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ITQ-26, NEW CRYSTALLINE MICROPOROUS MATERIALBACKGROUND 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 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 Brønsted 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 molecular sieves, which exhibit the ion- exchange and/or adsorption characteristics of zeolites are 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

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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 AlPO, 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. The present invention is a new molecular sieve having a unique framework structure.

[0003] 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.

[0004] There are currently over 150 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-26 is a new framework material.

SUMMARY OF THE INVENTION

[0005] ITQ-26 (INSTITUTO DE TECNOLOGÍA QUÍMICA number 26) 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-26 is stable to calcination in air, absorbs hydrocarbons, and is catalytically active for hydrocarbon conversion.

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[0006] In one embodiment, the present invention is directed to a new crystalline material that is a silicate compound having a composition $mR:aX_2O_3:YO_2 \cdot nH_2O$ 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, 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, and Y is Si alone or in combination with any other tetravalent metal capable of tetrahedral coordination such as Ge and Ti and where $m = 0.01 - 1$, $a = 0.00 - 0.2$, and $n = 0 - 10$ and having a unique diffraction pattern as given in Table 2.

[0007] In a more specific embodiment, the present invention is directed to a calcined crystalline silicate compound that has a composition $aX_2O_3:YO_2 \cdot nH_2O$, 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, 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, and Y is Si alone or in combination with any other tetravalent metal capable of tetrahedral coordination such as Ge and Ti and where $a = 0.00 - 0.2$ and $n = 0 - 10$ and having a unique diffraction pattern as given in Table 3.

[0008] 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 silica, organic structure directing agent (SDA), water, and optional metal and heating at a temperature and time sufficient to crystallize the silicate.

[0009] The invention includes the use of ITQ-26 to separate hydrocarbons from a hydrocarbon containing stream.

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[0010] The invention also includes the use of ITQ-26 as a hydrocarbon conversion catalyst for converting an organic feedstock to conversion products.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIGURE 1 is a representation of 1, 3-bis-(triethylphosphonium-methyl)-benzene the organic structure directing agent (SDA).

[0012] FIGURE 2 shows the framework structure of ITQ-26 showing only the tetrahedral atoms. There is one unit cell, whose edges are defined by the gray box.

[0013] FIGURE 3 shows the X-ray diffraction pattern of as-synthesized ITQ-26.

[0014] FIGURE 4 shows the X-ray diffraction pattern of calcined/dehydrated ITQ-26.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0015] The present invention is a new structure of crystalline material. As with any porous crystalline material, the structure of ITQ-26 can be defined by the interconnections between the tetrahedrally coordinated atoms in its framework. In particular, ITQ-26 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.

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Table 1
ITQ-26 tetrahedral atom interconnections

T atom	Connected to:
T1	T2, T5, T56, T68
T2	T1, T4, T57, T69
T3	T4, T17, T24, T43
T4	T2, T3, T6, T75
T5	T1, T7, T116, T120
T6	T4, T20, T27, T44
T7	T5, T14, T34, T70
T8	T9, T12, T53, T65
T9	T8, T11, T54, T66
T10	T11, T17, T24, T49
T11	T9, T10, T13, T72
T12	T8, T14, T111, T115
T13	T11, T20, T27, T50
T14	T7, T12, T40, T67
T15	T16, T19, T62, T71
T16	T15, T18, T63, T72
T17	T3, T10, T18, T31
T18	T16, T17, T20, T69
T19	T15, T21, T106, T110
T20	T6, T13, T18, T32
T21	T19, T28, T52, T73
T22	T23, T26, T59, T74
T23	T22, T25, T60, T75
T24	T3, T10, T25, T37
T25	T23, T24, T27, T66
T26	T22, T28, T101, T105
T27	T6, T13, T25, T38
T28	T21, T26, T46, T76
T29	T30, T33, T56, T68
T30	T29, T32, T57, T69
T31	T17, T32, T43, T49
T32	T20, T30, T31, T63
T33	T29, T34, T95, T100
T34	T7, T33, T40, T58
T35	T36, T39, T53, T65
T36	T35, T38, T54, T66
T37	T24, T38, T43, T49
T38	T27, T36, T37, T60
T39	T35, T40, T89, T94
T40	T14, T34, T39, T55
T41	T42, T45, T59, T74
T42	T41, T44, T60, T75

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T43	T3, T31, T37, T44
T44	T6, T42, T43, T57
T45	T41, T46, T83, T88
T46	T28, T45, T52, T61
T47	T48, T51, T62, T71
T48	T47, T50, T63, T72
T49	T10, T31, T37, T50
T50	T13, T48, T49, T54
T51	T47, T52, T77, T82
T52	T21, T46, T51, T64
T53	T8, T35, T54, T55
T54	T9, T36, T50, T53
T55	T40, T53, T100, T135
T56	T1, T29, T57, T58
T57	T2, T30, T44, T56
T58	T34, T56, T94, T133
T59	T22, T41, T60, T61
T60	T23, T38, T42, T59
T61	T46, T59, T82, T131
T62	T15, T47, T63, T64
T63	T16, T32, T48, T62
T64	T52, T62, T88, T129
T65	T8, T35, T66, T67
T66	T9, T25, T36, T65
T67	T14, T65, T120, T127
T68	T1, T29, T69, T70
T69	T2, T18, T30, T68
T70	T7, T68, T115, T125
T71	T15, T47, T72, T73
T72	T11, T16, T48, T71
T73	T21, T71, T105, T123
T74	T22, T41, T75, T76
T75	T4, T23, T42, T74
T76	T28, T74, T110, T121
T77	T51, T78, T123, T131
T78	T77, T80, T124, T132
T79	T80, T91, T97, T113
T80	T78, T79, T81, T136
T81	T80, T93, T99, T114
T82	T51, T61, T88, T105
T83	T45, T84, T121, T129
T84	T83, T86, T122, T130
T85	T86, T91, T97, T118
T86	T84, T85, T87, T134
T87	T86, T93, T99, T119
T88	T45, T64, T82, T110
T89	T39, T90, T127, T133
T90	T89, T92, T128, T134

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T91	T79, T85, T92, T103
T92	T90, T91, T93, T132
T93	T81, T87, T92, T104
T94	T39, T58, T100, T120
T95	T33, T96, T125, T135
T96	T95, T98, T126, T136
T97	T79, T85, T98, T108
T98	T96, T97, T99, T130
T99	T81, T87, T98, T109
T100	T33, T55, T94, T115
T101	T26, T102, T123, T131
T102	T101, T104, T124, T132
T103	T91, T104, T113, T118
T104	T93, T102, T103, T128
T105	T26, T73, T82, T110
T106	T19, T107, T121, T129
T107	T106, T109, T122, T130
T108	T97, T109, T113, T118
T109	T99, T107, T108, T126
T110	T19, T76, T88, T105
T111	T12, T112, T125, T135
T112	T111, T114, T126, T136
T113	T79, T103, T108, T114
T114	T81, T112, T113, T124
T115	T12, T70, T100, T120
T116	T5, T117, T127, T133
T117	T116, T119, T128, T134
T118	T85, T103, T108, T119
T119	T87, T117, T118, T122
T120	T5, T67, T94, T115
T121	T76, T83, T106, T122
T122	T84, T107, T119, T121
T123	T73, T77, T101, T124
T124	T78, T102, T114, T123
T125	T70, T95, T111, T126
T126	T96, T109, T112, T125
T127	T67, T89, T116, T128
T128	T90, T104, T117, T127
T129	T64, T83, T106, T130
T130	T84, T98, T107, T129
T131	T61, T77, T101, T132
T132	T78, T92, T102, T131
T133	T58, T89, T116, T134
T134	T86, T90, T117, T133
T135	T55, T95, T111, T136
T136	T80, T96, T112, T135

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[0016] 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.

[0017] In one embodiment, this new crystalline silicate compound has a composition $mR:aX_2O_3:YO_2 \cdot nH_2O$ 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, 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, and Y is Si alone or in combination with any other tetravalent metal capable of tetrahedral coordination such as Ge and Ti and where $m = 0.01 - 1$, $a = 0.00 - 0.2$, and $n = 0 - 10$. This compound has the unique diffraction pattern given in Table 2 and shown in FIGURE 3.

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Table 2
X-ray diffraction lines for as-synthesized ITQ-26

d (Å) (%)	relative int.
13.8-13.0	60-100
12.3-11.6	5-40
9.09-8.73	30-80
6.55-6.37	5-50
4.76-4.66	5-50
4.49-4.40	20-70
4.20-4.12	50-100
3.81-3.75	5-50
3.69-3.63	5-50
3.36-3.31	30-80
2.998-2.959	5-40
2.846-2.811	5-40
2.624-2.594	5-40
2.503-2.476	5-40
2.366-2.342	5-40

[0018] Other embodiments of the new structure include a calcined compound of composition $aX_2O_3:YO_2 \cdot nH_2O$, 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, 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, Fe, and Y is Si alone or in combination with any other tetravalent metal capable of tetrahedral coordination such as Ge and Ti and where $a = 0.00 - 0.2$, and $n = 0 - 10$. This compound has the unique diffraction pattern given in Table 3 and FIGURE 4.

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Table 3
X-ray diffraction lines for calcined/dehydrated ITQ-26

d (Å)	relative int. (%)
13.7-13.0	60-100
12.2-11.6	20-70
9.63-9.27	1-10
9.03-8.72	20-70
6.55-6.39	1-10
5.01-4.91	1-10
4.75-4.66	1-20
4.50-4.42	1-20
4.39-4.32	1-10
4.21-4.14	1-20
4.17-4.10	1-20
3.82-3.76	1-10
3.70-3.65	1-20
3.37-3.32	1-20
3.33-3.29	1-10
3.14-3.10	1-10

[0019] This new compound is made by the method of mixing together a source of silica, organic structure directing agent (SDA), water, and optional source of metal and heating at a temperature and time sufficient to crystallize the silicate. The method is described below.

[0020] The synthetic porous crystalline material of this invention, ITQ-26, is a crystalline phase which has a unique 3-dimensional channel system comprising intersecting 12-membered rings of tetrahedrally coordinated atoms. The 12-membered ring channels have cross-sectional dimensions between the bridging oxygen atoms of about 7.8 Ångströms by about 6.8 Ångströms along one direction and about 7.1 Ångströms by about 6.6 Ångströms along the other two directions.

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[0021] Variations in the X-ray diffraction pattern may occur between the different chemical composition forms of ITQ-26, such that the exact ITQ-26 structure can vary due its particular composition and whether or not it has been calcined and rehydrated.

[0022] In the as-synthesized form ITQ-26 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.

[0023] The ITQ-26 material of the present invention may be calcined to remove the organic templating 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-26 are shown in Table 3 measured with synchrotron 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.

[0024] In addition, to describing the structure of ITQ-26 by the interconnections of the tetrahedral atoms as in Table 1 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-26 is illustrated in FIGURE 2 (which shows only the tetrahedral atoms) down the direction of the 12-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

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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.

[0025] 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 have been seen in the zirconium diphosphonate, MIL-57. See: C. Serre, G. Férey, *J. Mater. Chem.* 12, p. 2367 (2002). 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. B* 29, 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 ± 1.0 Ångström is implied for the x and y coordinate positions and a range of ± 0.5 Ångström for the z coordinate positions.

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Table 4

Positions of tetrahedral (T) atoms for the ITQ-26 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)
T1	1.559	8.591	1.558
T2	1.559	5.478	1.559
T3	1.559	1.559	5.056
T4	2.791	2.791	2.490
T5	2.352	11.023	3.307
T6	1.531	1.531	0.000
T7	0.000	11.844	5.084
T8	25.191	18.159	1.558
T9	25.191	21.272	1.559
T10	25.191	25.191	5.056
T11	23.959	23.959	2.490
T12	24.398	15.727	3.307
T13	25.219	25.219	0.000
T14	0.000	14.906	5.084
T15	18.159	1.559	1.558
T16	21.272	1.559	1.559
T17	25.191	1.559	5.056
T18	23.959	2.791	2.490
T19	15.727	2.352	3.307
T20	25.219	1.531	0.000
T21	14.906	0.000	5.084
T22	8.591	25.191	1.558
T23	5.478	25.191	1.559
T24	1.559	25.191	5.056
T25	2.791	23.959	2.490
T26	11.023	24.398	3.307
T27	1.531	25.219	0.000
T28	11.844	0.000	5.084
T29	25.191	8.591	11.672
T30	25.191	5.478	11.671
T31	25.191	1.559	8.174
T32	23.959	2.791	10.740
T33	24.398	11.023	9.922
T34	0.000	11.844	8.146
T35	1.559	18.159	11.672
T36	1.559	21.272	11.671
T37	1.559	25.191	8.174
T38	2.791	23.959	10.740
T39	2.352	15.727	9.922

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T40	0.000	14.906	8.146
T41	8.591	1.559	11.672
T42	5.478	1.559	11.671
T43	1.559	1.559	8.174
T44	2.791	2.791	10.740
T45	11.023	2.352	9.922
T46	11.844	0.000	8.146
T47	18.159	25.191	11.672
T48	21.272	25.191	11.671
T49	25.191	25.191	8.174
T50	23.959	23.959	10.740
T51	15.727	24.398	9.922
T52	14.906	0.000	8.146
T53	25.191	18.159	11.672
T54	25.191	21.272	11.671
T55	24.398	15.727	9.922
T56	1.559	8.591	11.672
T57	1.559	5.478	11.671
T58	2.352	11.023	9.922
T59	8.591	25.191	11.672
T60	5.478	25.191	11.671
T61	11.023	24.398	9.922
T62	18.159	1.559	11.672
T63	21.272	1.559	11.671
T64	15.727	2.352	9.922
T65	1.559	18.159	1.558
T66	1.559	21.272	1.559
T67	2.352	15.727	3.307
T68	25.191	8.591	1.558
T69	25.191	5.478	1.559
T70	24.398	11.023	3.307
T71	18.159	25.191	1.558
T72	21.272	25.191	1.559
T73	15.727	24.398	3.307
T74	8.591	1.559	1.558
T75	5.478	1.559	1.559
T76	11.023	2.352	3.307
T77	14.934	21.966	8.173
T78	14.934	18.853	8.174
T79	14.934	14.934	11.671
T80	16.166	16.166	9.105
T81	14.906	14.906	6.615
T82	13.375	25.219	11.699
T83	11.816	4.784	8.173
T84	11.816	7.897	8.174
T85	11.816	11.816	11.671
T86	10.584	10.584	9.105
T87	11.844	11.844	6.615
T88	13.375	1.531	11.699

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T89	4.784	14.934	8.173
T90	7.897	14.934	8.174
T91	11.816	14.934	11.671
T92	10.584	16.166	9.105
T93	11.844	14.906	6.615
T94	1.531	13.375	11.699
T95	21.966	11.816	8.173
T96	18.853	11.816	8.174
T97	14.934	11.816	11.671
T98	16.166	10.584	9.105
T99	14.906	11.844	6.615
T100	25.219	13.375	11.699
T101	11.816	21.966	5.057
T102	11.816	18.853	5.056
T103	11.816	14.934	1.559
T104	10.584	16.166	4.125
T105	13.375	25.219	1.531
T106	14.934	4.784	5.057
T107	14.934	7.897	5.056
T108	14.934	11.816	1.559
T109	16.166	10.584	4.125
T110	13.375	1.531	1.531
T111	21.966	14.934	5.057
T112	18.853	14.934	5.056
T113	14.934	14.934	1.559
T114	16.166	16.166	4.125
T115	25.219	13.375	1.531
T116	4.784	11.816	5.057
T117	7.897	11.816	5.056
T118	11.816	11.816	1.559
T119	10.584	10.584	4.125
T120	1.531	13.375	1.531
T121	11.816	4.784	5.057
T122	11.816	7.897	5.056
T123	14.934	21.966	5.057
T124	14.934	18.853	5.056
T125	21.966	11.816	5.057
T126	18.853	11.816	5.056
T127	4.784	14.934	5.057
T128	7.897	14.934	5.056
T129	14.934	4.784	8.173
T130	14.934	7.897	8.174
T131	11.816	21.966	8.173
T132	11.816	18.853	8.174
T133	4.784	11.816	8.173
T134	7.897	11.816	8.174
T135	21.966	14.934	8.173
T136	18.853	14.934	8.174

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[0026] The complete structure of ITQ-26 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-26, 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.

[0027] 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.

[0028] 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.

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

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Table 5

Coordination sequence for ITQ-26 structure.

atom number	atom label	coordination sequence													
1	T(1)	4	9	18	31	47	66	94	127	159	188	226	287	345	
2	T(2)	4	9	17	29	44	68	97	125	154	190	240	292	338	
3	T(3)	4	9	18	30	42	60	89	126	162	188	222	281	349	
4	T(4)	4	12	18	27	48	69	94	124	160	201	237	285	330	
5	T(5)	4	12	17	30	46	67	90	124	158	186	230	279	344	
6	T(6)	4	11	20	24	36	72	110	126	136	182	256	306	326	
7	T(7)	4	11	20	28	42	70	100	120	146	186	232	291	349	

[0029] 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)).

[0030] The coordination sequence for the ITQ-26 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.

[0031] 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-

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atoms. When this occurs it is found that T-atoms may be also coordinated to one or two oxygen atoms of water molecules ($-\text{OH}_2$), or of hydroxyl groups ($-\text{OH}$). For example, the molecular sieve $\text{AlPO}_4\text{-34}$ 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 ($-\text{F}$) 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).

[0032] The invention also includes a method of synthesizing a crystalline silicate composition of ITQ-26 having the diffraction pattern similar to Table 2 by mixing together a source of silica, organic structure directing agent (SDA), water, and optional metal, X, with a composition, in terms of mole ratios, within the following ranges:

R/ YO_2	0.01 - 1
$\text{H}_2\text{O}/\text{YO}_2$	2-50
X/ YO_2	0 - .2

and preferably within the following ranges:

R/ YO_2	0.1 - .5
$\text{H}_2\text{O}/\text{YO}_2$	5 - 20
X/ YO_2	0 - .1

and 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, and Y is Si alone or in combination with any other tetravalent metal capable of tetrahedral coordination such as Ge and Ti.

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[0033] Said organic structure directing agent (SDA) is preferably 1, 3-bis-(triethylphosphoniummethyl)-benzene. See FIGURE 1. Sources of silica can be colloidal, fumed or precipitated silica, silica gel, sodium or potassium silicates, or organic silicon such as 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 and various salts of the metals X such as iron nitrate, iron chloride, and gallium nitrate, etc. The mixture is then heated at a temperature and time sufficient to crystallize the silicate.

[0034] 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-26 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.

[0035] 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.

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[0036] Thus, in its active form ITQ-26 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).

[0037] 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 and ammonium forms, is particularly useful in the catalysis of certain organic, e.g., hydrocarbon, conversion reactions.

[0038] 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

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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-26 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.

[0039] 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-26 in a vacuum, but a longer time is required to obtain a sufficient amount of dehydration.

[0040] 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

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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.

[0041] 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.

[0042] 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.

[0043] 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

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composite is prepared in the form of beads, in the range of about 2 to about 80 weight percent of the composite.

[0044] In order to more fully illustrate the nature of the invention and the manner of practicing same, the following example is presented.

Example 1: Synthesis of ITQ-26

[0045] The germanium containing gel was prepared, according to the following description: 0.62 of germanium oxide were dissolved in 24.19 g of a solution of 1, 3-bis-(triethylphosphoniummethyl)-benzene hydroxide (FIGURE 1) with a concentration of 0.62 mol of OH⁻ in 1000 g of solution. Then, 5.02 g of tetraethylorthosilicate were hydrolyzed in that solution and the mixture was left to evaporate under stirring until complete evaporation of the ethanol formed was achieved. When the weight reached 8.62 g of gel, 0.62 g of HF (48.1 %wt.) were added and the mixture was homogenized. The final composition of the gel was:

0.80 SiO₂: 0.20 GeO₂: 0.25 *m*-B(Et₃P)₂(OH)₂: 0.50 HF: 7.50 H₂O

[0046] The mixture was transferred to Teflon-lined stainless steel autoclaves and heated under stirring for 6 days at 175 °C. Longer crystallization times gave impure ITQ-26 with a small amount of polymorph C of Beta zeolite.

[0047] The powder X-ray diffractogram of the sample as made and calcined is shown in FIGURE 3 and FIGURE 4 below. The sample was calcined in air to 550 °C for 3 hours, cooled down to 300 °C, and then sealed under vacuum in a 2 mm quartz capillary tube to minimize structural damage.

[0048] The X-ray diffraction patterns are given in Table 6 and Table 7, respectively.

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[0049] The porosity of the calcined material was measured by adsorbing nitrogen and argon. Adsorption measurements were carried out by manipulating the sample in an inert atmosphere. The results obtained are:

- BET surface area: 257 m²/g
- Micropore area: 243 m²/g
- Micropore volume: 0.12 cm³/g
- Pore diameter: 7.1 Å

[0050] That data suggest that ITQ-26 is a large pore (12-ring pore aperture) zeolite. This is confirmed by the structure discussed above.

Example 2: ^kSynthesis of ITQ-26

[0051] The germanium containing gel was prepared, according to the following description: 0.75 of germanium oxide were dissolved in 22.5 g of a solution of 15 % wt. 1, 3-bis-(triethylphosphoniummethyl)-benzene hydroxide. Then, 6.01 g of tetraethylorthosilicate were hydrolyzed in that solution and the mixture was left to evaporate under stirring until complete evaporation of the ethanol formed was achieved. When the weight reached 10.3 g of gel, 0.74 g of HF (49 % wt.) were added and the mixture was homogenized. The final composition of the gel was:

0.80 SiO₂: 0.20 GeO₂: 0.25 *m*-B(Et₃P)₂(OH)₂: 0.50 HF: 7.50 H₂O

[0052] The mixture was transferred to a Teflon-lined stainless steel autoclave and heated for 6 days at 175 °C with a tumbling rate of 20 rpm. The sample was recovered by filtration, washed with deionized water and then dried in an 115 °C oven. The X-ray diffraction pattern was measured with Cu Kα

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radiation and is similar to that given in Table 6 and Figure 3. Analysis of the X-ray diffraction pattern showed the sample to be pure ITQ-26.

Table 6
X-ray powder diffraction lines of as-made ITQ-26
(Cu K α radiation)

2-Theta	d(Å)	I%
4.63	19.086	3
6.62	13.348	100
7.40	11.944	19
9.43	9.376	8
9.92	8.907	60
10.47	8.440	3
11.94	7.407	6
13.70	6.460	29
14.11	6.273	9
15.21	5.819	1
16.29	5.437	2
16.96	5.224	6
17.87	4.960	10
18.83	4.709	25
19.98	4.441	37
20.26	4.379	5
21.34	4.160	79
22.99	3.866	1
23.30	3.815	5
23.39	3.801	1
23.53	3.779	23
24.29	3.661	30
25.30	3.518	6
26.08	3.414	5
26.72	3.334	54
27.57	3.233	8
28.54	3.125	6
29.98	2.979	19
31.61	2.828	16
33.08	2.705	7
33.65	2.661	5
34.34	2.609	13
36.04	2.490	14
37.08	2.423	8
38.20	2.354	16
40.65	2.218	8

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43.52	2.078	8
46.32	1.959	6
48.38	1.880	4

Table 7

X-ray powder diffraction lines of calcined/dehydrated ITQ-26
(Synchrotron radiation, $\lambda = 0.8702 \text{ \AA}$)

2-Theta	d(Å)	I%
2.64	18.907	1
3.73	13.376	100
4.20	11.864	41
5.28	9.449	4
5.62	8.873	42
6.75	7.390	1
7.46	6.692	1
7.54	6.622	2
7.71	6.469	4
7.97	6.259	1
9.58	5.210	2
10.07	4.959	4
10.60	4.709	8
11.20	4.459	7
11.47	4.353	3
11.80	4.232	2
11.97	4.173	9
12.07	4.139	9
13.00	3.845	1
13.09	3.819	1
13.20	3.767	4
13.61	3.672	5
14.23	3.514	1
14.70	3.402	2
14.95	3.344	9
15.12	3.307	4
15.23	3.284	1
15.46	3.236	2
15.58	3.211	2
16.05	3.117	3
16.74	2.989	2
16.89	2.963	3
17.67	2.832	3
19.20	2.608	3
21.31	2.353	2

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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 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 claims 1 or 2 wherein said bridging atoms include one or more elements selected from the group consisting of O, N, F, S, Se, and C.
4. A synthetic porous crystalline material, as synthesized, characterized by an X-ray diffraction pattern including the peaks as substantially set forth in Table 2 of the specification.
5. The crystalline material of any one of the preceding claims wherein said crystalline material has a composition $mR:aX_2O_3:YO_2 \cdot nH_2O$ 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 real number less than or equal to 1, a is a real number less than or equal to 0.2 and n is a real number less than or equal to 10.

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6. A calcined dehydrated material characterized by an X-ray diffraction pattern including the most significant lines substantially, as set forth in Table 3 of the specification.

7. The calcined dehydrated material of Claim 6 wherein said crystalline material has a composition $aX_2O_3:YO_2 \cdot nH_2O$ where 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 a is a real number less than or equal to 0.2 and n is a real number less than or equal to 10.

8. A process for the separation of hydrocarbons from a hydrocarbon-containing stream using any of the materials of claims 1 through claim 7.

9. 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 any of the materials of claims 1 through claim 7.

10. The process for converting a feedstock of claim 9 wherein the catalyst is combined with a hydrogenating metal.

11. The process for converting a feedstock of claim 10 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

12. A method of synthesizing a crystalline silicate composition of ITQ-26 having the diffraction pattern similar to Table 2 by mixing together at

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least one source of silica, at least one organic structure directing agent (R), water, and optionally a source of metal (X) to form a 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 - .2

wherein X is any trivalent metal capable of tetrahedral coordination and Y is silicon and optionally any other tetravalent metal capable of tetrahedral coordination.

13. The method according to claim 12 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.

14. A method of synthesizing a crystalline silicate composition of ITQ-26 having the diffraction pattern similar to Table 2 by mixing together a source of silica, organic structure directing agent (R), water, and optionally a source of metal (X), to form a 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 - .2

and wherein X is one or more metals selected from the group consisting of B, Ga, Al, Fe, Li, Be, P, Zn, Cr, Mg, Co, Ni, Mn, As, In, Sn, Sb, Ti, and Zr , and Y is silicon and may include one or more metals selected from the group consisting of Ge and Ti.

15. A method of synthesizing a crystalline silicate composition of any of the claims 12 through 14 wherein said organic structure directing agent (SDA) is 1, 3-bis-(triethylphosphoniummethyl)-benzene.

16. The crystalline silicate composition produced using the method of any one of claims 12 to 15.