

ITQ-34, NEW CRYSTALLINE MICROPOROUS MATERIAL

The present invention relates to a new crystalline microporous material.

BACKGROUND OF THE INVENTION

[0001] Microporous materials, including zeolites and silicoaluminophosphates, are widely used in the petroleum industry as absorbents, catalysts and catalyst supports. Their crystalline structures consist of three-dimensional frameworks containing uniform pore openings, channels and internal cages of dimensions ($<20\text{\AA}$) similar to most hydrocarbons. The microporous structures of these materials allow them to absorb molecules whose size is equal to or less than the size of the pore openings. The composition of the frameworks can be such that they are anionic, which requires the presence of non-framework cations to balance the negative charge. These non-framework cations, such as alkali or alkaline earth metal cations, are exchangeable, either entirely or partially with another type of cation utilizing ion exchange techniques in a conventional manner. If these non-framework cations are converted to the proton form by, for example, acid treatments or exchange with ammonium cations followed by calcination to remove the ammonia, it imparts the material with acid sites having catalytic activity. The combination of acidity and restricted pore openings gives these materials catalytic properties unavailable with other materials due to their ability to exclude or restrict some of the products, reactants, and/or transition states in many reactions. Non-reactive materials, such as pure silica and aluminophosphate frameworks are also useful and can be used in absorption and separation processes of liquids, gases, and reactive molecules such as alkenes.

[0002] The family of crystalline microporous compositions known as zeolites exists as mineral and synthetic species. Their microporous frameworks contain tetravalent silicon tetrahedra atoms connected by bridging oxygen atoms. It is possible that some or all of the silicon atoms can be substituted with other tetravalent atoms capable of tetrahedral coordination, such as germanium, titanium, or zirconium. Some of the tetrahedral atoms can also be replaced with trivalent metal atoms such as aluminum, gallium, and/or iron to form an anionic framework as described above. U.S. Patent 6,471,941 discloses one such microporous zeolite composition designated ITQ-13, which has a three-dimensional framework of channels containing 9, 10, and 10 tetrahedral atoms in the pore openings along the three crystallographic directions.

[0003] Another family of crystalline microporous compositions known as molecular sieves, which exhibit the ion-exchange and/or adsorption characteristics of zeolites is the aluminophosphates, identified by the acronym AIPO, and substituted aluminophosphates as disclosed in U.S. Pat. Nos. 4,310,440 and 4,440,871. U.S. Pat. No. 4,440,871 discloses a class of silica aluminophosphates, which are identified by the acronym SAPO and which have different structures as identified by their X-ray diffraction pattern. The structures are identified by a numerical number after AIPO, SAPO, MeAPO (Me = metal), etc. (Flanigen et al., *Proc. 7th Int. Zeolite Conf.*, p. 103 (1986) and may include Al and P substitutions by B, Si, Be, Mg, Ge, Zn, Fe, Co, Ni, etc.

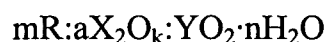
[0004] ExxonMobil and others extensively use various microporous materials, such as faujasite, mordenite, and ZSM-5 in many commercial applications. Such applications include reforming, cracking, hydrocracking, alkylation, oligomerization, dewaxing and isomerization. Any new material has the potential to improve the catalytic performance over those catalysts presently employed.

[0005] There are currently over 160 known microporous framework structures as tabulated by the International Zeolite Association. There exists the need for new structures, having different properties than those of known materials, for improving the performance of many hydrocarbon processes. Each structure has unique pore, channel and cage dimensions, which gives its particular properties as described above. ITQ-34 is a new molecular sieve having a unique framework structure.

SUMMARY OF THE INVENTION

[0006] ITQ-34 (INSTITUTO DE TECNOLOGÍA QUÍMICA number 34) is a new crystalline microporous material having a framework of tetrahedral atoms connected by bridging atoms, the tetrahedral atom framework being defined by the interconnections between the tetrahedrally coordinated atoms in its framework. ITQ-34 is stable to calcination in air, absorbs hydrocarbons, and is catalytically active for hydrocarbon conversion.

[0007] In one embodiment, the present invention is directed to a new crystalline material that is a silicate compound having a composition



where R is an organic compound, X is any metal capable of tetrahedral coordination such as one or more of B, Ga, Al, Fe, Li, Be, P, Zn, Cr, Mg, Co, Ni, Mn, As, In, Sn, Sb, and Zr, more preferably one or more trivalent metals capable of tetrahedral coordination, and even more preferably one or more of the elements B, Ga, Al, and Fe, k is the oxidation state of X and represents a number from 1 to 3, and Y is Si alone or in combination with any other tetravalent metal capable of tetrahedral coordination such as Ge and Ti and where m represents a

number greater than or equal to 0.01 and less than or equal to 1, a represents a number less than or equal to 0.2 and n represents a number less than or equal to 10 and having a unique diffraction pattern as given in Table 2.

[0008] In a more specific embodiment, the present invention is directed to a calcined crystalline silicate compound that has a composition



where X, Y, a, k and n have the same meaning as above and having a unique diffraction pattern as given in Table 3.

[0009] The present invention also includes a method of synthesizing a crystalline silicate compound having the diffraction pattern similar to Table 2, by mixing together a source of tetravalent element Y, where Y is Si alone or in combination with Ge and/or Ti, an organic structure directing agent (SDA) R, water, and optionally a source of metal X and optionally a source of fluoride, and heating at a temperature and for a period of time sufficient to crystallize the silicate.

[0010] The invention includes the use of ITQ-34 to separate hydrocarbons from a hydrocarbon containing stream.

[0011] The invention also includes the use of ITQ-34 as a hydrocarbon conversion catalyst for converting an organic feedstock to conversion products.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Figure 1 is a representation of ethane-1,2-bis-(trimethylphosphonium) hydroxide ($Me_3P(CH_2)_2PMe_3(OH)_2$) and

propane 1,3-bis-(trimethylphos-phonium)hydroxide ($\text{Me}_3\text{P}(\text{CH}_2)_3\text{PMe}_3(\text{OH})_2$) used as organic structure directing agents (SDA) in the examples.

[0013] Figure 2 shows the framework structure of ITQ-34 showing only the tetrahedral atoms. There is one unit cell, whose edges are defined by the box.

[0014] Figure 3 shows the X-ray diffraction pattern of as-synthesized ITQ-34 prepared with ethane-1,2-bis (trimethylphosphonium) hydroxide.

[0015] Figure 4 shows the X-ray diffraction pattern of as-synthesized ITQ-34 prepared with propane-1,3-bis (trimethylphosphonium) hydroxide.

[0016] Figure 5 shows the X-ray diffraction pattern of calcined ITQ-34.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0017] The present invention is a new structure of crystalline material. As with any porous crystalline material, the structure of ITQ-34 can be defined by the interconnections between the tetrahedrally coordinated atoms in its framework. In particular, ITQ-34 has a framework of tetrahedral (T) atoms connected by bridging atoms, wherein the tetrahedral atom framework is defined by connecting the nearest tetrahedral (T) atoms in the manner given in Table 1.

Table 1

ITQ-34 tetrahedral atom interconnections

T atom	Connected to:
T1	T3, T8, T69, T71
T2	T9, T68, T70, T72
T3	T1, T44, T54, T67
T4	T46, T51, T55, T66
T5	T45, T50, T56, T67
T6	T24, T34, T66, T93
T7	T25, T33, T67, T94
T8	T1, T18, T26, T52

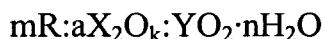
T9	T2, T17, T27, T53
T10	T12, T17, T60, T62
T11	T18, T59, T61, T63
T12	T10, T39, T49, T58
T13	T41, T50, T56, T57
T14	T40, T51, T55, T58
T15	T25, T33, T57, T98
T16	T24, T34, T58, T99
T17	T9, T10, T35, T47
T18	T8, T11, T36, T48
T19	T21, T26, T87, T89
T20	T27, T86, T88, T90
T21	T19, T44, T54, T85
T22	T41, T45, T56, T84
T23	T40, T46, T55, T85
T24	T6, T16, T84, T103
T25	T7, T15, T85, T104
T26	T8, T19, T36, T42
T27	T9, T20, T35, T43
T28	T30, T35, T78, T80
T29	T36, T77, T79, T81
T30	T28, T39, T49, T76
T31	T40, T46, T51, T75
T32	T41, T45, T50, T76
T33	T7, T15, T75, T108
T34	T6, T16, T76, T109
T35	T17, T27, T28, T37
T36	T18, T26, T29, T38
T37	T35, T39, T62, T101
T38	T36, T63, T100, T102
T39	T12, T30, T37, T99
T40	T14, T23, T31, T98
T41	T13, T22, T32, T99
T42	T26, T44, T71, T96
T43	T27, T72, T95, T97
T44	T3, T21, T42, T94
T45	T5, T22, T32, T93
T46	T4, T23, T31, T94
T47	T17, T49, T80, T111
T48	T18, T81, T110, T112
T49	T12, T30, T47, T109
T50	T5, T13, T32, T108
T51	T4, T14, T31, T109
T52	T8, T54, T89, T106
T53	T9, T90, T105, T107
T54	T3, T21, T52, T104
T55	T4, T14, T23, T103
T56	T5, T13, T22, T104

T57	T13, T15, T59, T64
T58	T12, T14, T16, T65
T59	T11, T57, T100, T110
T60	T10, T102, T107, T111
T61	T11, T101, T106, T112
T62	T10, T37, T80, T90
T63	T11, T38, T81, T89
T64	T57, T74, T82, T108
T65	T58, T73, T83, T109
T66	T4, T6, T68, T73
T67	T3, T5, T7, T74
T68	T2, T66, T95, T105
T69	T1, T97, T106, T112
T70	T2, T96, T107, T111
T71	T1, T42, T81, T89
T72	T2, T43, T80, T90
T73	T65, T66, T91, T103
T74	T64, T67, T92, T104
T75	T31, T33, T77, T82
T76	T30, T32, T34, T83
T77	T29, T75, T100, T110
T78	T28, T97, T101, T112
T79	T29, T96, T102, T111
T80	T28, T47, T62, T72
T81	T29, T48, T63, T71
T82	T64, T75, T92, T98
T83	T65, T76, T91, T99
T84	T22, T24, T86, T91
T85	T21, T23, T25, T92
T86	T20, T84, T95, T105
T87	T19, T96, T102, T107
T88	T20, T97, T101, T106
T89	T19, T52, T63, T71
T90	T20, T53, T62, T72
T91	T73, T83, T84, T93
T92	T74, T82, T85, T94
T93	T6, T45, T91, T95
T94	T7, T44, T46, T92
T95	T43, T68, T86, T93
T96	T42, T70, T79, T87
T97	T43, T69, T78, T88
T98	T15, T40, T82, T100
T99	T16, T39, T41, T83
T100	T38, T59, T77, T98
T101	T37, T61, T78, T88
T102	T38, T60, T79, T87
T103	T24, T55, T73, T105
T104	T25, T54, T56, T74

T105	T53, T68, T86, T103
T106	T52, T61, T69, T88
T107	T53, T60, T70, T87
T108	T33, T50, T64, T110
T109	T34, T49, T51, T65
T110	T48, T59, T77, T108
T111	T47, T60, T70, T79
T112	T48, T61, T69, T78

[0018] Tetrahedral atoms are those capable of having tetrahedral coordination, including one or more of, but not limiting, lithium, beryllium, boron, magnesium, aluminum, silicon, phosphorous, titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, zirconium, gallium, germanium, arsenic, indium, tin, and antimony.

[0019] In one embodiment, this new crystalline silicate compound has a composition



where R is an organic compound, and X is any metal capable of tetrahedral coordination such as one or more of B, Al, Ga, Fe, Li, Be, P, Zn, Cr, Mg, Co, Ni, Mn, As, In, Sn, Sb, and Zr, more preferably one or more trivalent metals capable of tetrahedral coordination, and even more preferably one or more of the elements B, Ga, Al, and Fe, k is the oxidation state of X and k represents a number from 1 to 3, and Y is Si alone or in combination with any other tetravalent metal capable of tetrahedral coordination such as Ge and Ti and where m represents a number greater than or equal to 0.01 and less than or equal to 1, a represents a number less than or equal to 0.2 and n represents less than or equal to 10. This compound has the unique diffraction pattern given in Table 2 and shown in Figure 3. The diffraction pattern in Table 2 was measured with Cu K α radiation using a PANalytical X'Pert diffractometer with a X'celerator

detector, Bragg-Brentano geometry, 45kV and 40 mA tube voltage and current, $1/16^\circ$ fixed divergence slit, 0.017° step size, and 1400 sec counting time per step.

Table 2

X-ray diffraction lines for as-synthesized ITQ-34

d-spacing (Å)	relative intensity
11.2-10.9	20-70
10.3-10.0	20-70
9.53-9.33	5-50
7.97-7.83	60-100
6.06-5.98	5-50
5.57-5.51	20-70
5.38-5.32	5-50
4.73-4.69	5-50
4.18-4.14	30-80
4.09-4.05	5-50
3.90-3.86	30-80
3.78-3.74	20-70
3.71-3.67	30-80
3.37-3.35	5-50
2.90-2.88	5-50
2.54-2.52	5-50
2.32-2.30	5-50

[0020] Other embodiments of the new structure include a calcined compound of composition



where X, Y, a, k and n have the same meaning as above. This compound has the unique diffraction pattern given in Table 3 and shown in Figure 5.

Table 3

X-ray diffraction lines for calcined/dehydrated ITQ-34

d-spacing (Å)	relative intensity
12.8-12.5	30-80
11.2-11.0	60-100
10.3-10.1	5-50
9.57-9.37	5-40
8.41-8.25	5-40
8.01-7.87	20-70
5.79-5.71	5-40
5.57-5.51	5-50
4.10-4.06	5-40
3.91-3.87	5-50
3.80-3.76	5-40
3.71-3.67	5-50

[0021] This new compound is made by the method of mixing together a source of tetravalent element Y, where Y is Si alone or in combination with Ge and/or Ti, an organic structure directing agent (SDA), water, and optionally a source of metal X and, optionally, a source of fluoride and heating at a temperature and for a period of time sufficient to crystallize the silicate. The method is described below.

[0022] The synthetic porous crystalline material of this invention, ITQ-34, is a crystalline phase which has a unique 3-dimensional channel system comprising intersecting 10, 10 and 9-member rings of tetrahedrally coordinated atoms. The interconnectivity of T atoms, as provided in Table 1, results in a new zeolite structure, different from other known 10, 10, 9-member rings structures, such as ITQ-13. The straight 10-member ring channels have cross-sectional dimensions between the bridging oxygen atoms of about 4.6 Ångströms by about 5.8 Ångströms and the sinusoidal 10-member ring channels have cross-sectional dimensions between the bridging oxygen atoms of about 4.8 Ångströms by about 5.9 Ångströms. The sinusoidal 9-member ring channels have cross-sectional

dimensions between the bridging oxygen atoms of about 3.9 Ångströms by about 4.8 Ångströms.

[0023] Variations in the X-ray diffraction pattern may occur between the different chemical composition forms of ITQ-34, such that the exact ITQ-34 structure can vary due its particular composition and whether or not it has been calcined and rehydrated.

[0024] In the as-synthesized form ITQ-34 has a characteristic X-ray diffraction pattern, the essential lines of which are given in Table 2 measured with Cu K α radiation. Variations occur as a function of specific composition and its loading in the structure. For this reason the intensities and d-spacings are given as ranges.

[0025] The ITQ-34 material of the present invention may be calcined to remove the organic structure directing agent without loss of crystallinity. This is useful for activating the material for subsequent absorption of other guest molecules such as hydrocarbons. The essential lines, which uniquely define calcined/ dehydrated ITQ-34 are shown in Table 3 measured with Cu K α radiation. Variations occur as a function of specific composition, temperature and the level of hydration in the structure. For this reason the intensities and d-spacings are given as ranges.

[0026] In addition, to describing the structure of ITQ-34 by the interconnections of the tetrahedral atoms as in above, it may be defined by its unit cell, which is the smallest repeating unit containing all the structural elements of the material. The pore structure of ITQ-34 is illustrated in FIGURE 2 (which shows only the tetrahedral atoms) down the direction of the straight 10-membered ring channels. There is a single unit cell unit in FIGURE 2, whose limits are

defined by the box. Table 4 lists the typical positions of each tetrahedral atom in the unit cell in units of Ångströms. Each tetrahedral atom is bonded to bridging atoms, which are also bonded to adjacent tetrahedral atoms. Tetrahedral atoms are those capable of having tetrahedral coordination, including one or more of, but not limiting, lithium, beryllium, boron, magnesium, aluminum, silicon, phosphorous, titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, zirconium, gallium, germanium, arsenic, indium, tin, and antimony. Bridging atoms are those capable of connecting two tetrahedral atoms, examples which include, but not limiting, oxygen, nitrogen, fluorine, sulfur, selenium, and carbon atoms.

[0027] In the case of oxygen, it is also possible that the bridging oxygen is also connected to a hydrogen atom to form a hydroxyl group (-OH-). In the case of carbon, it is also possible that the carbon is also connected to two hydrogen atoms to form a methylene group (-CH₂-). For example, bridging methylene groups are present in the zirconium diphosphonate, MIL-57. See: C. Serre, G. Férey, *J. Mater. Chem.* **12**, p. 2367 (2002). In the case of nitrogen, it is also possible that the nitrogen bridging atom is part of an imidazolate anion. For example, bridging imidazolate groups are present in the zinc(II) imidazolate zeolite-type compounds, Zn(mim)₂·2H₂O, Zn(eim)₂·H₂O, and Zn(eim/mim)₂·1.25H₂O. See: X-C. Huang, Y-Y. Lin, J-P. Zhang, X-M. Chen, *Angew. Chem. Int. Ed.* **45**, p. 1557-1559 (2006). Bridging sulfur and selenium atoms have been seen in the UCR-20-23 family of microporous materials. See: N. Zheng, X. Bu, B. Wang, P. Feng, *Science* **298**, p. 2366 (2002). Bridging fluorine atoms have been seen in lithium hydrazinium fluoroberyllate, which has the ABW structure type. See: M. R. Anderson, I. D. Brown, S. Vilminot, *Acta Cryst.* **B29**, p. 2626 (1973). Since tetrahedral atoms may move about due to other crystal forces (presence of inorganic or organic species, for example), or by the choice of tetrahedral and bridging atoms, a range of ±0.5 Ångström is implied for

the x and coordinate positions and a range of ± 1.0 Ångström for the y and z coordinate positions.

Table 4

Positions of tetrahedral (T) atoms for the ITQ-34 structure. Values, in units of Ångströms, are approximate and are typical when T = silicon and the bridging atoms are oxygen.

Atom	x (Å)	y (Å)	z (Å)
T001	2.460	2.655	3.814
T002	2.877	2.967	16.438
T003	1.516	5.436	4.751
T004	1.592	9.473	14.173
T005	1.603	9.484	1.527
T006	1.554	9.287	18.894
T007	1.592	9.752	6.298
T008	0.000	0.899	4.769
T009	0.000	2.163	17.332
T010	9.029	19.489	16.410
T011	8.612	19.177	3.842
T012	9.972	16.708	17.347
T013	9.896	12.671	1.577
T014	9.886	12.660	14.123
T015	9.934	12.857	6.298
T016	9.896	12.392	18.894
T017	0.000	21.245	17.365
T018	0.000	19.981	4.736
T019	9.029	2.655	8.782
T020	8.612	2.967	21.350
T021	9.972	5.436	7.845
T022	9.896	9.473	23.615
T023	9.886	9.484	11.069
T024	9.934	9.287	18.894
T025	9.896	9.752	6.298
T026	0.000	0.899	7.827
T027	0.000	2.163	20.456
T028	2.460	19.489	21.378
T029	2.877	19.177	8.754
T030	1.516	16.708	20.441
T031	1.592	12.671	11.019
T032	1.603	12.660	23.666
T033	1.554	12.857	6.298
T034	1.592	12.392	18.894
T035	0.000	21.245	20.423
T036	0.000	19.981	7.860

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T037	9.029	19.489	21.378
T038	8.612	19.177	8.754
T039	9.972	16.708	20.441
T040	9.896	12.671	11.019
T041	9.886	12.660	23.666
T042	2.460	2.655	8.782
T043	2.877	2.967	21.350
T044	1.516	5.436	7.845
T045	1.592	9.473	23.615
T046	1.603	9.484	11.069
T047	2.460	19.489	16.410
T048	2.877	19.177	3.842
T049	1.516	16.708	17.347
T050	1.592	12.671	1.577
T051	1.603	12.660	14.123
T052	9.029	2.655	3.814
T053	8.612	2.967	16.438
T054	9.972	5.436	4.751
T055	9.896	9.473	14.173
T056	9.886	9.484	1.527
T057	8.204	13.727	3.814
T058	8.621	14.039	16.438
T059	7.261	16.509	4.751
T060	7.337	20.545	14.173
T061	7.347	20.557	1.527
T062	7.299	20.359	18.894
T063	7.337	20.824	6.298
T064	5.744	11.971	4.769
T065	5.744	13.236	17.332
T066	3.285	8.417	16.410
T067	2.868	8.105	3.842
T068	4.228	5.636	17.347
T069	4.152	1.599	1.577
T070	4.142	1.588	14.123
T071	4.190	1.785	6.298
T072	4.152	1.320	18.894
T073	5.744	10.173	17.365
T074	5.744	8.909	4.736
T075	3.285	13.727	8.782
T076	2.868	14.039	21.350
T077	4.228	16.509	7.845
T078	4.152	20.545	23.615
T079	4.142	20.557	11.069
T080	4.190	20.359	18.894
T081	4.152	20.824	6.298
T082	5.744	11.971	7.827
T083	5.744	13.236	20.456
T084	8.204	8.417	21.378

T085	8.621	8.105	8.754
T086	7.261	5.636	20.441
T087	7.337	1.599	11.019
T088	7.347	1.588	23.666
T089	7.299	1.785	6.298
T090	7.337	1.320	18.894
T091	5.744	10.173	20.423
T092	5.744	8.909	7.860
T093	3.285	8.417	21.378
T094	2.868	8.105	8.754
T095	4.228	5.636	20.441
T096	4.152	1.599	11.019
T097	4.142	1.588	23.666
T098	8.204	13.727	8.782
T099	8.621	14.039	21.350
T100	7.261	16.509	7.845
T101	7.337	20.545	23.615
T102	7.347	20.557	11.069
T103	8.204	8.417	16.410
T104	8.621	8.105	3.842
T105	7.261	5.636	17.347
T106	7.337	1.599	1.577
T107	7.347	1.588	14.123
T108	3.285	13.727	3.814
T109	2.868	14.039	16.438
T110	4.228	16.509	4.751
T111	4.152	20.545	14.173
T112	4.142	20.557	1.527

[0028] The complete structure of ITQ-34 is built by connecting multiple unit cells as defined above in a fully-connected three-dimensional framework. The tetrahedral atoms in one unit cell are connected to certain tetrahedral atoms in all of its adjacent unit cells. While Table 1 lists the connections of all the tetrahedral atoms for a given unit cell of ITQ-34, the connections may not be to the particular atom in the same unit cell but to an adjacent unit cell. All of the connections listed in Table 1 are such that they are to the closest tetrahedral (T) atoms, regardless of whether they are in the same unit cell or in adjacent unit cells.

[0029] Although the Cartesian coordinates given in Table 4 may accurately reflect the positions of tetrahedral atoms in an idealized structure, the true

structure can be more accurately described by the connectivity between the framework atoms as shown in Table 1 above.

[0030] Another way to describe this connectivity is by the use of coordination sequences as applied to microporous frameworks by W. M. Meier and H. J. Moeck, in the *Journal of Solid State Chemistry* **27**, p. 349 (1979). In a microporous framework, each tetrahedral atom, N_0 , (T-atom) is connected to $N_1 = 4$ neighboring T-atoms through bridging atoms (typically oxygen). These neighboring T-atoms are then connected to N_2 T-atoms in the next shell. The N_2 atoms in the second shell are connected to N_3 T-atoms in the third shell, and so on. Each T-atom is only counted once, such that, for example, if a T-atom is in a 4-membered ring, at the fourth shell the N_0 atom is not counted second time, and so on. Using this methodology, a coordination sequence can be determined for each unique T-atom of a 4-connected net of T-atoms. The following line lists the maximum number of T-atoms for each shell.

$$N_0 = 1 \quad N_1 \leq 4 \quad N_2 \leq 12 \quad N_3 \leq 36 \quad N_k \leq 4 \cdot 3^{k-1}$$

Table 5

Coordination sequence for ITQ-34 structure.

Atom	coordination sequence												
T1	4	12	21	36	55	83	113	155	194	232	283	346	409
T2	4	12	22	37	57	84	114	153	192	235	290	350	405
T3	4	11	22	39	57	80	112	152	203	243	278	335	421
T4	4	9	19	36	59	88	119	148	187	240	300	349	385
T5	4	9	18	36	62	88	114	149	192	242	294	340	396
T6	4	11	22	32	51	85	116	141	183	239	296	349	392
T7	4	11	20	32	55	87	112	139	185	245	294	333	400
T8	4	11	20	34	57	81	115	153	192	232	285	353	413
T9	4	11	22	36	53	83	121	155	180	228	303	365	397

[0031] One way to determine the coordination sequence for a given structure is from the atomic coordinates of the framework atoms using the computer

program zeoTsites (see G. Sastre, J.D. Gale, *Microporous and mesoporous Materials* **43**, p. 27 (2001)).

[0032] The coordination sequence for the ITQ-34 structure is given in Table 5. The T-atom connectivity as listed in Table 1 and is for T-atoms only. Bridging atoms, such as oxygen usually connects the T-atoms. Although most of the T-atoms are connected to other T-atoms through bridging atoms, it is recognized that in a particular crystal of a material having a framework structure, it is possible that a number of T-atoms may not connected to one another. Reasons for non-connectivity include, but are not limited by T-atoms located at the edges of the crystals and by defects sites caused by, for example, vacancies in the crystal. The framework listed in Table 1 and Table 5 is not limited in any way by its composition, unit cell dimensions or space group symmetry.

[0033] While the idealized structure contains only 4-coordinate T-atoms, it is possible under certain conditions that some of the framework atoms may be 5- or 6-coordinate. This may occur, for example, under conditions of hydration when the composition of the material contains mainly phosphorous and aluminum T-atoms. When this occurs it is found that T-atoms may be also coordinated to one or two oxygen atoms of water molecules ($-OH_2$), or of hydroxyl groups ($-OH$). For example, the molecular sieve $AlPO_4$ -34 is known to reversibly change the coordination of some aluminum T-atoms from 4-coordinate to 5- and 6-coordinate upon hydration as described by A. Tuel et al. in *J. Phys. Chem. B* **104**, p. 5697 (2000). It is also possible that some framework T-atoms can be coordinated to fluoride atoms ($-F$) when materials are prepared in the presence of fluorine to make materials with 5-coordinate T-atoms as described by H. Koller in *J. Am. Chem Soc.* **121**, p. 3368 (1999).

[0034] The invention also includes a method of synthesizing a crystalline silicate composition of ITQ-34 having the diffraction pattern similar to Table 2

by mixing together a source of tetravalent element Y, where Y represents Si alone or in combination with Ge and/or Ti, an organic structure directing agent (SDA) R, water, and optionally a source of metal X, and, optionally, a source of fluoride F, with a composition, in terms of mole ratios, within the following ranges:

R/YO ₂	0.01 - 1
H ₂ O/YO ₂	2 - 50
X/YO ₂	0 - 0.2
F/YO ₂	0 - 2

and preferably within the following ranges:

R/YO ₂	0.1 - 0.5
H ₂ O/YO ₂	5 - 20
X/YO ₂	0 - 0.1
F/YO ₂	0 - 0.5

where X is any metal capable of tetrahedral coordination such as one or more of B, Ga, Al, Fe, Li, Be, P, Zn, Cr, Mg, Co, Ni, Be, Mn, As, In, Sn, Sb, Ti, and Zr, more preferably one or more trivalent metals capable of tetrahedral coordination, and even more preferably one or more of the elements B, Ga, Al, and Fe.

[0035] The organic structure directing agents (SDA) are preferably ethane-1,2-bis (trimethylphosphonium) or propane-1,3-bis (trimethylphosphonium), the structure of which is shown in FIGURE 1. Sources of silica can be colloidal, fumed or precipitated silica, silica gel, sodium or potassium silicates, or organic silicon such as tetraalkylorthosilicates, e.g. tetraethylorthosilicate, etc. Sources of metal can be boric acid, germanium (IV) ethoxide, germanium oxide,

germanium nitrate, aluminum nitrate, sodium aluminate, aluminum sulfate, aluminum hydroxide, aluminum chloride, iron nitrate, iron chloride, and gallium nitrate, etc. Sources of fluoride can be ammonium fluoride, hydrogen fluoride, hydrofluoric acid, and other suitable fluoride-containing compounds. The mixture is then heated at a temperature and time sufficient to crystallize the silicate material, typically in sealed autoclaves for several hours or days.

[0036] Non-limiting suitable crystallization conditions include heating at a temperature between 125°C and 200°C for periods of 1 to 100 days. Stirring or tumbling may be applied during crystallization.

[0037] To the extent desired and depending on the X_2O_3/YO_2 molar ratio of the material, any cations present in the as-synthesized ITQ-34 can be replaced in accordance with techniques well known in the art by ion exchange with other cations. Preferred replacing cations include metal ions, hydrogen ions, and hydrogen precursor, e.g., ammonium ions and mixtures thereof. Particularly preferred cations are those which tailor the catalytic activity for certain hydrocarbon conversion reactions. These include hydrogen, rare earth metals and metals of Groups IIA, IIIA, IVA, VA, IB, IIB, IIIB, IVB, VB, VIB, VIIB and VIII of the Periodic Table of the Elements.

[0038] The crystalline material of this invention can be used to catalyze a wide variety of chemical conversion processes, particularly organic compound conversion processes, including many of present commercial/industrial importance. Examples of chemical conversion processes which are effectively catalyzed by the crystalline material of this invention, by itself or in combination with one or more other catalytically active substances including other crystalline catalysts, include those requiring a catalyst with acid activity.

[0039] Thus, in its active form ITQ-34 can exhibit a high acid activity, which can be measured with the alpha test. Alpha value is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst and it gives the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time). It is based on the activity of silica-alumina cracking catalyst taken as an Alpha of 1 (Rate Constant=0.016 sec⁻¹). The Alpha Test is described in U. S. Pat. No. 3,354,078; in the *Journal of Catalysis* **4**, 527 (1965); **6**, 278 (1966); and **61**, 395 (1980), each incorporated herein by reference as to that description. The experimental conditions of the test used herein include a constant temperature of 538° C. and a variable flow rate as described in detail in the *Journal of Catalysis* **61**, 395 (1980).

[0040] When used as a catalyst, the crystalline material of the invention may be subjected to treatment to remove part or all of any organic constituent. This is conveniently effected by thermal treatment in which the as-synthesized material is heated at a temperature of at least about 370° C for at least 1 minute and generally not longer than 20 hours. While subatmospheric pressure can be employed for the thermal treatment, atmospheric pressure is desired for reasons of convenience. The thermal treatment can be performed at a temperature up to about 927° C. The thermally treated product, especially in its metal, hydrogen or ammonium forms, is particularly useful in the catalysis of certain organic, e.g., hydrocarbon, conversion reactions.

[0041] When used as a catalyst, the crystalline material can be intimately combined with a hydrogenating component such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt, chromium, manganese, or a noble metal such as, but not limited to, platinum or palladium where a hydrogenation-dehydrogenation function is to be performed. Such component can be in the composition by way of co-crystallization, exchanged into the composition to the extent a Group IIIA element, e.g., aluminum, is in the structure, impregnated

therein or intimately physically admixed therewith. Such component can be impregnated in or on to it such as, for example, by, in the case of platinum, treating ITQ-34 with a solution containing a platinum metal-containing ion. Thus, suitable platinum compounds for this purpose include chloroplatinic acid, platinous chloride and various compounds containing the platinum amine complex.

[0042] The crystalline material of this invention, when employed either as an adsorbent or as a catalyst in an organic compound conversion process should be dehydrated, at least partially. This can be done by heating to a temperature in the range of 100° C to about 370° C. in an atmosphere such as air, nitrogen, etc., and at atmospheric, subatmospheric or superatmospheric pressures for between 30 minutes and 48 hours. Dehydration can also be performed at room temperature merely by placing the ITQ-34 in a vacuum, but a longer time is required to obtain a sufficient amount of dehydration.

[0043] As in the case of many catalysts, it may be desirable to incorporate the new crystal with another material resistant to the temperatures and other conditions employed in organic conversion processes. Such materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica and/or metal oxides such as alumina. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Use of a material in conjunction with the new crystal, i.e., combined therewith or present during synthesis of the new crystal, which is active, tends to change the conversion and/or selectivity of the catalyst in certain organic conversion processes. Inactive materials suitably serve as diluents to control the amount of conversion in a given process so that products can be obtained economically and orderly without employing other means for controlling the rate of reaction. These materials may be incorporated into naturally occurring clays, e.g.,

bentonite and kaolin, to improve the crush strength of the catalyst under commercial operating conditions. Said materials, i.e., clays, oxides, etc., function as binders for the catalyst. It is desirable to provide a catalyst having good crush strength because in commercial use it is desirable to prevent the catalyst from breaking down into powder-like materials. These clay and/or oxide binders have been employed normally only for the purpose of improving the crush strength of the catalyst.

[0044] Naturally occurring clays which can be composited with the new crystal include the montmorillonite and kaolin family, which families include the subbentonites, and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite, or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification. Binders useful for compositing with the present crystal also include inorganic oxides, such as silica, zirconia, titania, magnesia, beryllia, alumina, and mixtures thereof.

[0045] In addition to the foregoing materials, the new crystal can be composited with a porous matrix material such as silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions such as silica-alumina-thoria, silica- alumina-zirconia silica-alumina-magnesia and silica-magnesia-zirconia.

[0046] The relative proportions of finely divided crystalline material and inorganic oxide matrix vary widely, with the crystal content ranging from about 1 to about 90 percent by weight and more usually, particularly when the composite is prepared in the form of beads, in the range of about 2 to about 80 weight percent of the composite.

[0047] In order to more fully illustrate the nature of the invention and the manner of practicing same, the following examples are presented.

Example 1 - Synthesis of ethane-1,2-bis(trimethylphosphonium) hydroxide:
 $((\text{Me}_3\text{P})_2(\text{CH}_2)_2(\text{OH})_2)$

[0048] Ethane-1,2-bis(trimethylphosphonium) bromide was synthesized by adding 25.0 g of trimethylphosphine (>97 wt.%) over a mixture of 28.20 g of 1,2-dibromoethane with 100 ml of methanol. The mixture is left under stirring at 60 °C for 2 days and a white solid precipitates, that after washing with diethyl ether, corresponds to: ethane-1,2-bis (trimethylphosphonium) bromide. This white solid, previously dissolved in water, is converted to the corresponding hydroxide using an anionic exchange resin in batch overnight, yielding a solution of ethane-1,2-bis (trimethylphosphonium) hydroxide with a concentration of 1.18 mol OH/Kg that will be used as structure directing agent source. The agent is shown in Figure 1(Upper).

Example 2 - Propane-1,3-bis(trimethylphosphonium) hydroxide:
 $((\text{Me}_3\text{P})_2(\text{CH}_2)_3(\text{OH})_2)$

[0049] Propane-1,3-bis(trimethylphosphonium) bromide was synthesized by adding 25.0 g of trimethylphosphine (>97 wt.%) over a mixture of 30.47 g of 1,3-dibromoethane with 100 ml of methanol. The mixture is left under stirring at room temperature for 24 hours and a white solid precipitates, that after washing with diethyl ether, corresponds to: propane-1,3-bis (trimethylphosphonium) bromide. This white solid, previously dissolved in water, is converted to the corresponding hydroxide using an anionic exchange resin in batch overnight, yielding a solution of propane-1,3-bis (trimethylphosphonium) hydroxide with a concentration of 0.89 mol OH/Kg that

will be used as structure directing agent source. The agent is shown in Figure 1(Lower).

Example 3 - Synthesis of ITQ-34

[0050] 0.38 g of germanium oxide were dissolved in 10.13 g of a solution of ethane-1,2-bis (trimethylphosphonium) hydroxide with a concentration of 1.18 mol OH/Kg. Then, 7.56 g of tetraethylorthosilicate (TEOS) were hydrolyzed in the solution formed and the mixture was maintained under stirring until all the ethanol formed in the hydrolysis was evaporated. Finally, 0.50 g of HF (48% wt.) were added and left stirring until the final composition was:

0.91 SiO₂ : 0.09 GeO₂ : 0.15 (Me₃P)₂(CH₂)₂ (OH)₂ : 0.30 HF : 3 H₂O
where (Me₃P)₂(CH₂)₂ (OH)₂ is ethane-1,2-bis (trimethylphosphonium) hydroxide

[0051] The gel was heated in Teflon-lined stainless steel autoclaves at 175 °C under tumbling for 18 days. The solid was filtered, washed with deionized water and dried at 100 °C to yield ITQ-34 and its XRD pattern is shown in Figure 3.

Example 4 - Synthesis of ITQ-34

[0052] The synthesis gel used for this synthesis had the following molar composition:

0.95 SiO₂ : 0.05 GeO₂ : 0.15 (Me₃P)₂(CH₂)₂ (OH)₂ : 0.30 HF : 3 H₂O
where (Me₃P)₂(CH₂)₂ (OH)₂ is ethane-1,2-bis (trimethylphosphonium) hydroxide

[0053] The gel was prepared by dissolving 0.21 g of germanium oxide in 10.12 g of a solution of ethane-1,2-bis (trimethylphosphonium) hydroxide with a

concentration of 1.18 mol OH/Kg and hydrolyzing 7.94 g of tetraethylorthosilicate (TEOS) in the solution formed under continuous mechanical stirring until all the ethanol and the appropriate amount of water were evaporated. Then, 0.50 g of HF (48% wt.) were added to yield the above gel reaction mixture.

[0054] The gel was autoclaved at 175 °C under stirring for 63 days. The solid, was recovered by filtration, washed with distilled water and dried at 100 °C. The XRD pattern is similar to Figure 3 indicates the product is ITQ-34.

Example 5 - Synthesis of ITQ-34

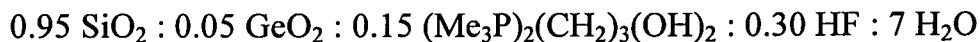
[0055] The ITQ-34 sample was prepared with the following gel composition:



where $(\text{Me}_3\text{P})_2(\text{CH}_2)_3(\text{OH})_2$ is propane-1,3-bis (trimethylphosphonium) hydroxide 0.39 g of germanium oxide were dissolved in 13.41 g of propane-1,3-bis (trimethylphosphonium) hydroxide with a concentration of 0.90 mol OH/Kg. Then, 7.57 g of tetraethylorthosilicate (TEOS) were hydrolyzed in the solution formed and the mixture was maintained under stirring until all the alcohol formed in the hydrolysis was evaporated and the desired composition was reached. Finally, 0.50 g of HF (48% wt.) were added. The gel was heated in Teflon-lined stainless steel autoclaves at 175 °C under stirring conditions for 6 days. The solid was filtered, washed with deionized water and dried at 100 °C. The XRD pattern of the sample corresponds to that of ITQ-34 and is shown in Figure 4.

Example 6 - Synthesis of ITQ-34

[0056] 0.25 g of germanium oxide were dissolved in 16.85 g of a solution of propane-1,3-bis (trimethylphosphonium) hydroxide with a concentration of 0.89 mol OH/Kg. Then, 9.95 g of tetraethylorthosilicate (TEOS) were hydrolyzed in the solution formed and the mixture was maintained under stirring until all the ethanol was evaporated. Then, 0.625 g of HF (48% wt.) were added and left stirring until the final composition was:

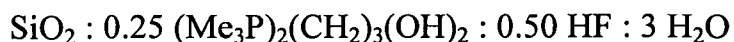


where $(\text{Me}_3\text{P})_2(\text{CH}_2)_3(\text{OH})_2$ is propane-1,3-bis (trimethylphosphonium) hydroxide.

[0057] The gel was autoclaved at 175 °C under tumbling for 8 days. The solid was filtered, washed with deionized water and dried at 100 °C. The XRD pattern is similar to Figure 4 indicates the product is ITQ-34.

Example 7 - Synthesis of ITQ-34

12.75 g of tetraethylorthosilicate (TEOS) were hydrolyzed in 33.73 g of a solution of propane-1,3-bis (trimethylphosphonium) hydroxide with a concentration of 0.89 mol OH/Kg and the mixture was maintained under stirring until all the ethanol formed in the hydrolysis was evaporated. Then, 1.275 g of HF (48% wt.) were added and left stirring to reach the final composition:

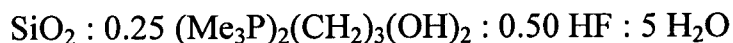


where $(\text{Me}_3\text{P})_2(\text{CH}_2)_3(\text{OH})_2$ is propane-1,3-bis (trimethylphosphonium) hydroxide.

[0058] The gel was heated in Teflon-lined stainless steel autoclaves at 175°C under tumbling for 18 days. The solid filtered, washed with deionized water and dried at 100 °C yield ITQ-34 impurified with ITQ-19.

Example 8 - Synthesis of ITQ-34

[0059] The synthesis gel used for this synthesis had the following molar composition:



where $(\text{Me}_3\text{P})_2(\text{CH}_2)_3(\text{OH})_2$ is propane-1,3-bis (trimethylphosphonium) hydroxide

The gel was prepared by hydrolyzing 14.57 g of tetraethylorthosilicate (TEOS) in 32.39 g of a solution of propane-1,3-bis (trimethylphosphonium) hydroxide with a concentration of 1.08 mol OH/Kg and maintaining under continuous mechanical stirring until all the ethanol and the appropriate amount of water were evaporated to yield the above gel reaction mixture. Finally, 1.46 g of HF (48% wt.) were added and the mixture homogenized.

[0060] The gel was autoclaved at 200°C under stirring for 7 days. The solid, ITQ-34 with a small impurity, was recovered by filtration, washed with distilled water and dried at 100°C.

CLAIMS

1. A synthetic crystalline material having a framework of tetrahedral atoms (T) connected by bridging atoms, the tetrahedral atom framework being defined by connecting the nearest tetrahedral (T) atoms in the manner shown in Table 1 of the specification.

2. The crystalline material of claim 1 wherein said tetrahedral atoms include one or more elements selected from the group consisting of B, Li, Be, Al, P, Si, Ga, Ge, Zn, Cr, Mg, Fe, Co, Ni, Mn, As, In, Sn, Sb, Ti, and Zr.

3. The crystalline material of claim 1 wherein said bridging atoms include one or more elements selected from the group consisting of O, N, F, S, Se, and C.

4. A process for the separation of hydrocarbons from a hydrocarbon-containing stream comprising contacting said hydrocarbon stream with the material of claim 1.

5. A process for converting a feedstock comprising organic compounds to at least one conversion product which comprises contacting said feedstock at organic compound conversion conditions with a catalyst comprising an active form of the material of claim 1.

6. A synthetic porous crystalline material, as synthesized, characterized by an X-ray diffraction pattern including the peaks as set forth below:

d-spacing (Å)	relative intensity
11.2-10.9	20-70
10.3-10.0	20-70
9.53-9.33	5-50
7.97-7.83	60-100
6.06-5.98	5-50
5.57-5.51	20-70
5.38-5.32	5-50
4.73-4.69	5-50
4.18-4.14	30-80
4.09-4.05	5-50
3.90-3.86	30-80
3.78-3.74	20-70
3.71-3.67	30-80
3.37-3.35	5-50
2.90-2.88	5-50
2.54-2.52	5-50
2.32-2.30	5-50.

7. The crystalline material of claim 6 wherein said crystalline material has a composition $mR:aX_2O_3:YO_2.nH_2O$ where R is an organic compound, X is one or more metals selected from the group consisting of B, Ga, Al and Fe, and Y is one or more metals selected from the group consisting of Si, Ge and Ti, and m is a number greater than or equal to 0.01 and less than or equal to 1, a is a number less than or equal to 0.2 and n is a number less than or equal to 10.

8. A calcined dehydrated material characterized by an X-ray diffraction pattern including the most significant lines as set forth below

d-spacing (Å)	relative intensity
12.8-12.5	30-80
11.2-11.0	60-100
10.3-10.1	5-50
9.57-9.37	5-40
8.41-8.25	5-40
8.01-7.87	20-70
5.79-5.71	5-40
5.57-5.51	5-50
4.10-4.06	5-40
3.91-3.87	5-50
3.80-3.76	5-40
3.71-3.67	5-50

9. A process for the separation of hydrocarbons from a hydrocarbon-containing stream comprising contacting said hydrocarbon stream with the material of claim **8**.

10. A process for converting a feedstock comprising organic compounds to at least one conversion product which comprises contacting said feedstock at organic compound conversion conditions with a catalyst comprising an active form of the material of claim **8**.

11. The process for converting a feedstock as in claim **10** wherein the catalyst is combined with a hydrogenating metal.

12. The process for converting a feedstock as in claim **11** wherein said hydrogenating metal is one or more metals selected from the group consisting of tungsten, vanadium, molybdenum, rhenium, nickel, cobalt, chromium, manganese, or a noble metal.

13. A method of synthesizing a crystalline silicate composition of ITQ-34 having the diffraction pattern as set forth below

d-spacing (Å)	relative intensity
11.2-10.9	20-70
10.3-10.0	20-70
9.53-9.33	5-50
7.97-7.83	60-100
6.06-5.98	5-50
5.57-5.51	20-70
5.38-5.32	5-50
4.73-4.69	5-50
4.18-4.14	30-80
4.09-4.05	5-50
3.90-3.86	30-80
3.78-3.74	20-70
3.71-3.67	30-80
3.37-3.35	5-50
2.90-2.88	5-50
2.54-2.52	5-50
2.32-2.30	5-50

by mixing together a source of tetravalent element Y, where Y is Si alone or in combination with Ge and/or Ti, an organic structure directing agent R, water, and optionally a source of metal X and optionally a source of fluoride F, the mixture having a composition, in terms of mole ratios, within the following ranges:

R/YO ₂	0.01-1
H ₂ O/YO ₂	2-50
X/YO ₂	0-0.2
F/YO ₂	0-2

and where X is any trivalent metal capable of tetrahedral coordination.

14. The method according to claim **13** wherein X is one or more metals selected from the group consisting of B, Ga, Al or Fe and Y is silicon and may include one or more metals selected from the group consisting of Ge and Ti.

15. The method of claim **13** wherein said molar ratio ranges are

R/YO ₂	0.1-0.5
H ₂ O/YO ₂	5-20
X/YO ₂	0-0.1
F/YO ₂	0-0.5.

16. The method of claim **14** wherein said molar ratio ranges are

R/YO ₂	0.1-0.5
H ₂ O/YO ₂	5-20
X/YO ₂	0-0.1
F/YO ₂	0-0.5.

17. The method of claim **13**, wherein said organic structure directing agent (R) is ethane-1,2-bis (trimethylphosphonium) or propane-1,3-bis (trimethylphosphonium).

18. The method of claim **14** wherein said organic structure directing agent (R) is ethane-1,2-bis (trimethylphosphonium) or propane-1,3-bis (trimethylphosphonium).