under higher crystallization temperature are two important advantages for the good results.

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References

1 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan, and E. M. Flangen, *J. Am. Chem. Soc.*, **104**, 1146 (1982).
2 M. Makarova, A. Ojo, K. Al-Ghefaili, and J. Dwyer, Proceedings of the IX International Zeolite Conference, Montreal, July 1992, Abstr., No. II, 259.
3 M. Alfonzo, J. Goldwasser, C. M. López, F. J. Machado, M. Matjushin, B. Mendéz, and M. M. Ramírez, *J. Mol. Catal.*, **98**, 35 (1995).
4 E. G. Derouane, L. Maistrian, Z. Zabelica, A. Tuel, J. B. Nagy, and R. von Ballmoos, *Appl. Catal.*, **51**, 13 (1989).
5 P. Mériaudeau, V. A. Tuan, F. Lefebvre, V. T. Nghiem, and C. Naccache, *Microporous Mesoporous Mater.*, **22**, 435 (1998).
6 L. J. Wang, X. D. Huang, W. Zhao, and Q. Z. Li, *Chinese J. Inorg. Chem.*, **18**, 559 (2002).
7 P. Mériaudeau, V. A. Tuan, V. T. Nghiem, S. Y. Lai, N. Hung, and C. Naccache, *J. Catal.*, **169**, 55 (1997).
8 N. J. Tapp, N. B. Milestone, and D. M. Bibby, *Zeolites*, **8**, 183 (1988).