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(54) Molecular sieves

(57) This invention relates to a class of microporous metal-silicoaluminophosphate molecular sieves(MeAPSOs) and the method of their fast preparation. These molecular sieves can be represented by the empirical formula on an anhydrous basis: mR· $(M_qSi_xAl_yP_z)O_2$, wherein *"R"* represents the templating agent presented in the intracrystalline pore system; "*m*" is the molar amount of *"R"* per mole of $(M_qSi_xAl_yP_zO_2$ and has a value from 0.01 to 8.00; "M" represents at least one metal element; "*q*", "*x*", "*y*" and "*z*" represent the molar fractions of metal, silicon, aluminum and phosphorus respectively, whose variations are q=0~0.98, x=0~0.98, y=0.01~0.60, z=0.01~0.60 and q+x+y+z=1. The crystallization time of the synthesis is 0.5-12 hours, which is defined as the method of fast preparation. This molecular sieve can be used as adsorbents and catalysts of many hydrocarbon conversion processes.

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Description

1. Field of the Invention

[0001] The present invention relates to a class of metal-containing crystalline microporous silicoaluminophosphates (denoted as MeAPSO here and after) and to the method of their fast preparation, and to their use as adsorbents and catalysts. In MeAPSO, "Me" represents Zr, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Mg, Ca, Sr, Ba and La etc. The fast synthesis of MeAPSO can be achieved by critically control of preparation of starting gels and of hydrothermal crystallization at programmed temperature.

2. Description of the Prior Art

[0002] Aluminophosphate is a type of molecular sieve containing AlO_2 and PO_2 tetrahedra and has electrovalently neutral framework that is different from the well-known crystalline aluminosilicate zeolite. In 1982, Wilson et al. disclosed the synthesis of aluminophosphate molecular sieves in U.S. Pat. No. 4,310,440. Subsequently, a class of silicoaluminophosphate crystalline was disclosed in U.S. Pat. No. 4,440,871 by Brent M. Lok et al in 1984, which included SAPO-5, SAPO-11, SAPO-16, SAPO-17, SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-37, SAPO-40, SAPO-41, SAPO-42, SAPO-44. In general, these silicoaluminophosphates can be taken as a replacement of some phosphorus by silicon in neutral framewok of aluminophosphate molecular sieves. The change of aluminophosphate to silicoaluminophosphates, even with same crystalline structure, resulted in a formation of new materials with novel chemical and physical properties.

[0003] Substitution of other elements than Si for Al, and/or P in aluminophosphate molecular sieve framework can also yield various kinds of new materials. U.S.Pat. No. 4,567,029 describes the synthesis of metal-aluminophosphate molecular sieves, which include MeAPO-5, 11, 12, 14, 16, 17, 20, 34, 35, 36, 39, 44, 47, wherein Me is Mg, Mn, Co and Zn. U.S.Pat. No. 5,126,308 discloses the preparation of ELAPO-34, wherein EL is Mg, Mn, Co, Fe, Ni, Ca and Zn. Crystalline ferroaluminophosphate (FAPOs) are disclosed in U.S.Pat. No. 4,554,143, titanium aluminophosphates (TAPOs) are disclosed in U.S.Pat. No. 4,500,651, MAPO metal aluminophosphates wherein M is As, Be, B, Cr, Ga, Ge, Li, or V are disclosed in U.S.Pat. No. 4,686,093. Binary and more metal aluminophosphates were disclosed in Canadian Pat. No. 1,241,943, which described the synthesis of FeMgAPO-5, FeMnAPO-11, TiZnAPO-31, FeMnAPO-44, FeCoMgAPO-17, FeTiCoAPO-34.

[0004] Substitution of other elements in silicoaluminophosphates molecular sieve framework can also yield various kinds of new materials. "ELAPSO" molecular sieves disclosed in patents, including GaAPSO as in U.S.Pat. No. 4,735,806, BaAPSO in U.S.Pat. No. 4,737,353, CrAPSO in U.S.Pat. No. 4,738,837, CoAPSO in U.S.Pat. No. 4,744,970, MgAPSO in U.S.Pat. No. 4,758,419, and MnAPSO in U.S.Pat. No. 4,793,833. U.S. Pat. No. 5,675,050 disclosed the preparation of MeAPO-FAU and MeAPSO-FAU wherein Me is Co, Zn, Cu, Ni, Mg and Mn.

[0005] It is well known that the synthesis of molecular sieve is a special art that strongly related to the preparation procedures and to the starting materials used for the preparation. In aforementioned patents, certain elements were incorporated into framework of the aluminophosphate and silicoaluminophosphate molecular sieves, which yields various kinds new materials of ELAPOs and ELAPSOs. However, these incorporations of other elements into aluminophosphate and silicoaluminophosphate were only effective for some special case (or to some given crystalline structure) and not valid for all $AlPO_4$ and SAPO types. A lot of MeAPSO materials have not been reported. For example, Zr in most $AlPO_4$s and SAPOs, most other elements in SAPO-56, etc.

[0006] In synthesis of molecular sieves, the control of crystallization speed is also a special art depending on the detail procedures of the preparation of starting gel, on the source of starting raw material and on the crystallization conditions. In the aforementioned patents, the crystallization speed was claimed in a wide range, in some cases for many days to achieve a successful synthesis. Fast crystallization of molecular sieve is with practical value. T. Inui reported *(J Chem Soc Chem Commun* 1990, 205; *Appl Catal* 1990, 58: 2:155-163) a method on fast synthesis of Ni-SAPO-34 by critically control the gel preparation procedure and by temperature programmed control of crystallization temperature.

SUMMARY OF THE INVENTION

[0007] The object of the present invention is to provide a class of microporous metal-silicoaluminophosphate molecular sieves having some new properties used for adsorption and catalysis.

[0008] The another object of the present invention is to provide a fast synthesis method for preparing the molecular sieves.

[0009] This invention provides a class of microporous metal-silicoaluminophosphate molecular sieves (MeAPSOs). Their chemical compositions can be represented by the empirical formula on an anhydrous basis: $mR\cdot(M_qSi_xAl_yP_z)$

O_2, wherein *"R"* represents the templating agent presented in the intracrystalline pore system; *"m* is the molar amount of *"R"* per mole of $(M_qSi_xAl_yP_z)O_2$ and has a value from 0.01to 8.00; "M" represents at least one metal element; *"q", "x", "y"* and "*z* " represent the molar fractions of metal, silicon, aluminum and phosphorus respectively, whose variations are q=0~0.98, x=0~0.98, y=0.01~0.60, z=0.01~0.60 and q+*x*+*y*+*z*=1.

[0010] According to the present invention, the microporous metal-silicoaluminophosphate molecular sieves (MeAPSOs) relate to MeAPSO-17, 18, 34, 35, 44 and 56, "Me" represents one or several metals among zirconium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, molybdenum, magnesium, calcium, strontium, barium, and lanthanum, and at least some of the metals are incorporated into the framework of molecular sieves in the form of MeO_2 tetrahedra.

[0011] The aforesaid metal-silicoaluminophosphates are quickly synthesized by aging of the mixture gel under microwave radiation or a temperature sufficiently high and by hydrothermal crystallization at programmed temperature from a mixture containing reactivated sources of silica, alumina and phosphate, one or several kinds organic templating agent(s) and one or several kinds soluble metal acetate(s), nitrate(s) or sulphate(s) etc.

[0012] The reaction mixture is placed in a stainless steel autoclave lined with polytetrafluoroethylene, sealed and heated, preferably under the autogeneous pressure in the system or the pressure of nitrogen, air or other inert gases filled in, is in the range of 0.1~1MPa at programmed temperature of 50~250°C, and kept for 0.5~12 hours, and preferably between 1~3 hours, until crystals of the metal-silicoaluminophosphates product are obtained. The product is recovered by any convenient method such as centrifugation or filtration.

DETAILED DESCRIPTION OF THE INVENTION

[0013] The present invention relates to several silicoaluminophosphates containing metals, which can be expressed on an anhydrous basis as follows: $mR\cdot(M_qSi_xAl_yP_z)O_2$, wherein *"R"* represents the templating agent presented in the intracrystalline pore system; *"m "* is the molar amount of "*R*" per mole of $(M_qSi_xAl_yP_z)O_2$ and has a value from 0.01 to 8.00; "M" represents at least one metal element; *"q", "x", "y"* and *"z"* represent the molar fractions of metal, silicon, aluminum and phosphorus respectively, whose variations are q=0~0.98, x=0~0.98, y=0.01~0.60, z=0.01~0.60 and q+*x*+*y*+*z*=1.

[0014] According to the present invention, at least some of the metals are incorporated into the framework of molecular sieves in the form of MeO_2 tetrahedra. In addition, the metal atom incorporated into the molecular sieve framework can be one or several metal(s) among zirconium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, molybdenum, magnesium, calcium, strontium, barium, and lanthanum.

[0015] The synthesis method of metal-silicoaluminophosphate molecular sieves according to the present invention is characterized by the synthesis process comprising steps of:

(1) The sources of silicon, alumnium, phosphorus, metal compound, templating agent and water are mixed in a suitable proportion and stirred to obtain the primary gel mixture.
(2) Aging of the primary gel mixture under microwave radiation for no less than 0.1 minutes, preferably 2~10 minutes or under a temperature sufficiently high for no less than lhour, preferably 2~12 hours.
(3) The gel mixture is transferred into a stainless-steel autoclave lined with polytetrafluoroethylene, sealed and heated at temperature programmed 50~250°C, and kept for no less than 0.1 hours, preferably 0.5-12 hours.
(4) The solid crystalline products are separated from the mother liquor, washed with de-ionized water to neutral and dried at 80~130°C in air, then a primary powder of synthesized MeAPSO molecular sieves are obtained.
(5) The microporous metal silicoaluminophosphate molecular sieves are prepared by calcining a primary powder at 300~700°C in air for no less than 3 hours.

[0016] In the above process, the source of silicon is one or several kinds of silica sol, sodium silicate sol, activated silica oxide or orthosilicate ester; the source of aluminum is one or several kinds of aluminum salt, aluminate, activated aluminum oxide, alkoxy aluminium, diaspore or pseudoboehmite; the source of phosphorus is one or several kinds of orthophosphoric acid, phosphate, organic phosphide or phosphoric oxide; the source of metal is one or several kinds of oxides, oxychloride, metal salts of inorganic or organic acids of titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, zirconium, molybdenum, magnesium, calcium, strontium, barium, and lanthanum or other metals; and the source of templating agent is one or several kinds of cyclohexylamine, triethylamine, diethylamine, n-propylamine, isopropylamine, n-dipropylamine, diisopropylamine, tripropylamine, n-butylamine, isobutylamine, hexamethyenlaminelidyne, hexanediamine, N, N-diisopropyl ethylamine, N, N-diisopropyl propylamine, N', N', N, N-tetramethyl-(1,6-)hexanediamine, ethanolamine, diethanolamine, triethanolamine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, or the corresponding alcohol.

[0017] In the preparation process said above, the formula ratio of the ingredients (the molecular ratio of oxides) is:

$$MeO_n/Al_2O_3 = 0.01\sim1.0;$$

$$SiO_2/Al_2O_3 = 0\sim10;$$

$$P_2O_5/Al_2O_3 = 0.01\sim15\ ;$$

$$H_2O/Al_2O_3 = 10\sim100;$$

$$R/Al_2O_3 = 0.1\sim10$$

("R " is one or a mixture of templating agent).

[0018] Additionally, the crystallization pressure, which can be the autogenous pressure in the system or the pressure of nitrogen, air or other inert gases filled in, is in the range of 0.1~1 Mpa.

[0019] With the present process, different molecular sieves MeAPSO can be prepared by changing the formula ratio of the ingredients or by choosing different templating agents.

[0020] The preparing process is described in detail as follows:

(1) Synthesis of the MeAPSO-17 molecular sieve

The templating agent is one or several kinds of cyclohexylamine, triethylamine, diethylamine, n-propylamine, isopropylamine, n-dipropylamine, diisopropylamine, tripropylamine, n-butylamine, isobutylamine, ethanolamine, diethanolamine, triethylamine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, or the corresponding alcohol. The prefered templating agent is one or several kinds of cyclohexylamine, triethylamine, or diethylamine.

The formula ratio (the molecular ratio of oxides) is

$$MeO_n/Al_2O_3 = 0.01\sim1.0;$$

$$SiO_2/Al_2O_3 = 0\sim10;$$

$$P_2O_5/Al_2O_3 = 0.01\sim15;$$

$$H_2O/Al_2O_3 = 10\sim100;$$

$$R/Al_2O_3 = 0.1\sim10$$

(*"R* " is one or a mixture of templating agents),

MeAPSO-17 molecular sieves of the present invention can be synthesized according to the aforesaid description.

The anhydrous chemical composition of the synthesized MeAPSO-17 molecular sieves can be expressed as $mR\cdot(M_qSi_xAl_yP_z)O_2$, wherein "*R*" represents the templating agent presented in the intracrystalline pore system; *"m"* is the molar amount of *"R"* per mole of $(M_qSi_xAl_yP_z)O_2$ and has a value from 0.01to 8.00; "M" represents at least one metal element; *"q", "x", "y"* and *"z"* represent the molar fractions of metal, silicon, aluminum and phosphorus respectively, whose variations are q=0~0.98, x=0~0.4, y=0.01~0.60, z=0.01~0.60 and q+*x*+*y*+*z*=1.

(2) Synthesis of the MeAPSO-18 molecular sieve

The templating agent is one or several kinds of N, N-diisopropyl ethylamine, N, N-diisopropyl propylamine, or tetraethylammonium hydroxide.

The formula ratio (the molecular ratio of oxides) is

$$MeO_n/Al_2O_3 = 0.01\sim1.0;$$

$$SiO_2/Al_2O_3 = 0\sim10;$$

$$P_2O_5/Al_2O_3 = 0.01\sim10;$$

$$H_2O/Al_2O_3 = 10\sim100;$$

$$R/Al_2O_3 = 0.1\sim10$$

("*R*" is one or a mixture of templating agents).

MeAPSO-18 molecular sieves of the present invention are then synthesized according to the aforesaid description.

The anhydrous chemical composition of the synthesized MeAPSO-18 molecular sieves can be expressed as $mR\cdot(M_qSi_xAl_yP_z)O_2$, wherein "*R*" represents the templating agent presented in the intracrystalline pore system; "*m*" is the molar amount of *"R"* per mole of $(M_qSi_xAl_yP_z)O_2$ and has a value from 0.01 to 8.00; "M" represents at least one metal element; *"q", "x", "y"* and *"z"* represent the molar fractions of metal, silicon, aluminum and phosphorus respectively, whose variations are $q=0\sim0.98$, $x=0\sim0.98$, $y=0.01\sim0.60$, $z=0.01\sim0.60$ and $q+x+y+z=1$.

The prefered metal is at least one of zirconium, titanium, cobalt, manganese, magnesium, iron, nickel, and zinc.

(3) Synthesis of the MeAPSO-34 molecular sieve

The templating agent is one or several kinds of triethylamine, diethylamine, n-propylamine, isopropylamine, n-dipropylamine, diisopropylamine, tripropylamine, n-butylamine, isobutylamine, ethanolamine, diethanolamine, triethanolamine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, or the corresponding alcohol. The prefered templating agent is a cheap one or several kinds of triethylamine, diethylamine, n-propylamine, isopropylamine, and tripropylamine.

The formula ratio (the molecular ratio of oxides) is

$$MeO_x/Al_2O_3 = 0.01\sim1.0;$$

$$SiO_2/Al_2O_3 = 0\sim10;$$

$$P_2O_5/Al_2O_3 = 0.01\sim15;$$

$$H_2O/Al_2O_3 = 10\sim100;$$

$$R/Al_2O_3 =0.1\sim10$$

("*R*" is one or a mixture of templating agents).

MeAPSO-34 molecular sieves of the present invention are then synthesized according to the aforesaid description.

The anhydrous chemical composition of the synthesized MeAPSO-34 molecular sieves can be expressed as $mR\cdot(M_qSi_xAl_yP_z)O_2$, wherein *"R"* represents the templating agent presented in the intracrystalline pore system; *"m"* is the molar amount of *"R"* per mole of $(M_qSi_xAl_yP_z)O_2$ and has a value from 0.01to 8.00; "M" represents at least one metal element; *"q ", "x", "y"* and "z" represent the molar fractions of metal, silicon, aluminum and phosphorus respectively, whose variations are $q=0\sim0.98$, $x=0\sim0.98$, $y=0.01\sim0.60$, $z=0.01\sim0.60$ and $q+x+y+z=1$.

(4) Synthesis of the MeAPSO-35 molecular sieve

The templating agent is one or several kinds of hexamethyleneimine, hexanediamine, triethylamine, diethylamine, n-dipropylamine, diisopropylamine, tripropylamine, n-butylamine, isobutylamine, ethanolamine, diethanolamine, triethylamine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, or the corresponding alcohol. The prefered templating agent is hexamethyleneimine.

The formula ratio (the molecular ratio of oxides) is

$$MeO_n/Al_2O_3 = 0.01\sim1.0;$$

$$SiO_2/Al_2O_3 = 0.3\sim0.6;$$

$$P_2O_5/Al_2O_3 = 0.01\sim10;$$

$$H_2O/Al_2O_3 = 10\sim100;$$

$$R/Al_2O_3 = 1.0\sim2.0$$

(*"R"* is one or a mixture of templating agent),

MeAPSO-35 molecular sieves of the present invention are then synthesized according to the aforesaid description.

The anhydrous chemical composition of the synthesized MeAPSO-35 molecular sieves can be expressed as $mR\cdot(M_qSi_xAl_yP_z)O_2$, wherein *"R"* represents the templating agent presented in the intracrystalline pore system; *"m"* is the molar amount of *"R"* per mole of $(M_qSi_xAl_yP_z)O_2$ and has a value from 0.01to 2.0; "M" represents at least one metal element; *"q", "x ", "y"* and *"z"* represent the molar fractions of metal, silicon, aluminum and phosphorus respectively, whose variations are $q=0\sim0.98$, $x=0.3\sim0.98$, $y=0.01\sim0.60$, $z=0.01\sim0.60$ and $q+x+y+z=1$.

(6) Synthesis of the MeAPSO-44 molecular sieve

The templating agent is one or several kinds of cyclohexylamine, triethylamine, diethylamine, n-propylamine, isopropylamine, n-dipropylamine, diisopropylamine, tripropylamine, n-butylamine, isobutylamine, ethanolamine, diethanolamine, triethylamine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, or the corresponding alcohol. The prefered templating agent is one or several kinds of cyclohexylamine, triethylamine, and diethylamine.

The formula ratio (the molecular ratio of oxides) is

$$MeO_n/Al_2O_3 = 0.01\sim1.0;$$

$$SiO_2/Al_2O_3 = 0.2\sim10;$$

$$P_2O_5/Al_2O_3 = 0.01\sim15;$$

$$H_2O/Al_2O_3 = 10\sim100;$$

$$R/Al_2O_3 = 1\sim10$$

(R is one or a mixture of templating agents).

The MeAPSO-44 molecular sieves of the present invention are then synthesized according to the aforesaid description.

The anhydrous chemical composition of as-synthesized MeAPSO-44 molecular sieves can be expressed as $mR\cdot (M_qSi_xAl_yP_z)O_2$, wherein "R" represents the templating agent presented in the intracrystalline pore system; "m" is the molar amount of "R" per mole of $(M_qSi_xAl_yP_z)O_2$ and has a value from 0.01to 8.00; "M" represents at least one metal element; *"q", "x", "y"* and "*z*" represent the molar fractions of metal, silicon, aluminum and phos-

phorus respectively, whose variations are q=0～0.98, x=0.2～0.98, y=0.01～0.60, z=0.01～0.60 and q+x+y+z=1.
(7) Synthesis of the MeAPSO-56 molecular sieve

[0021] The templating agent is one or several kinds of N', N', N, N-tetramethyl- (1,6)-hexanediamine, tripropylamine, or n-propylamine.

[0022] The formula ratio (the molecular ratio of oxides) is

$$MeO_n/Al_2O_3 = 0.01\sim0.7;$$

$$SiO_2/Al_2O_3 = 0.1\sim10;$$

$$P_2O_5/Al_2O_3 = 0.01\sim15;$$

$$H_2O/Al_2O_3 = 10\sim100;$$

$$R/Al_2O_3 = 0.7\sim6$$

(R is one or a mixture of templating agents).

[0023] Thus, MeAPSO-56 molecular sieves of the present invention are then synthesized according to the aforesaid description.

[0024] The anhydrous chemical composition of the as-synthesized MeAPSO-56 molecular sieves can be expressed as $mR\cdot(M_qSi_xAl_yP_z)O_2$, wherein "*R*" represents the templating agent presented in the intracrystalline pore system; *"m"* is the molar amount of "*R*" per mole of $(M_qSi_xAl_yP_z)O_2$ and has a value from 0.01to 6.00; "M" represents at least one metal element; *"q", "x", "y"* and "*z*" represent the molar fractions of metal, silicon, aluminum and phosphorus respectively, whose variations are q=0～0.98, x=0.01～0.98, y=0.01～0.60, z=0.01～0.60 and q+x+y+z=1.

[0025] Preferably, the metal is one or more selected from the group consisting of vanadium, copper, molybdenum, zirconium, titanium, cobalt, manganese, magnesium, iron, nickel, and zinc.

[0026] The present invention is illustrated by the following examples:

Example 1

(Preparation of TAPSO-17)

[0027] A reaction mixture was prepared by combining 6.88g of pseudo-boehmite(74.2wt% Al_2O_3) and 11.53g of orthophosphoric acid (85wt% H_3PO_4) plus 14ml of water in a beaker, and stirring until homogeneous. To this mixture was first added 1.2g of silica sol(25%SiO_2) and stirred for 10 minutes. After that 1.7ml tetrabutylorthotitanate, 17 ml de-ionized water and 7.5ml cyclohexylamine were added to the mixture under stirring and the mixture was stirred for 15 minutes until homogeneous. The composition of the final reaction mixture in molar oxide ratio was: $1.5C_6H_{11}NH_2$: $0.1SiO_2$:Al_2O_3:P_2O_5:$0.05TiO_2$:$39H_2O$.

[0028] The gel mixture is radiated in microwave oven for 2 minutes, then the mixture was sealed in a autoclave lined with polytetrafluoroethylene and crystallized for 2 hours under temperature programmed 50～200°C. The autoclave was then taken out and cooled in the cold water to room temperature. The solid product was separated from the mother liquor and washed with de-ionized water until neutral. Then it was dried at 100°C. XRD pattern of the product was characterized by following data (Table 1), which can be identified that the product was TAPSO-17 molecular sieve. Its water adsorption capacity was determined to be 26.8wt% at 25°C.

[0029] The chemical composition was: 2.8wt.%C, 0.5wt.%N, 3.5wt.%SiO_2, 41.2wt.%Al_2O_3, 47.3 wt.%P_2O_5, 2.6wt%TiO_2, 2.1wt.%H_2O.

Table 1

No.	2θ	d(Å)	100× I/I_0
1	7.560	11.6798	100

Table 1 (continued)

No.	2θ	d(Å)	100× I/I_0
2	9.579	9.1955	35
3	13.180	6.6919	83
4	15.260	5.7739	40
5	16.420	5.3907	27
6	19.450	4.5548	43
7	20.340	4.3468	98
8	21.190	4.1714	51
9	23.110	3.8288	39
10	23.660	3.7321	35
11	25.200	3.5253	33
12	26.790	3.3087	40
13	27.250	3.2535	18
14	28.590	3.1107	19
15	31.040	2.8706	35
16	31.630	2.8081	52
17	33.350	2.6660	22

Comparison Example 1

[0030] By using essentially the same composition and procedure as in Example 1, while changing only the 1.2g silica sol in Example 1 to 1.8g silica sol, then the product so obtained was a mixture crystal of the TAPSO-17 and the TAPSO-44 molecular sieves.

Comparison Example 2

[0031] By using essentially the same composition and procedure in Example 1, while changing only the 1.2g silica sol in Example 1 to 3.6g silica sol, then the product so obtained was the TAPSO-44 molecular sieve.

Example 2

(Preparation of VAPSO-17)

[0032] A reaction mixture was prepared by combining 6.88g of pseudo-boehmite(74.2wt% Al_2O_3) and 11.53g of orthophosphoric acid (85wt% H_3PO_4) plus 14ml water in a beaker, and stirring until homogeneous. To this mixture was first added 1.2g of silica sol and stirred for 10 minutes. After that 0.59g NH_4VO_3, 17 ml de-ionized water and 7.5ml cyclohexylamine were added to the mixture under stirring, and the mixture was stirred for 15 minutes until homogeneous. The composition of the final reaction mixture in molar oxide ratio was: $1.5C_6H_{11}NH_2$: $0.1SiO_2$: Al_2O_3: P_2O_5: $0.05V_2O_5$: $39H_2O$.

[0033] The gel mixture is radiated in microwave oven for 2 minutes, then the mixture was sealed in a autoclave lined with polytetrafluoroethylene at 0.4Mpa after pressurized with nitrogen, and crystallized for 2 hours under temperature programmed 50~200°C. The autoclave was then taken out and cooled in cold water to the room temperature. The solid product was separated from the mother liquor and washed with de-ionized water until neutral. It was dried at 100°C. XRD pattern of the product was characterized by following data (Table 2), which can be identified that the product was VAPSO-17 molecular sieve. Its water adsorption capacity was determined to be 24.5wt% at 25°C.

Table 2

No.	2θ	d(Å)	100× I/I_0
1	7.570	11.6582	100
2	9.610	9.1964	31
3	13.220	6.6967	87
4	15.300	5.7926	44
5	16.420	5.3976	29

Table 2 (continued)

No.	2θ	d(Å)	100× I/I_0
6	17.810	4.9806	13
7	19.440	4.5778	38
8	20.320	4.3725	90
9	21.210	4.1915	47
10	23.120	3.8622	38
11	23.630	3.7789	35
12	25.200	3.5411	30
13	26.760	3.3363	39
14	27.250	3.2788	17
15	28.560	3.1318	18
16	31.030	2.8988	29
17	31.620	2.8355	48
18	33.350	2.6937	18

Example 3

(Preparation of CrAPSO-17)

[0034] By using essentially the same composition and procedure as in Example 2, while changing only the 0.59g NH_4VO_3 in Example 2 to 2.00g $Cr(NO_3)_3 \cdot 9H_2O$, the so obtained product was determined by XRD to be the CrAPSO-17 molecular sieve. Its water adsorption capacity was measured to be 25.8 wt % at 25°C.

Example 4

(Preparation of ZrAPSO-17)

[0035] A reaction mixture was prepared by combining 6.88g of pseudo-boehmite(74.2wt% Al_2O_3) and 11.53g of orthophosphoric acid (85wt% H_3PO_4) plus 14ml of water in a beaker, and stirring until homogeneous. To this mixture was first added 1.2g of silica sol(25%SiO_2) and stirred for 10 minutes. After that 1.06g $Zr(NO_3)_4 \cdot 5H_2O$, 17ml de-ionized water and 7.5ml cyclohexylamine were added to the mixture under stirring and the mixture was stirred for 15 minutes until homogeneous. The composition of the final reaction mixture in molar oxide ratio was: $1.5C_6H_{11}NH_2$: $0.1SiO_2$: Al_2O_3: P_2O_5: $0.05ZrO_2$: $39H_2O$.

[0036] The gel mixture is radiated in microwave oven for 2 minutes, then the mixture was sealed in a autoclave lined with polytetrafluoroethylene and crystallized for 2 hours under temperature programmed 50~200°C. The autoclave was then taken out and cooled in the cold water to the room temperature. The solid was separated from the mother liquor and washed with de-ionized water to neutral. It was then dried at 100°C. XRD pattern of the product was characterized by following data(Table 3), which can be identified that the product was ZrAPSO-17 molecular sieve. Its water adsorption capacity was determined to be 24.1 wt % at 25°C.

Table 3

No.	2θ	d(Å)	100× I/I_0
1	7.750	11.5992	100
2	9.639	9.1053	35
3	13.250	6.6017	83
4	15.380	5.6536	41
5	16.520	5.3203	25
6	19.480	3.4645	45
7	20.420	4.2566	98
8	21.250	4.0818	48
10	23.150	3.7287	37
11	23.700	3.6320	42

Table 3 (continued)

No.	2θ	d(Å)	100× I/I_0
12	25.260	3.4152	35
13	26.860	3.2137	45
14	27.320	3.1625	18
15	28.630	3.0204	19
16	31.130	2.6803	36
17	31.680	2.6251	53
18	33.440	2.5740	24

Example 5

(Preparation of MgAPSO-17)

[0037] By using essentially the same composition and procedure as in Example 4, while changing only the 1.07g $Zr(NO_3)_4 \cdot 5H_2O$ and the 7.5ml cyclohexylamine in Example 4 to 1.08g $Mg(CH_3COO)_2 \cdot 4H_2O$ and 8.1ml triethylamine respectively, the product so obtained was determined to be MgAPSO-17 molecular sieve by XRD. Its water adsorption capacity was measured to be 23.1 wt% at 25°C.

Example 6

(Preparation of CaAPSO-17)

[0038] By using essentially the same composition and procedure as in Example 4, while changing only the 1.07g $Zr(NO_3)_4 \cdot 5H_2O$ and the 7.5ml cyclohexylamine in Example 4 to 1.19g $Ca(NO_3)_2 \cdot 5H_2O$ and 6.9ml diethylamine respectively, the product so obtained was determined to be the CaAPSO-17 molecular sieve by XRD. Its water adsorption capacity was measured to be 20.5 wt% at 25°C.

Example 7

(Preparation of SrAPSO-17)

[0039] By using essentially the same composition and procedure as in Example 4, while changing only the 1.07g $Zr(NO_3)_4 \cdot 5H_2O$ and the 7.5ml cyclohexylamine in Example 4 to 1.06g $Sr(NO_3)_2$ and 6.1ml isopropylamine respectively, and the product so obtained was determined to be the SrAPSO-17 molecular sieve by XRD. Its water adsorption capacity was measured to be 25.1 wt % at 25°C.

Example 8

(Preparation of BaAPSO-17)

[0040] By using essentially the same composition and procedure as in Example 4, while changing only the 1.07g $Zr(NO_3)_4 \cdot 5H_2O$ and the 7.5ml cyclohexylamine in Example 4 to 1.31g $Ba(NO_3)_3$ and 8.7ml triethylamine respectively, the product so obtained was determined to be the BaAPSO-17 molecular sieve by XRD. Its water adsorption capacity was measured to be 24.3%wt at 25°C.

Example 9

(Preparation of FAPSO-17)

[0041] By using essentially the same composition and procedure as in Example 4 , while changing only the 1.07g $Zr(NO_3)_4 \cdot 5H_2O$ and the 7.5ml cyclohexylamine in Example 4 to 1.02g $Fe(NO_3)_2 \cdot 9H_2O$ and 8.2ml dipropylamine respectively, the product so obtained was determined to be the FAPSO-17 molecular sieve by XRD. Its water adsorption capacity was measured to be 25.8wt% at 25°C.

Example 10

(Preparation of CoAPSO-17)

[0042] By using essentially the same composition and procedure as in Example 4, while changing only the 1.07g $Zr(NO_3)_4 \cdot 5H_2O$ in Example 4 to 1.25g $Co(CH_3COO)_4 \cdot 4H_2O$, the product so obtained was determined by XRD to be the CoAPSO-17 molecular sieve. Its water adsorption capacity was measured to be 24.5wt% at 25°C.

Example 11

(Preparation of NiAPSO-17)

[0043] By using essentially the same composition and procedure as in Example 4, while changing only the 1.07g $Zr(NO_3)_4 \cdot 5H_2O$ in Example 4 to 1.48g $Ni(NO_3)_2 \cdot 6H_2O$, and at same time using 4.2ml cyclohexylamine and 2.6ml diethylamine as the template, the product so obtained was determined by XRD to be the NiAPSO-17 molecular sieve. Its water adsorption capacity was 26.8wt% at 25 °C.

Example 12

(Preparation of CuAPSO-17)

[0044] By using essentially the same composition and procedure as in Example 4, while changing only the 1.07g $Zr(NO_3)_4 \cdot 5H_2O$ in Example 4 to 1.21g $Cu(NO_3)_2 \cdot 3H_2O$, and at the same time using the 3.7ml of triethylamine and 3.4ml of diethylamine as the template, the product so obtained was determined by XRD to be the CuAPSO-17 molecular sieve. Its water adsorption capacity was measured to be 22.5wt% at 25°C.

Example 13

(Preparation of ZnAPSO-17)

[0045] By using essentially the same composition and procedure as in Example 4, while changing only the 1.07g $Zr(NO_3)_4 \cdot 5H_2O$ in Example 4 to 1.11g $Zn(CH_3COO)_2 \cdot 2H_2O$, and at same time using 3.1ml of triethylamine and 3.5ml of propylamine as the template, the product so obtained was determined by XRD to be ZnAPSO-17 molecular sieve. Its water adsorption capacity was measured to be 25.3wt% at 25°C.

Example 14

(Preparation of MnAPSO-17)

[0046] By using essentially the same composition and procedure as in Example 4, while changing only the 1.07g $Zr(NO_3)_4 \cdot 5H_2O$ in Example 4 to 1.25g $Mn(CH_3COO)_2 \cdot 4H_2O$, and then sealing after pressurizing it with nitrogen to 0.1Mpa. The product so obtained by XRD was determined to be the MnAPSO-17 molecular sieve. Its water adsorption capacity was measured to be 23.1wt% at 25 °C.

Example 15

(Preparation of MoAPSO-17)

[0047] By using essentially the same composition and procedure as in Example 4, while changing the 1.07g $Zr(NO_3)_4 \cdot 5H_2O$ in Example 4 to 0.89g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and then sealing after pressurizing it with air to 0.1 Mpa. The product so obtained was determined by XRD to be the MoAPSO-17 molecular sieve. Its water adsorption capacity was measured to be 21.1wt% at 25°C.

Example 16

(Preparation of LaAPSO-17)

[0048] By using essentially the same composition and procedure as in Example 4, while changing only the 1.07g Zr

$(NO_3)_4 \cdot 5H_2O$ in Example 4 to 1.85g $La(NO_3)_3 \cdot nH_2O$, and sealing the autoclave after pressurizing it with air to 0.4Mpa. The product so obtained was determined by XRD to be the LaAPSO-17 molecular sieve. Its water adsorption capacity was measured to be 25.6wt% at 25°C.

Example 17

(Preparation of TAPO-17)

[0049] A reaction mixture was prepared by combining 6.88g of pseudo-boehmite(74.2wt% Al_2O_3) and 11.53g of orthophosphoric acid (85wt% H_3PO_4) plus 14ml water in a beaker, and stirring until homogeneous. Then 1.7ml of Ti $(OC_4H_9)_4$ was added to the mixture and stirred for 10 minutes. After that 17ml de-ionized water and 7.5ml cyclohexylamine were added under stirring and the mixture was further stirred for 15 minutes until homogeneous. The composition of the final reaction mixture in molar oxide ratio was: $1.5C_6H_{11}NH_2$: Al_2O_3: P_2O_5: $0.05TiO_2$: $39H_2O$.

[0050] The mixture was sealed in a autoclave lined with polytetrafluoroethylene, heated at a temperature sufficiently high for 12 hours and crystallized for 2 hours under temperature programmed 50~200°C. The autoclave was taken out and cooled in cold water to room temperature. The solid product was separated from the mother liquor and washed with de-ionized water to neutral. It was then dried at 100°C. XRD determination confirmed that the product was the TAPO-17 molecular sieve. Its water adsorption capacity was measured to be 24.0wt% at 25°C.

[0051] The chemical composition was: 2.6wt.%C, 0.5wt.%N, 42.9wt.%Al_2O_3, 48.0wt.%P_2O_5, 3.1wt%TiO_2, 2.9wt.%H_2O.

Example 18

(Preparation of ZrAPO-17)

[0052] A reaction mixture was prepared by combining 7.06g of pseudo-boehmite(72.2Mt% Al_2O_3) and 11.53g orthophosphoric acid (85wt% H_3PO_4) plus 14ml water in a beaker, and stirring until homogeneous. After that, 2.15g $Zr(NO_3)_4 \cdot 5H_2O$ plus 17 ml de-ionized water and 7.5ml of cyclohexylamine were added to the mixture, further stirred for 15 minutes until homogeneous. The composition of the final reaction mixture in molar oxide ration was: $1.5C_6H_{11}NH_2$: Al_2O_3: P_2O_5: $0.1ZrO_2$: $39H_2O$.

[0053] The gel mixture is radiated in microwave oven for 2 minutes, then the mixture was sealed in a autoclave lined with polytetrafluoroethylene and crystallized for 2 hours under temperature programmed 50~200°C. The autoclave was then taken out and cooled in cold water to room temperature. The solid product was separated from the mother liquor and washed with de-ionized water to neutral. Then it was dried at 100°C. XRD determination verified that the product was the ZrAPO-17 molecular sieve. Its water adsorption capacity was measured to be 23.50wt% at 25°C.

Example 19

(Preparation of CoAPO-17)

[0054] By using essentially the same composition and procedure as in Example 18, while changing only the 1.07g $Zr(NO_3)_4 \cdot 5H_2O$ plus 17ml de-ionized water in Example 18 to 2.50g $Co(CH_3COO)_4 \cdot 4H_2O$ plus 17ml de-ionized water, a final product was obtained. The product was determined by XRD to be CoAPO-17 molecular sieve. Its water adsorption capacity was measured to be 23.1wt% at 25°C.

Example 20

(Preparation of MnAPO-17)

[0055] By using essentially the same composition and procedure as in Example 18, while changing only the 1.07g $Zr(NO_3)_4 \cdot 5H_2O$ plus 17ml de-ionized water in Example 18 to 2.50g $Mn(CH_3COO)_4 \cdot 4H_2O$ plus 17ml de-ionized water, a final product was obtained. The product was determined by XRD to be MnAPO-17 molecular sieve. Its water adsorption capacity was measured to be 22.4wt% at 25°C.

Example 21

(Preparation of ZrAPSO-18)

[0056] 7.06g activated alumina (72.2wt% Al_2O_3) was dissolved in 39.64ml de-ionized water, and then 10.95g ortho-phosphoric acid (85wt% H_3PO_4), 2.35g silica sol(SiO_2 25.5wt%) and 2.35g $Zr(NO_3)_4 \cdot 5H_2O$ were added to the prepared alumina sol, stirring for no less than 30 minutes. Finally 10.34g N, N-diisopropylamine was added to the mixture with continuous stirring until attaining a homogeneous phase.

[0057] The gel mixture is radiated in microwave oven for 2 minutes, then the mixture was sealed in a autoclave lined with polytetrafluoroethylene and crystallized under autogeneous pressure for 3 hours under programmed temperature 50~170°C. The solid product was washed with de-ionized water to neutral. It was then dried at 100°C in the air. The product was determined by XRD(Table 4) to be the ZrAPSO-18 molecular sieve.

Table 4

No.	2θ	d(Å)	100× I/I_0
1	9.450	9.3513	100
2	10.540	8.3865	17
3	12.870	6.6730	10
4	14.740	6.0050	14
5	15.920	5.5624	32
6	16.910	5.2389	68
7	19.530	4.5416	22
8	20.020	4.4315	27
9	20.510	4.3268	36
10	21.280	4.1719	27
11	23.830	3.7309	28
12	26.250	3.3922	27
13	27.800	3.2065	22
14	30.300	2.9474	17
15	30.980	2.8842	26
16	32.150	2.7819	20

Example 22

(Preparation of CoAPSO-18)

[0058] By using essentially the same composition and procedure as in Example 21, while changing only the 7.06g activated alumina(72.2wt% Al_2O_3) and 2.15g $Zr(NO_3)_4 \cdot 5H_2O$ in Example 21 to 6.00g psudo-boemite(85.0wt% Al_2O_3) and 1.46g $Co(NO_3)_3 \cdot 6\ H_2O$, respectively, a final product was obtained. The product was determined by XRD(Table 5) to be the CoAPSO-18 molecular sieve.

Table 5

No.	2θ	d(Å)	100× I/I_0
1	9.460	9.3414	100
2	10.500	8.4184	12
3	12.800	6.9104	10
4	13.950	6.3432	9
5	14.750	6.0009	8
6	15.920	5.5624	37
7	16.920	5.2359	50
8	19.570	4.5324	17
9	20.490	4.3309	37
10	21.210	4.1855	24

Table 5 (continued)

No.	2θ	d(Å)	100× I/I_0
11	23.890	3.7217	19
12	25.730	3.4596	14
13	26.210	3.3973	21
14	27.750	3.2122	13
15	30.320	2.9455	17
16	30.920	2.8897	24

Example 23

(Preparation of TAPSO-18)

[0059] By using essentially the same composition and procedure as in Example 21, while changing the 2.35g silica sol and 2.15g $Zr(NO_3)_4 \cdot 5H_2O$ in Example 21 to 1.50g activated dioxide silica(40% SiO_2) and 0.63g $Ti(SO_4)_2$, respectively, a final product was obtained. The product was determined by XRD(Table 6) to be TAPSO-18 molecular sieve.

Table 6

No.	2θ	d(Å)	100× I/I_0
1	9.490	9.3119	100
2	10.430	8.4747	14
3	10.860	8.1401	12
4	12.950	6.8307	9
5	14.760	5.9969	11
6	15.520	5.7049	30
7	15.910	5.5659	17
8	16.880	5.2482	73
9	17.680	5.0125	21
10	19.500	4.5485	15
11	20.020	4.4315	31
12	20.810	4.2651	35
13	21.740	4.0847	15
14	23.820	3.7325	16
15	26.170	3.4024	23
16	26.720	3.3336	14
17	27.930	3.1919	22
18	30.090	2.9675	18
19	30.720	2.9080	18
20	32.330	2.7668	20

Comparison Example 3

[0060] By using essentially the same composition and procedure as in Example 21, while changing the 2.15g $Zr(NO_3)_4 \cdot 5H_2O$ in Example 21 to 13.65g $Ti(SO_4)_2$(96%), a final product was obtained. The product was a mixture of TAPSO-18 and TAPSO-44 crystals. The XRD result is shown in Table 7.

Table 7

No.	2θ	D(Å)	100× I/I_0
1	9.450	9.3513	17
2	12.840	6.8890	12
3	14.860	5.9567	26
4	15.940	5.5555	12

Table 7 (continued)

No.	2θ	D(Å)	100× I/I_0
5	16.880	5.2482	13
6	19.710	4.5005	60
7	20.880	4.2509	100
8	22.330	3.9781	76
9	23.830	3.7309	10
10	25.910	3.4359	38
11	28.930	3.0838	16
12	30.020	2.9742	21
13	34.550	2.5939	17
14	37.530	2.3945	12

Example 24

(Preparation of MnAPSO-18)

[0061] By using essentially the same composition and procedure as in Example21, while changing the 2.15g $Zr(NO_3)_4 \cdot 5H_2O$ in Example 21 to 1.23g $Mn(CH_3COO)_2 \cdot 4H_2O$, a final product was obtained. The product was MnAPSO-18 molecular sieve(Table 8).

Table 8

No.	2θ	d(Å)	100× I/I_0
1	9.480	9.3217	100
2	10.540	8.3865	14
3	12.820	6.8997	10
4	14.750	6.0009	10
5	15.940	5.5555	33
6	16.960	5.2236	62
7	19.560	4.5347	20
8	20.030	4.4294	22
9	20.510	4.3268	34
10	21.290	4.1700	28
11	23.860	3.7263	22
12	25.820	3.4477	15
13	26.250	3.3922	21
14	27.910	3.1941	17
15	30.250	2.9521	17
16	31.010	2.8815	24

Example 25

(Preparation of MgAPSO-18)

[0062] By using essentially the same composition and procedure as in Example 21, while changing the 2.15g $Zr(NO_3)_4 \cdot 5H_2O$ in Example 21 to 1.07g $Mg(CH_3COO)_2 \cdot 4H_2O$, a final product was obtained. The product was MgAPSO-18 molecular sieve(Table 9).

Table 9

No.	2θ	d(Å)	100× I/I_0
1	9.490	9.3119	100
2	10.460	8.4505	17

Table 9 (continued)

No.	2θ	d(Å)	100× I/I_0
3	10.910	8.1029	15
4	15.540	5.6976	32
5	16.910	5.2389	93
6	17.730	4.9984	24
7	19.530	4.5416	22
8	20.060	4.4228	39
9	20.870	4.2529	45
10	21.960	4.0442	20
11	22.360	3.9728	16
12	23.880	3.7232	20
13	24.320	3.6569	16
14	26.220	3.3960	27
15	27.970	3.1874	23
16	30.110	2.9655	22
17	31.070	2.8761	22
18	32.350	2.7651	25

Example 26

(Preparation of FAPSO-18)

[0063] By using essentially the same composition and procedure as in Example 21, while changing the 2.15g $Zr(NO_3)_4 \cdot 5H_2O$ and 10.34g N,N-diisopropylethylamine in Example 21 to 2.02g $Fe(NO_3)_3 \cdot 9H_2O$ and 10.61g N,N-diisopropylpropylamine respectively, a final product was obtained. The product was determined by XRD(Table 10) to be FAPSO-18 molecular sieve.

Table 10

No.	2θ	d(Å)	100× I/I_0
1	9.510	9.2924	100
2	10.440	8.4666	14
3	10.860	8.1401	14
4	15.560	5.6903	28
5	16.950	5.2267	71
6	17.670	5.0153	18
7	19.540	4.5393	16
8	20.060	4.4228	32
9	20.820	4.2630	40
10	21.780	4.0773	18
11	23.990	3.7064	14
12	24.320	3.6569	16
13	26.210	3.3973	25
14	30.120	2.9646	17
15	31.090	2.8743	19
16	32.340	2.7660	21

Example 27

(Preparation of NiAPSO-18)

[0064] By using essentially the same composition and procedure as in Example21, while changing the 2.15g $Zr(NO_3)_4 \cdot 5H_2O$ and 10.34g N,N-diisopropylethylamine in Example 21 to 1.45g $Ni(NO_3)_2 \cdot 6H_2O$ and 9.96g tetraethyl hydroxide amine, a final product was obtained. The product was determined by XRD(Table 11) to be NiAPSO-18 molecular sieve.

Table 11

No.	2θ	d(Å)	100× I/I_0
1	9.450	9.3513	100
2	10.550	8.3786	15
3	12.780	6.9212	12
4	14.740	6.0050	9
5	15.960	5.5486	48
6	16.880	5.2482	47
7	19.560	4.5347	21
8	20.510	4.3268	43
9	21.290	4.1700	35
10	23.830	3.7309	31
11	25.760	3.4556	19
12	26.270	3.3897	24
13	27.790	3.2076	21
14	30.330	2.9445	18
15	31.020	2.8806	28

Example 28

(Preparation of ZnAPSO-18)

[0065] By using essentially the same composition and procedure as in Example 21, while changing the 2.15g $Zr(NO_3)_4 \cdot 5H_2O$ in Example 21 to 1.10g $Zn(CH_3COO)_2 \cdot 2H_2O$, a final product was obtained. The product was ZnAPSO-18 molecular sieve(Table 12).

Table 12

No.	2θ	d(Å)	100× I/I_0
1	9.430	9.3711	100
2	10.500	8.4184	12
3	12.790	6.9158	11
4	15.920	5.5624	45
5	16.880	5.2482	55
6	19.560	4.5347	20
7	20.460	4.3372	41
8	21.240	4.1797	30
9	23.810	3.7340	26
10	25.720	3.4609	16
11	26.270	3.3897	22
12	27.780	3.2088	15
13	30.310	2.9464	17
14	30.980	2.8842	27

Comparison Example 4

[0066] By using essentially the same composition and procedure as in Example 21, while changing 10.34g N, N-diisopropylpropylamine in Example 21 to 5.82g N, N-diisopropylethylamine, a product of unknown phase was obtained. The XRD analysis result is shown in the table 13

Table 13

No.	2θ	d(Å)	100× I/I_0
1	7.500	11.7777	8
2	13.000	6.8045	2
3	14.930	5.9290	3
4	19.800	4.4803	6
5	20.530	4.3226	17
6	21.160	4.1953	6
7	21.890	4.0570	100
8	22.480	3.9518	11
9	23.260	3.8211	7
10	25.970	3.4281	4
11	28.320	3.1488	8
12	30.050	2.9713	4
13	31.270	2.8581	9
14	35.920	2.4981	12
15	42.400	2.1301	3
16	46.710	1.9431	5
17	48.310	1.8824	5
18	53.790	1.7028	3
19	56.700	1.6221	3

Example 29

(Preparation of CUZrAPSO-18)

[0067] By using essentially the same composition and procedure as in Example 21, while changing the 2.15g $Zr(NO_3)_4 \cdot 5H_2O$ in Example 21 to 1.08g $Zr(NO_3)_4 \cdot 5H_2O$ and 1.08g $Cu(NO_3)_2 \cdot 3H_2O$, a final product was obtained. The product was determined CuZrAPSO-18 molecular sieve.

Example 30

(Preparation of ZrAPSO-34)

[0068] 7.06g psudo-bromite(72.2wt% Al_2O_3) was dissolved in 19ml de-ionized water, and then 4.8g silica sol was added to the prepared alumina sol under stirring. 10.95g orthophosphoric acid (85wt% H_3PO_4) and 10ml de-ionized water was then added slowly under continual stirring for 10 minutes. After that, 1.07g $Zr(NO_3)_4 \cdot 5H_2O$ plus 10ml de-ionized water were added to the prepared mixture, and stirred for 20 minutes. Finally, 15.15g triethylamine was added to the mixture under continuous stirring until attaining a homogeneous phase. The composition of the final reaction mixture in molar oxide ratio was: $3Et_3N$: $0.4SiO_2$: Al_2O_3: P_2O_5:$0.05ZrO_2$: $39H_2O$.

[0069] The gel mixture is radiated in microwave oven for 2 minutes, then the mixture was sealed in a autoclave lined with polytetrafluoroethylene and crystallized under autogeneous pressure for 2.5 hours under temperature programmed 50~200°C. The solid product was washed to neutral, and then dried at 100°C in air. The product was determined by XRD (Table 14) to be the ZrAPSO-34 by XRD. Its water adsorption capacity was 31.2wt% at 25°C.

[0070] The chemical composition of the product was: 2.6wt.%C, 0.5wt.%N, 4.6wt.%SiO_2, 37.1wt.%Al_2O_3, 49.4wt.%P_2O_5, 2.2wt%ZrO_2, 3.6wt.%H_2O.

Table 14

No.	2θ	d(Å)	100× I/I_0
1	9.660	9.1485	100
2	13.010	6.7993	10
3	16.200	5.4669	35
4	17.040	5.1992	13

Table 14 (continued)

No.	2θ	d(Å)	100× I/I_0
5	20.750	4.2773	37
6	21.380	4.1526	15
7	24.270	3.6643	10
8	26.040	3.4191	14
9	30.590	2.9201	14
10	31.230	2.8617	18
11	49.090	1.8543	7

Example 31

(Preparation of TAPSO-34)

[0071] By using essentially the same composition and procedure as in Example 30, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 30 to 0.63g titanium sulfate(containing 96wt% $Ti(SO_4)_2$). The mixture was sealed in a autoclave lined with polytetrafluoroethylene after pressurizing with nitrogen to 0.4Mpa, heated at a temperature sufficiently high for 12 hours and crystallized for 2 hours under temperature programmed 50~200°C, a final product was obtained. The product was determined by XRD to be the TAPSO-34 molecular sieve, as shown in Table 15. Its water adsorption capacity was measured to be 35.1wt% at 25°C.

Table 15

No.	2θ	d(Å)	100× I/I_0
1	9.430	9.3711	100
2	12.780	6.9292	18
3	13.980	6.3297	8
4	15.940	5.5555	49
5	17.900	4.9513	12
6	18.940	4.6817	8
7	20.510	4.3268	79
8	21.000	4.2269	13
9	23.040	3.8570	10
10	25.140	3.5394	17
11	25.780	3.4530	20
12	30.490	2.9294	24
13	31.590	2.8299	9

Example 32

(Preparation of CoAPSO-34)

[0072] By using essentially the same composition and procedure as in Example 30, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 30 to 1.25g of $Co(CH_3COO)_4.4H_2O$, a final product was obtained. The product was determined by XRD to be the CoAPSO-34 molecular sieve, as shown in Table 16. Its water adsorption capacity was measured to be 34.0wt% at 25°C.

Table 16

No.	2θ	d(Å)	100× I/I_0
1	9.430	9.3711	100
2	12.760	6.9320	20
3	13.940	6.3477	8
4	15.930	5.5589	49

Table 16 (continued)

No.	2θ	d(Å)	100× I/I_0
5	17.860	4.9623	14
6	20.490	4.3309	81
7	23.010	3.8620	11
8	25.080	3.5477	21
9	25.790	3.4517	23
10	30.470	2.9313	28
11	31.110	2.8725	22

Example 33

(Preparation of MnAPSO-34)

[0073] By using essentially the same composition and procedure as in Example 30, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 30 to 0.62g of $Mn(CH_3COO)_4.4H_2O$, a final product was obtained. The product was determined by XRD to be the MnAPSO-34 molecular sieve, as shown in Table 17. Its water adsorption capacity was measured to be 32.3wt% at 25°C.

Table 17

No.	2θ	d(Å)	100× I/I_0
1	9.430	9.3711	100
2	12.780	6.9212	16
3	13.960	6.3387	8
4	15.930	5.5589	47
5	20.490	4.3309	73
6	23.020	3.8603	11
7	25.090	3.5463	15
8	25.770	3.4543	20
9	30.510	2.9276	24
10	31.100	2.8734	21

Example 34

(Preparation of NiAPSO-34)

[0074] By using essentially the same composition and procedure as in Example 30, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 30 to 0.62g of $Ni(NO_3)_2.6H_2O$, a final product was obtained. The product was determined by XRD to be the NiAPSO-34 molecular sieve, as shown in Table 18. Its water adsorption capacity was measured to be 34.6wt% at 25°C.

Table 18

No.	2θ	d(Å)	100× I/I_0
1	9.410	9.3909	100
2	12.760	6.9320	11
3	13.890	6.3707	4
4	15.930	5.5589	30
5	16.740	5.2917	8
6	17.800	4.9789	6
7	20.480	4.3330	45
8	21.190	4.1894	10
9	23.020	3.8603	7

Table 18 (continued)

No.	2θ	d(Å)	100× I/I_0
10	25.020	3.5561	8
11	25.770	3.4543	12
12	27.620	3.2270	9
13	29.390	3.0365	6
14	30.960	2.8860	4

Example 35

(Preparation of ZnAPSO-34)

[0075] By using essentially the same composition and procedure as in Example 30, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 30 to 0.62g of $Zn(NO_3)_2.6H_2O$, a final product was obtained. The product was determined by XRD to be the ZnAPSO-34 molecular sieve, as shown in Table 19. Its water adsorption capacity was measured to be 32.9wt% at 25°C.

Table 19

No.	2θ	d(Å)	100× I/I_0
1	9.450	9.3513	100
2	12.780	6.9212	23
3	14.000	6.3207	10
4	15.950	5.5520	48
5	17.910	4.9486	20
6	20.510	4.3268	96
7	23.020	3.8603	9
8	25.130	3.5408	27
9	25.780	3.4530	23
10	30.490	2.9294	35
11	31.160	2.8680	24
12	34.330	2.6100	9

Example 36

(Preparation of MgAPSO-34)

[0076] By using essentially the same composition and procedure as in Example 30, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 30 to 1.28g of $Mg(NO_3)_2.6H_2O$, a final product was obtained. The product was determined by XRD to be the MgAPSO-34 molecular sieve, as shown in Table 20. Its water adsorption capacity was measured to be 31.5wt% at 25°C.

Table 20

No.	2θ	d(Å)	100× I/I_0
1	9.430	9.3711	100
2	12.760	6.9320	15
3	13.930	6.3523	7
4	15.940	5.5555	44
5	17.890	4.9541	9
6	20.480	4.3330	70
7	21.030	4.2209	14
8	23.040	3.8570	9
9	25.110	3.5436	11

Table 20 (continued)

No.	2θ	d(Å)	100× I/I_0
10	25.780	3.4530	18
11	30.490	2.9294	20
12	30.970	2.8851	18

Example 37

(Preparation of LaAPSO-34)

[0077] By using essentially the same composition and procedure as in Example 30, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 30 to 2.17g of $La(NO_3)_3.6H_2O$, a final product was obtained. The product was determined by XRD to be the LaAPSO-34 molecular sieve, as shown in Table 21. Its water adsorption capacity was measured to be 31.6 wt% at 25°C.

Table 21

No.	2θ	d(Å)	100× I/I_0
1	9.420	9.3810	100
2	12.760	6.9320	16
3	15.930	5.5589	45
4	16.940	5.2297	12
5	20.480	4.3330	58
6	21.270	4.1738	14
7	25.780	3.4530	20
8	30.450	2.9332	19
9	30.990	2.8833	23

Example 38

(Preparation of FAPSO-34)

[0078] By using essentially the same composition and procedure as in Example 30, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 30 to 2.17g of $Fe(NO_3)_3.9H_2O$, a final product was obtained. The product was determined by XRD to be the FAPSO-34 molecular sieve, as shown in Table 22. Its water adsorption capacity was measured to be 34.2 wt% at 25°C.

Table 22

No.	2θ	d(Å)	100× I/I_0
1	9.440	9.3612	100
2	12.790	6.9158	15
3	13.970	6.3342	6
4	15.950	5.5520	39
5	17.910	4.9486	9
6	20.500	4.3289	60
7	25.090	3.5463	15
8	25.820	3.4477	16
9	30.480	2.9304	19
10	31.040	2.8788	19

Example 39

(Preparation of VAPSO-34)

[0079] By using essentially the same composition and procedure as in Example 30, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 30 to 0.59g of NH_4VO_3, a final product was obtained. The product was determined by XRD to be the VAPSO-34 molecular sieve, as shown in Table 23. Its water adsorption capacity was measured to be 33.5 wt% at 25°C.

Table 23

No.	2θ	d(Å)	100× I/I_0
1	9.450	9.3513	67
2	12.790	6.9158	12
3	15.960	5.5486	33
4	16.830	5.2636	9
5	20.510	4.3268	50
6	21.470	4.1354	100
7	23.010	3.8620	17
8	25.810	3.4490	15
9	30.520	2.9066	14
10	31.020	2.8806	19

Example 40

(Preparation of CrAPSO-34)

[0080] By using essentially the same composition and procedure as in Example 30, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 30 to 2.00g of $Cr(NO_3)_3.9H_2O$, a final product was obtained. The product was determined by XRD to be the CrAPSO-34 molecular sieve, as shown in Table 24. Its water adsorption capacity was measured to be 32.4 wt% at 25°C.

Table 24

No.	2θ	d(Å)	100× I/I_0
1	9.440	9.3612	100
2	12.790	6.9158	17
3	13.970	6.3342	7
4	15.940	5.5555	53
5	16.830	5.2636	11
6	17.900	4.9513	13
7	20.510	4.3268	79
8	21.040	4.2190	15
9	23.030	3.8587	12
10	25.110	3.5436	17
11	25.780	3.4530	23
12	30.480	2.9304	25
13	31.020	2.8806	24

Example 41

(Preparation of CuAPSO-34)

[0081] By using essentially the same composition and procedure as in Example 30, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 30 to 2.17g of $Cu(NO_3)_2.3H_2O$, a final product was obtained. The product was determined by XRD to be the CuAPSO-34 molecular sieve, as shown in Table 25. Its water adsorption capacity was measured to be 30.1 wt% at 25°C.

Table25

No.	2θ	d(Å)	100× I/I_0
1	9.450	9.3513	100
2	12.800	6.9104	16
3	14.000	6.3207	7
4	15.970	5.5451	49
5	17.900	4.9513	10
6	20.520	4.3247	66
7	21.140	4.1992	14
8	23.060	3.8537	12
9	25.120	3.5422	15
10	25.800	3.4503	20
11	30.530	2.9257	21
12	31.040	2.8788	21

Example 42

(Preparation of MoAPSO-34)

[0082] By using essentially the same composition and procedure as in Example 30, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 30 to 0.89g of $(NH_4)_6Mo_7O_{24}.4H_2O$, a final product was obtained. The product was determined by XRD to be the MoAPSO-34 molecular sieve, as shown in Table 26 Its water adsorption capacity was measured to be 36.8 wt% at 25°C.

Table 26

No.	2θ	d(Å)	100× I/I_0
1	9.410	9.3909	100
2	12.750	6.9374	15
3	13.910	6.3613	6
4	15.920	5.5624	47
5	16.890	5.2451	12
6	17.870	4.9596	10
7	20.480	4.3330	63
8	21.250	4.1777	14
9	25.090	3.5463	12
10	25.760	3.4556	19
11	30.430	2.9351	18
12	30.990	2.8833	19

Example 43

(Preparation of CaAPSO-34)

[0083] By using essentially the same composition and procedure as in Example 30, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 30 to 1.19g of $Ca(NO_3)_2.3H_2O$, a final product was obtained. The product was determined by XRD to be the CaAPSO-34 molecular sieve, as shown in Table 27. Its water adsorption capacity was measured to be 30.1 wt% at 25°C.

Table 27

No.	2θ	d(Å)	100× I/I_0
1	9.460	9.3414	100

Table 27 (continued)

No.	2θ	d(Å)	100× I/I_0
2	12.820	6.8997	18
3	14.000	6.3207	8
4	15.970	5.5451	47
5	17.930	4.9431	13
6	20.530	4.3226	75
7	21.030	4.2209	14
8	23.070	3.8521	11
9	25.160	3.5366	18
10	25.820	3.4477	22
11	30.530	2.9257	26
12	31.070	2.8761	21

Example 44

(Preparation of SrAPSO-34)

[0084] By using essentially the same composition and procedure as in Example 30, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 30 to 2.17g of $Sr(NO_3)_2$, a final product was obtained. The product was determined by XRD to be the SrAPSO-34 molecular sieve, as shown in Table 28. Its water adsorption capacity was measured to be 32.3 wt% at 25°C.

Table 28

No.	2θ	d(Å)	100× I/I_0
1	9.420	9.3810	100
2	12.760	6.9320	16
3	14.000	6.3207	6
4	15.930	5.5589	45
5	16.730	5.2949	11
6	17.910	4.9486	9
7	20.490	4.3309	59
8	21.210	4.1855	15
9	25.110	3.5436	15
10	25.780	3.4530	18
11	30.440	2.9341	21
12	31.000	2.8824	19

Example 45

(Preparation of BaAPSO-34)

[0085] By using essentially the same composition and procedure as in Example 30, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 30 to 1.31g of $Ba(NO_3)_2$, a final product was obtained. The product was determined by XRD to be the BaAPSO-34 molecular sieve, as shown in Table 29. Its water adsorption capacity was measured to be 32.2 wt% at 25°C.

Table 29

No.	2θ	d(Å)	100× I/I_0
1	9.460	9.3414	100
2	12.810	6.9050	16
3	15.980	5.5417	48

Table 29 (continued)

No.	2θ	d(Å)	100× I/I_0
4	17.920	4.9459	12
5	20.530	4.3224	69
6	21.240	4.1797	17
7	25.180	3.5339	15
8	25.830	3.4464	21
9	30.530	2.9257	20
10	31.050	2.8779	24

Example 46

(Preparation of ZrAPSO-34)

[0086] By using essentially the same composition and procedure as in Example 30, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 30 to 1.61g of $ZrOCl_2.8H_2O$, a final product was obtained. The product was determined by XRD to be the ZrAPSO-34 molecular sieve, as shown in Table 30. Its water adsorption capacity was measured to be 32.2 wt% at 25°C.

Table 30

No.	2θ	d(Å)	100× I/I_0
1	9.400	9.4009	100
2	12.740	6.9428	14
3	15.920	5.5624	41
4	16.860	5.2543	11
5	20.460	4.3372	59
6	21.070	4.2130	14
7	21.240	4.1797	12
8	23.010	3.8620	8
9	25.050	3.5519	10
10	25.740	3.4582	17
11	29.420	3.0335	7
12	30.940	2.8878	20
13	31.550	2.8334	9
14	48.910	1.8607	8

Example 47

(Preparation of ZrAPO-34)

[0087] A reaction mixture was prepared by combining 21ml of de-ionized water and 7.06g of hydrated aluminum oxide (a pseudo-boehmite phase, 72.2 wt% Al_2O_3), to which was added 11.53g of 85 wt% orthophosphoric acid (H_3PO_4) and 10ml of de-ionized water with stirring. After stirring for 10 minutes, to this mixture was added 2.15g of $Zr(NO_3)_4.5H_2O$ and 10ml of de-ionized water, and then stirred for 20 minutes. Finally 15.15g of triethylamine was added, and the mixture stirred until homogeneous. The following gel composition was prepared in terms of mole ratios of oxides: $3Net_3$: Al_2O_3: P_2O_5: $0.1ZrO_2$: $50H_2O$.

[0088] The gel mixture is radiated in :microwave oven for 2 minutes, then the mixture was sealed in a autoclave lined with polytetrafluoroethylene and crystallized under autogeneous pressure for 2.5 hours under temperature programmed 50~200°C. The solid product was washed with de-ionized water to neutral, and dried in air at 100°C. ZrAPO-34 molecular sieve was produced, as evidenced by the X-ray powder diffraction pattern of solid product. The analysis result of XRD was shown in Table 31.The water adsorption capacity of ZrAPO-34 at 25 °C measured to be 34.3 wt%.

Table 31

No.	2θ	d(Å)	100× I/I_0
1	9.610	9.1959	100
2	15.560	5.6903	15
3	16.910	5.2389	38
4	17.840	4.9679	23
5	20.180	4.3968	16
6	21.100	4.2071	23
7	22.070	4.0243	9
8	22.420	3.9623	9
9	24.460	3.6362	8
10	24.850	3.5801	9
11	25.530	3.4862	11
12	26.280	3.3884	10
13	26.870	3.3153	8
14	28.100	3.1729	18
15	30.190	2.9579	14
16	30.810	2.8997	9
17	31.300	2.8554	15
18	32.510	2.7519	17

Example 48

(Preparation of ZrAPSO-34)

[0089] A reaction mixture was prepared by combining 19ml of de-ionized water and 7.06g of hydrated aluminum oxide (a pseudo-boehmite phase, 72.2 wt% Al_2O_3), to which was added slowly and with stirring 4.8g of silica sol (25.0 wt%SiO_2).Then 11.53g of 85 wt% orthophosphoric acid (H_3PO_4) and 10ml of de-ionized water was added. After stirring for 10 minutes, to this mixture was added a solution of 1.07g of $Zr(NO_3)_4.5H_2O$ and 10ml of de-ionized water, and then stirred for 20 minutes. Finally 7.58g of triethylamine and 5.40g of diethylamine was added, and the mixture stirred until homogeneous. The following gel composition was prepared in terms of mole ratios of oxides: $1.5(Net_3+Net_2): 0.4SiO_2: Al_2O_3: P_2O_5: 0.05ZrO_2: 50H_2O$.

[0090] The gel mixture is radiated in microwave oven for 2 minutes, then the mixture was sealed in a autoclave lined with polytetrafluoroethylene and pressurizing with nitrogen gas to 0.4Mpa, and crystallized for 2.5 hours under temperature programmed 50~200°C. The solid product was washed with de-ionized water to neutral, and dried in air at 100°C. ZrAPSO-34 molecular sieve was produced, as evidenced by the X-ray powder diffraction pattern of solid product. The analysis result of XRD was shown in Table 32. The water adsorption capacity of ZrAPSO-34 at 25°C measured to be 27.7 wt%.

Table 32

No.	2θ	d(Å)	100× I/I_0
1	9.750	9.0642	100
2	13.130	6.7374	12
3	16.290	5.4369	26
4	20.860	4.2549	42
5	22.100	4.0189	96
6	25.500	3.4902	12
7	26.140	3.4062	14
8	28.510	3.1282	9
9	30.450	2.9332	9
10	30.900	2.8915	17
11	31.400	2.8466	21

Table 32 (continued)

No.	2θ	d(Å)	100× I/I_0
12	36.060	2.4887	9
13	36.240	2.4767	10
14	49.270	1.8479	7

Example 49

(Preparation of ZrAPSO-35)

[0091] A reaction mixture was prepared by combining 19ml of de-ionized water and 7.06g of hydrated aluminum oxide (a pseudo-boehmite phase,72.2 wt% Al_2O_3), to which was added slowly and with stirring 3.60g of silica sol(25 wt%SiO_2).Then 11.53g of 85 wt% orthophosphoric acid (H_3PO_4) and 10ml of de-ionized water was added. After stirring for 10 minutes, to this mixture was added a solution of 1.07g of $Zr(NO_3)_4.5H_2O$ and 20ml of de-ionized water, and then stirred for 20 minutes. Finally 7.50g of hexamethyleneimine was added, and the mixture stirred for about 20 minutes until homogeneous. The composition of the final reaction mixture in mole oxide ratios was: $1.5HN(CH_2)_6$: $0.3SiO_2$: Al_2O_3: P_2O_5: $0.05ZrO_2$: $55.5H_2O$.

[0092] The gel mixture is radiated in microwave oven for 1 minutes, then the mixture was sealed in a autoclave lined with polytetrafluoroethylene and crystallized under autogeneous pressure for 2 hours under temperature programmed 50~200°C. The solid product was washed with de-ionized water to neutral, and dried in air at 100°C. ZrAPSO-35 molecular sieve was produced, as evidenced by the X-ray powder diffraction pattern of solid product. The analysis result of XRD was shown in Table 33.The water adsorption capacity of ZrAPSO-35 at 25°C measured to be 35.5 wt%.

[0093] Chemical analysis established that the solid product was comprised of 3.2 wt% C, 0.6wt% N, 6.9wt% SiO_2, 39.1 wt% Al_2O_3, 45.4 wt% P_2O_5, 2.4 wt% ZrO_2 and 2.3 wt% H_2O.

Table 33

No.	2θ	d(Å)	100×I/I_0
1	8.590	10.2855	21
2	10.930	8.0881	50
3	13.300	6.6517	45
4	15.870	5.9290	8
5	17.270	5.1305	77
6	17.740	4.9956	10
7	21.020	4.2229	33
8	21.880	4.0588	100
9	23.180	3.8341	21
10	24.970	3.5631	10
11	26.830	3.3202	25
12	28.540	301250	24
13	29.050	3.0713	12
14	32.090	2.7869	48
15	34.490	2.5983	8

Comparison Example 5

[0094] By using essentially the same composition and procedure as in Example 49, while changing the 7.50g hexamethylene tetramine in Example 49 to 15.0g of the same templating agent(R/Al_2O_3 = 3.0), a final product was obtained. The product was not pure ZrAPSO-35 molecular sieve, but was a mixed crystal with unknown structure.

Comparison Example 6

[0095] By using essentially the same composition and procedure as in Example 49, while changing the 7.50g hexamethyleneimine in Example 49 to 2.5g of the same templating agent(R/Al_2O_3 = 0.5), a final product was obtained. The product was not pure ZrAPSO-35 molecular sieve, but was a mixed crystal that containing ZrAPSO-5 molecular sieve.

Comparison Example 7

[0096] By using essentially the same composition and procedure as in Example 49, while changing the 3.60g silica sol in Example 49 to 2.4g of the same silica sol(SiO_2/Al_2O_3 = 0.2), a final product was obtained. The product was not pure ZrAPSO-35 molecular sieve, but was a mixed crystal that containing small amount of ZrAPSO-5 molecular sieve.

Comparison Example 8

[0097] By using essentially the same composition and procedure as in Example 49, while changing the 3.60g silica sol in Example 49 to 1.2g of the same silica sol(SiO_2/Al_2O_3 = 0.1), a final product was obtained. The product was not pure ZrAPSO-35 molecular sieve, but was a mixed crystal that containing ZrAPSO-5 molecular sieve, as evidenced by the XRD pattern.

Comparison Example 9

[0098] By using essentially the same composition and procedure as in Example 49, while changing the 3.60g silica sol in Example 49 to 0g of silica sol(SiO_2/Al_2O_3 = 0), a final product was obtained. The product was not pure ZrAPO-35 molecular sieve, but was ZrAPO-16 molecular sieve.

Comparison Example 10

[0099] By using essentially the same composition and procedure as in Example 49, while changing the 3.60g silica sol in Example 49 to 8.4g of the same silica sol(SiO_2/Al_2O_3 = 0.7), a final product was obtained. The product was not pure ZrAPSO-35 molecular sieve, but was a mixed crystal that containing ZrAPSO-5 molecular sieve.

Example 50

(Preparation of TAPSO-35)

[0100] By using essentially the same composition and procedure as in Example 49, while changing the 1.07g Zr $(NO_3)_4.5H_2O$ in Example 49 to 0.63g of titanium sulfate(containing $Ti(SO_4)_2$ 96%), a final product was obtained. The product was determined by XRD to be the TAPSO-35 molecular sieve, as shown in Table 34. Its water adsorption capacity was measured to be 37.1 wt% at 25°C.

Table 34

No.	2θ	D(Å)	100× I/I_0
1	8.520	10.3698	18
2	10.840	8.1551	46
3	13.220	6.6918	37
4	15.800	5.6044	8
5	17.170	5.1602	65
6	20.930	4.2409	46
7	21.780	4.0773	100
8	23.080	3.8504	17
9	24.870	3.5772	11
10	26.730	3.3324	20
11	28.450	3.1347	34
12	28.950	3.0817	12
13	32.000	2.7946	47

Example 51

(Preparation of CoAPSO-35)

[0101] By using essentially the same composition and procedure as in Example 49, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 49 to 1.25g of $Co(CH_3COO).4H_2O$, then aging for 2 hours at room temperature and crystallizing for 12 hours at 200°C, a final product was obtained. The product was determined by XRD to be the CoAPSO-35 molecular sieve, as shown in Table 35. Its water adsorption capacity was measured to be 33.2 wt% at 25°C.

Table 35

No.	2θ	d(Å)	100× I/I_0
1	8.520	10.3698	16
2	10.850	8.1476	48
3	13.240	6.6817	38
4	15.800	6.0090	10
5	17.190	5.1542	65
6	17.670	5.0756	12
7	20.940	4.2389	33
8	21.790	4.0754	100
9	23.100	3.8472	21
10	24.890	3.5744	13
11	26.750	3.3299	21
12	28.450	3.1347	38
13	28.960	2.8646	11
14	32.000	2.7946	45
15	34.380	2.6064	12

Example 52

(Preparation of MnAPSO-35)

[0102] By using essentially the same composition and procedure as in Example 49, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 49 to 0.62g of $Mn(CH_3COO).4H_2O$, a final product was obtained. The product was determined by XRD to be the MnAPSO-35 molecular sieve, as shown in Table 36. Its water adsorption capacity was measured to be 31.3 wt% at 25°C.

Table 36

No.	2θ	d(Å)	100× I/I_0
1	8.530	10.3577	22
2	10.860	8.1401	49
3	13.230	6.6867	37
4	15.810	5.9982	9
5	17.190	5.1542	69
6	17.680	5.0655	10
7	20.940	4.2389	45
8	21.790	4.0754	100
9	23.090	3.8488	20
10	24.900	3.5730	11
11	26.760	3.3288	22
12	28.340	3.1466	34
13	28.980	3.1013	11
14	32.010	2.7937	48
15	34.410	2.6042	11

Example 53

(Preparation of NiAPSO-35)

[0103] By using essentially the same composition and procedure as in Example 49, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 49 to 1.45g of $Ni(NO_3)_2.6H_2O$, a final product was obtained. The product was determined by XRD to be the NiAPSO-35 molecular sieve, as shown in Table 37. Its water adsorption capacity was measured to be 36.4 wt% at 25°C.

Table 37

No.	2θ	d(Å)	$100\times I/I_0$
1	8.550	10.3335	50
2	10.930	8.0881	48
3	13.320	6.6418	38
4	15.890	5.5729	7
5	17.280	5.1276	65
6	17.770	4.9873	11
7	21.040	4.2190	30
8	21.890	4.0570	100
9	23.190	3.8324	23
10	24.980	3.5617	9
11	26.860	3.3165	23
12	28.450	3.1347	29
13	29.060	3.0703	13
14	32.110	2.7852	48
15	34.450	2.6381	8

Example 54

(Preparation of ZnAPSO-35)

[0104] By using essentially the same composition and procedure as in Example 49, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 49 to 1.49g of $Zn(NO_3)_2.6H_2O$, a final product was obtained. The product was determined by XRD to be the ZnAPSO-35 molecular sieve. Its water adsorption capacity was measured to be 29.9 wt% at 25°C.

Example 55

(Preparation of MgAPSO-35)

[0105] By using essentially the same composition and procedure as in Example 49, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 49 to 1.49g of $Mg(NO_3)_2.6H_2O$, a final product was obtained. The product was determined by XRD to be the MgAPSO-35 molecular sieve. Its water adsorption capacity was measured to be 33.3 wt% at 25°C.

Example 56

(Preparation of LaAPSO-35)

[0106] By using essentially the same composition and procedure as in Example 49, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 49 to 2.17g of $La(NO_3)_3.6H_2O$, a final product was obtained. The product was determined by XRD to be the LaAPSO-35 molecular sieve. Its water adsorption capacity was measured to be 35.6 wt% at 25°C.

Example 57

(Preparation of FAPSO-35)

[0107] By using essentially the same composition and procedure as in Example 49, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 49 to 2.02g of $Fe(NO_3)_3.9H_2O$, a final product was obtained. The product was determined by XRD to be the FAPSO-35 molecular sieve. Its water adsorption capacity was measured to be 30.8 wt% at 25°C.

Example 58

(Preparation of VAPSO-35)

[0108] By using essentially the same composition and procedure as in Example 49, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 49 to 0.59g of NH_4VO_3, a final product was obtained. The product was determined by XRD to be the VAPSO-35 molecular sieve. Its water adsorption capacity was measured to be 32.2 wt% at 25°C.

Example 59

(Preparation of CrAPSO-35)

[0109] By using essentially the same composition and procedure as in Example 49, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 49 to 2.00g of $Cr(NO_3)_2.9H_2O$, a final product was obtained. The product was determined by XRD to be the CrAPSO-35 molecular sieve. Its water adsorption capacity was measured to be 34.4 wt% at 25°C.

Example 60

(Preparation of CuAPSO-35)

[0110] By using essentially the same composition and procedure as in Example 49, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 49 to 1.21g $Cu(NO_3)_2.3H_2O$, a final product was obtained. The product was determined by XRD to be the CuAPSO-35 molecular sieve. Its water adsorption capacity was measured to be 33.1 wt% at 25°C.

Example 61

(Preparation of MoAPSO-35)

[0111] By using essentially the same composition and procedure as in Example 49, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ and the 7.50g hexamethyleneimine in Example 49 to 0.89g of $(NH_4)_6Mo_7O_{24}.4H_2O$ and a mixture of 2.56g of hexamethyleneimine and 4.67g of diethylamine, respectively, a final product was obtained. The product was determined by XRD to be the MoAPSO-35 molecular sieve. Its water adsorption capacity was measured to be 31.8 wt% at 25°C.

Example 62

(Preparation of CaAPSO-35)

[0112] By using essentially the same composition and procedure as in Example 49, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ and the 7.50g hexamethyleneimine in Example 49 to 1.19g of $Ca(NO_3)_2.3H_2O$ and a mixture of 4.21g of triethylamine and 2.56g of hexamethyleneimine, respectively, a final product was obtained. The product was determined by XRD to be the CaAPSO-35 molecular sieve. Its water adsorption capacity was measured to be 29.1 wt% at 25°C.

Example 63

(Preparation of SrAPSO-35)

[0113] By using essentially the same composition and procedure as in Example 49, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 49 to 1.06g of $Sr(NO_3)_2$ and the autoclave was sealed after pressurizing it with nitrogen to 0.2Mpa, a final product was obtained. The product was determined by XRD to be the SrAPSO-35 molecular sieve. Its water adsorption capacity was measured to be 30.3 wt% at 25°C.

Example 64

(Preparation of BaAPSO-35)

[0114] By using essentially the same composition and procedure as in Example 49, while changing the 1.07g $Zr(NO_3)_4.5H_2O$ in Example 49 to 1.31g of $Ba(NO_3)_2$ and the autoclave was sealed after pressurizing it with nitrogen to 0.2Mpa, a final product was obtained. The product was determined by XRD to be the BaAPSO-35 molecular sieve. Its water adsorption capacity was measured to be 30.8 wt% at 25°C.

Example 65

(Preparation of ZrAPSO-35)

[0115] A reaction mixture was prepared by combining 3.60g of silica sol (25wt.% SiO_2) under stirring, to which were added 7.06g of diaspore (74.2wt.% Al_2O_3) and 19ml of de-ionized water. Then 11.53g of 85wt.% orthophosphoric acid (H_3PO_4) and 10ml of de-ionized water were added slowly, and stirred for 10min. To this mixture 1.07g of $Zr(NO_3)_4 \cdot 5H_2O$ (AR) and 10ml of de-ionized water were added, and stirred for 20min. Then a mixture of 3.75g of hexamethyleneimine and 3.75g of cyclohexylamine were added as the templating agent, and the mixture was stirred for 15min until homogeneous.

[0116] The mixture was sealed in a autoclave lined with polytetrafluoroethylene, heated at a temperature sufficiently high for 12 hours and crystallized under autogeneous pressure for 2 hours under temperature programmed 50~200°C. The solid product was recovered by centrifuging and washing with water until neutral, and dried in air at 100°C. XRD analysis of the isolated product established that ZrAPSO-35 molecular sieve was produced. Its water adsorption capacity was 36.0 wt.%at25°C.

Example 66

(Preparation of ZrAPSO-35)

[0117] By using essentially the same composition and procedure as in Example 65, while changing the 7.06g of diaspore in Example 65 to 6.80g of pseudoboehmite (75.0wt% Al_2O_3), a final product was obtained. The product was determined by XRD to be the ZrAPSO-35 molecular sieve. Its water adsorption capacity was measured to be 32.2 wt% at 25°C.

Example 67

(Preparation of CoAPSO-44)

[0118] A reaction mixture was prepared by slowly combining 11.53g of 85wt.% orthophosphoric acid (H_3PO_4) and 14ml of de-ionized water, to which was added 6.88g of diaspore (74.2wt.% Al_2O_3) with stirring until homogeneous. Then 7.2g of silica sol (25wt.% SiO_2) was added, and stirred for 10min. To this mixture 1.25g of $Co(CH_3COO)_4 \cdot 4H_2O$ (AR) and 12ml of de-ionized water were added, and stirred for 10min. 12ml of cyclohexylamine was added as the templating agent, and the mixture was stirred for 15min until homogeneous. The composition of the final reaction mixture in molar oxide ratios was: $2.5C_6H_{11}NH_2$: $0.6SiO_2$: Al_2O_3: P_2O_5: $0.05CoO_2$: $39H_2O$

[0119] The gel mixture is radiated in microwave oven for 2 minutes, then the mixture was sealed in a autoclave lined with polytetrafluoroethylene and crystallized under autogeneous pressure for 3 hours under temperature programmed 50~200°C. The autoclave was then taken out and cooled to room temperature. The solid product was separated from the mother liquid and washed with water until neutral, then dried in air at 100°C. X-ray analysis(Table 38) of the isolated product established that the product was CoAPSO-44 molecular sieve. Its water adsorption capacity was measured to be 32.2 wt.% at 25°C.

Table 38

No.	2θ	d(Å)	100× I/I_0
1	9.400	9.4009	77

Table 38 (continued)

No.	2θ	d(Å)	100× I/I_0
2	12.950	6.8307	21
3	16.060	5.5142	52
4	18.930	4.6842	10
5	20.710	4.2854	100
6	21.670	4.0977	26
7	22.600	3.9311	10
8	23.030	3.8587	12
9	24.330	3.6554	70
10	26.150	3.4049	23
11	27.840	3.2020	10
12	30.020	2.9742	20
13	30.840	2.8970	51
14	35.450	2.5301	11

Comparison Example 11

[0120] By using essentially the same composition and procedure as in Example 67, while changing the 7.2g of silica sol in Example 65 to 1.80g of the same material, a final product was obtained. The product was determined by XRD to be a mixture of TAPSO-17 and TAPSO-44 molecular sieves.

Comparison Example 12

[0121] By using essentially the same composition and procedure as in Example 67, while changing the 7.2g of silica sol in Example 65 to 0.96g of the same material, a final product was obtained. The product was determined by XRD to be the TAPSO-17 molecular sieve.

Example 68

(Preparation of MnAPSO-44)

[0122] By using essentially the same composition and procedure as in Example 67, while changing the 1.25g of Co $(CH_3COO)_4.4H_2O$ in Example 67 to 1.24g of $Mn(CH_3COO)_4.4H_2O$, a final product was obtained. The product was determined by XRD(Table 39) to be the MnAPSO-44 molecular sieve. Its water adsorption capacity was measured to be 31.5 wt% at 25°C.

Table 39

No.	2θ	d(Å)	100× I/I_0
1	9.360	9.4410	80
2	12.890	6.8623	26
3	15.900	5.5382	57
4	18.870	4.6989	9
5	20.640	4.2998	100
6	21.610	4.1089	26
7	22.520	3.9449	11
8	22.970	3.8686	13
9	24.250	3.6673	70
10	26.080	3.4139	24
11	27.740	3.2133	11
12	29.940	2.9820	19
13	30.720	2.9080	47
14	35.370	2.5356	11

Example 69

(Preparation of CrAPSO-44)

[0123] By using essentially the same composition and procedure as in Example 67, while changing the 1.25g of Co $(CH_3COO)_4.4H_2O$ in Example 67 to 2.00g of $Cr(NO_3)_3.4H_2O$, a final product was obtained. The product was determined by XRD(Table 40) to be the CrAPSO-44 molecular sieve. Its water adsorption capacity was measured to be 30.8 wt% at 25°C.

Table 40

No.	2θ	d(Å)	100× I/I_0
1	9.410	9.3909	76
2	12.970	6.8202	24
3	16.070	5.5108	52
4	18.930	4.6842	10
5	20.730	4.2813	100
6	21.700	4.0921	30
7	22.600	3.9311	12
8	23.050	3.8554	14
9	24.350	3.6524	74
10	26.190	3.3998	26
11	27.890	3.1963	12
12	30.050	2.9713	22
13	30.870	2.8942	52
14	35.490	2.5273	12

Example 70

(Preparation of CuAPSO-44)

[0124] By using essentially the same composition and procedure as in Example 67, while changing the 1.25g of Co $(CH_3COO)_4.4H_2O$ in Example 67 to 1.21g of $Cu(NO_3)_3.4H_2O$, a final product was obtained. The product was determined by XRD(Table 41) to be the CuAPSO-44 molecular sieve. Its water adsorption capacity was measured to be 28.9 wt% at 25°C.

Table 41

No.	2θ	d(Å)	100× I/I_0
1	9.420	9.3810	84
2	12.960	6.8254	20
3	16.080	5.5074	60
4	18.960	4.6768	12
5	20.740	4.2793	99
6	21.690	4.0940	40
7	23.050	3.8554	14
8	24.340	3.6539	100
9	26.190	3.3998	20
10	27.870	3.1986	11
11	30.030	2.9733	31
12	30.870	2.8942	48
13	35.480	2.5280	17

Example 71

(Preparation of VAPSO-44)

[0125] By using essentially the same composition and procedure as in Example 67, while changing the 1.25g of Co $(CH_3COO)_4.4H_2O$ in Example 67 to 0.59g of NH_4VO_3, a final product was obtained. The product was determined by XRD(Table 42) to be the VAPSO-44 molecular sieve. Its water adsorption capacity was measured to be 28.5 wt% at 25°C.

Table 42

No.	2θ	d(Å)	$100\times I/I_0$
1	9.420	9.3810	74
2	12.980	6.8150	26
3	16.080	5.5074	49
4	17.290	5.1246	8
5	18.960	4.6768	10
6	20.740	4.2793	100
7	21.680	4.0958	23
8	22.610	3.9294	12
9	23.060	3.8537	16
10	24.350	3.6524	57
11	26.170	3.4024	18
12	27.920	3.1930	10
13	30.040	2.9723	22
14	30.860	2.8952	45
15	35.480	2.5280	14

Example 72

(Preparation of MoAPSO-44)

[0126] By using essentially the same composition and procedure as in Example 67, while changing the 1.25g of Co $(CH_3COO)_4.4H_2O$ in Example 67 to 0.89g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, a final product was obtained. The product was determined by XRD(Table 43) to be the MoAPSO-44 molecular sieve. Its water adsorption capacity was measured to be 28.6 wt% at 25°C.

Table 43

No.	2θ	d(Å)	$100\times I/I_0$
1	9.400	9.4009	95
2	12.970	6.8202	29
3	16.050	5.5177	42
4	18.940	4.6817	12
5	20.720	4.2834	100
6	21.680	4.0958	24
7	23.040	3.8570	16
8	24.350	3.6524	100
9	26.140	3.4062	28
10	30.030	2.9733	26
11	30.760	2.9043	44
12	35.470	2.5287	15

Example 73

(Preparation of TAPSO-44)

[0127] A reaction mixture was prepared by slowly combining 11.53g of 85wt.% orthophosphoric acid (H_3PO_4) and 14ml of de-ionized water, to which was added 6.88g of diaspore (74.2wt.% Al_2O_3) with stirring until homogeneous. Then 7.2g of silica sol (25wt.% SiO_2) was added, and stirred for 10min. To this mixture 1.7ml of tetrabutylorthotitanate ($Ti(OC_4H_{10})_4$) and 12ml of de-ionized water was added, and stirred for 10min. Then 12.5ml of cyclohexylamine was added as the templating agent, and the mixture was stirred for 15min until homogeneous. The composition of the final reaction mixture in molar oxide ratios was: $2.5C_6H_{11}NH_2$: $0.6SiO_2$: Al_2O_3: P_2O_5: $0.05TiO_2$: $39H_2O$

[0128] The gel mixture is radiated in microwave oven for 2 minutes, then the mixture was sealed in a autoclave lined with polytetrafluoroethylene after filled with 0.2MPa N_2, and crystallized for 3 hours under temperature programmed 50~200°C. The autoclave was then taken out and cooled to room temperature. The solid product was separated from the mother liquid and washed with water until neutral, and dried in air at 100°C. X-ray analysis of the isolated product established that the product was TAPSO-44 molecular sieve (Table 44). Its water adsorption capacity was 33.0 wt.% at 25°C.

Table 44

No.	2θ	d(Å)	100× I/I_0
1	9.410	9.3909	82
2	12.960	6.8254	21
3	13.720	6.4490	5
4	16.070	5.5108	56
5	17.280	5.1276	8
6	18.940	4.6817	10
7	20.720	4.2834	100
8	21.690	4.0940	28
9	23.050	3.8554	14
10	24.350	3.6524	83
11	26.160	3.4037	23
12	27.890	3.1963	9
13	30.040	2.9723	23
14	30.870	2.8942	50
15	35.500	2.5266	13

Example 74

(Preparation of ZrAPSO-44)

[0129] A reaction mixture was prepared by slowly combining 11.53g of 85wt.% orthophosphoric acid (H_3PO_4) and 14ml of de-ionized water, to which was added 7.06g of pseudoboehmite (72.2wt.% Al_2O_3) with stirring until homogeneous. Then 7.2 g of silica sol (25wt.% SiO_2) was added, and stirred for 10min. To this mixture 1.07g of $Zr(NO_3)\cdot5H_2O$ and 12ml of de-ionized water were added and stirred for 10min. Then 12.5ml of cyclohexylamine was added as the templating agent, and the mixture was stirred for 15min until homogeneous. The composition of the final reaction mixture in molar oxide ratios was: $2.5C_6H_{11}NH_2$: $0.6SiO_2$: Al_2O_3: P_2O_5: $0.05ZrO_2$: $39H_2O$.

[0130] The gel mixture is radiated in microwave oven for 2 minutes, then the mixture was sealed in a autoclave lined with polytetrafluoroethylene, filled with 0.2MPa N_2, and crystallized for 3 hours under temperature programmed 50~200°C. The autoclave was then taken out and cooled to room temperature. The solid product was separated from the mother liquid and washed with water until neutral, and dried in air at 100°C. X-ray analysis of the isolated product established that the product was ZrAPSO-44 molecular sieve(Table 45). Its water adsorption capacity was 34.1wt% at 25°C.

Table 45

No.	2θ	d(Å)	100× I/I_0
1	9.400	9.4009	80
2	12.940	6.8359	19
3	16.060	5.5142	48
4	17.250	5.1364	12
5	20.710	4.2854	88
6	21.680	4.0958	39
7	22.600	3.9311	14
8	23.030	3.8587	15
9	24.320	3.6569	100
10	26.150	3.4049	23
11	30.010	2.9752	31
12	30.850	2.8961	46
13	35.460	2.5294	15

Example 75

(Preparation of NiAPSO-44)

[0131] By using essentially the same composition and procedure as in Example 74, while changing the 1.07g of Zr $(NO_3)\cdot 5H_2O$ in Example 74 to 1.45g of $Ni(NO_3)_2\cdot 6H_2O$ (AR, 98%), a final product was obtained. The product was determined by XRD to be the NiAPSO-44 molecular sieve (Table 46). Its water adsorption capacity was measured to be 32.5 wt% at 25°C.

Table 46

No.	2θ	d(Å)	100× I/I_0
1	9.450	9.3513	67
2	12.990	6.8097	14
3	16.100	5.5006	36
4	17.330	5.1129	10
5	18.970	4.6744	9
6	20.750	4.2773	65
7	21.740	4.0847	29
8	23.080	3.8504	11
9	24.380	3.6480	100
10	26.190	3.3998	18
11	30.070	2.9694	28
12	30.890	2.8924	42
13	32.900	2.7201	9
14	35.510	2.5260	13

Example 76

(Preparation of ZnAPSO-44)

[0132] By using essentially the same composition and procedure as in Example 74, while changing the 1.07g of Zr $(NO_3)\cdot 5H_2O$ in Example 74 to 1.49g of $Zn(NO_3)_2\cdot 6H_2O$ (AR), a final product was obtained. The product was determined by XRD to be the ZnAPSO-44 molecular sieve(Table 47). Its water adsorption capacity was measured to be 29.8 wt% at 25°C.

Table 47

No.	2θ	d(Å)	100× I/I_0
1	9.370	9.4309	86
2	12.930	6.8412	22
3	16.030	5.5245	52
4	17.230	5.1423	9
5	18.900	4.6914	11
6	20.690	4.2895	100
7	21.650	4.1014	26
8	22.570	3.9363	11
9	23.010	3.8620	14
10	24.290	3.6613	93
11	26.120	3.4088	24
12	27.830	3.2031	11
13	29.990	2.9771	24
14	30.830	2.8979	52
15	35.430	2.5315	13

Example 77

(Preparation of FAPSO-44)

[0133] By using essentially the same composition and procedure as in Example 74, while changing the 1.07g of $Zr(NO_3)\cdot 5H_2O$ and 12.5ml of cyclohexylamine in Example 74 to 2.02g of $Fe(NO_3)_3\cdot 6H_2O$ (AR) and 13.1ml tetrabutylammonium hydroxide respectively, a final product was obtained. The product was determined by XRD to be the FAPSO-44 molecular sieve(Table 48). Its water adsorption capacity was measured to be 28.8 wt% at 25°C.

Table 48

No.	2θ	d(Å)	100× I/I_0
1	9.349	9.4511	79
2	12.900	6.8571	19
3	16.000	5.5348	47
4	17.210	5.1483	10
5	18.880	4.6965	12
6	20.670	4.2936	91
7	21.610	4.1089	31
8	22.530	3.9432	10
9	22.980	3.8670	16
10	24.260	3.6658	100
11	26.100	3.4114	21
12	27.800	3.2065	9
13	29.950	2.9810	35
14	30.810	2.8997	53
15	32.760	2.7314	10
16	35.410	2.5329	15

Example 78

(Preparation of MgAPSO-44)

[0134] By using essentially the same composition and procedure as in Example 74, while changing the 1.07g of $Zr(NO_3).5H_2O$ in Example 74 to 1.28g of $Mg(NO_3)_2\cdot 6H_2O$ (AR), a final product was obtained. The product was determined by XRD to be the ZnAPSO-44 molecular sieve(Table 49). Its water adsorption capacity was measured to be 33.0 wt% at 25°C.

Table 49

No.	2θ	d(A)	100× I/I_0
1	9.420	9.3810	100
2	12.970	6.8202	20
3	16.070	5.5108	50
4	18.960	4.6768	13
5	20.730	4.2813	99
6	21.690	4.0940	30
7	23.050	3.8554	14
8	24.340	3.6539	93
9	26.190	3.3998	22
10	30.040	2.9723	26
11	30.760	2.9043	38
12	30.860	2.8952	47
13	35.470	2.5287	12

Example 79

(Preparation of CaAPSO-44)

[0135] By using essentially the same composition and procedure as in Example 74, while changing the 1.07g of Zr $(NO_3)\cdot 5H_2O$ in Example 74 to 0.59g of $Ca(NO_3)_2\cdot 4H_2O$ (AR), a final product was obtained. The product was determined by XRD to be the CaAPSO-44 molecular sieve(Table 50). Its water adsorption capacity was measured to be 32.2 wt% at 25°C.

Table 50

No.	2θ	d(Å)	100× I/I_0
1	9.340	9.4612	69
2	12.910	6.8518	17
3	16.010	5.5313	34
4	17.240	5.1394	12
5	18.870	4.6989	7
6	20.660	4.2957	60
7	21.620	4.1071	23
8	22.980	3.8670	9
9	24.290	3.6613	100
10	26.090	3.4126	16
11	27.810	3.2054	8
12	29.980	2.9781	31
13	30.770	2.9034	29
14	32.930	2.7258	8
15	35.410	2.5329	13

Example 80

(Preparation of SrAPSO-44)

[0136] By using essentially the same composition and procedure as in Example 74, while changing the 1.07g of Zr $(NO_3)\cdot 5H_2O$ in Example 74 to 0.53g of $Sr(NO_3)_2$ (AR), a final product was obtained. The product was determined by XRD to be the SrAPSO-44 molecular sieve(Table 51). Its water adsorption capacity was measured to be 30.5 wt% at

25°C.

Table 51

No.	2θ	d(Å)	100× I/I_0
1	9.400	9.4009	63
2	12.950	6.8307	16
3	16.060	5.5142	36
4	17.280	5.1276	9
5	20.720	4.2834	77
6	21.680	4.0958	36
7	23.060	3.8537	13
8	24.330	3.6554	100
9	26.150	3.4049	18
10	27.870	3.1986	9
11	30.030	2.9733	33
12	30.740	2.9062	29
13	30.870	2.8942	37
14	35.470	2.5287	12

Example 81

(Preparation of BaAPSO-44)

[0137] By using essentially the same composition and procedure as in Example 74, while changing the 1.07g of $Zr(NO_3)\cdot5H_2O$ in Example 74 to 0.65g of $Ba(NO_3)_2$ (AR), a final product was obtained. The product was determined by XRD to be the BaAPSO-44 molecular sieve(Table 52). Its water adsorption capacity was measured to be 31.8 wt% at 25°C.

Table 52

No.	2θ	d(Å)	100× I/I_0
1	9.410	9.3909	65
2	12.940	6.8359	15
3	16.080	5.5074	41
4	20.740	4.2793	81
5	21.700	4.0921	23
6	23.050	3.8554	14
7	24.350	3.6524	100
8	26.170	3.4024	24
9	30.020	2.9742	25
10	30.740	2.9062	30
11	30.880	2.8933	41
12	35.490	2.5273	13

Example 82

(Preparation of LaAPSO-44)

[0138] By using essentially the same composition and procedure as in Example 74, while changing the 1.07g of $Zr(NO_3)\cdot5H_2O$ in Example 74 to 2.17g of $La(NO_3)_3\cdot6H_2O$ (AR), a final product was obtained. The product was determined by XRD to be the LaAPSO-44 molecular sieve(Table 53). Its water adsorption capacity was measured to be 31.3 wt% at 25°C.

Table 53

No.	2θ	d(Å)	100× I/I_0
1	9.400	9.4009	80
2	12.970	6.8202	20
3	16.070	5.5108	61
4	18.940	4.6817	10
5	20.730	4.2813	100
6	21.690	4.0940	34
7	22.600	3.9311	10
8	23.050	3.8554	13
9	24.330	3.6554	90
10	26.170	3.4024	20
11	27.870	3.1986	10
12	30.030	2.9733	34
13	30.880	2.8933	54
14	32.860	2.7234	9
15	35.460	2.5294	13

Example 83

(Preparation of SAPO-56)

[0139] A reaction mixture was prepared by orderly combining 10.40g of silica sol (40wt.% SiO_2) and 26.28g of 85wt.% orthophosphoric acid (H_3PO_4), to which was added 12.75g of activated alumina (73.0wt.% Al_2O_3) and 75ml of deionized water. To this mixture 40g of N', N', N, N-tetramethyl-1,6-hexanediamine was added as the templating agent, and the mixture was stirred until homogeneous.

[0140] The gel mixture is radiated in microwave oven for 2 minutes, then the mixture was sealed in a autoclave lined with polytetrafluoroethylene and crystallized under autogeneous pressure for 2 hours under temperature programmed 50~200°C. The solid product was recovered by centrifuging and washed with water until neutral, then dried in air at 100°C, the SAPO-56 had been produced. The above product has an X-ray powder diffraction pattern characterized by the following data(Table 54):

Table 54

No.	2θ	d(Å)	100×I/I_0
1	7.380	11.9689	18
2	8.610	10.2616	58
3	11.530	7.6686	56
4	12.840	6.8890	35
5	15.490	5.7158	36
6	17.310	5.1188	44
7	17.720	5.0012	65
8	20.180	4.3968	78
9	21.610	4.1089	100
10	21.960	4.0442	24
11	23.440	3.7921	36
12	25.870	3.4412	36
13	27.780	3.2088	67
14	29.900	2.9859	24
15	30.320	2.9455	38
16	31.310	2.8546	33
17	33.430	2.6782	27
18	34.470	2.5998	19

Example 84

(Preparation of TAPSO-56)

[0141] Reaction mixture A was prepared by orderly combining 10.40g of silica sol (40wt.% SiO_2) and 26.28g of 85wt.% orthophosphoric acid (H_3PO_4), to which was added 12.10g of activated alumina (73.0wt.% Al_2O_3) and 70ml of de-ionized water and stirred until homogeneous. Solution B was prepared by combining 2.85g of $Ti(SO_4)_2$ (96wt.%) and 5ml of de-ionized water and stirring until homogeneous. Solusion B was added to mixture A with intensively stirring for all of 30min. To this mixture 40g of N', N', N, N-tetramethyl-1, 6-hexanediamine was added as the templating agent, and the mixture was stirred until homogeneous.

[0142] The gel mixture is radiated in microwave oven for 2 minutes, then the mixture was sealed in a autoclave lined with polytetrafluoroethylene and crystallized under autogeneous pressure for 2 hours under temperature programmed 50~200°C. The solid product was recovered by centrifuging and washed with water until neutral, then dried in air at 100°C, the TAPSO-56 molecular sieve had been produced. The above product has an X-ray powder diffraction pattern characterized by the following data in Table 55.

Table 55

No.	2θ	d(Å)	100× I/I_0
1	7.340	12.0341	20
2	8.559	10.3215	64
3	11.480	7.7018	61
4	12.790	6.9158	35
5	15.440	5.7342	35
6	17.260	5.1335	42
7	17.680	5.0125	47
8	19.650	4.5141	18
9	20.140	4.4054	79
10	21.570	4.1165	100
11	23.410	3.7969	32
12	25.840	3.4451	36
13	27.760	3.2110	60
14	30.280	2.9493	36
15	31.270	2.8581	30
16	33.410	2.6798	26
17	34.440	2.6020	15

Comparison Example 13

[0143] By using essentially the same composition and procedure as in Example 84, while changing the 40g of N', N', N, N-tetramethyl-1, 6-hexanediamine in Example 84 to 10g of the same material. The proportion of the template and Al_2O_3 was 0.62g. A final product was obtained. The product was determined by XRD to be TAPSO-11 molecular sieve. The product has an X-ray powder diffraction pattern characterized by the following data(Table 56).

Table 56

No.	2θ	d(Å)	100× I/I_0
1	8.070	10.9470	20
2	9.450	9.3513	56
3	13.200	6.7019	24
4	15.700	5.6399	47
5	20.510	4.3268	77
6	21.050	4.2170	93
7	22.760	3.9039	91
8	23.240	3.8243	100

Table 56 (continued)

No.	2θ	d(Å)	100× I/I_0
9	24.780	3.5900	29
10	26.700	3.3360	30
11	28.740	3.1037	33
12	33.020	2.7105	25

Example 85

(Preparation of FAPSO-56)

[0144] Reaction mixture A was prepared by orderly combining 12.80g of silica sol (40wt.% SiO_2) and 19.50g of 85wt.% orthophosphoric acid (H_3PO_4), to which was added 15.90g of activated alumina (73.0wt.% Al_2O_3) and 70ml of de-ionized water and stirred until homogeneous. Solution B was prepared by combining 2.85g of $Fe_2(SO_4)_3$ (96wt.%) and 5ml of de-ionized water and stirring until homogeneous. Solution B was added to mixture A with intensively stirring for all of 30min. To this mixture 40g of N', N', N, N-tetramethyl-1, 6-hexanediamine was added as the templating agent, and the mixture was stirred until homogeneous.

[0145] The mixture was sealed in a autoclave lined with polytetrafluoroethylene, heated at a temperature sufficiently high for 12 hours and crystallized under autogeneous pressure for 2 hours under temperature programmed 50~200°C. The solid product was recovered by centrifuging and washed with water until neutral, then dried in air at 100°C, the FAPSO-56 had been produced. The above product has an X-ray powder diffraction pattern characterized by the following data in Table 57.

Table 57

No.	2θ	d(Å)	100× I/I_0
1	7.360	12.0041	14
2	8.559	10.3215	49
3	11.480	7.7018	60
4	12.810	6.9050	28
5	15.450	5.7306	28
6	17.270	5.1305	40
7	17.700	5.0068	100
8	19.660	4.5119	15
9	20.150	4.4032	65
10	21.580	4.1146	76
11	23.420	3.7953	45
12	25.840	3.4451	35
13	27.770	3.2099	98
14	29.870	2.9888	21
15	30.280	2.9493	31
16	31.280	2.8572	26
17	33.420	2.6790	27
18	34.460	2.6005	17

Example 86

(Preparation of ZrAPSO-56)

[0146] By using essentially the same composition and procedure as in Example 84, while changing the 2.85g of $Ti(SO_4)_2$ (96wt.%) and 5ml of de-ionized water in preparing solution B and 40g of N', N', N, N-tetramethyl-1, 6-hexanediamine as the templating agent in Example 84 to 3.71g of $ZrOCl_2 \cdot 8H_2O$ (99wt.%) and 5ml of de-ionized water and a mixture of 20g of N', N', N, N-tetramethyl-1, 6-hexanediamine and 13g of tripropylamine respectively, a final product was obtained. The product was ZrAPSO-56 molecular sieve. The above product has an X-ray powder diffraction pattern characterized by the following data in Table 58.

Table 58

No.	2θ	d(Å)	100× I/I_0
1	7.360	11.9851	21
2	8.580	10.2855	61
3	11.510	7.6855	63
4	12.820	6.8997	40
5	15.480	5.7269	35
6	17.280	5.1246	46
7	17.700	5.0125	67
8	20.180	4.3968	77
9	21.610	4.1089	100
10	23.430	3.7937	39
11	25.890	3.4386	44
12	27.750	3.2122	78
13	30.330	2.9445	37
14	31.340	2.8519	36
15	33.420	2.6790	29
16	34.500	2.5976	22
17	50.650	1.8008	18

Example 87

(Preparation of MnAPSO-56)

[0147] By using essentially the same composition and procedure as in Example 84, while changing the 2.85g of Ti $(SO_4)_2$ (96wt.%) and 5ml of de-ionized water in preparing solution B and 40g of N', N', N, N-tetramethyl-1, 6-hexanediamine as the templating agent in Example 84 to 2.82g of $MnAc_2{\cdot}4H_2O$ (99wt.%) and 5ml of de-ionized water and a mixture of 10g of N', N', N, N-tetramethyl-1, 6-hexanediamine and 25g of *n*-propylamine respectively, a final product was obtained. The product was MnAPSO-56 molecular sieve. The above product has an X-ray powder diffraction pattern characterized by the following data in Table 59.

Table 59

No.	2θ	d(Å)	100× I/I_0
1	7.380	11.9689	19
2	8.600	10.2735	56
3	11.520	7.6752	58
4	12.830	6.8943	38
5	14.810	5.9767	12
6	15.490	5.7158	37
7	17.290	5.1246	44
8	17.710	5.0040	68
9	19.660	4.5119	19
10	20.170	4.3989	81
11	21.600	4.1108	100
12	21.940	4.0479	22
13	23.450	3.7905	37
14	25.860	3.4425	37
15	27.790	3.2076	71
16	29.900	2.9859	25
17	30.280	2.9493	39
18	31.300	2.8554	33

Table 59 (continued)

No.	2θ	d(Å)	100× I/I_0
19	33.440	2.6774	29
20	34.470	2.5998	20

Example 88

(Preparation of CoAPSO-56)

[0148] By using essentially the same composition and procedure as in Example 84, while changing the 2.85g of $Ti(SO_4)_2$ (96wt.%) and 5ml of de-ionized water in preparing solution B in Example 84 to 2.05g of $CoAc_2.4H_2O$ (99.5wt.%) and 5ml of de-ionized water, a final product was obtained. The product was CoAPSO-56 molecular sieve.

Example 89

(Preparation of NiAPSO-56)

[0149] By using essentially the same composition and procedure as in Example 84, while changing the 2.85g of $Ti(SO_4)_2$ (96wt.%) and 5ml of de-ionized water in preparing solution B in Example 84 to 2.45g of $Ni(NO_3)_2 \cdot 6H_2O$ (98wt.%) and 5ml of de-ionized water, a final product was obtained. The product was NiAPSO-56 molecular sieve.

Example 90

(Preparation of CuAPSO-56)

[0150] By using essentially the same composition and procedure as in Example 84, while changing the 2.85g of $Ti(SO_4)_2$ (96wt.%) and 5ml of de-ionized water in preparing solution B in Example 84 to 3.05g of $CuSO_4 \cdot 6H_2O$ (98wt.%) and 5ml of de-ionized water, a final product was obtained. The product was CuAPSO-56 molecular sieve.

Example 91

(Preparation of TCuAPSO-56)

[0151] By using essentially the same composition and procedure as in Example 84, while changing the 2.85g of $Ti(SO_4)_2$ (96wt.%) and 5ml of de-ionized water in preparing solution B in Example 84 to 1.42g of $Ti(SO_4)_2$ (96wt.%) and 1.52g of $CuSO_4 \cdot 6H_2O$ (98wt.%) and 5ml of de-ionized water, a final product was obtained. The product was TCuAPSO-56 molecular sieve.

Example 92

[0152] A portion of solid product of Example 84 was placed in crucible pot and calcined in air at 550°C for no less than 1, preferred 3~8 hours. The calcined sample was quantified exactly and placed in the desiccator that was loaded with the saturated NaCl solution at room temperature for 24 hours. The value of saturated water adsorption capacity was measured by the changed weight of the calcined sample. The experiment indicated that the water adsorption capacity of TAPSO-56 molecular sieve was 29.6%.

Example 93

(Catalytic reaction)

[0153] The primary powder of synthesized MeAPSO-17 molecular sieves of Example 1~16 were calcined in air at 550°C for 5 hours, thus the microporous MeAPSO-17 molecular sieves were obtained, which can be used as catalysts. The MTO(*Methanol to olefins)* reactions were performed with reaction temperature of 450°C. The weight hour's space velocity of methanol was $2h^{-1}$. The results showed that the conversion of methanol was 100% and the selectivity of $C_2^=-C_3^=$ was the following data in Table 60.

Table 60

Samples	$C_2^=\sim C_3^=$(wt%)
TAPSO-17	56.84
VAPSO-17	56.28
CrAPSO-17	53.44
ZrAPSO-17	53.32
MgAPSO-17	52.55
CaAPSO-17	52.10
SrAPSO-17	48.55
BaAPSO-17	48.47
FAPSO-17	46.78
CoAPSO-17	48.65
NiAPSO-17	55.62
CuAPSO-17	47.87
ZnAPSO-17	57.84
MnAPSO-17	49.81
MoAPSO-17	46.24
LaAPSO-17	51.22

Example 94

[0154] The primary powder of synthesized ZrAPSO-18 molecular sieves of Example 21 The Sample of Example 21 were calcined in air at 550°C for 4 hours, thus the microporous ZrAPSO-18 molecular sieve was obtained, which can be used as catalyst. Then the catalyst was pressed, crushed and sorted into 20~40 mesh. 1.28g of the sample was placed in a fixed-bed quartz reactor for estimating the catalytic activity of methanol to olefins (MTO) reaction. The MTO reaction was performed with reaction temperature of 450°C. Methanol was carried by N_2, the weight hour's space velocity of which was $2h^{-1}$. The products were analyzed by on-line gas chromatogram. The results showed that the conversion of methanol was 100%, the selectivity of $C_2^=$-$C_3^=$ was upwards of 85%, which indicated that ZrAPSO-18 molecular sieve had high activity on MTO reaction.

Example 95

(Catalytic reactions)

[0155] The primary powder of synthesized MeAPSO-34 molecular sieves of Example 30~45 were calcined in air at 550°C for 5 hours, thus the microporous MeAPSO-34 molecular sieves were obtained, which can be used as catalysts. The MTO(*Methanol to olefins*) reactions were performed with reaction temperature of 450°C. The weight hour's space velocity of methanol was about $2h^{-1}$. The results showed that the conversions of methanol were 100% and the selectivity of $C_2^=$-$C_3^=$ were the following data in Table 61.

Table 61

Samples	$C_2^=\sim C_3^=$(wt%)
ZrAPSO-34	89.41
TAPSO-34	86.67
CoAPSO-34	92.93
MnAPSO-34	88.27
NiAPSO-34	87.15
ZnAPSO-34	91.62
MgAPSO-34	91.57
LaAPSO-34	88.97
FAPSO-34	88.41
VAPSO-34	84.96

Table 61 (continued)

Samples	$C_2^{=}\sim C_3^{=}$(wt%)
CrAPSO-34	88.06
CuAPSO-34	88.45
MoAPSO-34	90.07
CaAPSO-34	89.90
SrAPSO-34	89.92
BaAPSO-34	89.40

Example 96

(Catalytic reactions)

[0156] The primary powder of synthesized MeAPSO-35 molecular sieves of Example 49~64 were calcined in air at 550°C for 5 hours, thus the microporous MeAPSO-35 molecular sieves were obtained, which can be used as catalysts. The MTO(*Methanol to olefins)* reactions were performed with reaction temperature of 450°C. The weight hour's space velocity of methanol was about $2h^{-1}$. The results showed that the conversions of methanol were 100% and the selectivity of $C_2^{=}$-$C_3^{=}$ were the following data in Table 62.

Table 62

Samples	$C_2^{=}\sim C_3^{=}$(wt%)
ZrAPSO-35	68.44
TAPSO-35	66.35
CoAPSO-35	64.78
MnAPSO-35	64.57
NiAPSO-35	62.22
ZnAPSO-35	65.88
MgAPSO-35	64.35
LaAPSO-35	64.21
FAPSO-35	63.27
VAPSO-35	63.11
CrAPSO-35	62.25
CuAPSO-35	61.92
MoAPSO-35	59.14
CaAPSO-3	58.66
SrAPSO-35	55.37
BaAPSO-35	52.83

Example 97

(Catalytic reactions)

[0157] The primary powder of synthesized MeAPSO-44 molecular sieves of Example 67~82 were calcined in air at 550°C for 5 hours, thus the microporous MeAPSO-44 molecular sieves were obtained, which can be used as catalysts. The MTO(*Methanol to olefins*) reactions were performed with reaction temperature of 450°C. The MTO reactions were performed with reaction temperature of 450°C. The weight hour's space velocity of methanol was about $2h^{-1}$. The results showed that the conversions of methanol were 100% and the selectivity of $C_2^{=}$-$C_3^{=}$ were the following data in Table 63.

Table 63

Samples	$C_2^{=}\sim C_3^{=}$(wt%)
CoAPSO-44	96.62

Table 63 (continued)

Samples	$C_2^{=}$~$C_3^{=}$(wt%)
MnAPSO-44	82.00
CrAPSO-44	60.94
CuAPSO-44	72.97
VAPSO-44	75.61
TAPSO-44	64.17
ZrAPSO-44	86.08
NiAPSO-44	74.66
ZnAPSO-44	70.93
MgAPSO-44	82.94
CaAPSO-44	91.59
SrAPSO-44	84.95
BaAPSO-44	83.38
LaAPSO-44	86.42
FAPSO-44	76.45
MOAPSO-44	62.77

Example 98

[0158] The primary powder of synthesized TAPSO-56 molecular sieves of Example 84 were calcined in air at 550°C for 5 hours, thus the microporous TAPSO-56 molecular sieves were obtained, which can be used as catalysts. Then the catalyst was pressed, crushed and sorted into 20~40 mesh. 1.28g of the sample was placed in a fixed-bed quartz reactor for estimating the catalytic activity of methanol to olefins (MTO) reaction. The MTO reaction was performed with reaction temperature of 450°C. Methanol was carried by N_2, the weight hour's space velocity of which was $2h^{-1}$. The products were analyzed by on-line gas chromatogram. The results showed that the conversion of methanol was 100%, the selectivity of $C_2^{=}$-$C_3^{=}$ was upwards of 70%, which indicated that TAPSO-56 molecular sieve had high activity on MTO reaction.

[0159] According to the results of the above full-scale tests and reference tests, we can conclude conveniently that MeAPSOs molecular sieves could be fast synthesized by the use of the above templating agents and by microwave preparation of the mixture gel and by hydrothermal crystallization at programmed temperature. Because the processes are simple and the technological conditions can be controlled easily, the processes are suitable for use in the commercial scale. Additionally, after calcination, MeAPSO molecular sieves can be used as absorbents or catalysts (for example, the reaction of catalytic cracking, polymerization, reforming, alkylation, dealkylation. oxidation, transalkyation, isomerization, hydrocyclization, dehydrogenation, and hydrogenation, etc.). Especially in the process of MTO reaction, the catalytic activity and selectivity are very high, which illustrated that these MeAPSO molecular sieves were promising to be used in a commercial scale.

Claims

1. A class of microporous metal-containing silicoaluminophosphate molecular sieves whose as-synthesized chemical composition on an anhydrous basis is: $mR\cdot(M_qSi_xAl_yP_z)O_2$, wherein *"R"* represents the templating agent presented in the intracrystalline pore system; *"m "* is the molar amount of *"R"* per mole of $(M_qSi_xAl_yP_z)O_2$ and has a value from 0.01to 8.00; "M" represents at least one metal element; *"q ", "x ", "y"* and *"z"* represent the molar fractions of metal, silicon, aluminum and phosphorus respectively, whose variations are q=0~0.98, x=0~0.98, y=0.01~0.60, z=0.01~0.60 and $q+x+y+z=1$.

2. The molecular sieves according to claim 1 wherein metal atoms in the microporous metal silicoaluminophosphate molecular sieves (MeAPSOs), at least in part, exist in the framework of the molecular sieve in the form of MeO_2 tetrahedra, and metal atom is at least one of Zr, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Mg, Ca, Sr, Ba and La.

3. The molecular sieves according to claim 1 or 2 wherein the metal-containing silicoaluminophosphate(MeAPSO-17) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table I.

Table I

No.	2θ	d(Å)	Relative Intensity
1	7.56-7.75	11.68-11.60	vs
2	13.18-13.25	6.69-6.60	s-vs
3	15.26-15.38	5.77-5.65	w-m
4	19.44-19.48	4.58-4.46	w-m
5	20.32-20.42	4.37-4.25	vs

4. The molecular sieves according to claim 1 or 2 wherein the metal-containing silicoaluminophosphate(MeAPSO-18) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table II.

Table II

No.	2θ	d(Å)	Relative Intensity
1	9.43-9.51	9.37-9.29	vs
2	10.50-10.86	8.42-8.14	w
3	16.88-16.95	5.25-5.22	m-s
4	19.56-20.06	4.53-4.42	w
5	20.46-20.82	4.34-4.26	m

5. The molecular sieves according to claim 1 or 2 wherein the metal-containing silicoaluminophosphate(MeAPSO-34) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table III.

Table III

No.	2θ	d(Å)	Relative Intensity
1	9.41-9.46	9.39-9.34	vs
2	15.93-15.97	5.56-5.54	w-m
3	17.80-17.93	4.98-4.94	w
4	20.48-20.53	4.33-4.32	m-s
5	25.02-25.16	3.55-3.53	w

6. The molecular sieves according to claim 1 or 2 wherein the metal-containing silicoaluminophosphate(MeAPSO-35) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table IV.

Table IV

No.	2θ	d(Å)	Relative Intensity
1	8.52-8.59	10.37-10.28	w
2	10.84-10.93	8.15-8.09	m-s
3	13.22-13.30	6.69-6.65	w-m
4	17.17-17.27	5.16-5.13	s
5	21.78-21.88	4.08-4.05	vs

7. The molecular sieves according to claim 1 or 2 wherein the metal-containing silicoaluminophosphate(MeAPSO-44) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table V.

Table V

No.	2θ	d(Å)	Relative Intensity
1	9.37-9.42	9.43-9.38	s

Table V (continued)

No.	2θ	d(Å)	Relative Intensity
2	16.03-16.08	5.52-5.50	m
3	20.69-20.74	4.29-4.28	vs
4	24.29-24.35	3.66-3.65	vs
5	30.83-30.86	2.90-2.89	s-vs

8. The molecular sieves according to claim 1 or 2 wherein the metal-containing silicoaluminophosphate(MeAPSO-56) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table VI.

Table VI

No.	2θ	d(Å)	Relative Intensity
1	7.34-7.38	12.03-11.97	w
2	11.48-11.52	7.70-7.67	m-s
3	17.68-17.71	5.01-5.00	m-s
4	20.14-20.17	4.41-4.40	s-vs
5	21.57-21.60	4.12-4.11	vs

9. The molecular sieves according to claim 1 or 2 wherein the zirconium-containing silicoaluminophosphate(ZrAPSO-17) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table VII.

Table VII

No.	2θ	d(Å)	Relative Intensity
1	~7.75	~11.60	vs
2	~13.25	~6.60	s-vs
3	~15.38	~5.65	w-m
4	~19.48	~3.46	m
5	~20.42	~4.26	vs

10. The molecular sieves according to claim 1 or 2 wherein the vanadium-containing silicoaluminophosphate(VAPSO-17) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table VIII

Table VIII

No.	2θ	d(Å)	Relative Intensity
1	~7.57	~11.66	vs
2	~13.22	~6.70	s-vs
3	~15.30	~5.79	w-m
4	~20.32	~4.37	s-vs
5	~21.21	~4.19	m

11. The molecular sieves according to claim 1 or 2 wherein the titanium-containing silicoaluminophosphate(TAPSO-17) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table IX.

Table IX

No.	2θ	d(Å)	Relative Intensity
1	~7.56	~11.68	vs
2	~13.18	~6.69	s

Table IX (continued)

No.	2θ	d(Å)	Relative Intensity
3	~15.26	~5.77	w-m
4	~20.34	~4.35	s-vs
5	~21.19	~4.17	m

12. The molecular sieves according to claim 1 or 2 wherein the zirconium-containing silicoaluminophosphate(ZrAPSO-18) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table X

Table X

No.	2θ	d(Å)	Relative Intensity
1	~9.45	~9.35	vs
2	~10.54	~8.39	w
3	~16.91	~5.24	s
4	~20.02	~4.43	w
5	~20.51	~4.33	w-m

13. The molecular sieves according to claim 1 or 2 wherein the titanium-containing silicoaluminophosphate(TAPSO-18) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XI

Table XI

No.	2θ	d(Å)	Relative Intensity
1	~9.49	~9.31	vs
2	~10.43	~8.47	w
3	~16.88	~5.25	s
4	~20.02	~4.43	w
5	~20.81	~4.26	w-m

14. The molecular sieves according to claim 1 or 2 wherein the cobalt-containing silicoaluminophosphate(CoAPSO-18) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XII

Table XII

No.	2θ	d(Å)	Relative Intensity
1	~9.46	~9.34	vs
2	~10.50	~8.42	w
3	~16.92	~5.23	m
4	~19.57	~4.53	w
5	~20.49	~4.33	w-m

15. The molecular sieves according to claim 1 or 2 wherein the manganese-containing silicoaluminophosphate(MnAPSO-18) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XIII

Table XIII

No.	2θ	d(Å)	Relative Intensity
1	~9.48	~9.32	vs
2	~15.94	~5.55	w
3	~16.96	~5.22	s

Table XIII (continued)

No.	2θ	d(Å)	Relative Intensity
4	~20.03	~4.49	w
5	~20.51	~4.33	w

16. The molecular sieves according to claim 1 or 2 wherein the magnesium-containing silicoaluminophosphate(MgAPSO-18) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XIV

Table XIV

No.	2θ	d(Å)	Relative Intensity
1	~9.49	~9.31	vs
2	~15.54	~5.70	w
3	~16.91	~5.24	s-vs
4	~20.06	~4.42	w
5	~20.87	~4.25	w-m

17. The molecular sieves according to claim 1 or 2 wherein the nickel-containing silicoaluminophosphate(NLAPSO-18) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XV

Table XV

No.	2θ	d(Å)	Relative Intensity
1	~9.45	~9.35	vs
2	~15.96	~5.55	w-m
3	~16.88	~5.25	w-m
4	~20.51	~4.33	w-m
5	~21.29	~4.17	w

18. The molecular sieves according to claim 1 or 2 wherein the iron-containing aluminophosphate(FeAPO-18) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XVI

Table XVI

No.	2θ	d(Å)	Relative Intensity
1	~9.51	~9.29	vs
2	~15.56	~5.69	w
3	~16.95	~5.23	s
4	~20.82	~4.26	m
5	~21.78	~4.08	w

19. The molecular sieves according to claim 1 or 2 wherein the zinc-containing silicoaluminophosphate(ZnAPSO-18) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XVII

TableXVII

No.	2θ	d(Å)	Relative Intensity
1	~9.43	~9.37	vs
2	~15.92	~5.56	m
3	~16.88	~5.25	s
4	~20.46	~4.34	w

TableXVII (continued)

No.	2θ	d(Å)	Relative Intensity
5	~21.24	~4.18	w

20. The molecular sieves according to claim 1 or 2 wherein the zirconium-containing silicoaluminophosphate(ZrAPSO-34) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XVIII.

Table XVIII

No.	2θ	d(Å)	Relative Intensity
1	9.40-9.66	9.40-9.15	vs
2	15.92-16.20	5.56-5.46	w-m
3	16.86-17.04	5.25-5.20	w
4	20.46-20.75	4.33-4.28	m-s
5	21.07-21.38	4.21-4.15	w

21. The molecular sieves according to claim 1 or 2 wherein the zirconium-containing aluminophosphate(ZrAPO-34) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XIX.

Table XIX

No.	2θ	d(Å)	Relative Intensity
1	~9.61	~9.19	vs
2	~16.91	~5.24	w-m
3	~17.84	~4.97	w
4	~20.18	~4.40	w
5	~21.10	~4.21	w

22. The molecular sieves according to claim 1 or 2 wherein the vanadium-containing silicoaluminophosphate(VAPSO-34) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XX

Table XX

No.	2θ	d(Å)	Relative Intensity
1	~9.45	~9.35	v
2	~15.96	~5.55	w
3	~16.83	~5.26	vw
4	~20.51	~4.33	m
5	~21.47	~4.13	vs

23. The molecular sieves according to claim 1 or 2 wherein the copper-containing silicoaluminophosphate(CuAPSO-34) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XXI

Table XXI

No.	2θ	d(Å)	Relative Intensity
1	~9.45	~9.35	vs
2	~15.97	~5.54	w
3	~17.90	~4.95	vw
4	~20.52	~4.32	m-s
5	~21.14	~4.20	vw

24. The molecular sieves according to claim 1 or 2 wherein the lanthanum-containing silicoaluminophosphate(LaAFSO-34) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XXII

Table XXII

No.	2θ	d(Å)	Relative Intensity
1	~9.42	~9.38	vs
2	~15.93	~5.56	w
3	~16.94	~5.23	vw
4	~20.48	~4.33	m-s
5	~21.27	~4.17	vw

25. The molecular sieves according to claim 1 or 2 wherein the molybdenum-containing silicoaluminophosphate (MoAPSO-34) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XXIII

Table XXIII

No.	2θ	d(Å)	Relative Intensity
1	~9.41	~9.39	vs
2	~15.92	~5.56	m
3	~16.89	~5.24	vw
4	~20.48	~4.33	m-s
5	~21.25	~4.18	vw

26. The molecular sieves according to claim 1 or 2 wherein the zirconium-containing silicoaluminophosphate (ZrAPSO-35) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XXIV.

Table XXIV

No.	2θ	d(Å)	Relative Intensity
1	~8.59	~10.28	w
2	~10.93	~8.09	m
3	~13.30	~6.65	m
4	~17.27	~5.13	s
5	~21.88	~4.06	vs

27. The molecular sieves according to claim 1 or 2 wherein the nickel-containing silicoaluminophosphate (NiAPSO-35) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XXV.

Table XXV

No.	2θ	d(Å)	Relative Intensity
1	~8.55	~10.33	m
2	~10.93	~8.09	w-m
3	~13.32	~6.64	w
4	~17.28	~5.13	s
5	~21.89	~4.06	vs

28. The molecular sieves according to claim 1 or 2 wherein the zirconium-containing silicoaluminophosphate (ZrAPSO-44) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XXVI

Table XXVI

No.	2θ	d(Å)	Relative Intensity
1	~9.40	~9.40	s-vs
2	~16.06	~5.51	m
3	~20.71	~4.29	s-vs
4	~24.32	~3.66	vs
5	~30.85	~2.90	m

29. The molecular sieves according to claim 1 or 2 wherein the chromium-containing silicoaluminophosphate (CrAPSO-44) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XXVII

Table XXVII

No.	2θ	d(Å)	Relative Intensity
1	~9.41	~9.39	s-vs
2	~16.07	~5.51	m
3	20.73	~4.28	vs
4	~24.35	~3.65	s
5	~30.87	~2.89	m

30. The molecular sieves according to claim 1 or 2 wherein the copper-containing silicoaluminophosphate (CuAPSO-44) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XXVIII

Table XXVIII

No.	2θ	d(Å)	Relative Intensity
1	~9.42	~9.38	s-vs
2	~16.08	~5.51	m-s
3	~20.74	~4.28	s-vs
4	~24.34	~3.65	vs
5	~30.87	~2.89	m

31. The molecular sieves according to claim 1 or 2 wherein the vanadium-containing silicoaluminophosphate (VAPSO-44) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XXIX

Table XXIX

No.	2θ	d(Å)	Relative Intensity
1	~9.42	~9.38	s
2	~16.08	~5.51	m
3	~20.74	~4.28	vs
4	~24.35	~3.65	m-s
5	~30.86	~2.89	m

32. The molecular sieves according to claim 1 or 2 wherein the nickel-containing silicoaluminophosphate (NiAPSO-44) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XXX

Table XXX

No.	2θ	d(Å)	Relative Intensity
1	~9.45	~9.35	s

Table XXX (continued)

No.	2θ	d(Å)	Relative Intensity
2	~16.10	~5.50	w
3	~20.75	~4.28	s
4	~24,38	~3.65	vs
5	~30.89	~2.89	m

33. The molecular sieves according to claim 1 or 2 wherein the iron-containing silicoaluminophosphate (FAPSO-44) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XXXI

Table XXXI

No.	2θ	d(Å)	Relative Intensity
1	~9.35	~9.45	s
2	~16.00	~5.53	m
3	~20.67	~4.29	s-vs
4	~24.26	~3.66	vs
5	~30.81	~2.90	m

34. The molecular sieves according to claim 1 or 2 wherein the lanthanum-containing silicoaluminophosphate (LaAPSO-44) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XXXII

Table XXXII

No.	2θ	d(Å)	Relative Intensity
1	~9.40	~9.40	s
2	~16.07	~5.51	m
3	~20.73	~4.28	vs
4	~24.33	~3.65	s
5	~30.88	~2.89	m

35. The molecular sieves according to claim 1 or 2 wherein the zirconium-containing silicoaluminophosphate (ZrAPSO-56) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XXXIII.

Table XXXIII

No.	2θ	d(Å)	Relative Intensity
1	~7.36	~11.98	w
2	~11.51	~7.69	m-s
3	~20.18	~4.40	s
4	~21.61	~4.11	vs
5	~27.75	~3.21	s

36. The molecular sieves according to claim 1 or 2 wherein the titanium-containing silicoaluminophosphate (TAPSO-56) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XXXIV.

Table XXXIV

No.	2θ	d(Å)	Relative Intensity
1	~7.34	~12.03	w
2	~11.48	~7.70	m-s

Table XXXIV (continued)

No.	2θ	d(Å)	Relative Intensity
3	~20.14	~4.41	s
4	~21.57	~4.12	vs
5	~27.76	~3.21	m-s

37. The molecular sieves according to claim 1 or 2 wherein the iron-containing silicoaluminophosphate (FAPSO-56) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XXXV.

Table XXXV

No.	2θ	d(Å)	Relative Intensity
1	~7.36	~12.00	vw
2	~11.48	~7.70	m-s
3	~17.70	~5.00	vs
4	~21,58	~4.11	s
5	~27.77	~3.21	vs

38. The molecular sieves according to claim 1 or 2 wherein the manganese-containing silicoaluminophosphate (MnAPSO-56) has a characteristic X-ray powder diffraction pattern containing at least the d-spacing which corresponds to the five main peaks set forth in Table XXXVI.

Table XXXVI

No.	2θ	d(Å)	Relative Intensity
1	~7.38	~11.97	vw
2	~11.52	~7.67	m-s
3	~20.17	~4.40	s
4	~21.60	~4.11	vs
5	~27.79	~3.21	s

39. Crystalline metal-silicoaluminophosphate molecular sieves prepared by calcining the primary powder of any one of claim 1-38 at a temperature sufficiently high to remove at least some of the templating agent present in the intracrystalline pore system.

40. The crystalline metal-silicoaluminophosphate molecular sieves according to claim 39 having a three-dimensional microporous framework structure of SiO_2, AlO_2^-, PO_2^+ and MeO2 tetrahedral units, and whose essential empirical chemical formula basis is as follows: $mR\cdot (M_qSi_xAl_yP_z)O_2$, wherein *"m* " has a value of zero.

41. The crystalline metal-silicoaluminophosphate molecular sieves according to claim 39 or claim 40 having a characteristic X-ray powder diffraction pattern containing at least the d-spacing set forth in any of Tables I to XXXVI in claims 3 to 38.

42. A process for preparing a primary mixture gel of metal-containing silicoaluminophosphate crystalline according to claim 1 or claim 2 comprising a step of mixing proportional silicon source, aluminum source, phosphorus source, metal compound, templating agent and water under stirring.

43. The process according to claim 42 wherein the silicon source is one or more of silica sol, sodium silicate sol, activated silica and orthosilicate ester.

44. The process according to claim 42 wherein the aluminum source is one or more of aluminum salt, aluminate, activated alumina, aluminum alkoxy, diaspore and pseudoboehmite.

45. The process according to claim 42 wherein the phosphorus source is one or more of orthophosphoric acid, phosphate, organic phosphide and phosphoric oxide.

46. The process according to claim 42 wherein the metal compound is one or more of metal oxide, metal oxychloride, metal salts of inorganic and organic acid of Zr, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Mg, Ca, Sr, Ba and La.

47. The process according to claim 42 wherein the templating agent is one or more kinds of cyclohexylamine, triethylamine, diethylamine, n-propylamine, isopropylamine, n-dipropylamine, diisopropylamine, tripropylamine, n-butylamine, isobutylamine, hexamethyenlaminelidyne, hexanediamine, N, N-diisopropyl ethylamine, N, N-diisopropyl propylamine, N', N', N, N-tetramethyl-(1,6-)hexanediamine, ethanolamine, diethanolamine, triethanolamine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, or the corresponding alcohol.

48. The process according to claim 42 wherein the formula ratio of the ingredients of the mixture gel in the synthesis of the microporous metal silicoaluminophosphate is in the following (the molecular ratio of oxides):

$$MeO_n/Al_2O_3 = 0.01\sim1.0;$$

$$SiO_2/Al_2O_3 = 0\sim10;$$

$$P_2O_5/Al_2O_3 = 0.01\sim15;$$

$$H_2O/Al_2O_3 = 10\sim100;$$

$$R/Al_2O_3 = 0.1\sim10$$

(*"R* " is one or a mixture of templating agents).

49. The process according to any one of claims 42 to 48 comprising aging under microwave radiation for 0.1 to 30 minutes.

50. The process according to any one of claims 42 to 48 comprising aging under a temperature sufficiently high for 1 to 24 hours.

51. The process according to any one of claims 42 to 50 wherein the crystallization pressure is at autogenous pressure or 0.1~0.5MPa of N_2, air or inert gas.

52. The process according to any one of claims 42 to 50 wherein the crystallization temperature is programmed at 50~250°C.

53. The process according to any one of claims 42 to 50 wherein the crystallization time is 1-24 hours.

54. The metal silicoaluminophosphate molecular sieves (MeAPSOs) according to claim 41 for use in ion exchangers, adsorbents and catalysts.

55. The metal silicoaluminophosphate molecular sieves (MeAPSOs) according to claim 41 for use as a catalyst of methanol to C_2-C_4 olefins.

56. The metal silicoaluminophosphate molecular sieves (MeAPSOs) according to claim 41 for use as a catalyst of dimethyl ether or a mixture of any ratio of methanol and dimethyl ether to C_2-C_4 olefins.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 30 3157

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	EP 0 159 624 A (UNION CARBIDE CORP) 30 October 1985 (1985-10-30) * claims 1,35 *	1,42	C01B37/06
A	EP 0 158 350 A (UNION CARBIDE CORP) 16 October 1985 (1985-10-16) * claims 1,21 *	1,42	
A	EP 0 344 837 A (SHELL INT RESEARCH) 6 December 1989 (1989-12-06) * claim 1 *	1	
A	EP 0 417 863 A (SHELL INT RESEARCH) 20 March 1991 (1991-03-20) * claim 1 *	1	
A	EP 0 587 215 A (SHELL INT RESEARCH) 16 March 1994 (1994-03-16) * claim 1 *	1	
A	EP 0 665 186 A (ELF AQUITAINE) 2 August 1995 (1995-08-02) * claim 1 *	1	**TECHNICAL FIELDS SEARCHED (Int.Cl.7)** C01B
A	EP 0 103 117 A (UNION CARBIDE CORP) 21 March 1984 (1984-03-21) * claim 1 *	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	7 June 2001	Clement, J-P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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