Synthesis and characterization of the silicoaluminophosphate SAPO-47

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Synthesis of a novel small-pore SAPO-47 molecular sieve was described. The effects of the templates and silica concentration in the synthesis gel on the crystallinity and phase purity of SAPO-47 were studied. The results show that pure SAPO-47 could be obtained in a wide range of SiO_2/Al_2O_3 using sec-butylamine, methylbutylamine or iso-butylamine as templating agent. It is evident that the strength and the amount of the acid sites are related closely to the silicon content and distribution in the framework. SAPO-47 molecular sieve catalyst with expectable acidity could be obtained by controlling the SiO_2/Al_2O_3 in the initial gel.

1. INTRODUCTION

A large number of microporous silicoaluminophosphates(SAPO-n) have been prepared by hydrothermal methods by varying the crystallization conditions and phosphorus source, aluminum source, silicon source and organic templates[1]. Among those, SAPO-34 and SAPO-44 both have a chabazite type framework topology, consisting of a two-dimensional system of channels, with free diameters of 3.8Å. They are kinds of medium acidic strength molecular sieves with small pore character. At present, the studies on SAPO-34 and SAPO-44 have been very abundant. It is revealed that the both could be synthesized using several templates and show well catalytic properties on MTO (*methanol to light olefins*) or SDTO (*syngas via dimethylether to light olefins*) processes.

The crystal structure of SAPO-47 molecular sieve synthesized by using methylbutylamine as a template was determined by J. J. Pluth and J.V. Smith in 1989. SAPO-47 has also a chabazite-type framework, [2] which is the same as SAPO-34 and SAPO-44. Afterwards, Emil Dumitriu et al. prepared pure SAPO-47 molecular sieve by using sec-butylamine as a template in 1998.[3] But the studies and reports on SAPO-47 are lesser than SAPO-34 and SAPO-44. In this paper, we demonstrate the synthesis of SAPO-47 molecular sieve, the effects of gel composition and templates on crystallization, and their catalytic properties on MTO process.

2. EXPERIMENTAL

2.1. Synthesis

All the syntheses were carried out hydrothermally. The reactants used were pseudobeohmite(72.2 wt% Al_2O_3, Purissimum grade) as the aluminum source, ortho-phosphorate (85 wt%, Analytical grade) as the phosphorous source, silica sol (25.0 wt% SiO_2) as silicon source, and methylbutylamine(99%), sec-butylamine(96%) or iso-butylamine(99%) as templating agent.

The reaction mixtures were prepared with composition: x template : y SiO_2 : 1.0 Al_2O_3 : 1.0

P_2O_5 : 70 H_2O, *x* and *y* represent the mole fractions of template and silica. The process of operation was as follows: to combine the measured ortho-phosphorate and the partial measured water, to which was added the measured pseudobeohmite, and stirred until homogeneous. To this mixture was added the measured silica sol and the mixture stirred until homogeneous. Finally the measured templates and surplus water were added and the mixture stirred until homogeneous.

This reaction mixture was sealed in Teflon-lined stainless steel autoclaves (100ml) and heated in an oven at 200°C under autogenous pressure for 64 hours. After crystallization, the autoclaves were cooled down to room temperature under running water and the solid reaction products were recovered by centrifugation, washed with water, and dried in air overnight at 100 °C.

2.2. Characterization

The structure type and crystallinity of all the samples were checked by powder X-ray diffraction (XRD) on a D/max-rb diffractmeter using CuK_{α} radiation, the voltage was 30-40kV, the electric current was 40-50 mA.

The measurement of acidity of all samples was performed on homemade ammonia-TPD apparatus. The samples were calcined to remove the templates at 550°C for 5 hours under a flow of dry air. The calcined samples were pressed to tablets without binder and then crashing to 20-40 mesh, and 0.1g of sample was filled in a small stainless reactor. The sample was pre-treated at 650°C for 20 minutes under He flow and the temperature was then decreased to 100°C. After 20 minutes, ammonia was adsorbed to saturation at 100°C and disadsorbed at a rate of 20°C/min to 650°C in a flow of He. The GC and TCD detector were used in ammonia analysis.

2.3 Catalytic tests

The MTO reactions were carried out on a fixed bed reactor with continuing flow of MeOH (WHSV=$2h^{-1}$) and nitrogen (75ml/min.). Before reaction, catalyst (1.50g) was pre-treated at 550°C for 1 hour in a 75 ml/min. nitrogen flow. Methanol was fed by nitrogen (75ml/min.) carrier gas through a saturator. Reaction conditions were as follows: 450°C, WHSV(MeOH)=$2h^{-1}$, N_2=75ml/min.. On- line GC with Porapak-Qs column incorporated with temperature program and FID detector was used in product analysis.

3. RESULTS AND DISCUSSION

First of all, it should be pointed out that the present work demonstrated that the synthesis of SAPO-47 molecular sieve using any of the sec-butylamine, methylbutyl-amine and iso-butylamine as the template. Especially, the iso-butylamine was used for the first time.

3.1. Effects of templates on the products

Crystallization of SAPO-47 molecular sieves from the gel composition: *x* template: $0.6SiO_2$: $1.0Al_2O_3$: $1.0P_2O_5$: $70H_2O$ was investigated (Table 1). The results showed that when sec-butylamine or methylbutylamine was used as the template, and template/Al_2O_3≥2, pure SAPO-47 could be obtained. When iso-butylamine was used as the template, only at the template/Al_2O_3 ratio was ~3, SAPO-47 molecular sieve could be synthesized. This also demonstrated that pure SAPO-47 could be obtained in a wide range of template/Al_2O_3 using sec-butylamine or methylbutylamine as a templating agent, but couldn't at low and high concentrations of the template using iso-butylamine as a templating agent.

Table 1
Effects of the template on the products

Templates	Template/Al_2O_3	Product composition
sec-butylamine	1	SAPO-47+impurity
	2	SAPO-47
	3	SAPO-47
	4	SAPO-47
methylbutylamine	1	Unknown phase
	2	SAPO-47
	3	SAPO-47
	4	SAPO-47
iso-butylamine	1	Unknown phase
	2	SAPO-47+impurity
	3	SAPO-47
	4	Unknown phase

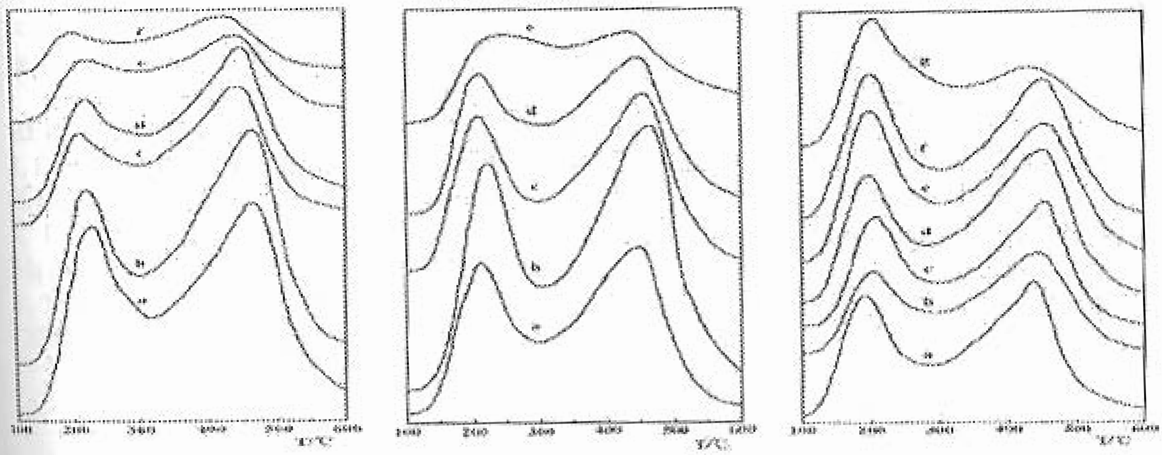
3.2. Effects of SiO_2/Al_2O_3 ratios of the gel on the products

From the gel composition: 3.0template: $y$$SiO_2$: 1.0$Al_2O_3$: 1.0$P_2O_5$: 70$H_2O$, the crystallization of SAPO-47 was studied with the variations of the SiO_2/Al_2O_3 ratio (Table 2). It is seen that pure SAPO-47 could be synthesized within a wide range of SiO_2/Al_2O_3 ratio. If sec-butylamine, methyl-butylamine or iso-butylamine was used as the template, and the range of the SiO_2/Al_2O_3 ratio of the gel was $SiO_2/Al_2O_3 \geq 0.1$, $0.2 \leq SiO_2/Al_2O_3 \leq 0.6$, or $0.2 \leq SiO_2/Al_2O_3 \leq 0.8$ respectively, pure SAPO-47 could be obtained. This provides a chance to adjust the strength of acidity of SAPO-47 molecular sieve by the variations of the SiO_2/Al_2O_3 ratio.

Table 2
Effects of SiO_2/Al_2O_3 ratios of the gel on the products

Templates	SiO_2/Al_2O_3	Product composition
sec-butylamine	0	Unknown phase
	0.1-1.2	SAPO-47
methylbutylamine	0-0.1	Unknown phase
	0.2-0.6	SAPO-47
	0.7	Amorphous phase
iso-butylamine	0	Unknown phase
	0.1	SAPO-47+impurity
	0.2-0.8	SAPO-47
	0.9	Amorphous phase

TPD profiles of ammonia desorption from SAPO-47 synthesized by using different templates and SiO_2/Al_2O_3 ratios of the gel were given in Figure 1. The results showed that for the SAPO-47 molecular sieve synthesized with different compositions, the number of both weak and strong acid sites increased first and then decreased with the increase of the SiO_2/Al_2O_3 ratio of the gel. This is reasonably associated with the silicon content, distribution and location in the framework. Generally, SAPO-n materials are formed by silicon replacing Al and/or P in the framework of AlPO-n materials. In SAPO molecular sieves, the order of acidity is as follows: Si(0Al)< Si(4Al)< Si(3Al)< Si(2Al)< Si(1Al). Moreover, it is proposed that Si atoms incorporate into AlPO structure by two different substitution mechanisms: the first one, the Si substitution for phosphorus forms Si(4Al) structure, which gives rise to negative charges forming a Brφnsted acid site; the second mechanism is the double substitution of neighboring aluminum and phosphorus by two silicon atoms forming Si(nAl)(n=3-0), which leads to the formation of stronger Brφnsted acid sites. The increase of Si(4Al) and appearance of the Si(3Al), Si(2Al), Si(1Al), Si(0Al) suggested that substitution of the Si atoms for the phosphorus and for the phosphorus and aluminum pair took place in the later stage of the crystallization.[4] So it is reasonable that the number of the acid sites would increase because of the addition of the units of Si(4Al), Si(3Al), Si(2Al) and / or Si(1Al), but decrease when Si(0Al) occurs. The strength and amount of the acid sites of SAPO-47 could be adjusted with the variations of the SiO_2/Al_2O_3 ratio in the gels.



(1) (2) (3)

Fig. 1 TPD profiles of SAPO-47 synthesized by using the different templates and gel SiO_2/Al_2O_3 ratios

(1) sec-butylamine as template, SiO_2/Al_2O_3: a 0.1, b 0.2, c 0.3, d 0.4, e 0.5, f 0.6

(2) methylbutylamine as template, SiO_2/Al_2O_3:a 0.2, b 0.3, c 0.4, d 0.5, e 0.6

(3) iso-butylamine as template, SiO_2/Al_2O_3: a 0.2, b 0.3, c 0.4, d 0.5, e 0.6, f 0.7, g 0.8

3.3. Catalytic activity

MTO performance over the SAPO-47 molecular sieve catalyst synthesized from the gel composition: 3.0iso-butylamine: $0.6SiO_2$: 1.0 Al_2O_3: 1.0 P_2O_5: $70H_2O$ was carried out. It is observed that the conversion of methanol could reach 100%, and the selectivity of ethylene and C_2+C_3 olefins were 54.51% and 83.27% respectively (Table 3). Compared with SAPO-44 and SAPO-34 (the selectivity of C_2+C_3 olefins are 84.10% and 90.86% respectively), SAPO-47 molecular sieve catalyst also shows higher activity of reaction on MTO process.

Table 3

The product distribution on MTO reaction of SAPO-47, 44 and 34 catalysts

Samples	Product distribution* (wt%)							
	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4^+	C_5^+	$C_2^=$~$C_3^=$
SAPO-47	1.52	54.51	0.89	28.76	0.00	11.64	2.69	83.27
SAPO-44[a]	1.63	42.95	1.79	41.15	0.00	9.51	2.97	84.10
SAPO-34[b]	1.19	61.88	0.18	28.98	0.00	5.66	2.21	90.86

*Conversion of MeOH: 100%

a, b: the former work

4. CONCLUSION

Pure and well crystalline SAPO-47 molecular sieve was synthesized by using any of sec-butylamine, methylbutylamine or iso-butylamine as templating agent for a wide range of SiO_2/Al_2O_3 ratio. The strength and amount of the acid sites could be adjusted with the variations of the SiO_2/Al_2O_3 ratio, and SAPO-47 molecular sieve catalyst with expectable acidity could be obtained by controlling the SiO_2/Al_2O_3 in the initial gel. The MTO performance illustrates that SAPO-47 molecular sieve is a kind of highly active catalyst.

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