

SAPO-34 molecular sieve and method for preparing the same

Technical Field

The present invention belongs to the field of SAPO molecular sieves, and specifically concerns a SAPO-34 molecular sieve containing the template agent of diisopropylamine, and hydrothermal method for preparing the same.

Background

In 1982, a series of novel silicoaluminophosphate SAPO molecular sieves were successfully synthesized by the Union Carbide Corporation, which was disclosed in patent US 4310440. Since then silicoaluminophosphate molecular sieve and its heteroatom-substituted derivatives have been one research focus in the field of materials and catalysis. Among these molecular sieves, silicoaluminophosphate SAPO-34 molecular sieve with CHA type framework has shown an excellent catalytic performance in methanol to olefins (MTO) process, due to its proper acidity and pore structure (Applied Catalysis, 1988, 40: 316).

SAPO-34 is a molecular sieve with chabazite-type framework containing 8-member ring ellipsoidal cage and 3-dimensional channel, which is formed by stacking of double six-rings according to ABC sequence. SAPO-34 is microporous molecular sieve with a pore size of 0.38×0.38 nm and cage size of 1.0×0.67 nm. Space group of SAPO-34 is R3m belonging to trigonal crystal system (J. Phys. Chem., 1990, 94: 2730). SAPO-34 is formed by Si, Al, P and O whose composition change at some range, generally in the order of $n(\text{Si}) < n(\text{P}) < n(\text{Al})$.

SAPO-34 molecular sieve is generally produced by a hydrothermal synthesis process which uses water as the solvent and is conducted in a sealed autoclave. The components for the synthesis comprise an aluminum source, a silicon source, a phosphorus source, a structural-directing agent and deionized water. The silicon source may be chosen from silica sol, active silica and orthosilicate ester. The aluminum source may be chosen from active alumina, pseudoboehmite and alkoxy aluminum. Preferable silicon source and aluminum source are silica sol and pseudoboehmite. Phosphorus source is generally 85% phosphoric acid. The structural-directing agent partly affects the microstructure, elemental composition, morphology of synthesized molecular sieve, thus producing an impact on the catalytic performance of synthesized molecular sieve. Preparation methods of multiple SAPO molecular sieves have been reported in US 4310440 and US 4440871, and the template agents used to synthesize SAPO-34 were tetraethyl ammonium hydroxide, isopropylamine, and a mixture of tetraethyl ammonium hydroxide and dipropylamine. A method for preparing SAPO-34 molecular sieve was published in Chinese patent ZL93112230 using triethylamine with low price as the temple agent, reducing the cost of synthesis. Hereafter, methods for preparing SAPO-34 molecular sieve were published in Chinese patent ZL93112015 and ZL94110059 using diethylamine and a mixture of diethylamine and triethylamine respectively, further reducing the cost of synthesis.

A method for preparing SAPO-34 molecular sieve was published in Chinese patent CN1131845C using multiple temple agents containing diisopropylamine. A method for preparing SAPO molecular sieves was published in international patent WO 03/040037A1 via a dry process of solid precursor, in which it was mentioned that diisopropylamine could be used as a template agent, and the product was uncertainly describe as SAPO molecular sieves, including SAPO-34 molecular sieve. It is worth noting that although the template agents included diisopropylamine, diisopropylamine was used as a template agent in none of above patent examples .

Usually, with the increase of Si content in SAPO molecular sieves, the Si coordination structures change from Si(4Al) to Si(nAl) (n=0 to 4) (in different kind of SAPO molecular sieves, the allowable maximum of single Si distribution in the frameworks are different, seeing *J. Phys. Chem.*, 1994, **98**, 9614). The Si coordination structures have significant effect on the acid density and the acid intensity, and the acid intensity is enhanced in the order of Si(1Al) > Si(2Al) > Si(3Al) > Si(4Al). In the other hand, the amount of acid center produced by each Si atom decrease with the appearance of Si islands in the framework of SAPO molecular sieves (Si(4Al) is 1, and the others are less 1), leading to the decrease of the acid density. It is supposed that using the SAPO molecular sieves as the acid catalyst, the catalytic performance must be effected by the distribution of Si in the framework since the non-uniform distribution of Si in crystal bring the non-uniform distribution of acidity. The enrichment of Si on the surface of crystal indicates that the Si coordination structures on the surface of crystal are more complex than inside the crystal. Weckhuysen et al have reported that in the process of methanol to olefin (MTO), reaction firstly occurs near the surface of crystal, and with the reaction going on, the large coke species form and block the pores progressively, making the diffusion of the products inside the crystal more difficult (*Chemistry - A European Journal*, 2008, **14**, 11320-11327; *J. Catal.*, 2009, **264**, 77-87). It indicates that the acid environment on the surface of crystal is very important to the catalytic performance, and it is significant to seek a control method of the degree of Si enrichment on the molecular sieve surfaces.

Disclosure

An object of the present invention is to provide a SAPO-34 molecular sieve containing template agent diisopropylamine. The chemical composition in the anhydrous state of said molecular sieve is expressed as: $m\text{DIPA} \cdot (\text{Si}_x\text{Al}_y\text{P}_z)\text{O}_2$; wherein, DIPA is diisopropylamine existing in cages and pore channels of said molecular sieve; m is the molar number of diisopropylamine per one mole of $(\text{Si}_x\text{Al}_y\text{P}_z)\text{O}_2$, and m is from 0.03 to 0.25; x, y, z respectively represents the molar number of Si, Al, P, and x is from 0.01 to 0.30, and y is from 0.40 to 0.60, and z is from 0.25 to 0.49, and $x + y + z = 1$. There is a slight Si enrichment phenomenon on the crystal surface of said molecular sieve crystal, and the ratio of the surface Si content to the bulk Si content of the crystal ranges from 1.48 to 1.01; wherein the Si content is calculated by the molar ratio of $\text{Si}/(\text{Si}+\text{Al}+\text{P})$.

In X-ray diffraction spectrogram of said SAPO-34 molecular sieve, the diffraction peaks are included shown in Table 2. There is a slight Si enrichment phenomenon on the crystal surface of said molecular sieve crystal, and the ratio of the surface Si content to the bulk Si content of the crystal ranges from 1.48 to 1.01, preferably ranges from 1.42 to 1.02, further preferably ranges from 1.36 to 1.03, and more further preferably ranges from 1.33 to 1.03; wherein the Si content is calculated by the molar ratio of $\text{Si}/(\text{Si}+\text{Al}+\text{P})$. The Si contents from core to shell of said molecular sieve crystals increase uniformly or non-uniformly.

Another object of the present invention is to provide a method for preparing SAPO-34 molecular sieve. Another object of the present invention is to provide a SAPO-34 molecular sieve prepared using the above method and catalysts prepared from the same for acid-catalyzed reaction or an oxygenate to olefins reaction.

The technical problem to be solved in the present invention is that the SAPO-34 molecular sieve with high purity is hydrothermally prepared directly using diisopropylamine as the template agent, and selecting the silicon source, the aluminum source, and the phosphorus source from traditional ingredients. There is a slight Si enrichment phenomenon on the crystal surface of said molecular sieve

crystal, and the ratio of the surface Si content to the bulk Si content of the crystal ranges from 1.48 to 1.01; wherein the Si content is calculated by the molar ratio of $\text{Si}/(\text{Si}+\text{Al}+\text{P})$. Through experimental research, the inventors of the present invention found that the degree of Si enrichment on the molecular sieve surfaces can be decreased by adding a surfactant.

The present invention provides a hydrothermal method for preparing said SAPO-34 molecular sieve.

The present invention reports said method for preparing SAPO-34 molecular sieve, characterized in including the steps as follows:

(a) a silicon source, an aluminum source, a phosphorus source, a surfactant BM, deionized water and structural-directing agent DIPA are mixed, and an initial gel mixture with following molar ratio is obtained:

$\text{SiO}_2/\text{Al}_2\text{O}_3$ is from 0.05 to 1.5;

$\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$ is from 0.5 to 1.5;

$\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ is from 16 to 150;

$\text{DIPA}/\text{Al}_2\text{O}_3$ is from 2.0 to 5.9;

$\text{BM}/\text{Al}_2\text{O}_3$ is from 0.001 to 0.05;

(b) the initial gel mixture obtained in said step (a) is transferred into a synthetic kettle, then sealed and heated to crystallization temperature range from 150°C to 220°C , crystallized for crystallization time range from 0.5h to 72h under an autogenous pressure;

(c) after finishing the crystallization, the solid product is centrifugal separated, washed to neutral using deionized water and dried to obtain said SAPO-34 molecular sieve;

wherein, said structural-directing agent DIPA is diisopropylamine; said surfactant BM is alkyl ammonium halide.

In said step (a), the silicon source is one or more selected from silica sol, active silica, orthosilicate esters and metakaolin; the aluminum source is one or more selected from aluminum salts, activated alumina, aluminum alkoxide and metakaolin; the phosphorus source is one or more selected from phosphoric acid, diammonium hydrogen phosphate, ammonium dihydrogen phosphate, organophosphorous compounds and phosphorus oxides.

Said surfactant BM is alkyl ammonium halide. Preferably said surfactant BM is one or more selected from dodecyl trimethyl ammonium chloride, tetradecyl trimethyl ammonium chloride, hexadecyl trimethyl ammonium chloride, octadecyl trimethyl ammonium chloride, dodecyl trimethyl ammonium bromide, tetradecyl trimethyl ammonium bromide, hexadecyl trimethyl ammonium bromide, octadecyl trimethyl ammonium bromide.

In the initial gel mixture obtained in said step (a), the preferable molar ratio of $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ is from 26 to 120, and further preferably the molar ratio of $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ is from 31 to 100.

In the initial gel mixture obtained in said step (a), the molar ratio of $\text{SDA}/\text{Al}_2\text{O}_3$ is from 3.0 to 5.0.

In the initial gel mixture obtained in said step (a), the molar ratio of $\text{CGP}/\text{Al}_2\text{O}_3$ is from 0.001 to 0.03.

In said step (b), preferably the crystallization condition are the crystallization temperature range from 170°C to 210°C and the crystallization time range from 1h to 60h; and further preferably the crystallization condition are the crystallization temperature range from 180°C to 210°C and the crystallization time range from 1h to 24h; and more further preferably the crystallization condition are the crystallization temperature range from 190°C to 210°C and the crystallization time range from 1h to 12h.

In said step (b), the crystallization is carried out dynamically or statically.

The SAPO-34 molecular sieves prepared by said methods can be used as catalysts for acid-catalyzed reaction after calcining at a temperature from 400 to 700 °C in air.

The SAPO-34 molecular sieves prepared by said methods can be used as catalysts for an oxygenate to olefins reaction after calcining at a temperature from 400 to 700 °C in air.

The present invention also refers to a catalyst for acid-catalyzed reaction, which is obtained by calcining at least one of said SAPO-34 molecular sieves or at least one of the SAPO-34 molecular sieves prepared by said methods, at a temperature from 400 to 700 °C in air.

The present invention also refers to a catalyst for an oxygenate to olefins reaction, which is obtained by calcining at least one of said SAPO-34 molecular sieves or at least one of the SAPO-34 molecular sieves prepared by said methods, at a temperature from 400 to 700 °C in air.

The present invention can bring the advantages including:

(1) obtaining a SAPO-34 molecular using diisopropylamine as the template agent, characterized in a slight Si enrichment phenomenon on the crystal and with the ratio of the surface Si content to the bulk Si content of the crystal ranging from 1.48 to 1.01.

(2) the SAPO-34 molecular sieves prepared by said methods in present invention having excellent catalytic performance in the MTO reaction and ethanol dehydration reaction.

Brief Description of the Drawings

Figure 1 is a scanning electron microscope image of the sample prepared in Example 1.

Specific Embodiments of the invention

The present invention will be described in details by Examples, but the present invention is not limited to these Examples.

In Examples, abbreviations are used as follows:

Diisopropylamine is abbreviated as DIPA; dodecyl trimethylammonium bromide is abbreviated as DTAB; tetradecyl trimethylammonium bromide is abbreviated as TTAB; cetyl trimethylammonium bromide is abbreviated as CTAB; octadecyl trimethylammonium bromide is abbreviated as OTAB; dodecyl trimethylammonium chloride is abbreviated as DTAC; tetradecyl trimethylammonium chloride is abbreviated as TTAC; cetyl trimethylammonium chloride is abbreviated as CTAC; octadecyl trimethylammonium chloride is abbreviated as OTAC.

The elemental analysis of the bulk composition was determined with X-ray Fluorescence (XRF) at PANalytical X'Pert PRO X-ray diffractometer with Cu target ($\lambda=0.15418$ nm), operated at 40KV and 100mA.

The elemental analysis of the surface composition was determined with X-ray photoelectron spectroscopy at Thermo ESCALAB 250Xi X-Ray Photoelectron Spectrometer (Mono AlK α X-ray source) using Al2p=74.7eV of Al₂O₃ in sample surface as internal standard to calibrate charge of sample surface.

Example 1

The amount of ingredients and the crystallization condition were shown in Table 1. The synthesis process was as follows: 14.06g of pseudoboehmite (with Al₂O₃ mass percent of 72.5%) and 90g of deionized water mixing homogeneously by stirring, and then 23.0g of phosphoric acid (with H₃PO₄ mass percent of 85%) was added by droplets and stirred to smooth, and then 6.4g of silica sol (with

SiO₂ mass percent of 30%) and 1.09g cetyl trimethyl ammonium bromide (CTAB) were added, and then 30.4g of diisopropylamine (abbreviated as DIPA, with a mass percent of 99%) was added into the mixture to obtain an initial gel mixture with the molar ratio of 3.0DIPA: 0.30SiO₂:1Al₂O₃:1P₂O₅:0.03CTAB:50H₂O. The initial gel mixture was transferred into a stainless steel synthetic kettle.

The synthetic kettle was heated to 200°C, dynamically crystallized for 24h. After finishing the crystallization, the solid product was centrifugal separated, washed and dried at 100°C in air to obtain 27.6g of raw powder sample. The sample was detected with XRD and XRD data were shown in Table 2, indicating that the sample prepared was SAPO-34 molecular sieve. The scanning electron microscope image of the sample was illustrated in Figure 1.

The elemental analysis of the surface composition and the bulk composition of the sample were detected with XPS and XRF, respectively. The ratio of the surface Si content to the bulk Si content was shown in Table 1. The bulk composition of the sample obtained in Example 1 was Al_{0.49}P_{0.43}Si_{0.08}.

The organic content of the sample obtained in Example 1 was detected with CHN analyzer, indicating the molar ratio of C/N was 6.01. The chemical compositions of the raw powder of molecular sieve were obtained by normalization of CHN and XRF results, which was 0.08DIPA·(Si_{0.08}Al_{0.49}P_{0.40})O₂.

The raw powder sample was detected with ¹³C MAS NMR analysis, and the result showed that only the characteristic ¹³C resonance of DIPA was observed without any characteristic ¹³C resonance of CTAB observed, indicating CTAB didn't enter into the final product.

Table 1: The list of amount of ingredients and crystallization conditions of the molecular sieves*

Example	Molar amount of DIPA	Aluminum source and molar amount of Al ₂ O ₃ thereof	Phosphorus source and molar amount of P ₂ O ₅ thereof	Silicon source and molar amount of SiO ₂ thereof	H ₂ O	BM and molar amount thereof	Crystallization Temperature	Crystallization Time	Si _{surface} /Si _{bulk}
1	0.3mol	pseudoboehmite 0.1mol	phosphoric acid 0.10mol	silica sol 0.03mol	5.0 mol	CTAB 0.003mol	200 °C	24h	1.06
2	0.59mol	aluminium isopropoxide 0.1mol	phosphoric acid 0.10mol	silica sol 0.005mol	1.6 mol	DTAB 0.0001mol	150 °C	48h	1.01
3	0.12mol	kaolinite 0.1mol	phosphoric acid 0.10mol	silica sol 0.15mol	15 mol	OTAB 0.001mol	180 °C	24h	1.29
4	0.18mol	γ-alumina 0.1mol	phosphoric acid 0.10mol	silica sol 0.12mol	8.3 mol	TTAB 0.005mol	200 °C	24h	1.48
5	0.5mol	aluminum sulfate 0.1mol	phosphoric acid 0.05mol	active silica 0.03mol	2.6 mol	CTAC 0.002mol	190 °C	12h	1.42
6	0.3mol	aluminium chloride 0.1mol	phosphoric acid 0.12mol	ethyl orthosilicate 0.08mol	12 mol	DTAC 0.003mol	200 °C	24h	1.25
7	0.033 mol	pseudoboehmite 0.1mol	phosphoric acid 0.09mol	silica sol 0.03mol	3.1 mol	OTAC 0.004mol	200 °C	24h	1.33
8	0.08mol	metakaolin 0.1mol	phosphoric acid 0.15mol	silica sol 0.05mol	10 mol	TTAC 0.002mol	200 °C	24h	1.36
9	0.26mol	pseudoboehmite 0.1mol	ammonium dihydrogen phosphate 0.10mol	silica sol 0.06mol	6.6 mol	OTAC 0.001mol	220 °C	0.5h	1.03
10	0.2mol	pseudoboehmite 0.1mol	diammonium hydrogen phosphate 0.10mol	metakaolin 0.06mol	5.2 mol	CTAC 0.0009mol	200 °C	24h	1.12
11	0.2mol	aluminum sulfate 0.1mol	diammonium hydrogen	silica sol 0.07mol	8.8 mol	DTAC 0.002mol	200 °C	18h	1.18

			phosphate 0.15mol						
12	0.3mol	pseudoboehmite 0.1mol	diammonium hydrogen phosphate 0.12mol	silica sol 0.12mol	6.5 mol	CTAB 0.002mol	180 °C	24h	1.27
13	0.4mol	pseudoboehmite 0.1mol	phosphoric anhydride 0.13mol	metakaolin 0.03mol	12 mol	DTAB 0.003mol	210 °C	1h	1.22
14	0.39mol	pseudoboehmite 0.1mol	phosphoric acid 0.10mol	silica sol 0.03mol	4.5 mol	OTAB 0.004mol	190 °C	12h	1.45
15	0.39mol	aluminum nitrate 0.1mol	phosphoric acid 0.10mol	tetramethyl orthosilicate 0.03mol	6.5 mol	TTAB 0.003mol	150 °C	72h	1.40
16	0.30mol	pseudoboehmite 0.1mol	trimethyl phosphine 0.10mol	silica sol 0.03mol	6.5 mol	CTAB 0.003mol	210 °C	5h	1.33
17	0.35mol	pseudoboehmite 0.1mol	triethyl phosphine 0.10mol	silica sol 0.03mol	6.5 mol	DTAB 0.003mol	170 °C	60h	1.12
18	0.24mol	pseudoboehmite 0.1mol	phosphoric acid 0.10mol	silica sol 0.03mol	5.0 mol	CTAB 0.002mol +OTAB 0.001mol	200 °C	24h	1.10
19	0.25mol	pseudoboehmite 0.1mol	phosphoric acid 0.10mol	silica sol 0.03mol	5.0 mol	CTAB 0.001mol +CTAC 0.001mol +DTAB 0.001mol	200 °C	24h	1.08

Table2: XRD result of the sample obtained in Example 1

No.	2 θ	d(Å)	100× I/I ₀
1	9.5177	9.29267	100
2	12.7987	6.91689	19.92
3	14.1388	6.26416	13.11
4	15.9829	5.5453	50.04
5	18.1242	4.89469	22.4
6	20.5413	4.32386	84.84
7	22.278	3.99057	6.09
8	23.0981	3.85071	4.97
9	25.3853	3.50871	23.15
10	25.7835	3.45542	18.75
11	27.5448	3.23834	3.71
12	28.5382	3.12783	2.09
13	29.5454	3.02346	5.07
14	30.4947	2.93147	25.16
15	31.3812	2.85065	18.51
16	34.3501	2.61076	6.33
17	36.4789	2.46314	2.67
18	39.6546	2.2729	3.18
19	43.4168	2.08427	5.1
20	47.4822	1.91487	2.79
21	49.1405	1.85407	5.48
22	50.4542	1.80883	3.22
23	51.1735	1.78508	3.43
24	53.0514	1.72624	2.25

25	53.9912	1.69839	1.01
26	54.7895	1.67552	1.62
27	55.7846	1.64797	2.24
28	56.4017	1.63139	1.57
29	59.6235	1.55071	0.97
30	60.8263	1.52163	1.28

Examples 2 to 17

The amount of ingredients and the crystallization conditions were shown in Table 1, and the synthesis processes were the same as Example 1.

The samples were detected with XRD. XRD data of samples were similar to Table 2, which showed that each corresponding peak had the same peak position and the $\pm 10\%$ difference of peak intensity, indicating the samples prepared were SAPO-34 molecular sieves.

The elemental analysis of the surface composition and the bulk composition of the sample were detected with XPS and XRF, and the ratios of the surface Si content to the bulk Si content were shown in Table 1.

The raw powder samples obtained in Examples 2 to 17 were detected with CHN elemental analysis respectively, and the results showed that the ratios of C/N fluctuated at a range of 6.0 ± 0.05 . The chemical compositions of the raw powders of molecular sieves were obtained by normalization of CHN and XRF results, which were $0.25\text{DIPA} \cdot (\text{Si}_{0.01}\text{Al}_{0.50}\text{P}_{0.49})\text{O}_2$, $0.04\text{DIPA} \cdot (\text{Si}_{0.30}\text{Al}_{0.45}\text{P}_{0.25})\text{O}_2$, $0.06\text{DIPA} \cdot (\text{Si}_{0.25}\text{Al}_{0.40}\text{P}_{0.35})\text{O}_2$, $0.20\text{DIPA} \cdot (\text{Si}_{0.09}\text{Al}_{0.47}\text{P}_{0.44})\text{O}_2$, $0.10\text{DIPA} \cdot (\text{Si}_{0.15}\text{Al}_{0.45}\text{P}_{0.40})\text{O}_2$, $0.03\text{DIPA} \cdot (\text{Si}_{0.10}\text{Al}_{0.48}\text{P}_{0.42})\text{O}_2$, $0.05\text{DIPA} \cdot (\text{Si}_{0.13}\text{Al}_{0.45}\text{P}_{0.42})\text{O}_2$, $0.07\text{DIPA} \cdot (\text{Si}_{0.10}\text{Al}_{0.49}\text{P}_{0.41})\text{O}_2$, $0.07\text{DIPA} \cdot (\text{Si}_{0.15}\text{Al}_{0.50}\text{P}_{0.35})\text{O}_2$, $0.08\text{DIPA} \cdot (\text{Si}_{0.07}\text{Al}_{0.60}\text{P}_{0.33})\text{O}_2$, $0.08\text{DIPA} \cdot (\text{Si}_{0.08}\text{Al}_{0.49}\text{P}_{0.43})\text{O}_2$, $0.12\text{DIPA} \cdot (\text{Si}_{0.09}\text{Al}_{0.49}\text{P}_{0.42})\text{O}_2$, $0.09\text{DIPA} \cdot (\text{Si}_{0.09}\text{Al}_{0.47}\text{P}_{0.44})\text{O}_2$ and $0.10\text{DIPA} \cdot (\text{Si}_{0.10}\text{Al}_{0.50}\text{P}_{0.40})\text{O}_2$, respectively.

The raw powder samples obtained in Examples 2 to 17 were detected with ^{13}C MAS NMR analysis respectively, only the characteristic ^{13}C resonance of DIPA was observed without any characteristic ^{13}C resonance of surfactant BM which had been added observed, indicating surfactant BM which had been added didn't enter into the final products.

Example 18

The amount of ingredients and the crystallization conditions were shown in Table 1, and the synthesis process was the same as Example 1, except that the crystallization is carried out statically and the surfactant BM was changed to a mixture of CTAB and OTAB. The sample was detected with XRD. XRD data of sample were similar to Table 2, which showed that each corresponding peak had the same peak position and the $\pm 10\%$ difference of peak intensity, indicating the sample prepared was SAPO-34 molecular sieve.

The elemental analysis of the surface composition and the bulk composition of the sample were detected with XPS and XRF, and the ratios of the surface Si content to the bulk Si content were shown in Table 1.

The raw powder sample obtained in Example 18 was detected with CHN elemental analysis respectively, and the result showed that the ratio of C/N was 5.95. The chemical compositions of the raw powders of molecular sieves were obtained by normalization of CHN and XRF results, which was $0.08\text{DIPA} \cdot (\text{Si}_{0.08}\text{Al}_{0.49}\text{P}_{0.43})\text{O}_2$.

The raw powder sample obtained in Example 18 was detected with ^{13}C MAS NMR analysis

respectively, only the characteristic ^{13}C resonance of DIPA was observed without any characteristic ^{13}C resonances of CTAB or OTAB observed, indicating CTAB or OTAB didn't enter into the final product.

Example 19

The amount of ingredients and the crystallization conditions were shown in Table 1, and the synthesis process was the same as Example 1, except that the crystallization is carried out statically and the surfactant was changed to a mixture of CTAB, CTAC and DTAB. The sample was detected with XRD. XRD data of sample were similar to Table 2, which showed that each corresponding peak had the same peak position and the $\pm 10\%$ difference of peak intensity, indicating the sample prepared was SAPO-34 molecular sieve.

The raw powder sample obtained in Example 18 was detected with CHN elemental analysis respectively, and the result showed that the ratio of C/N was 5.99. The chemical compositions of the raw powders of molecular sieves were obtained by normalization of CHN and XRF results, which was $0.09\text{DIPA} \cdot (\text{Si}_{0.08}\text{Al}_{0.50}\text{P}_{0.42})\text{O}_2$.

The raw powder sample obtained in Example 19 was detected with ^{13}C MAS NMR analysis respectively, only the characteristic ^{13}C resonance of DIPA was observed without any characteristic ^{13}C resonances of CTAB, CTAC or DTAB observed, indicating CTAB, CTAC or DTAB didn't enter into the final product.

Example 20

3g of the samples obtained in Examples 1 to 19 respectively, were put into plastic beaker, adding 3ml of 40% hydrofluoric acid to dissolve the framework of molecular sieve under ice-bath condition, and then adding 15ml of tetrachloromethane to dissolve the organic compounds. The organic compounds were analyzed with GC-MS. The results indicated that the organic compound in the samples obtained in Examples 1 to 19 all was diisopropylamine.

Example 21

The sample obtained in Example 1 was immobilized using epoxy resin and polished at a glazing machine. The composition analysis from the core to the shell was detected with SEM-EDX linear scanning of the crystal section near the crystal core. The result indicated that the atomic ratio of Si/Al near the core area of the crystal was about 0.14 and the atomic ratio of Si/Al near the surface area of the crystal was about 0.17.

The sample obtained in Example 11 (with the morphology of rhombic octahedron and the crystal size from $1\mu\text{m}$ to $5\mu\text{m}$ according to the SEM photo) was immobilized using epoxy resin and polished at a glazing machine. The composition analysis from the core to the shell was detected with SEM-EDX linear scanning of the crystal section near the crystal core. The result indicated that the atomic ratio of Si/Al near the core area of the crystal was about 0.16 and the atomic ratio of Si/Al near the surface area of the crystal was about 0.22.

Comparative Example 1 (without addition of a surfactant)

The amount of ingredients, the synthesis process and the crystallization conditions were the same as Example 1, except without addition of CTAB in the initial gel mixture. The sample was detected with XRD. XRD data of sample were similar to Table 2, which showed that each corresponding peak had the same peak position and the $\pm 10\%$ difference of peak intensity, indicating the sample prepared was

SAPO-34 molecular sieve. The relative crystallinity of the sample obtained in Comparative Example 1 was 90% of the sample obtained in Example 1 (defining the crystallinity of the sample obtained in Example 1 as 100%).

Relative crystallinity = $(I_1 + I_2 + I_3) \times 100\% / (I_1' + I_2' + I_3')$, wherein I_1 , I_2 and I_3 are the intensities of the three strongest diffraction peaks in X-ray diffraction spectrogram of the sample obtained in Comparative Example 1; I_1' , I_2' and I_3' are the intensities of the three strongest diffraction peaks in X-ray diffraction spectrogram of the sample obtained in Example 1.

The elemental analysis of the surface composition and the bulk composition of the sample were detected with XPS and XRF, respectively, showing that the ratio of the surface Si content to the bulk Si content $Si_{\text{surface}}/Si_{\text{bulk}}$ was 2.2.

Example 22

The sample obtained in Example 1 was calcined at 600°C for 4 hours in air, then pressed, crushed and sieved to 20-40 mesh. 5.0g of the sample was added into a batch reactor loaded 30mL of ethanol to carry out an ethanol dehydration evaluation. The reaction was carried out at 150°C under stirring. The result showed that ethanol conversion reached 90% and the selectivity for ether in products was 90%.

Example 23

The sample obtained in Example 1 was calcined at 600°C for 4 hours in air, then pressed, crushed and sieved to 20-40 mesh. 1.0g of a sample was weighted and loaded into a fixed bed reactor to carry out a methanol to olefins reaction evaluation. The sample was activated at 550°C for 1 hour in nitrogen gas and reduced to 450°C to perform a reaction. Methanol was carried by nitrogen gas with a flow rate of 40 mL/min and the Weight Hour Space Velocity of the methanol was 2.0 h⁻¹. The reaction products were analyzed by an on-line gas chromatograph (Varian3800, FID detector, capillary column was PorapLOT Q-HT). The results were shown in Table 3.

Table 3: The result of methanol to olefins on the sample

Sample	Life (min)	Selectivity (mass%) *							
		CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄ ⁺	C ₅ ⁺	C ₂ H ₄ +C ₃ H ₆
Example 1	206	1.2	51.0	0.64	37.2	0.64	7.3	1.2	88.2

* The highest (ethylene + propylene) selectivity when methanol conversion was 100%.

Comparative Example 2

The sample obtained in Comparative Example 1 was calcined at 600°C for 4 hours in air, then pressed, crushed and sieved to 20-40 mesh. 1.0g of a sample was weighted and loaded into a fixed bed reactor to carry out a methanol to olefins reaction evaluation. The sample was activated at 550°C for 1 hour in nitrogen gas and reduced to 450°C to perform a reaction. Methanol was carried by nitrogen gas with a flow rate of 40 mL/min and the Weight Hour Space Velocity of the methanol was 2.0 h⁻¹. The reaction products were analyzed by an on-line gas chromatograph (Varian3800, FID detector, capillary column was PorapLOT Q-HT). The results were shown in Table 4.

Table 4: The result of methanol to olefins on the sample

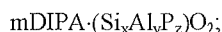
Sample	Life	Selectivity (mass%) *
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	(min)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4^+	C_5^+	$\text{C}_2\text{H}_4 + \text{C}_3\text{H}_6$
Example 1	106	1.37	41.14	0.50	38.60	1.23	12.07	3.97	80.6

* The highest (ethylene + propylene) selectivity when methanol conversion was 100%.

Claims

1. A SAPO-34 molecular sieve whose chemical composition in the anhydrous state is expressed as:



wherein, DIPA is diisopropylamine existing in cages and pore channels of said molecular sieve; m is the molar number of diisopropylamine per one mole of $(\text{Si}_x\text{Al}_y\text{P}_z)\text{O}_2$, and m is from 0.03 to 0.25;

x, y, z respectively represents the molar number of Si, Al, P, and x is from 0.01 to 0.30, and y is from 0.40 to 0.60, and z is from 0.25 to 0.49, and $x + y + z = 1$.

2. A SAPO-34 molecular sieve according to claim 1, wherein in X-ray diffraction spectrogram of said SAPO-34 molecular sieve, the diffraction peaks are included as follows:

No.	2θ
1	9.5177
2	12.7987
3	14.1388
4	15.9829
5	18.1242
6	20.5413
7	22.278
8	23.0981
9	25.3853
10	25.7835
11	27.5448
12	28.5382
13	29.5454
14	30.4947
15	31.3812
16	34.3501
17	36.4789
18	39.6546
19	43.4168
20	47.4822
21	49.1405
22	50.4542
23	51.1735
24	53.0514
25	53.9912
26	54.7895
27	55.7846
28	56.4017
29	59.6235
30	60.8263

3. A SAPO-34 molecular sieve according to claim 1, wherein there is a slight Si enrichment phenomenon on the crystal surface of said molecular sieve crystal, and the ratio of the surface Si content to the bulk Si content of the crystal ranges from 1.48 to 1.01; wherein the Si content is calculated by the molar ratio of $\text{Si}/(\text{Si}+\text{Al}+\text{P})$.

4. A SAPO-34 molecular sieve according to claim 1, wherein the ratio of the surface Si content to the bulk Si content of the crystal ranges from 1.42 to 1.02, preferably ranges from 1.36 to 1.03, and further

preferably ranges from 1.33 to 1.03.

5. A SAPO-34 molecular sieve according to claim 1, wherein the Si contents from core to shell of said molecular sieve crystals increase uniformly.

6. A SAPO-34 molecular sieve according to claim 1, wherein the Si contents from core to shell of said molecular sieve crystals increase non-uniformly.

7. A method for preparing said SAPO-34 molecular sieve according to claim 1, including the steps as follows:

(a) a silicon source, an aluminum source, a phosphorus source, a surfactant BM, deionized water and structural-directing agent DIPA are mixed, and an initial gel mixture with following molar ratio is obtained:

$\text{SiO}_2/\text{Al}_2\text{O}_3$ is from 0.05 to 1.5;

$\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$ is from 0.5 to 1.5;

$\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ is from 16 to 150;

$\text{DIPA}/\text{Al}_2\text{O}_3$ is from 2.0 to 5.9;

$\text{BM}/\text{Al}_2\text{O}_3$ is from 0.001 to 0.05;

(b) the initial gel mixture obtained in said step (a) is transferred into a synthetic kettle, then sealed and heated to crystallization temperature range from 150°C to 220°C, crystallized for crystallization time range from 0.5h to 72h under an autogenous pressure;

(c) after finishing the crystallization, the solid product is separated, washed and dried to obtain said SAPO-34 molecular sieve;

wherein, said structural-directing agent DIPA is diisopropylamine; said surfactant BM is alkyl ammonium halide.

8. A method according to claim 7, wherein in said step (a), the silicon source is one or more selected from silica sol, active silica, orthosilicate esters and metakaolin; the aluminum source is one or more selected from aluminum salts, activated alumina, aluminum alkoxide and metakaolin; the phosphorus source is one or more selected from phosphoric acid, diammonium hydrogen phosphate, ammonium dihydrogen phosphate, organophosphorous compounds and phosphorus oxides.

9. A method according to claim 7, wherein in the initial gel mixture obtained in said step (a), the surfactant BM is one or more selected from dodecyl trimethylammonium chloride, tetradecyl trimethylammonium chloride, cetyl trimethylammonium chloride, octadecyl trimethylammonium chloride, dodecyl trimethylammonium bromide, tetradecyl trimethylammonium bromide, cetyl trimethylammonium bromide, octadecyl trimethylammonium bromide.

10. A method according to claim 7, wherein in the initial gel mixture obtained in said step (a), the molar ratio of $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ is from 26 to 120, and preferably the molar ratio of $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ is from 31 to 100.

11. A method according to claim 7, wherein in the initial gel mixture obtained in said step (a), the molar ratio of $\text{DIPA}/\text{Al}_2\text{O}_3$ is from 3.0 to 5.0.

12. A method according to claim 7, wherein in the initial gel mixture obtained in said step (a), the molar ratio of $\text{BM}/\text{Al}_2\text{O}_3$ is from 0.001 to 0.03.

13. A method according to claim 3, wherein in said step (b), the crystallization temperature ranges from 180°C to 210°C, and preferably the crystallization temperature ranges from 190°C to 210°C; the crystallization time ranges from 1h to 24h, and preferably the crystallization time ranges from 1h to 12h.

14. A method according to claim 7, wherein in said step (b), the crystallization is carried out statically.

15. A method according to claim 7, wherein in said step (b), the crystallization is carried out dynamically.
16. A catalyst for acid-catalyzed reaction, which is obtained by calcining at least one of said SAPO-34 molecular sieves according to claims from 1 to 6 or at least one of the SAPO-34 molecular sieve prepared by said methods according to claims from 7 to 14, at a temperature from 400 to 700 °C in air.
17. A catalyst for an oxygenate to olefins reaction, which is obtained by calcining at least one of said SAPO-34 molecular sieves according to claims from 1 to 6 or at least one of the SAPO-34 molecular sieves prepared by said methods according to claims from 7 to 14, at a temperature from 400 to 700 °C in air.