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A one-step route to SAPO-46 using H_3PO_3-containing gel and its application as the catalyst for methanol dehydration

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ABSTRACT

SAPO-46 molecular sieve has been synthesized on a new one-step route by using phosphorous acid (H_3PO_3) or the mixture of H_3PO_3 and phosphoric acid (H_3PO_4) as the phosphorus source. It has been found that the pure phase of SAPO-46 could be obtained more conveniently from the H_3PO_3-containing gels at 200 °C. Meanwhile, SAPO-46 with higher crystallinity can be synthesized in a wide range of gel compositions, containing higher silica in the product. As the catalyst for the dehydration of methanol to dimethyl ether (DME), it has exhibited high selectivity for the formation of DME as well as the activity of methanol conversion. Raman and IR have been employed to characterize the initial gel and as-synthesized sample to investigate the formation of SAPO-46 and the one-template-multiple-structures phenomena in the new one-step route, where SAPO-41 or SAPO-46 can be formed according to silica concentration. The transformation of P(III) species in the initial gels to P(V) species during crystallization have been found. It may be the key role for the formation of SAPO-46 on the new route. Besides, the correlation between silica content and the structure type of crystalline products with di-n-propylamine as the template has also been obtained.

1. Introduction

Silicoaluminophosphates (SAPOs) molecular sieves have generated considerable interest as solid acid catalysts since their first synthesis in 1984 [1]. These structures, in general less acidic than aluminosilicates and have been found practical applications as catalysts in industrial processes, such as the selective isomerization of hydrocarbon chains and the conversion of methanol to light olefins (MTO process) [2–7]. In recent years, dimethyl ether (DME), which is now used as a raw material for making chemicals and aerosol propellant such as hair spray, shaving cream to replace ozone-destroying chlorofluorocarbons (CFC), has received attentions as an LPG alternative, transportation fuel in substitution to diesel and power generation [2–5].

Among the various SAPOs, AFS-structure type molecular sieves, which has a unique three-dimensional structure with large-pore, present potential applications. This type molecular sieve is first synthesized in the form of MeAPO and MeASPO by Flanigen and co-workers [8–10]. The structure is based on capped six-membered rings with a unidimensional 12-ring channel system with a free aperture between 7 Å and 8 Å cross-linked through 8-ring windows. AFO-structure contains only 10-ring with a pore size of 4.3 Å × 7.0 Å [11]. AFS-structure silicoaluminophosphates (SAPO-46) appears in 1994 [12]. Similar to other SAPO-based molecular sieves, it is generally synthesized by using phosphoric acid as the source of phosphorus, silica sol and reactive alumina as silica and aluminum source, respectively in the presence of di-n-propylamine (DPA) as the structure directing agent [12]. However the pure SAPO-46 is relatively difficult to be synthesized, as it tends to crystallize along with other DPA directing molecular sieves such as SAPO-11 and SAPO-41 [10,13,14]. So the formation of SAPO-46 needs two crystallizing steps. Firstly it has to be crystallized at 150 °C for 96 h, secondly reacted at 180 °C for a further period of 120 h [12]. Recently, the usages of non-conventional phosphorus sources have shown some distinct effects for crystallizing phosphate-based molecular sieves [15–17]. We have reported the synthesis of SAPO-41 and SAPO-47 molecular sieves by using H_3PO_3 as phosphorus source. H_3PO_3-containing gels have exhibited some competitive effects with organic amines on directing the formation of aluminophosphate-based molecular sieves [18,19]. In the present work, by using H_3PO_3 or the mixture of H_3PO_3 and H_3PO_4 as the source of phosphorus (denoted as P source afterwards), the preparation of SAPO-46 in aqueous system is described. Meanwhile, thermal stability of the as-synthesized SAPO-46, which is lower than that of like SAPO-5 [20] and SAPO-37 [21], has been improved by increasing the Si content of the framework. IR and Raman spectroscopes have been used to detect the transformation of P(III) species to P(V) species during the crystallization procedure

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and the slight interaction of the template-framework in SAPO-46. Additionally, the catalytic properties of SAPO-46 on the transformation of methanol to dimethyl ether (DME) have been studied. It has showed high selectivity to DME in collective products with less coke formation tendency.

2. Experimental

2.1. Reactants

Phosphorous acid (>99%) and di-n-propylamine (>95%) were purchased from Tianjin Yaohua Chemical and Acros Organics. Pseudoboehmite (water loss at 600 °C being 34.75 wt.%) was purchased from Shandong Aluminum Plant. Phosphoric acid (>99%) was purchased from Tianjin Chemical. Silica sol (5.9 M SiO_2) was purchased from Qindao Chemical.

2.2. Synthesis of SAPO-46

2.2.1. Using H_3PO_3 as the phosphorus source

Typically, 1.8 g of solid H_3PO_3 was dissolved in 20 ml deionized water, and then H_3PO_3 solution was added slowly to 1.7 g of pseudoboehmite. The mixture was stirred for about half an hour until it became homogeneous. Subsequently, 4.6 ml of di-n-propylamine (denoted as DPA afterwards) were added into it dropwise under vigorous stirring. Then, 1.1 ml aqueous silica sol was added. The reaction mixture had the following molar composition: $1.0Al_2O_3$:$2.0H_3PO_3$:4.0DPA:$100H_2O$: $0.6SiO_2$ with gel pH = 8. The mixture was sealed in a Teflon-lined stainless-steel autoclave and heated at 200 °C under autogeneous pressure.

2.2.2. Using H_3PO_3 and H_3PO_4 as the mixed phosphorus source

Typically, 0.91 g of H_3PO_3 was dissolved in 10 ml of deionized water, then 1.1 ml H_3PO_4 was added slowly to H_3PO_3 solution. The mixture was added to 2.1 g of pseudoboehmite and then 10 ml of deionized water was added in. After stirred for about half an hour, then 6.1 ml DPA was added in dropwise under vigorous stirring. Subsequently, 1.1 ml aqueous silica sol was added. The typical molar composition of the reaction mixture is $1.2Al_2O_3$:$1.0H_3PO_3$:$1.5H_3PO_4$:4.0DPA:$100H_2O$:$0.6SiO_2$. The mixture was sealed in a Teflon-lined stainless-steel autoclave and heated at 200 °C under autogenous pressure (Table 1).

2.3. Characterization

X-ray powder diffraction (XRD) patterns of the as-synthesized products were recorded on a Rigaku D/MAX-2500 diffractometer with Ni-filtered Cu Kα radiation ($\lambda = 1.5418$ Å). The IR spectra were recorded by Brucker Vector 22 FT-IR spectrometer. Raman spectrometer used was Renishaw in via spectroscopy system. The laser used was argon ion laser with 514.5 nm excitation source with power output of 20 mW. Element analysis was performed on an Elementar Varioel element analyzer. Thermal analysis was performed on Netzsch STA 409 PC thermal analyzer at a heating rate of 10 °C/min in nitrogen. The crystal morphology and electron probe microanalysis and chemical compositions of the products were performed with a Hitachi X-650 scanning microscope.

2.4. Catalytic reaction

Before the test, the SAPO-46 was calcined in air at 550 °C for 2 h to remove the organic template completely. The dehydration of methanol to DME was carried out on a fixed-bed stainless-steel reactor and detected with an on-line GC. The experiments were performed on atmospheric pressure at 350 °C, 450 °C and 585 °C, respectively. For each case, 0.6 g of HSAPO-46 catalyst (grain size 20–40 mesh) was used. Nitrogen saturated by pure methanol (11% MeOH in N_2) was used as feed with the gas mass space velocity (WHSV) 1.0 h^{-1}. It was 30 min for saturating the N_2 stream with methanol.

3. Results and discussion

3.1. Synthesis and initial characterization

In conventional synthesis procedure using H_3PO_4 as phosphorus source, SAPO-46 can only be obtained from a two-step route. It needs first to be crystallized at 150 °C for an initial period of 96 h, and then another period of 120 h at 180 °C would be expended [12]. However, in the present studies by using H_3PO_3 as the source of phosphorus, the pure SAPO-46 can be crystallized directly at 200 °C for only 72 h in the system of $Al_2O_3/SiO_2/H_3PO_3$/DPA/H_2O or $Al_2O_3/SiO_2/H_3PO_3/H_3PO_4$/DPA/$H_2O$. X-ray powder diffraction patterns of as-synthesized samples are shown in Fig. 1. It closely resembles to that of SAPO-46 phase reported in the literature [12]. SEM photographs confirm the phase purity prepared in this synthesis route (Fig. 2). Apart from this, the range of silica concentration for crystallizing pure SAPO-46 phase has been extended from $0.3 < SiO_2/Al_2O_3 < 0.6$ [13] to $0.3 \leq SiO_2/Al_2O_3 \leq 1.25$. Samples in Fig. 1 have shown the result for synthesizing SAPO-46 in gels with different silica concentration (the molar ratio of SiO_2/Al_2O_3 are 0.4, 0.8, 1.0, 1.3, respectively). Especially in the gels with $SiO_2/Al_2O_3 = 0.8$, the product shows the best crystallinity (Fig. 1B). A lower silica concentration, for example, in the range of $0.2 < SiO_2/Al_2O_3 < 0.3$, it led to the mixtures of SAPO-41 and SAPO-46 (Table 1 E). $SiO_2/Al_2O_3 \leq 0.2$ is the identical synthesis conditions to prepare pure SAPO-41 phase (Table 1 F). On the opposite, if $SiO_2/Al_2O_3 > 1.5$, no crystallization product can be obtained even if the duration was prolonged from 3 to 7 days.

Other factors, such as amounts of H_2O, DPA have also shown their impact on the formation of SAPO-46. It can also be seen from Table 1 and Fig. 3 that when $H_2O/Al_2O_3 < 150$, pure SAPO-46 is obtained (Fig. 3A). A higher H_2O content ($150 \leq H_2O/Al_2O_3 < 200$)

Table 1
Gel compositions and crystallization conditions of SAPO-46.

Sample	Reactant composition						Crystallization condition		Product
	Al_2O_3	H_3PO_3	H_3PO_4	SiO_2	DPA	H_2O	Temp (°C)	Time (day)	
I	1.0	2.0	0	0.6	3.0	100	200	6	Pure SAPO-46
A	1.2	1.0	1.5	0.6	4.0	100	200	3	Pure SAPO-46
B	1.2	0.5	1.5	1.5	4.0	100	200	3	Pure SAPO-46
C	1.2	1.0	1.5	0.4	4.0	100	200	3	Pure SAPO-46
D	1.2	1.5	1.5	0.6	4.0	100	200	3	Pure SAPO-46
E	1.2	0	2.0	0.6	4.0	100	200	3	SAPO-11, SAPO-46
F	1.2	1.0	1.5	0.2	4.0	100	200	3	Pure SAPO-41
G	1.2	1.0	1.5	0.6	2.0	100	200	3	Pure SAPO-11
H	1.2	1.0	1.5	0.6	2.0	180	200	3	SAPO-43, SAPO-46