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A SAPO-11 Silicoaluminophosphate Molecular Sieve with Stable Crystal Structure

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Abstract: A SAPO-11 silicoaluminophosphate molecular sieve with stable crystal structure was synthesized for the first time. After removing template by calcination, its crystal space group still retains Icm2 which the as-synthesized has. The catalyst deriving from the present SAPO-11 materials shows higher isomerization selectivity and higher paraffin hydroisomerization yield than those reported elsewhere.

Keywords: SAPO-11, molecular sieve, crystal cell, hydroisomerization, catalyst.

The SAPO-11 molecular sieve shows potential applications in hydrocarbon isomerization due to its special pore structure and tunable acidity[1,2]. The aluminophosphate ($AlPO_4$-11) molecular sieve with AEL-type structure is a member of the aluminophosphate molecular sieve family[3], which belongs to the orthorhombic crystal system with space group Icm2, and the mono-dimensional pore size of its 10-member rings is 3.6×6.3Å. After removing amine (as template) by calcination, it still belongs to the orthorhombic crystal system, but its symmetry changes and the space group turns to $Pna2_1$[3,4]. The main difference is that the positions of the XRD peaks are apparently different from those before calcination[3], typically, with the disappearance of the diffraction peak at 2θ=21.00~21.20° and the appearance of the diffraction peak at 2θ=21.80~21.95°. SAPO-11 is a member of silicoaluminophosphate molecular sieve family[5], having the same structure and XRD pattern as $AlPO_4$-11 before calcination, but the calcined samples synthesized by different methods may exhibit different space groups. In most case, the space group is $Pna2_1$, as for $AlPO_4$-11, but a mixture of Icm2 and $Pna2_1$ has also been observed[5,6]. To our knowledge, the pure Icm2 space group phase after calcination has not yet been reported.

Here, for the first time we present the SAPO-11 molecular sieve with stable crystal structure having space group Icm2 after removing template by calcination, and it shows

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higher paraffin hydroisomerization selectivity and higher hydroisomers yield than those reported previously.

For the preparation of SAPO-11 molecular sieve with stable crystal structure, the mixed precursors were phosphoric acid (containing 85 wt% of H_3PO_4), hydrated alumina (*pseudo*-boehmite containing 72 wt% of Al_2O_3), silica sol (containing 26 wt% of SiO_2), di-*n*-propylamine (chemically pure) and diisopropylamine (chemically pure). Typical procedure: 145.3 g of phosphoric acid and 217.6 g of deionized water were added into a gelation autoclave heated in a water-bath at 35℃, and after stirring for 30 min, 99.2 g of hydrated alumina was added and stirred for 2 hours. Subsequently, 14.17 g of di-*n*-propylamine and 21.25 g of diisopropylamine were mixed to uniformity and then added into the aforesaid gelation autoclave, and the mixture was stirred for 2 hours. Finally, 66.62 g of silica sol was added and stirred thoroughly for 2 hours, thus a reaction mixture was prepared. We found that the gelation temperature is very important, which has not been mentioned in the literature. A part of the reaction mixture sealed in a stainless steel crystallization autoclave was heated at 160℃ for 24 hours under autogenous pressure. The crystallized product was then filtrated, washed and dried at 100~110℃ overnight to obtain the molecular sieve product as raw powder. A part of raw powder was detected by XRD (the apparatus is a Bruker 5005 model), and the results are coincident with the data (**Table 1**) from the reference[5]. This denotes that the synthesized molecular sieve is a molecular sieve having AEL structure.

Table 1 Typical X-ray diffraction data of as-synthesized SAPO-11[5]

2θ/°	d	$100\times I/I_o$*
8.05~8.15	10.97~10.84	w~m
9.40~9.50	9.40~9.30	m
13.10~13.25	6.75~6.68	m
15.65~15.85	5.66~5.59	m
20.35~20.55	4.36~4.32	m
21.00~21.20	4.23~4.19	vs
22.10~22.25	4.02~3.99	m
22.50~22.90(doublet)	3.99~3.88	m
23.10~23.35	3.85~3.81	m~s

*w~m: <20; m: 20~70; s: 70~90; vs: 90~100

Table 2 X-ray diffraction data of calcined SAPO-11 synthesized by the present method

2θ/°	d	$100\times I/I_o$
8.08	10.93	78.3
9.50	9.30	76.4
13.09	6.76	38.2
13.79	6.42	14.3
15.76	5.62	61.1
20.29	4.37	39.0
21.22	4.18	100
22.24(doublet)	3.99	54.3
22.89(doublet)	3.88	46.0
23.31	3.81	55.7
24.48	3.36	13.6

Table 3 Hydroisomer results of n-C_8° over Pd/SAPO-11 at 350 ℃*

Catalyst No.	Space group of calcined SAPO-11	Conversion /%	i-C_8° Yield/%	i-C_8° Selectivity/%
A	Icm2	42.83	39.84	93.0
B	$Pna2_1$	50.62	33.51	66.2

*Reaction conditions: 0.10 g catalyst, 0.5 μL n-octane, 30 mL · min^{-1} carrier gas (H_2), product was determined by on-line GC analysis.

Another part of raw powder was heated in a muffle furnace at 550℃ for 3 hours, and then cooled automatically in air to room temperature. The XRD data of calcined sample are shown in Table 2. It can be seen that the diffraction peaks' position is coincident with the data listed in Table 1, suggesting that the structure of the molecular sieve substantially remains unchanged after calcination, that is, it still retains the space group Icm2. The molar composition of the molecular sieve after calcination was Al2O3:0.83P2O5: 0.55SiO2 (detected by 3013 model X-ray fluorescence spectroscopy).

Catalysts loaded with 0.56 wt% of Pd, using saturated impregnation with a Pd-$[NH_3]_4Cl_2$ solution, were crushed to 20~40 mesh particles. The catalytic activity for paraffin hydroisomerization was evaluated on a pulse microreaction[7,8] using n-octane as reactant. The catalyst containing SAPO-11 obtained by the present method was denoted as A (**Table 3**). The comparative catalyst containing SAPO-11 synthesized by the previous method[5] was denoted as B (**Table 3**), which has the molar composition of Al_2O_3:$0.86P_2O_5$:$0.51SiO_2$. The target products were the hydroisomers of C_8° (i-C_8°). The results are listed in **Table 3**.

The results in **Table 3** showed that catalyst A, which was prepared from SAPO-11 whose structure remains unchanged after calcination, exhibits significantly higher selectivity and higher yield for paraffin hydroisomerization than catalyst B, which contains SAPO-11 that has different structure different from its precursor.

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