

SAPO-34 molecular sieve and method for preparing the same

Technical Field

The present invention concerns a silicoaluminophosphate molecular sieve with the CHA framework, and method for preparing the same, and applications of the same in acid catalyzed reaction and an oxygenate to olefins reaction.

Background

In 1984, a series of novel silicoaluminophosphate SAPO molecular sieves were developed in the Union Carbide Corporation (UCC) (USP 4440871). SAPO molecular sieves are crystallized silicoaluminophosphates with three dimensional frameworks formed by PO_2^+ , AlO_2^- , and SiO_2 tetrahedrons. Among this kind of molecular sieves, SAPO-34 with chabazite-type framework contains 8-member ring pore, wherein the orifice size is $0.38 \text{ nm} \times 0.38 \text{ nm}$. SAPO-34 has attracted attention because it has shown the excellent catalytic performance in methanol to olefins (MTO) process, due to its proper acidity and pore structure.

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 template agent, and deionized water. The silicon source may be chosen from silica sol, active silica, and orthosilicate esters. The aluminum source may be chosen from active alumina, pseudo boehmite, or alkoxy aluminum. Preferable silicon source and aluminum source are silica sol and pseudo boehmite. Phosphorus source is generally 85% phosphoric acid. The template agent commonly used comprises tetraethyl ammonium hydroxide (TEAOH), morpholine (MOR), piperidine, isopropylamine ($i\text{-PrNH}_2$), triethylamine (TEA), diethylamine (DEA), dipropylamine, and the like, or a mixture thereof. In the traditional hydrothermal synthesis of SAPO-34, the molar amount of the organic amine template agent used is significantly less than the molar amount of water. Water is used as the continuous phase and the main solvent, and the molar ratio of water to organic amine template agent is generally larger than 10. In our research on hydrothermal synthesis process of SAPO-34 using diethylamine as the template agent, we found that with the amount increase of the template agent gradually, both of the product yield and crystallinity decrease to some degrees, seeing Table 1 in *Microporous and Mesoporous Materials*, 2008, 114(1-3): 4163.

Concerning the synthesized SAPO molecular sieves, several researchers have reported there is a Si enrichment phenomenon on the crystal surface. The reason is that the initial reaction mixtures to produce SAPO molecular sieves are acid or nearly neutral, and with the proceeding of crystallization, the pH values of the initial reaction mixtures rise gradually because the consumption of phosphoric acid which enters into molecular sieves. In the beginning of crystallization, the silicon source exists generally in the form of polymers. Because of the low isoelectric point, the silicon source decomposes by degrees with the rise of pH value, making the proportion of silicon entering in the framework of SAPO molecular sieves increase, leading to the Si enrichment phenomenon on the crystal surface. For instance, in our research on hydrothermal synthesis process of SAPO-34 using diethylamine as the template agent, we found that a non-uniform distribution of Si in the crystal shows a gradual increase of the Si content from the core to the surface, and the ratio of the Si content (molar ratio $\text{Si}/(\text{Si}+\text{Al}+\text{P})$) on the surface to the Si content in the crystal bulk is 1.41 (*Microporous and Mesoporous Materials*, 2008, 114(1-3): 4163). Akolekar et al found that in the SAPO-44 crystal, the molar ratio of the Si content (molar ratio

Si/(Si+Al+P)) on the surface to the Si content in the crystal bulk is from 6 to 10 (*Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 146 (1999) 375–386). In general, SAPO molecular sieves show the character of an obvious Si enrichment phenomenon on the crystal surface, but it has been noticed that, even for the same kind of SAPO molecular sieve, there are obvious difference between the elementary composition on the crystal surface and inside the crystal, which changes with the synthesis conditions and the template agents.

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 concentration 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 concentration. 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 molecular sieve 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.

The elementary analysis of molecular sieve surfaces generally is detected using the XPS method, and the elementary distribution from the core to shell is detected using the EDX method of SEM by line scan after cutting the crystal.

The hydrothermal synthesis of AlPO-21 molecular sieve was reported in European patent 0043562 using N,N,N',N'-tetramethyl ethylenediamine as the template agent. The synthesis of aluminum phosphate molecular sieve SCS-24 was reported in European patent 0538958 using N,N,N',N'-tetramethyl ethylenediamine as the template agent. The synthesis of AlPO-21 molecular sieve was reported in US patent 4898660 using N,N,N',N'-tetramethyl-1,3-diaminopropane and N,N,N',N'-tetramethyl ethylenediamine as the template agents. The synthesis of SAPO-56 was reported in US patent 5370851 using N,N,N',N'-tetramethyl-1,6-hexanediamine as the template agent. Wilson et al reported the synthesis of AlPO-17, SAPO-17, and SAPO-56 using N,N,N',N'-tetramethyl-1,6-hexanediamine as the template agent (*Mico. Meso. Mater.* 1999, **28**(1), 117-126). M. Goepper from France reported the synthesis of AlPO-34 in his doctoral dissertation (Universite Haute Alsace, Mulhouse, France, 1990), using N,N,N',N'-tetramethyl ethylenediamine (TMED) as the template agent, under the existence of hydrogen fluoride (with the mixture ratio of 1.0HF: 1.5TMED: 1Al₂O₃: 1P₂O₅: 80H₂O, crystallized at 200 °C for 24h). According to the above doctoral dissertation, the product with CHA framework could not be obtained as adding the divalent metal ions in the synthesis system, and when there was no fluorion in the synthesis system, the product obtained was AlPO-21. The hydrothermal synthesis of AlPO-34 and SAPO-34 with low content of silicon was reported in US patent 6835363 using the organic amines with two

dimethylamino- as the template agents, under the existence of hydrogen fluoride. Accordance to the above report, in research of synthesis of the molecular sieves using the organic amines with two dimethylamino- as the template agents, AIPO-34 and SAPO-34 could be obtained under proper synthesis condition and existence of fluorine. When there was no fluorine in the hydrothermal synthesis system, the products obtained were the molecular sieves with other frameworks. It indicates that the fluorine plays important role in the hydrothermal synthesis of the molecular sieves with CHA framework.

It is well known that the fluorine has strong corrosiveness to steel. In the large-scale produce of AIPO-34 and SAPO-34 molecular sieves, the corrosion of steel autoclave by the fluorine in the synthesis system is a problem which cannot be ignored. It has an important scientific value and utility value to seek a fast and efficient synthesis method of SAPO-34 without use of fluorine-containing system.

Disclosure

An object of the present invention is to provide a SAPO-34 molecular sieve, whose chemical composition in the anhydrous state is expressed as: $m\text{SDA} \cdot (\text{Si}_x\text{Al}_y\text{P}_z)\text{O}_2$; wherein, SDA represents the template agent existing in micropore of said molecular sieve; m is the molar number of said template agent per one mole of $(\text{Si}_x\text{Al}_y\text{P}_z)\text{O}_2$, and m is from 0.08 to 0.3; x, y, z respectively represents the molar number of Si, Al, P, and x is from 0.01 to 0.60, and y is from 0.2 to 0.60, and z is from 0.2 to 0.60, and $x + y + z = 1$. SDA is organic amine with the structural formula as $(\text{CH}_3)_2\text{NRN}(\text{CH}_3)_2$, wherein R is saturated straight-chain or branch-chain alkylene group with the number of carbon atoms at a range from 2 to 5. Said template agent SDA is one or more selected from N,N,N',N'-tetramethyl ethylenediamine, N,N,N',N'-tetramethyl-1,3-diaminopropane, N,N,N',N'-tetramethyl-1,4-butanediamine, N,N,N',N'-tetramethyl-1,5-pentane diamine, N,N,N',N'-tetramethyl-1,2-diaminopropane, N,N,N',N'-tetramethyl-1,3-butanediamine, N,N,N',N'-tetramethyl-1,4-pentane diamine. 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 (the Si content is calculated by the molar ratio of $\text{Si}/(\text{Si}+\text{Al}+\text{P})$) ranges from 1.50 to 1.01, preferably ranges from 1.42 to 1.02, further preferably ranges from 1.35 to 1.03, and more further preferably ranges from 1.30 to 1.03. 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.

Another object of the present invention is to provide a SAPO-34 molecular sieve prepared using the above method and a gas adsorbent prepared from the same.

The technical problem to be solved in the present invention is that the SAPO-34 molecular sieve is fast prepared in high yield without use of fluorine, using the organic amine with the structural formula as $(\text{CH}_3)_2\text{NRN}(\text{CH}_3)_2$ as the template agent. The inventors of the present invention found by experimental research that the SAPO-34 molecular sieve can be fast prepared by using the organic amine with the structural formula as $(\text{CH}_3)_2\text{NRN}(\text{CH}_3)_2$ as the template agent and main solvent, controlling the molar ratio of $(\text{CH}_3)_2\text{NRN}(\text{CH}_3)_2/\text{H}_2\text{O}$ and using the proper order of ingredients addition. Comparing with the SAPO-34 molecular sieve prepared by the hydrothermal method using the same template agent in

fluorine-containing system, the yield of the SAPO-34 molecular sieve prepared by said method in present invention is obviously improved. It is more important that there is a slight Si enrichment phenomenon on the surface of the product crystals prepared by the method in the present invention. This phenomenon might have relationship with the strong basicity environment in the synthesis system. The pH values alteration is not obviously at the crystallization process of initial period to the final period, and in the initial of crystallization, the silicon source exists in low degree of polymerization, making the proportion of silicon taking part in the formation of the molecular sieve crystal higher than using traditional methods, leading to a significant decrease of the Si enrichment degree on the molecular sieve surfaces.

The present invention refers to a method for preparing SAPO-34 molecular sieve, including the steps as follows:

(a) a silicon source, an aluminum source, a phosphorus source, deionized water and SDA are mixed, and an initial gel mixture with following molar ratio is obtained:

$\text{SiO}_2/\text{Al}_2\text{O}_3$ is from 0.01 to 1;

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

$\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ is from 1 to 19;

$\text{SDA}/\text{Al}_2\text{O}_3$ is from 5 to 30;

$\text{SDA}/\text{H}_2\text{O}$ is from 0.27 to 30;

wherein, SDA is organic amine with the structural formula as $(\text{CH}_3)_2\text{NRN}(\text{CH}_3)_2$, wherein R is saturated straight-chain or branch-chain alkylene group with the number of carbon atoms at a range from 2 to 5;

(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 170°C to 220°C , crystallized for crystallization time range from 0.5h to 48h under the 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.

In the initial gel mixture obtained 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.

In the initial gel mixture obtained in said step (a), the molar ratio of organic amine SDA to water $\text{SDA}/\text{H}_2\text{O}$ is from 0.5 to 30, and preferably the molar ratio of SDA to water $\text{SDA}/\text{H}_2\text{O}$ is from 1.0 to 30.

In the initial gel mixture obtained in said step (a), the molar ratio of organic amine SDA to Al_2O_3 $\text{SDA}/\text{Al}_2\text{O}_3$ is from 7.0 to 30.

The organic amine SDA in said step (a) is selected from N,N,N',N'-tetramethyl ethylenediamine,

N,N,N',N'-tetramethyl-1,3-diaminopropane, N,N,N',N'-tetramethyl-1,4-butanediamine,

N,N,N',N'-tetramethyl-1,5-pentane diamine, N,N,N',N'-tetramethyl-1,2-diaminopropane,

N,N,N',N'-tetramethyl-1,3-butanediamine, N,N,N',N'-tetramethyl-1,4-pentane diamine.

In said step (a), the order of ingredients addition is as follows: firstly, mixing homogeneously the aluminum source and the organic amine SDA by stirring to obtain the mixture A; after continuously stirring the mixture of the silicon source, the phosphorus source and deionized water, mixing

homogeneously the mixture A and the mixture of the silicon source, the phosphorus source and deionized water by stirring to obtain the initial gel mixture.

In said step (b), the crystallization condition are the crystallization temperature range from 180°C to 210°C and the crystallization time range from 1h to 24h; and 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.

The yield of SAPO-34 product is greater than 85%. The calculation method of product yield is: the mass of solid product after calcined at 600 °C to remove the template agent $\times 100\%$ /the total mass of inorganic oxides in the initial gel mixture.

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 sieve using organic amine $(\text{CH}_3)_2\text{NRN}(\text{CH}_3)_2$ 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 (the Si content is calculated by the molar ratio of $\text{Si}/(\text{Si}+\text{Al}+\text{P})$) ranging from 1.50 to 1.01.
- (2) obtaining a SAPO-34 molecular sieve using organic amine $(\text{CH}_3)_2\text{NRN}(\text{CH}_3)_2$ as the organic solvent and the template agent simultaneously, without use of toxic and corrosive fluorine which is liable to cause environmental.
- (3) comparing with the SAPO-34 molecular sieve prepared by the hydrothermal method using organic amine $(\text{CH}_3)_2\text{NRN}(\text{CH}_3)_2$ template agent in fluorine-containing system, the yield of the SAPO-34 molecular sieve prepared by said method in present invention is obviously improved (calculation method: the mass of solid product after calcined/ the total mass of inorganic oxides in the initial gel mixture $\times 100\%$).
- (4) less usage of water in the synthesis system which is environment-friendly and benefit to separate and recycle of organic amine, and reduce the production of waste water.
- (5) the SAPO-34 molecular prepared by said method in present invention having excellent catalytic performance and gas adsorption performance.

Specific Embodiments of the invention

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 XPS at Thermo ESCALAB 250Xi X-Ray Photoelectron Spectrometer (Mono AlK α X-ray source) using Al₂O₃ in sample surface as internal standard to calibrate charge of sample surface.

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

these Examples.

Examples 1 to 18

The amount of ingredients and the crystallization condition are shown in Table 1. The synthesis process was as follows: the aluminum sources were mixed with the organic amines (with purity of 99.5wt%), mixing homogeneously by stirring to obtain the mixture A. The silicon sources were mixed with the phosphorus sources and deionized water and the mixtures were stirred for 30min and added into the mixture A, then under sealed condition vigorously stirred for 30min to obtain initial gel mixtures. The initial gel mixtures were transferred into the stainless steel synthetic kettle, then sealed and heated to crystallization temperature, crystallized dynamically for crystallization time. After finishing the crystallization, the solid product was centrifugal separated, washed, and dried at 100°C in air to obtain raw powder samples. The samples prepared were detected by XRD, indicating that the sample prepared was SAPO-34 molecular sieve. XRD data of the sample obtained in Example 1 were shown in Table 2. XRD results of the samples obtained in Examples 2 to 18 were similar to the sample obtained in Example 1, which showed that each corresponding peak had the same peak position and the $\pm 10\%$ difference of peak intensity, indicating that all the samples prepared in Examples 2 to 18 were SAPO-34 molecular sieve. The inorganic elemental analysis of the surface composition and the bulk composition of the samples were detected with XPS and XRF, respectively, and results were shown in Table 1. The organic content of the samples were detected with CHN analyzer. The chemical compositions of the raw powders of molecular sieves were obtained by normalization of CHN and XRF results, which were shown in Table 1.

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

Example	organic amine	Aluminum source	Phosphorus source	Silicon source	H ₂ O	Crystallization Temperature	Crystallization Time	Product Yield ^a	A ^f	Chemical Composition ^g
1	N,N,N',N'-tetramethyl ethylenediamine 60g	10g	14.7g	4.3g	1.0g	190°C	12h	90.4%	1.37	0.15R-(Al _{0.49} P _{0.40} Si _{0.11})O ₂
2	N,N,N',N'-tetramethyl-1,3-diaminopropane 65.3g	10g	14.7g	4.3g	1.0g	190°C	12h	88.2%	1.30	0.13R-(Al _{0.50} P _{0.40} Si _{0.10})O ₂
3	N,N,N',N'-tetramethyl-1,4-butanediamine 72g	10g	14.7g	2.2g	1.0g	180°C	12h	87.6%	1.35	0.11R-(Al _{0.52} P _{0.42} Si _{0.06})O ₂
4	N,N,N',N'-tetramethyl-1,5-pentane diamine 79g	10g	14.7g	4.3g	1.0g	190°C	12h	88.9%	1.21	0.08R-(Al _{0.50} P _{0.41} Si _{0.09})O ₂
5	N,N,N',N'-tetramethyl-1,2-diaminopropane 65.3g	10g	14.7g	4.3g	1.0g	210°C	12h	91.5%	1.02	0.13R-(Al _{0.50} P _{0.40} Si _{0.10})O ₂
6	N,N,N',N'-tetramethyl-1,3-butanediamine 72g	10g	14.7g	2.2g	1.0g	190°C	12h	88.9%	1.23	0.10R-(Al _{0.53} P _{0.42} Si _{0.05})O ₂
7	N,N,N',N'-tetramethyl-1,4-pentane diamine 79g	10g	14.7g	4.3g	1.0g	190°C	1h	85.2%	1.30	0.10R-(Al _{0.50} P _{0.42} Si _{0.08})O ₂
8	N,N,N',N'-tetramethyl ethylenediamine 60g	7.8g ^c	14.7g	4.3g ^b	0g	210°C	24h	92.1%	1.35	0.17R-(Al _{0.50} P _{0.40} Si _{0.10})O ₂
9	N,N,N',N'-tetramethyl ethylenediamine 60g	7.8g ^c	11.5g	2.8g ^d	0g	190°C	12h	90.0%	1.30	0.14R-(Al _{0.48} P _{0.39} Si _{0.13})O ₂
10	N,N,N',N'-tetramethyl ethylenediamine 60g	20g ^e	14.7g	4.3g	0g	190°C	12h	89.3%	1.20	0.13R-(Al _{0.50} P _{0.40} Si _{0.10})O ₂
11	N,N,N',N'-tetramethyl ethylenediamine 120g	7.8g ^c	14.7g	4.3g ^b	0g	190°C	12h	90.3%	1.25	0.14R-(Al _{0.50} P _{0.41} Si _{0.09})O ₂

12	N,N,N',N'-tetramethyl ethylenediamine 120g	7.8g ^c	14.7g	4.3g ^b	0g	210°C	6h	91.0%	1.01	0.14R·(Al _{0.50} P _{0.41} Si _{0.09})O ₂
13	N,N,N',N'-tetramethyl ethylenediamine 60g	7.8g ^c	14.7g	4.3g ^b	0g	170°C	48h	87.6%	1.39	0.13R·(Al _{0.50} P _{0.41} Si _{0.09})O ₂
14	N,N,N',N'-tetramethyl -1,3-diaminopropane 58g	2.5g	3.6g	1.1g	0g	220°C	0.5h	85.3%	1.40	0.11R·(Al _{0.50} P _{0.42} Si _{0.08})O ₂
15	N,N,N',N'-tetramethyl -1,4-butanediamine 92g	7.8g ^c	14.7g	4.3g ^b	0g	180°C	24h	86.8%	1.30	0.10R·(Al _{0.50} P _{0.41} Si _{0.09})O ₂
16	N,N,N',N'-tetramethyl-1,2-diaminopropane 84g	7.8g ^c	19.6g	4.3g ^d	0g	185°C	20h	88.2%	1.10	0.11R·(Al _{0.42} P _{0.31} Si _{0.27})O ₂
17	N,N,N',N'-tetramethyl ethylenediamine 60g	10g	16.4g	4.3g	5.3g	210°C	1.0h	86.1%	1.35	0.14R·(Al _{0.50} P _{0.43} Si _{0.07})O ₂
18	N,N,N',N'-tetramethyl ethylenediamine 60g	10g	16.4g	2.2g	1.0g	190°C	12h	89.2%	1.25	0.14R·(Al _{0.50} P _{0.44} Si _{0.06})O ₂

*: All of the organic amines were analytically pure (with the mass percent of 99.5%); the aluminum source was pseudoboehmite (with Al₂O₃ mass percent of 72.5%); the phosphorus source was phosphoric acid (with H₃PO₄ mass percent of 85%); the silicon source was silica sol (with SiO₂ mass percent of 30%).

^a: Product yield= the mass of solid product (after calcined at 600 °C to remove the template agent) × 100%/the total mass of inorganic oxides in the initial gel mixture. ^b: the silicon source was tetraethoxysilane. ^c: the aluminum source was γ-alumina with Al₂O₃ mass percent of 93%. ^d: the silicon source was fumed silica (with SiO₂ mass percent of 93%). ^e: the aluminum source was aluminium isopropoxide. ^f: $A = \text{Si}_{\text{surface}} / \text{Si}_{\text{bulk}}$, wherein Si_{surface} is the surface Si content calculated by the molar ratio of Si/(Si+Al+P) according to the result of XPS; Si_{bulk} is the bulk Si content calculated by the bulk molar ratio of Si/(Si+Al+P) according to the result of XRF. ^g: R represented the organic amines.

Table2: XRD result of the sample obtained in Example 1

No.	2θ	d(Å)	100× I/I ₀
1	9.4545	9.35457	95.82
2	12.8344	6.8977	18.65
3	13.9189	6.3626	15.31
4	15.9622	5.55246	46.38
5	17.6853	5.01515	28.06
6	18.5142	4.79245	4.10
7	18.9682	4.67876	9.28
8	20.5336	4.32546	100
9	21.9097	4.05682	4.38
10	22.3181	3.98348	1.91
11	22.9725	3.87147	3.98
12	24.0990	3.69299	31.06
13	24.8162	3.58786	43.74
14	25.8284	3.44951	14.2
15	27.5669	3.23579	6.67
16	28.0275	3.18365	5.6
17	29.4615	3.03188	3.28
18	30.5062	2.92796	28.80
20	30.9433	2.88759	14.27
21	31.4801	2.83956	18.49
22	32.2688	2.77194	1.71
23	33.3591	2.68379	2.51
24	34.4001	2.60492	6.21

25	34.8399	2.57304	1.75
26	35.8666	2.50171	3.61
27	38.3234	2.34679	1.02
28	39.5752	2.27539	2.70
29	42.6257	2.11935	3.96
30	43.2903	2.08834	2.09
31	47.5413	1.91105	4.00
32	48.6651	1.86951	3.80
33	49.0438	1.85596	3.21

Example 19

The synthesis process, the amount of ingredients and the crystallization condition were the same as Example 1, except that the organic amine template was changed to 30g of N,N,N',N'-tetramethyl ethylenediamine and 30g of N,N,N',N'-tetramethyl-1,3-diaminopropan. After the crystallization, the solid product was centrifuged for separation, washed and dried at 100°C in air. 19.4g of the raw powder sample was obtained (with mass loss of 15% after calcined at 600 °C) and the product yield was 88.5%. The sample was detected with XRD. XRD data of sample were similar to the sample obtained in Example 1, 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, showing the ratio of $Si_{surface}/Si_{bulk}$ was 1.25.

Example 20

The synthesis process, the amount of ingredients and the crystallization condition were the same as Example 1, except that the organic amine template agent was changed to 40g of N,N,N',N'-tetramethyl-1,3-diaminopropan and 20g of N,N,N',N'-tetramethyl-1,2-diaminopropan. After the crystallization, the solid product was centrifuged for separation, washed and dried at 100°C in air. 20.1g of the raw powder sample was obtained (with mass loss of 16.5% after calcined at 600 °C) and the product yield was 90.1%. The sample was detected with XRD. XRD data of sample were similar to the sample obtained in Example 1, 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, showing the ratio of $Si_{surface}/Si_{bulk}$ was 1.15.

Example 21

3g of the samples obtained in Examples 1 to 3 respectively, were put into plastic beakers, adding 3ml of 40% hydrofluoric acid to dissolve the framework of molecular sieve, 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 compounds in the samples obtained in Examples 1 to 3 were N,N,N',N'-tetramethyl ethylenediamine, N,N,N',N'-tetramethyl-1,3-diaminopropan, and N,N,N',N'-tetramethyl butanediamine, respectively.

Example 22

The sample obtained in Example 1 (with the rhombohedral morphology and the crystal size from 1 μ m to 5 μ 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 0.18 and the atomic ratio of Si/Al near the surface area of the crystal was about 0.28.

The sample obtained in Example 2 (with the rhombohedral morphology and the crystal size from 1 μ m to 5 μ 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 0.17 and the atomic ratio of Si/Al near the surface area of the crystal was about 0.25.

The sample obtained in Example 3 (with the rhombohedral morphology and the crystal size from 1 μ m to 5 μ 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 0.10 and the atomic ratio of Si/Al near the surface area of the crystal was about 0.16.

The sample obtained in Example 18 (with the rhombohedral morphology and the crystal size from 1 μ m to 5 μ 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 0.09 and the atomic ratio of Si/Al near the surface area of the crystal was about 0.14.

Example 23 (Recycle of organic amine solution)

The synthesis process, the amount of ingredients and the crystallization condition were the same as Example 1. The stainless steel synthetic kettle was kept at 190°C for 12h, taken out from the oven and cooled rapidly with water. Then, the stainless steel synthetic kettle was open, from which the organic amine was separated in fume cupboard (Due to the low water amount in the synthesis system, after finishing the crystallization, under quiescent condition the synthesis system automatically separated into two phases which were the organic amine phase in upper layer and the gel-like substance phase with low fluidity in under layer. 57.6g of the organic amine solution was collected and analyzed with gas chromatography and combination of gas chromatography and mass spectrometry (capillary column SE-30). The result indicated there were 1.5g of water and 56.1g of N,N,N',N'-tetramethyl ethylenediamine.

The organic amine solution collected was recycled in the preparation of molecular sieve (adding a few fresh N,N,N',N'-tetramethyl ethylenediamine), and the synthesis process, the amount of ingredients and the crystallization condition were the same as Example 1. After the crystallization, the solid product was centrifuged for separation, washed and dried at 100°C in air. 20.3g of the raw powder sample was obtained (with mass loss of 16.1% after calcined at 600 °C) and the product yield was 91.4%. The sample was detected with XRD, indicating that the sample prepared was SAPO-34 molecular sieve. XRD data of the sample were similar to Table 2, which showed that each corresponding peak had the same peak position and peak shape, and the intensity of the strongest peak was about 105% of the sample obtained in Example 1.

Comparative Example 1

16.4g of phosphoric acid (85wt%), 17.6g of water and 10g of pseudo-boehmite (72.5wt%) were added into the synthetic kettle in sequence, stirred for 30min to obtain a homogeneous mixture. 8.3g of N,N,N',N'-tetramethyl ethylenediamine, 2.3g of tetraethoxysilane, 1.4g of HF solution (50%) and 11.2g of deionized water were homogeneously mixed by stirring, and added to the homogeneous mixture obtained above. After stirring for 2h under sealed condition, an initial gel mixture was obtained. The initial gel mixture was transferred into the stainless steel synthetic kettle, then heated to 150°C, dynamically crystallized for 12h. The stainless steel synthetic kettle was taken out from the oven and cooled. The solid product was centrifugal separated, washed to neutral using deionized water and dried at 100°C in air to obtain a raw powder sample. 8.5g of the raw powder sample was obtained (with mass loss of 16.4% after calcined at 600 °C) and the product yield was 39.5%. The sample was detected with XRD, indicating that the sample prepared was SAPO-34 molecular sieve. XRD data of sample were similar to Table 2, which showed that each corresponding peak had the same peak position, and the intensity of each corresponding peak was less than the sample obtained in Example 1, and the intensity of the strongest peak was about 70% 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 bulk composition was $Al_{0.50}P_{0.44}Si_{0.06}$ and the ratio of $Si_{surface}/Si_{bulk}$ was 2.0.

The sample (with the rhombohedral morphology and the crystal size from 1μm to 3μm 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 0.08 and the atomic ratio of Si/Al near the surface area of the crystal was about 0.22.

Comparative Example 2

16.4g of phosphoric acid (85wt%), 17.6g of water and 10g of pseudo-boehmite (72.5wt%) were added into the synthetic kettle in sequence, stirred for 30min to obtain a homogeneous mixture. 8.3g of N,N,N',N'-tetramethyl ethylenediamine, 4.6g of tetraethoxysilane, 1.4g of HF solution (50%) and 11.2g of deionized water were homogeneously mixed by stirring, and added to the homogeneous mixture obtained above. After stirring for 2h under sealed condition, an initial gel mixture was obtained. The initial gel mixture was transferred into the stainless steel synthetic kettle, then heated to 190°C, dynamically crystallized for 12h. The stainless steel synthetic kettle was taken out from the oven and cooled. The solid product was centrifugal separated, washed to neutral using deionized water and dried at 100°C in air to obtain a raw powder sample. 16.1g of the raw powder sample was obtained (with mass loss of 16.0% after calcined at 600 °C) and the product yield was 75.1%. The sample was detected with XRD, indicating that the sample prepared was SAPO-34 molecular sieve. XRD data of sample were similar to Table 2, which showed that each corresponding peak had the same peak position, and the intensity of each corresponding peak was less than the sample obtained in Example 1, and the intensity of the strongest peak was about 80% of the sample obtained in Example 1. The elemental analysis of the surface composition and the bulk composition of the samples were detected with XPS and XRF, respectively, showing that the bulk composition was $Al_{0.49}P_{0.41}Si_{0.10}$ and the ratio of $Si_{surface}/Si_{bulk}$ was 2.15.

The sample (with the rhombohedral morphology and the crystal size from 1μm to 3μm 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 0.15 and the atomic ratio of Si/Al near the surface area of the crystal was about 0.41.

Comparative Example 3

16.4g of phosphoric acid (85wt%), 17.6g of water and 10g of pseudo-boehmite (72.5wt%) were added into the synthetic kettle in sequence, stirred for 30min to obtain a homogeneous mixture. 12.5g of N,N,N',N'-tetramethyl ethylenediamine, 2.3g of tetraethoxysilane and 11.2g of deionized water were homogeneously mixed by stirring, and added to the homogeneous mixture obtained above. After stirring for 2h under sealed condition, an initial gel mixture was obtained. The initial gel mixture was transferred into the stainless steel synthetic kettle, then heated to 190°C, dynamically crystallized for 12h. The stainless steel synthetic kettle was taken out from the oven and cooled. The solid product was centrifugal separated, washed to neutral using deionized water and dried at 100°C in air to obtain the sample which was not SAPO-34 molecular sieve according to the result of XRD analysis.

Comparative Example 4 (change of the order of ingredients addation)

The amount of ingredients and the crystallization condition were the same as Example 1, except that the order of ingredients addation was changed. The process of ingredients addation was as follows: the aluminum source and the organic amine were mixed homogeneously by stirring, and then the phosphorus source was added, stirred for 20min under sealed condition, and then the silicon source and deionized water were added, stirred vigorously for 30min under sealed condition to obtain a homogenous gel mixture. The gel mixture was transferred into the stainless steel synthetic kettle, then heated to 190°C, dynamically crystallized for 12h. After finishing the crystallization, the stainless steel synthetic kettle was taken out from the oven and cooled. The solid product was centrifugal separated, washed to neutral using deionized water and dried at 100°C in air to obtain a raw powder sample. 18.5g of the raw powder sample was obtained (with mass loss of 15.6% after calcined at 600 °C) and the product yield was 83.7%. The sample was detected with XRD, indicating that the sample prepared was SAPO-34 molecular sieve. XRD data of sample were similar to Table 2, which showed that each corresponding peak had the same peak position, and the intensity of each corresponding peak was less than the sample obtained in Example 1, and the intensity of the strongest peak was about 85% 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 $Si_{surface}/Si_{bulk}$ was 1.69.

Comparative Example 5 (change of the order of ingredients addation)

The amount of ingredients and the crystallization condition were the same as Example 4, except that the order of ingredients addation was changed. The process of ingredients addation was as follows: the aluminum source and the organic amine were mixed homogeneously by stirring, and then the phosphorus source was added, stirred for 20min under sealed condition, and then the silicon source and deionized water were added, stirred vigorously for 30min under sealed condition to obtain a homogenous gel mixture. The gel mixture was transferred into the stainless steel synthetic kettle, then heated to 190°C, dynamically crystallized for 12h. After finishing the crystallization, the stainless steel synthetic kettle was taken out from the oven and cooled. The solid product was centrifugal separated, washed to neutral using deionized water and dried at 100°C in air to obtain a raw powder sample. 17.9g of the raw powder sample was obtained (with mass loss of 15.1% after calcined at 600 °C) and the

product yield was 81.6%. The sample was detected with XRD, indicating that the sample prepared was SAPO-34 molecular sieve. XRD data of sample were similar to Table 2, which showed that each corresponding peak had the same peak position and the slightly different peak intensity ($< \pm 10\%$). 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 $\text{Si}_{\text{surface}}/\text{Si}_{\text{bulk}}$ was 1.79.

Comparative Example 6 (change of the order of ingredients addition)

The amount of ingredients and the crystallization condition were the same as Example 4, except that the order of ingredients addition was changed, and a small quantity of ethanol was added into the synthesis system, and an ageing process was used. The process of ingredients addition was as follows: the aluminum source and the organic amine were mixed homogeneously by stirring, and then the silicon source was added, stirred for 20min under sealed condition, and then the phosphorus source, 1.0g of ethanol and deionized water were added, stirred vigorously for 30min under sealed condition, and then the mixture was aged by being stirred for 12h at 40°C to obtain a homogenous gel mixture. The gel mixture was transferred into the stainless steel synthetic kettle, then heated to 190°C , dynamically crystallized for 12h. After finishing the crystallization, the stainless steel synthetic kettle was taken out from the oven and cooled. The solid product was centrifugal separated, washed to neutral using deionized water and dried at 100°C in air to obtain a raw powder sample. 16.9g of the raw powder sample was obtained (with mass loss of 14.7% after calcined at 600°C) and the product yield was 77.4%. The sample was detected with XRD, indicating that the sample prepared was SAPO-34 molecular sieve. XRD data of sample were similar to Table 2, which showed that each corresponding peak had the same peak position and the slightly different peak intensity ($< \pm 10\%$). 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 $\text{Si}_{\text{surface}}/\text{Si}_{\text{bulk}}$ was 2.15.

Example 24

The samples obtained in Example 18 and Comparative Example 1 were calcined at 600°C for 4 hours in air, then pressed, crushed and sieved to 20-40 mesh. 1.0g of this 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 470°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 reaction result of methanol to olefins on the sample

Sample	Life (min)	Selectivity (mass%) *							
		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 18	200	1.8	44.9	0.8	40.0	1.4	9.1	2.0	84.9
Comparative Example 1	120	2.3	43.8	1.0	38.0	2.0	10.8	2.1	81.8

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

Example 25

The samples obtained in Example 1 and Comparative Example 2 were calcined at 600°C for 4 hours in air, then pressed, crushed and sieved to 20-40 mesh. 1.0g of this sample was weighted and loaded into a fixed bed reactor to carry out ethanol dehydration reaction evaluation. The sample was activated at 550°C for 1 hour in nitrogen gas and reduced to 260°C to perform a reaction. Ethanol was carried by nitrogen gas with a flow rate of 40 ml/min and the Weight Hour Space Velocity of the ethanol 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 indicated that on the sample obtained in Example 1, ethanol conversion was 95% and selectivity for ethylene was 99.5%. On the sample obtained in Comparative Example 2, ethanol conversion was 70% and selectivity for ethylene was 90%, and the product containing the hydrocarbon by-products, such as methane, and the like.

Example 26

The sample obtained in Example 1 was used for propylene adsorbent. The adsorption isotherm of the sample was detected by ASAP2020 of US Micromeritics. The adsorbed gases were propylene (99.99%), propane (99.99%). In order to avoid the influence of physical absorb water in molecular sieve, the sample was calcined at 600°C for 4 hours in air before the adsorption isotherm detection. Then the sample was heated to 350°C at the rate of 1°C/min in an extremely low vacuum (5×10^{-3} mmHg) and kept for 8 hours. The adsorbent temperature was 298K and controlled by thermostatic water bath (accuracy: $\pm 0.05^\circ\text{C}$). The result indicated that the adsorption capacities of propylene and propane were 1.95 and 1.0mmol/g (at 101kPa) respectively. The adsorption selectivity was propylene/propane = 1.95.

The sample after the adsorption was vacuumed at room temperature for 30 min by ASAP2020, and then detected again for the adsorption isotherm. The adsorption capacities of propylene and propane were 2.00 and 1.05mmol/g (at 101kPa) respectively. The result indicated that the sample had good regeneration performance which can be regenerated under very mild conditions.

Claims

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



wherein,

SDA represents the template agent existing in micropores of said molecular sieve;

SDA is organic amine with the structural formula as $(\text{CH}_3)_2\text{NRN}(\text{CH}_3)_2$, wherein R is saturated straight-chain or branch-chain alkylene group with the number of carbon atoms at a range from 2 to 5;

m is the molar number of said template agent per one mole of $(\text{Si}_x\text{Al}_y\text{P}_z)\text{O}_2$, and m is from 0.08 to 0.3;

x, y, z respectively represents the molar number of Si, Al, P, and x is from 0.01 to 0.60, and y is from 0.2 to 0.60, and z is from 0.2 to 0.60, and $x + y + z = 1$.

2. 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 1.50 to 1.01, preferably ranges from 1.42 to 1.02, further preferably ranges from 1.35 to 1.03, and more further preferably ranges from 1.30 to 1.03; wherein the Si content is calculated by the molar ratio of $\text{Si}/(\text{Si}+\text{Al}+\text{P})$.

3. A SAPO-34 molecular sieve according to claim 1, wherein said template agent SDA is one or more selected from N,N,N',N'-tetramethyl ethylenediamine, N,N,N',N'-tetramethyl-1,3-diaminopropane, N,N,N',N'-tetramethyl-1,4-butanediamine, N,N,N',N'-tetramethyl-1,5-pentane diamine, N,N,N',N'-tetramethyl-1,2-diaminopropane, N,N,N',N'-tetramethyl-1,3-butanediamine, N,N,N',N'-tetramethyl-1,4-pentane diamine.

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

5. 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.

6. 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, deionized water and SDA are mixed, and an initial gel mixture with following molar ratio is obtained:

$\text{SiO}_2/\text{Al}_2\text{O}_3$ is from 0.01 to 1;

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

$\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ is from 1 to 19;

$\text{SDA}/\text{Al}_2\text{O}_3$ is from 5 to 30;

$\text{SDA}/\text{H}_2\text{O}$ is from 0.27 to 30;

wherein, SDA is organic amine with the structural formula as $(\text{CH}_3)_2\text{NRN}(\text{CH}_3)_2$, wherein R is saturated straight-chain or branch-chain alkylene group with the number of carbon atoms at a range from 2 to 5;

(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 170°C to 220°C, crystallized for crystallization time range from 0.5h to 48h under the 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.

7. A method according to claim 6, wherein in the initial gel mixture obtained 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.

8. A method according to claim 6, wherein in the initial gel mixture obtained in said step (a), the molar ratio of organic amine SDA to water SDA/H₂O is from 0.5 to 30, and preferably the molar ratio of SDA to water SDA/H₂O is from 1.0 to 30.

9. A method according to claim 6, wherein in the initial gel mixture obtained in said step (a), the molar ratio of organic amine SDA to Al₂O₃ SDA/Al₂O₃ is from 7.0 to 30.

10. A method according to claim 6, wherein the organic amine SDA in said step (a) is selected from N,N,N',N'-tetramethyl ethylenediamine, N,N,N',N'-tetramethyl-1,3-diaminopropane, N,N,N',N'-tetramethyl-1,4-butanediamine, N,N,N',N'-tetramethyl-1,5-pentane diamine, N,N,N',N'-tetramethyl-1,2-diaminopropane, N,N,N',N'-tetramethyl-1,3-butanediamine, N,N,N',N'-tetramethyl-1,4-pentane diamine.

11. A method according to claim 6, wherein in said step (a), the order of ingredients addition is as follows: firstly, mixing homogeneously the aluminum source and the organic amine SDA by stirring to obtain the mixture A; after continuously stirring the mixture of the silicon source, the phosphorus source and deionized water, mixing homogeneously the mixture A and the mixture by stirring to obtain the initial gel mixture.

12. A method according to claim 6, 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.

13. A method according to claim 6, wherein in said step (b), the crystallization is carried out dynamically.

14. 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 5 or at least one of the SAPO-34 molecular sieve prepared by said methods according to claims from 6 to 13, at a temperature from 400 to 700 °C in air.

15. A catalyst for an oxygenate to olefin reaction, which is obtained by calcining at least one of said SAPO-34 molecular sieves according to claims from 1 to 5 or at least one of the SAPO-34 molecular sieves prepared by said methods according to claims from 6 to 13, at a temperature from 400 to 700 °C in air.