Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Characterization and hydroisomerization performance of SAPO-11 molecular sieves synthesized by dry gel conversion

Chun-Min Song *, Yi Feng, Li-Li Ma

School of Chemistry & Chemical Engineering, China University of Petroleum, Qingdao 266555, Shandong, China

ARTICLE INFO

ABSTRACT

SAPO-11 molecular sieves were synthesized by two types of dry gel conversion (DGC) methods, namely, steam-assisted conversion (SAC) and vapor phase transport (VPT), and by conventional hydrothermal (CHT) method. The properties of these samples were characterized by XRD, XRF, SEM, N_2-adsorption, Pyridine-IR and ^{29}Si MAS NMR methods. The results show that di-n-propylamine (DPA) is a suitable structure-directing agent (SDA) for the preparation of impurity-free SAPO-11. SAPO-11 molecular sieves synthesized by SAC and VPT exhibit higher crystallinity, higher Si content and more strongly acidic sites than that synthesized by CHT. ^{29}Si MAS NMR results demonstrated that the two samples obtained by the DGC methods contain more Si(nAl)(0 < n < 4) species than that obtained by CHT. These facts suggest that the SAC and VPT methods contribute either to better Si incorporation into the $AlPO_4$ framework or to better Si dispersal, thus decreasing the size of Si islands and increasing the number and strength of acidic sites. The results from the hydroisomerization of n-dodecane indicate that the Pt/SAPO-11 synthesized by SAC possesses the highest hydroconversion activity and isomer yield among those three catalysts, due to the high acidity of the molecular sieve supporter.

1. Introduction

SAPO-11 is a member of the silico-aluminophosphate (SAPO-n) family and was first synthesized by Union Carbide Corporation [1]. Many of these SAPO materials have novel pore structures and exhibit milder acidity due to the presence of phosphorus. The void volume of SAPO-11 consists of elliptical, non-intersecting 10-membered rings with a pore opening of 0.39 nm × 0.63 nm. When Pt/SAPO-11 catalysts are applied to the hydroisomerization of long-chain n-paraffins (isodewaxing process of lubricant oils [2,3]), cracking reactions are suppressed. Owing to its narrow pore size, the formation of multi-branched isomers was prevented, which are susceptible to cracking. Similar results were found over Pt- or Pd-supported SAPO-31 [4], SAPO-41 [5], ZSM-22 [6,7] and ZSM-23 [8] catalysts with uni-dimensional pore channels and 10-membered ring window openings. On those catalysts, the predominant products were mono-branched isomers, which are ideal for lubricants with high viscosity indices and low pouring points. In addition, the medium acidity of SAPO-11 is beneficial for further improving hydroisomerization selectivity. Thus, Pt- or Pd-supported SAPO-11 catalysts exhibit excellent hydroisomerization performance in the production of high-quality lubricants.

Compared with aluminosilicate zeolites, SAPOs exhibit weaker acidity and thus show low catalytic activity for the hydroisomerization of paraffins [9]. The acidity of SAPO molecular sieves depends strongly on the Si content and the distribution of Si in the framework [10–13]. A high Si content with more dispersed environments is often desired to increase the number of negative charges in the framework and therefore the number of acidic sites. SAPO molecular sieves are normally synthesized by conventional hydrothermal (CHT) method. However, these SAPOs often suffer from poor crystallinity, low Si incorporation and the formation of large Si islands in the framework, resulting in low acidity and poor catalytic properties [4,14–16]. As a result, much effort has been devoted to developing methods that enhance Si incorporation, thus improving Si dispersal and enhancing acidity, including the use of new structure-directing agents (SDA) [17], novel synthesis methods (two-phase [18–20] and non-aqueous synthesis [4,21]) and modifying the pH of the synthesis gel [22].

The synthesis of porous materials from dry gel conversion (DGC) was first reported by Xu et al. [23]. DGC has many advantages over CHT, including minimizing waste water disposal, enhancing the efficiency of synthesis reactors and reducing the use of SDAs, resulting in lower production costs. Numerous molecular sieves, such as Beta [24], MAPOs [25–26], SAPOs [26], SBA-15 [27] and $AlPO_4$-11[28], have been synthesized by this approach. DGC can be classified into two types: steam-assisted conversion

* Corresponding author. Tel.: +86 532 86984710; fax: +86 532 86981787.
E-mail address: songchm@upc.edu.cn (C.-M. Song).

(SAC) and vapor-phase transport (VPT). In the SAC approach, prior to heating, the predried gel powder containing organic SDAs is placed in a sample holder located in the upper part of an antoclave while a very small amount of pure water which is physically separated from gel powder is added to the bottom of the autoclave, and the dry gel powder is converted to a zeolite in evaporated steam. The VPT method is similar to SAC except that the SDA is not contained in the initial dry gel; instead of pure water, a small amount of aqueous solution containing SDA is placed at the bottom of the autoclave, and the water and volatile organic template are simultaneously evaporated in an autoclave.

Previously, studies investigating the hydroisomerization performance of SAPO-11 synthesized by SAC and VPT have been rare. In this work, we report the synthesis of SAPO-11 molecular sieves by the SAC, VPT and CHT methods. The influence of drying temperature and SDA type on the synthesis of SAPO-11 by DGC was investigated, and the physico-chemical properties of all the samples were compared. n-Dodecane was used as a model long-chain n-paraffin reactant to evaluate the hydroisomerization activity of Pt/SAPO-11 catalysts obtained by the SAC and VPT methods.

2. Experimental

2.1. Preparation of catalysts

Pseudoboethmite (PB, 78.4 wt.% Al_2O_3), silica colloidal gel (40 wt% SiO_2), orthophosphoric acid (H_3PO_4, 85 wt%) were used as sources of Al, Si and P. Di-n-propylamine (DPA), di-ethylamine (DEA), di-butylamine (DBA) and di-isopropylamine (DIPA) were used as structure-directing agents (SDA).

In each synthesis, the typical hydrogel composition was $0.6SiO_2:1.0Al_2O_3:1.0P_2O_5:1.2SDA:50.0H_2O$. Samples synthesized by conventional hydrothermal (CHT), steam-assisted conversion (SAC) and vapor phase transport (VPT) methods are denoted as CHT, SAC and VPT, respectively. Details of those samples are presented in Table 1.

In a typical procedure for the synthesis of SAPO-11 by CHT, PB was first mixed with phosphoric acid and distilled water and stirred for 2 h. Then, SDA was added and the mixture was stirred for another 2 h. Finally, Silica colloidal gel was added and this mixture was stirred continuously for 2 h. The final hydrogel was transferred into a stainless-steel autoclave and heated at 473 K for 48 h.

In the SAC method, the hydrogel was prepared as described above for CHT; the resulting hydrogel was dried at different temperatures (353 K, 373 K, 393 K and 413 K) for 12 h. Prior to heating, the predried gel powder containing organic SDA was placed in a sample holder located in the upper part of an autoclove while a very small amount of pure water which was physically separated from gel powder, is added to the bottom of the autoclave in the amount of 0.3 g H_2O per gram of dried gel. Finally, crystallization of the SAC was carried out at 473 K for 96 h.

In the VPT method, the hydrogel was similarly prepared as described for SAC, with the omission of SDA. The resulting hydrogel was dried at different temperatures (353 K, 373 K, 393 K and 413 K) for 12 h. The SDA was finally mixed with external bulk water and placed at the bottom of the autoclave, and SDA molecules were brought in contact with the dry-gel powder through the vapor phase. Crystallization was performed as described above for SAC.

The as-synthesized products were washed, dried at 393 K for 12 h and then calcined at 873 K for 24 h in order to completely remove the SDA. All Pt/SAPO-11 catalysts with 1.0 wt.% Pt were prepared by a wetness impregnation method using a Pt(NH$_3$)$_4$ Cl$_2$ solution.

Table 1
Synthesis details of samples obtained by different synthetic methods.

Sample	SDA	Synthesis parameters		Crystallinity
		Gel drying temperature (K)	Crystallization time (h)	
CHT[a]	DPA	/	48	SAPO-11(53%) + trace of AlPO$_4$-T
SAC[b]-1	DPA	353	96	SAPO-11(100%)
SAC-2	DPA	373	96	SAPO-11(95%)
SAC-3	DPA	393	96	SAPO-11(92%)
SAC-4	DPA	413	96	SAPO-11(96%)
SAC-5	DEA	353	96	SAPO-11(92%) + trace SAPO-5
SAC-6	DIPA	353	96	SAPO-11(92%) + trace SAPO-5
SAC-7	DBA	353	96	SAPO-11(92%) + trace SAPO-5
VPT[c]-1	DPA	353	96	SAPO-11(97%)
VPT-2	DPA	373	96	SAPO-11(93%)
VPT-3	DPA	393	96	SAPO-11(94%) + trace AlPO$_4$-T
VPT-4	DPA	413	96	SAPO-11(92%) + trace AlPO$_4$-T
VPT-5	DEA	353	96	SAPO-11(93%) + trace SAPO-5
VPT-6	DIPA	353	96	SAPO-11(96%) + trace SAPO-5
VPT-7	DBA	353	96	SAPO-11(89%) + trace SAPO-5

[a] Synthesized by CHT.
[b] Synthesized by SAC.
[c] Synthesized by VPT.

2.2. Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded on a Rigadu D/MAX-1400X diffractometer using CuK$_\alpha$ radiation ($\lambda = 0.15404$ nm) and Ni filter, operating at 40 kV, 40 mA and 2θ scanning speed of 5° min^{-1}. The relative crystallinities of the samples were calculated by summing the areas of the peaks in the 2θ range from 20° to 23°. X-ray fluorescence (XRF) analysis was performed on a Philips Magix X X-ray fluorescence apparatus. Surface areas and pore distributions were determined on a Micromeritics ASAP 2910 physical analyzer by N_2 adsorption (77 K). Microporous distributions were determined by the HK method, and the external surface areas of the samples were calculated by the t-plot method. The morphology of the products was examined using a Philips XL30E scanning electron microscope (SEM).

H_2–O_2 titration experiments for measuring the dispersion of Pt/SAPO-11 were carried out in a pulsed system with Ar as the carrier gas and a TCD detector. H_2 (or O_2) was injected into the catalyst bed through a six-port valve with a sample loop. All the gases used were properly purified before use. IR spectra of desorbed pyridine were recorded on a Bruker IFS-88 IR spectrometer at a scanning range of 400–4000 cm^{-1}. Self-supporting IR wafers of about 10 mg/cm^2 were first evacuated in situ at 673 K for 1 h, then the spectra were recorded after cooling to room temperature. Pyridine was then admitted, and after equilibration the samples were degassed at 423, 523 and 623 K and their spectra were recorded. ^{29}Si solid NMR spectra were measured at room temperature on a Varian Infinityplus-400 spectrometer using 7.5 mm ZrO_2 rotors.