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 Si/(Si+Al+P). Through experimental research, the inventers 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, charactered 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:

SiO_2/Al_2O_3 is from 0.05 to 1.5;

P_2O_5/Al_2O_3 is from 0.5 to 1.5;

H_2O/Al_2O_3 is from 16 to 150;

DIPA/Al_2O_3 is from 2.0 to 5.9;

BM/Al_2O_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 H_2O/Al_2O_3 is from 26 to 120, and further preferably the molar ratio of H_2O/Al_2O_3 is from 31 to 100.

In the initial gel mixture obtained in said step (a), the molar ratio of ~~SDA~~DIPA/Al_2O_3 is from 3.0 to 5.0.

In the initial gel mixture obtained in said step (a), the molar ratio of ~~CGP~~BM/Al_2O_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.

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 ±10% difference of peak intensity, indicating the sample prepared was SAPO-34 molecular sieve.

The raw powder sample obtained in Example ~~18~~19 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 $0.09DIPA{\cdot}(Si_{0.08}Al_{0.50}P_{0.42})O_2$.

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 1μm to 5μm 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 ±10% difference of peak intensity, indicating the sample prepared was

	(min)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4^+	C_5^+	$C_2H_4+C_3H_6$
Comparative 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%.

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:

SiO_2/Al_2O_3 is from 0.05 to 1.5;

P_2O_5/Al_2O_3 is from 0.5 to 1.5;

H_2O/Al_2O_3 is from 16 to 150;

$DIPA/Al_2O_3$ is from 2.0 to 5.9;

BM/Al_2O_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 H_2O/Al_2O_3 is from 26 to 120, and preferably the molar ratio of H_2O/Al_2O_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 $DIPA/Al_2O_3$ 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 BM/Al_2O_3 is from 0.001 to 0.03.

13. A method according to claim ~~3~~7, 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.