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(54) Crystalline Zeolite Composition

(57) The invention provides a crystalline aluminosilicate zeolite composition related to the family of ZSM-5 zeolites having formula, in terms of mole ratios of oxides, of

$[R_2O, M'_{2/n}O]_w$:
$[Al_2O_3]_x$
$[S_1O_2]_y$:
$[M''_{2/n}O]_z$

wherein $0.5<W/x<3$, y/x is >20, $0<z/x<100$ R is N containing cation, M′ is Group IA metal and M″ is a metal selected from the rare earth metals, chromium, vanadium, molybdenum, indium, boron, mercury, tellurium, silver, ruthenium, platinum and palladium. The invention also provides a process for converting an organic charge with the zeolite and method for preparing it.

GB 2 033 358 A

SPECIFICATION

Crystalline Zeolite Composition

Background of the Invention

Field of the Invention

The invention relates to crystalline aluminosilicate zeolite compositions. More particularly, it relates to crystalline zeolites that are crystallized in the presence of certain metals or metal compounds. It relates further to hydrocarbon conversion with such catalysts.

Description of the Prior Art

Zeolitic materials, both natural and synthetic, have been demonstrated in the past to have catalytic capabilities for various types of hydrocarbon conversion. Certain zeolitic materials are ordered, porous crystalline aluminosilicates having a definite crystalline structure within which there are a large number of small cavities which are interconnected by a number of still smaller channels. These cavities and channels are precisely uniform in size. Since the dimensions of these pores are such as to accept for adsorption molecules of certain dimensions, while rejecting those of larger dimensions, these materials, have come to be known as "molecular sieves" and are utilized in a variety of ways to take advantage of these properties.

Such molecular sieves include a wide variety of positive ion-containing crystalline aluminosilicates, both natural and synthetic. These aluminosilicates can be described as a rigid three-dimensional network of SiO_4 and AlO_4 in which the tetrahedra are crosslinked by the sharing of oxygen atoms whereby the ratio of the total aluminum and silicon atoms to oxygen is 1:2. The electrovalence of the tetrahedra-containing aluminum is balanced by the inclusion in the crystal of a cation, for example, an alkali metal or an alkaline earth metal cation. This can be expressed by formula wherein the ratio of Al to the number of the various cations, such as Ca/2, Sr/2, Na, K or Li, is equal to unity. One type of cation has been exchanged either in entirety or partially by another type of cation utilizing ion exchange techniques in a conventional manner. By means of such cation exchange, it has been possible to vary the size of the pores in the given aluminosilicate by suitable selection of the particular cation. The spaces between the tetrahedra are occupied by molecules of water prior to dehydration.

U.S. 3,941,871 discloses and claims a crystalline metal organosilicate having a high silica-to-alumina ratio and containing, in addition to sodium, calcium, nickel or zinc.

Other prior art techniques have resulted in the formation of a great variety of synthetic crystalline aluminosilicates. These aluminosilicates have come to be designated by letter or other convenient symbol, as illustrated by zeolite A (U.S. 2,882,243), zeolite X (U.S. 2,882,244), zeolite ZSM-5 (U.S. 3,702,886), zeolite ZSM-11 (U.S. 3,709,979), ZSM-12 (U.S. 3,832,449) and zeolite ZSM-35 (U.S. 4,016,245), merely to name a few.

Summary of the Invention

The present invention relates to stable synthetic crystalline aluminosilicate zeolite compositions, to a method for their preparation and to hydrocarbon conversion processes conducted therewith. These compositions, as synthesized, have a definite x-ray diffraction pattern, characteristic of the ZSM-5 zeolites and shows the significant lines set forth in Table 1.

Table 1

Interplanar spacing d(A):		*Relative Intensity*
11.1	±0.2	s
10.0	±0.2	s
7.4	±0.15	w
7.1	±0.15	w
6.3	±0.1	w
6.04	±0.1	w
5.97		
5.56	±0.1	w
5.01	±0.1	w
4.60	±0.08	w
4.25	±0.08	w
3.85	±0.07	vs
3.71	±0.05	s
3.04	±0.03	w
2.99	±0.02	w
2.94	±0.02	w

These values were determined by standard techniques. The radiation was the K-alpha doublet of copper, and a scintillation counter spectrometer with a strip chart pen recorder was used. The peak

heights, I, and the positions as a function of 2 times theta, where theta is the Bragg angle, were read from the spectrometer chart. From these, the relative intensitives, $100\ I/I_o$, where I_o is the intensity of the strongest line or peak, and d (obs.), the interplanar spacing in A, corresponding to the recorded lines, were calculated. In Table 1 the relative intensities are given in terms of the symbols s=strong, w=weak and vs=very strong. It should be understood that this X-ray diffraction pattern is characteristic of all the species of the present compositions. Ion exchange of the sodium ion with cations reveals substantially the same pattern with some minor shifts in interplanar spacing and variation in relative intensity. Other minor variations can occur depending on the silicon to aluminum ratio of the particular sample and the extent of thermal conditioning.

The anhydrous composition can also be identified, in terms of mole ratios of oxides, as follows:

$$[R_2O, M'_{2/n}O]_W : [Al_2O_3]_X : [SiO_2]_Y : [M''_{2/n}O]_Z$$

wherein W/X is from >0.5 to <3, Y/X is >20 and Z/X is from >zero to <~100, R is a nitrogen containing cation. R may include primary amines containing 2 to 10 carbon atoms and ammonium cations, preferably the tetraalkylammonium cation in which the alkyl contains from 2 to 5 carbon atoms, M' is a metal from Group IA of the Periodic Table, ammonium, hydrogen or mixtures thereof, and n is the valence of M' or M''. With respect to M'', the preferred metals are those selected from the rare earth metals, (i.e. metals having atomic numbers from 57 to 71), chromium, vanadium, molybdenum, indium, boron, mercury, tellurium, silver and one of the platinum group metals, which latter group includes platinum, palladium and ruthenium.

It is no known whether the M'' is present as a metal or as a metal compound. The above formula will be understood to take into account the presence in any of the M'' various states and also to allow for varying amounts thereof. For example, if it is present in the occluded state, then its concentration relative to aluminum in the zeolite as synthesized can range up to but less than about 100.

Description of Specific Embodiments

A reaction mixture containing sources of the tetrapropylammonium cation (as from the hydroxide), sodium oxide, silica, water, and sources of, for example, indium, boron, ruthenium, platinum, chromium, rare earth, vandium, mercury, tellurium, silver, palladium, molybdenum and, optionally, alumina, will yield a ZSM-5 zeolite, but having unexpectedly improved properties. The content of indium, boron, etc. listed above can range in the final product from about 0.005% by weight to 5.0% by weight.

The crystalline aluminosilicates prepared by the method of the present invention have high thermal stability and exhibit superior catalytic performance.

The original alkali metal can be replaced, at least in part, in accordance with techniques well-known in the art by ion exchange with other cations. Preferred replacing cations include metal ions, ammonium ions, hydrogen ions, and mixtures of the same. Particularly preferred cations are those which render the zeolite catalytically active, especially for hydrocarbon conversion. These include hydrogen, metals of Group II and VIII of the Periodic Table and manganese.

In a preferred embodiment of the zeolite, the silica/alumina mole ratio is greater than 35 and ranges up to about 3000.

The present zeolites have a high degree of thermal stability thereby rendering them particularly effective for use in processes involving elevated temperatures.

The composition can be prepared utilizing materials which supply the appropriate components of the zeolite. Such components include, for an aluminosilicate, sodium aluminate, alumina, sodium silicate, silica hydrosol, silica gel, silicic acid, sodium hydroxide and a tetrapropylammonium compound, e.g., tetrapropylammonium hydroxide. It will be understood that each component utilized in the reaction mixture for preparing the zeolite can be supplied by one or more initial reactants and they can be mixed together in any order. For example, sodium can be supplied by an aqueous solution of sodium hydroxide, or by an aqueous solution of sodium silicate; tetrapropylammonium cation can be supplied by the bromide salt. The reaction mixture can be prepared either batchwise or continuously. Crystal size and crystallization time of the composition will vary with the nature of the reaction mixture employed. It will be further understood that in the very high silica-to-alumina ratios, which can in this invention preferably range from greater than 35 to about 3000 or more, and more preferably about 70 to about 500, it may not be necessary to add a source of alumina to the reaction mixture since residual amounts in other reactants may suffice.

The zeolite can be prepared from a reaction mixture having a composition, in terms of mole ratios of oxides or in % of total moles of oxides, falling within the following ranges:

Table 2

	Broad	*Preferred*	*Most Preferred*
OH^-/SiO_2	0.07—1.0	0.1—0.8	0.2—0.75
$R_4N^+/(R_4N^+ + Na^+)$	0.2—0.95	0.3—0.9	0.4—0.9
H_2O/OH^-	10—300	10—300	10—300
SiO_2/Al_2O_3	50—3000	70—1000	70—500
Other metal Oxide (% of total oxides)	1×10^{-6}—1.0	1×10^{-5}—0.1	1×10^{-5}—0.01

R is as defined hereinabove in the Summary.

Typical reaction conditions consist of heating the foregoing reaction mixture to a temperature of from about 95°C to 175°C for a period of time of from about six hours to 120 days. A more preferred temperature range is from about 100°C to 175°C with the amount of time at a temperature in such range being from about 12 hours to 8 days.

The digestion of the gel particles is carried out until crystals form. The solid product is separated from the reaction medium, as by cooling the whole to room temperature, filtering and water washing.

The foregoing product is dried, e.g. at 230°F, for from about 8 to 24 hours. Of course, milder conditions may be employed if desired, e.g. room temperature under vacuum.

The zeolite can have the alkali metal associated therewith replaced by a wide variety of other cations according to techniques well-known in the art. Typical replacing cations would include hydrogen, ammonium and metal cations including mixtures of the same. Of the replacing metallic cations, particular preference is given to cation of metals such as rare earth metal, manganese and calcium, as well as metals of Groups II and VIII of the Periodic Table, e.g., zinc or platinum.

Typical ion exchange techniques include contacting the zeolite with a salt of the desired replacing cation or cations. Although a wide variety of salts can be employed, particular preference is given to chlorides, nitrates and sulfates.

Representative ion exchange techniques are disclosed in a wide variety of patents including United States 3,140,249; United States 3,140,251; and United States 3,140,253.

Following contact with the salt solution of the desired replacing cations, the zeolites are then preferably washed with water and dried at a temperature ranging from 150°F to about 600°F and thereafter calcined in air or other inert gas at temperatures ranging from about 500°F to 1500°F for periods of time ranging from 1 minute to 48 hours or more.

Regardless of the cations replacing the sodium in its synthesized form, the spatial arrangement of the aluminum, silicon and oxygen atoms which form the basic crystal lattices of the zeolite remains essentially unchanged by the described replacement of sodium or other alkali metal as determined by taking an X-ray powder diffraction pattern of the ion-exchanged materials. Such X-ray diffraction pattern of the ion-exchanged product reveals a pattern substantially the same as that set forth in Table 1 above.

The aluminosilicates prepared by the instant invention are formed in a wide variety of particular sizes. Generally speaking, the particles can be in the form of a powder,, a granule, or a molded product, such as extrudate having particle size sufficient to pass through a 2 mesh (Tyler) screen and be retained on a 400 mesh (Tyler) screen. In cases where the catalyst is molded, such as by extrusion, the aluminosilicate can be extruded before drying or dried or partially dried and then extruded.

As in the case of many catalysts, it is desired to incorporate the zeolite 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. 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 an active material in conjunction with the present composition, i.e., combined therewith, tends to improve 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 in orderly manner without employing other means for controlling the rate of reaction. Normally, zeolite materials have been incorporated into naturally occurring clays, e.g. bentonite and kaolin, to improve the crush strength of the catalyst under commercial operating conditions. These 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 a petroleum refinery the catalyst is often subjected to rough handling, which tends to break the catalyst down into powderlike materials which cause problems in processing. These clay binders have been employed for the purpose of improving the crush strength of the catalyst.

Naturally occurring clays which can be composited with the catalyst include the montmorillonite and kaolin families, which families include the sub-bentonites 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 they can be initially subjected to calcination, acid treatment or chemical modification.

In addition to the foregoing materials, the catalyst can be composited with a porous matrix material such as silica, alumina, 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. The matrix can be in the form of a cogel. The relative proportions of finely divided crystalline aluminosilicate and inorganic oxide gel matrix vary widely, with the crystalline aluminosilicate 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 about 50 percent by weight of the composite.

While the catalyst is useful in cracking and hydrocracking, it is outstandingly useful in other petroleum refining processes, indicating again the unique catalytic characteristics of these zeolites. The latter processes include isomerization of n-paraffins and naphthenes, polymerization of compounds containing an olefinic or acetylenic carbon-to-carbon linkage such as isobutylene and butene-1, reforming, alkylation, isomerization of polyalkyl substituted aromatics, e.g., ortho-xylene, and disproportionation of aromatics, such as toluene, to provide a mixture of benzene, xylenes and higher methylbenzenes. The catalysts have exceptional high selectivity and, under the conditions of hydrocarbon conversion, provides a high percentage of desired products relative to total products compared with known zeolitic hydrocarbon conversion catalysts.

As indicated above, the zeolite is also useful in other catalytic processes, such as catalytic cracking of hydrocarbons and hydrocracking. In addition to the thermal stability of this family of zeolites under these conditions, they provide conversion of the cracked oil to materials having lower molecular weights and boiling points, which are of greater economic value. The ability to be physically stable under high temperatures and/or in the presence of high temperature steam is extremely important for a cracking catalyst. During catalytic conversion, the reaction which takes place is essentially a cracking to produce hydrocarbons. However, this cracking is accompanied by a number of complex side reactions such as aromatization, polymerization, alkylation and the like. As a result of these complex reactions, a carbonaceous deposit is laid down on the catalyst which is referred to by petroleum engineers, as "coke". The deposit of coke on the catalyst tends to seriously impair the catalyst efficiency for the principal reaction desired and to substantially decrease the rate of conversion and/or the selectivity of the process. Thus, it is common to remove the catalyst after coke has been deposited thereon and to regenerate it by burning the coke in a stream of oxidizing gas. The regenerated catalyst is returned to the conversion stage of the process cycle. The thermal stability of the zeolite is advantageous in this regard.

The products can be used either in the alkali metal form, e.g., the sodium form, in the ammonium form, the hydrogen form, or another univalent or multivalent cationic form. Preferably, one of the other of the last two forms is employed. They can also be used in intimate combination with a hydrogenating component such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt, chromium, manganese, or a noble metal such as platinum or palladium where a hydrogenation dehydrogenation function is to be performed. Such component can be exchanged into the composition, impregnated therein or physically intimately admixed therewith. Such component can be impregnated in or onto the zeolite, such as, for example, by, in the case of platinum, treating the zeolite with a platinum metal-containing ion. Thus, suitable platinum compounds include chloroplatinic acid, platinous chloride and various compounds containing the platinum ammine complex.

The compounds of the useful platinum or other metals can be divided into compounds in which the metal is present in the cation of the compound and compounds in which it is present in the anion of the compound. Both types of compounds which contain the metal in the ionic state can be used. A solution in which platinum metals are in the form of a cation or cationic complex, e.g., $Pt(NH_3)_6Cl_4$ is particularly useful. For some hydrocarbon conversion processes, this noble metal form of the catalyst is unnecessary such as in low temperature, liquid phase ortho-xylene isomerization.

When it is employed either as an adsorbent or as a catalyst in one of the aforementioned processes, the catayst should be at least partially dehydrated. This can be done by heating to a temperature in the range of 200 to 600°C, in an atmosphere such as air, nitrogen, etc. and at atmospheric or subatmospheric pressures for between 1 minute and 48 hours. Dehydration can also be performed at lower temperatures merely by placing the catalyst in a vacuum, but a longer time is required to obtain a sufficient amount of dehydration.

The following examples will illustrate the invention.

Example 1

Solution 1

Q Brand Silicate	240 gms
Distilled H_2O	300
	540

Solution 2

Distilled H_2O	410 gms
Tetrapropyl Ammonium Bromide	30
Conc. H_2SO_4	20
$CrK(SO_4)_2 \cdot 12H_2O$	12.25

Q Brand is a Philadelphia Quartz Co. commercial brand of sodium silicate. Typical Analysis: 8.9% Na_2O, 28.7 SiO_2, 62.4% H_2O.

Solution 1 was placed into a 4-neck 2 l. flask with overhead stirrer. Solution 2 was added with stirring. The solution became very gelatinous. A small amount of H-ZSM-5 (about 0.1 g) was added for seeding. Heating was begun and the solution was allowed to heat to about 205°F. The variac setting was the only control on the temperature so it varied ±3°C depending on voltage variations during the day. After a few days, the solution lost its gelatinous character and became more chalk-like. Crystallization, as determined by X-ray took 5—6 days. The catalyst was filtered and washed with about 4 liters of distilled H_2O. The yield was 60—70 gms of catalyst.

The catalyst was dried at 70°C and calcined in a crucible in a muffle furnace at 75 to 1000°F for 12 hours. The catalyst was placed in a 200 ml flask with 100 cc of H_2O and 10 gm of NH_4NO_3 and refluxed at 100°C for 1 hour. The catalyst was filtered, washed and NH_4NO_3 exchanged repeatedly for 5 hours. The catalyst was again filtered, washed and exchanged repeatedly for about 16 hours. The catalyst was filtered, washed thoroughly and dried at 70°C for about 6 hours. The catalyst was calcined again in a muffle furnace at 75 to 1000°F for 6 hours.

X-ray powder diffraction patterns of the crystalline product, both in the as-synthesized form and after the treatments described above, are given in Table 3.

While this Example illustrates the use of the ammonium cation, other cations such as alkyl ammonium, metals and hydrogen may be used.

As set forth in Table 3, minor differences are observed between the X-ray diffraction patterns of the as-synthesized zeolite and the same zeolite after ion exchange and thermal treatments. These differences are changes from singlets to doublets and other doublets to singlets between the two patterns resulting from minor shifts in interplanar spacings and variations in relative intensities. These observed differences reflect minor variations in lattice parameters and crystal symmetry.

Table 3

As Synthesized			*Finished Catalyst*		
2θ	d(A)	I/I(0)	2θ	d(A)	I/I(0)
7.89	11.20	36	7.85	11.26	100
8.78	10.07	26	8.75	10.11	59
9.01	9.81	9	9.05	9.77	14
9.84	8.99	3	9.80	9.02	1
10.98	8.06	1	10.95	8.08	1
11.88	7.45	11	11.85	7.47	1
12.49	7.09	5	12.50	7.08	1
13.15	6.73	6	13.17	6.72	8
13.89	6.38	14	13.88	6.38	11
14.60	6.07	9	14.72	6.02	17
14.79	5.99	10			
			14.90	5.95	2
15.48	5.72	9	15.50	5.72	8
15.89	5.58	11	15.85	5.59	11
16.46	5.39	3	16.50	5.37	3
17.25	5.14	4	17.23	5.15	2
17.65	5.02	2	17.60	5.04	4
17.75	5.00	4	17.76	4.99	5
			18.13	4.89	1
			18.80	4.72	1
19.25	4.61	9	19.21	4.62	4
19.90	4.46	3	19.85	4.47	1
20.35	4.36	11	20.32	4.37	6
20.85	4.26	12	20.82	4.27	8

Table 3 (cont'd.)

As Synthesized			Finished Catalyst		
21.75	4.09	2	21.75	4.09	3
22.19	4.01	8	22.16	4.01	4
23.15	3.84	100	23.13	3.85	65
			23.25	3.83	28
23.67	3.76	24	23.63	3.76	16
23.92	3.72	45	23.90	3.72	30
24.38	3.65	30	24.30	3.66	8
			24.52	3.63	8
24.75	3.60	2			
25.55	3.49	4	25.50	3.49	3
25.90	3.44	12	25.84	3.45	5
26.35	3.38	2	26.15	3.41	2
26.68	3.34	7	26.53	3.36	5
26.95	3.31	9	26.92	3.31	7
27.45	3.25	3	27.38	3.26	3
			27.63	3.23	1
28.05	3.18	2	28.13	3.17	1
28.45	3.14	3	28.40	3.14	1
29.25	3.05	11	29.15	3.06	3
			29.35	3.04	3
29.95	2.98	12	29.85	2.99	12
			30.18	2.96	5
30.35	2.94	6	30.52	2.93	1
31.23	2.86	2	31.20	2.87	2
			31.50	2.84	1
32.15	2.78	1	32.12	2.79	1
32.80	2.73	3	32.71	2.74	2
33.45	2.68	1	33.36	2.69	1
33.80	2.65	1	33.69	2.66	1
34.38	2.61	4	34.33	2.61	2
34.71	2.58	1	34.55	2.60	2
34.95	2.57	1			
35.18	2.55	1	35.06	2.56	2
35.75	2.51	3	35.63	2.52	2
36.10	2.49	5	36.04	2.49	3
			36.28	2.48	2
36.72	2.45	1	36.58	2.46	1
37.11	2.42	3	37.18	2.42	2
37.53	2.40	4	37.56	2.39	2
38.31	2.35	1			
38.79	2.32	1			
39.17	2.30	1			
40.39	2.23	1			
40.62	2.22	1	40.45	2.23	1
40.99	2.20	1	40.99	2.20	1
41.45	2.18	1	41.43	2.18	1
41.78	2.16	1	41.80	2.16	1
42.50	2.13	1	42.48	2.13	1
42.88	2.11	1	42.83	2.11	1
43.24	2.09	1	43.13	2.10	1
43.56	2.08	1	43.53	2.08	1
43.81	2.07	1			
45.15	2.01	9	45.02	2.01	6
45.48	1.99	9	45.50	1.99	5
46.25	1.96	1			
46.51	1.95	3	46.50	1.95	2
47.50	1.91	3	47.42	1.92	2
48.60	1.87	4	48.44	1.88	2
			48.83	1.86	1
49.48	1.84	1	49.53	1.84	1
49.78	1.83	1	49.92	1.83	1
50.18	1.82	1	50.27	1.81	1

Table 3 (cont'd.)

As Synthesized			*finished Catalyst*		
			50.87	1.79	1
51.40	1.78	1	51.27	1.78	1
51.60	1.77	2	51.66	1.77	1
51.90	1.76	1	51.94	1.76	1
			52.25	1.75	1
53.21	1.72	1	53.17	1.72	1
53.50	1.71	1	53.65	1.71	1
			54.23	1.69	1
54.93	1.67	2	54.92	1.67	1
55.25	1.66	3	55.05	1.67	1
55.55	1.65	1	55.70	1.65	1
55.92	1.64	1	56.19	1.64	1
56.69	1.62	1	56.55	1.63	1
56.90	1.62	<1			
57.19	1.61	1	57.13	1.61	1
			58.25	1.58	1
59.04	1.56	1	58.96	1.57	1

In the following Examples (i.e. Examples 2—8) X-ray diffraction pattern for the catalytic form of the respective materials is shown in the table following the Example.

Example 2

Same as Example 1 with the exception that 5 gm of $RuCl_3 \cdot 3H_2O$ and 35 gm of HCl were used in place of the chromium compound and the sulfuric acid.

X-ray diffraction patterns for this material show substantially all the characteristic lines for the ZSM-5 zeolites as shown in Table 1. As in the first example, treatments of the zeolites of this and the six following examples by ion exchange, thermal conditioning or other treatments lead to similar minor variations in interplanar spacings, lattice symmetry, and relative intensity.

Table 4

2θ	*d(A)*	I/I_o
7.90	11.2	100
8.79	10.0	57
9.07	9.7	11
9.81	9.0	1
10.95	8.08	1
11.87	7.46	1
12.48	7.09	1
13.20	6.71	8
13.90	6.37	11
14.75	6.01	18
14.92	5.94	3
15.52	5.71	9
15.88	5.58	12
16.50	5.37	3
17.27	5.13	3
17.61	5.04	5
17.81	4.98	6
18.15	4.89	1
18.83	4.71	1
19.23	4.62	4
19.87	4.47	1
20.35	4.36	7
20.84	4.26	8
21.79	4.08	2
22.18	4.01	3
23.08	3.85	66
23.28	3.82	32
23.65	3.76	16
23.92	3.72	36
24.29	3.66	9

Table 4 (cont'd.)

2θ	$d(A)$	I/I_o
24.53	3.63	9
24.78	3.59	3
24.54	3.49	3
25.85	3.45	5
26.18	3.40	2
26.52	3.36	4
26.92	3.31	6
27.38	3.26	3
27.63	3.23	1
28.04	3.18	7
28.43	3.14	2
29.22	3.06	2
29.30	3.05	2
29.87	2.99	9
30.20	2.96	6
30.55	2.93	1
31.23	2.86	2
31.55	2.84	<1
32.15	2.78	1
32.73	2.74	2
33.37	2.69	1
33.75	2.66	1
34.30	2.61	2
34.60	2.59	2
35.04	2.56	6
35.63	2.52	2
36.09	2.49	3
36.33	2.47	2
36.60	2.46	1
37.18	2.42	2
37.54	2.40	2
40.50	2.23	1
40.99	2.20	1
41.45	2.18	1
41.73	2.16	1
42.50	2.13	<1
42.88	2.11	1
43.14	2.10	1
43.53	2.08	1
45.04	2.01	7
45.52	1.99	5
46.48	1.95	2
47.40	1.92	2
48.47	1.88	2
48.83	1.86	1
49.50	1.84	1
49.83	1.83	1
50.23	1.82	<1
50.90	1.79	<1
51.24	1.78	1
51.74	1.77	1
52.05	1.76	1
52.33	1.75	1
53.15	1.72	<1

Table 7 (cont'd.)

2θ	d(A)	I/I_o
53.65	1.71	<1
54.30	1.69	3
54.98	1.67	3
55.30	1.66	1
55.75	1.65	1
56.05	1.64	<1
56.55	1.63	1
57.20	1.61	1
59.03	1.56	1

Example 3

Same as Example 1 except that 2 gm of $H_2PtCl_6 \cdot nH_2O$ was used instead of the chromium compound. Also, 35 gm of HCl replaced the H_2SO_4.

Table 5

2θ	d(A)	I/I_o
7.90	11.2	100
8.80	10.0	60
9.10	9.7	14
9.85	9.0	2
11.02	8.03	1
11.92	7.42	2
12.53	7.06	1
13.23	6.69	8
13.93	6.36	12
14.77	6.00	18
15.04	5.89	3
15.54	5.70	10
15.89	5.58	13
16.54	5.36	4
17.27	5.13	2
17.58	5.04	5
17.80	4.98	6
18.20	4.87	1
18.80	4.72	1
19.25	4.61	5
19.90	4.46	2
20.37	4.36	7
20.85	4.26	10
21.80	4.08	3
22.21	4.00	5
22.50	3.95	3
23.10	3.85	65
23.34	3.81	35
23.72	3.75	22
23.95	3.72	39
24.33	3.66	14
24.57	3.62	13
24.86	3.58	3
25.53	3.49	3
25.87	3.44	6
26.13	3.41	3
26.57	3.35	5
26.97	3.31	8
27.42	3.25	4
27.62	3.23	1
28.08	3.18	1
28.44	3.14	1

Table 5 (cont'd.)

2θ	d(A)	I/I_o
29.17	3.06	2
29.40	3.04	4
29.90	2.99	13
30.22	2.96	7
30.55	2.93	1
31.23	2.86	2
31.58	2.83	1
32.15	2.78	1
32.79	2.73	3
33.47	2.68	1
33.79	2.65	1
34.37	2.61	2
34.67	2.59	2
35.05	2.56	2
35.70	2.52	3
36.12	2.49	4
36.25	2.48	2
36.70	2.45	1
37.23	2.42	2
37.56	2.39	3
38.25	2.35	1
38.72	2.33	1
39.20	2.30	1
39.75	2.27	2
40.30	2.24	1
40.62	2.22	1
41.03	2.20	1
41.48	2.18	1
41.81	2.16	1
42.50	2.13	<1
42.95	2.11	1
43.20	2.10	1
43.53	2.08	1
45.13	2.01	8
45.60	1.99	7
46.13	1.97	2
46.55	1.95	3
47.45	1.92	2
48.51	1.88	2
48.83	1.86	2
49.55	1.84	1
49.85	1.83	1
50.20	1.82	<1
50.88	1.80	<1
51.18	1.78	<1
51.70	1.77	<1
51.98	1.75	1
52.27	1.75	1
53.25	1.72	<1
53.63	1.71	<1
54.93	1.67	3
55.18	1.66	2
55.65	1.65	1
55.93	1.64	<1
56.50	1.63	1
56.90	1.62	<1

Table 5 Contd.

2θ	d(A)	I/I_o
57.20	1.61	1
58.30	1.58	<1
58.98	1.57	1

Example 4

Same as Example 1 except 6.3 gm of $In_2(SO_4)_3$ was used in place of the chromium potassium sulfate.

Table 6

2θ	d(A)	I/I_o
7.90	11.2	100
8.80	10.0	41
9.05	9.8	13
9.85	9.0	1
10.98	8.06	1
11.85	7.47	1
12.50	7.08	1
13.22	6.70	8
13.92	6.36	12
14.75	6.01	13
14.90	5.95	2
15.53	5.71	8
15.91	5.57	11
16.52	5.37	3
17.25	5.14	2
17.63	5.03	4
17.82	4.98	5
18.18	4.88	1
18.83	4.71	1
19.27	4.61	4
19.93	4.45	1
20.40	4.35	6
20.88	4.25	8
21.83	4.07	2
22.22	4.00	4
23.10	3.85	75
23.30	3.82	40
23.68	3.76	17
23.95	3.72	30
24.30	3.66	8
24.55	3.63	8
25.57	3.48	2
25.90	3.44	5
26.22	3.40	2
26.57	3.35	4
26.97	3.31	7
27.40	3.26	3
27.65	3.23	1
28.08	3.18	1
28.45	3.14	1
29.23	3.06	2
29.33	3.05	2
29.90	2.99	8
30.18	2.96	5
30.50	2.93	1
31.25	2.86	2
31.53	2.84	1
32.17	2.78	1

Table 6 (cont'd.)

2u	d(A)	I/I_o
32.78	2.73	2
33.43	2.68	1
33.73	2.66	1
34.33	2.61	2
34.60	2.59	1
35.10	2.56	1
35.68	2.52	2
36.10	2.49	3
36.30	2.47	1
36.62	2.45	1
37.24	2.41	2
37.57	2.39	2
40.50	2.23	<1
41.03	2.20	1
41.50	2.18	1
41.80	2.16	<1
42.50	2.13	<1
42.95	2.11	1
43.25	2.10	1
43.63	2.07	1
45.05	2.01	5
45.53	1.99	4
46.53	1.95	2
47.47	1.92	2
48.50	1.88	2
48.88	1.86	1
49.53	1.84	1
49.90	1.83	1
50.38	1.81	<1
50.90	1.79	<1
51.29	1.78	<1
51.75	1.77	1
52.03	1.76	1
52.37	1.75	1
53.20	1.72	<1
53.65	1.71	<1
54.20	1.69	<1
54.99	1.67	2
55.30	1.66	1
55.75	1.65	1
56.10	1.64	1
56.60	1.63	1
57.20	1.61	1
58.35	1.58	<1
59.08	1.56	1

Example 5

Same as Example 1 except that 5.8 gm of $Ce(SO_4)_2$ plus 3.7 of $Al_2(SO_4)_3 \cdot 14H_2O$ were used, the former to replace the chromium compound.

Table 7

2θ	d(A)	I/I_o
7.91	11.2	100
8.83	10.0	60
9.10	9.7	21
9.80	9.0	2

Table 7 Contd.

2θ	d(A)	I/I_o
11.02	8.03	1
11.91	7.43	2
12.50	7.08	1
13.23	6.69	15
13.92	6.36	17
14.80	5.99	20
15.03	5.89	4
15.55	5.70	12
15.93	5.56	14
16.54	5.36	4
17.30	5.13	3
17.68	5.02	5
17.86	4.97	9
18.22	4.87	1
18.85	4.71	1
19.38	4.58	6
19.93	4.45	2
20.40	4.35	10
20.88	4.25	13
21.80	4.08	4
22.19	4.01	7
22.60	3.93	3
23.09	3.85	82
23.33	3.81	38
23.70	3.75	24
23.98	3.71	47
24.35	3.66	14
24.58	3.62	13
24.85	3.58	3
25.59	3.48	3
25.91	3.44	8
26.34	3.38	3
26.60	3.35	5
26.98	3.30	11
27.42	3.25	4
27.58	3.23	1
28.12	3.17	2
28.47	3.14	2
29.23	3.06	5
29.43	3.04	5
29.92	2.99	15
30.25	2.95	8
30.54	2.93	2
31.25	2.86	3
31.60	2.83	1
32.19	2.78	2
32.79	2.73	4
33.42	2.68	2
33.74	2.66	2
33.99	2.64	1
34.37	2.61	3
34.68	2.59	2
35.13	2.55	2
35.71	2.51	3
36.12	2.49	5
36.33	2.47	3
36.64	2.45	1

Table 7 Contd.

2θ	d(A)	I/I_o
37.20	2.42	3
37.56	2.39	3
38.32	2.25	1
38.77	2.32	1
40.54	2.23	1
41.03	2.20	1
41.47	2.18	1
42.54	2.13	1
42.93	2.11	2
43.58	2.08	1
45.11	2.01	9
45.58	1.99	9
46.03	1.97	1
46.55	1.95	3
47.49	1.92	3
48.51	1.88	2
48.88	1.86	2
49.50	1.84	1
49.98	1.82	1
50.37	1.81	1
50.88	1.80	1
51.30	1.78	1
51.71	1.77	1
52.00	1.76	1
52.33	1.75	1
54.93	1.67	2
55.18	1.66	2
55.55	1.65	1
55.82	1.65	1
56.55	1.63	<1
56.98	1.62	<1
57.25	1.61	<1
58.35	1.58	<1
59.00	1.57	1

Example 6

Same as Example 1 except that 2.28 gm of V_2O_5 was used in place of the chromium compound.

Table 8

2θ	d(A)	I/I_o
7.85	11.3	100
8.76	10.1	55
9.03	9.8	14
9.75	9.1	2
10.90	8.12	1
11.80	7.50	1
12.47	7.10	1
13.23	6.69	7
13.85	6.39	9
14.71	6.02	17
15.00	5.91	3
15.48	5.72	7
15.83	5.60	11
16.48	5.38	3
17.20	5.16	2
17.55	5.05	5

Table 8 Contd.

2θ	$d(A)$	I/I_o
17.76	4.99	5
18.10	4.90	1
18.80	4.72	1
19.20	4.62	4
19.90	4.46	1
20.30	4.37	6
20.79	4.27	7
21.71	4.09	2
22.13	4.02	3
22.49	3.95	2
23.02	3.86	60
23.25	3.83	31
23.62	3.77	14
23.88	3.73	34
24.23	3.67	8
24.47	3.64	8
24.72	3.60	2
25.50	3.49	3
25.80	3.45	5
26.13	3.41	2
26.51	3.36	5
26.88	3.32	6
27.33	3.26	2
27.58	3.23	1
28.09	3.18	1
28.38	3.14	1
29.13	3.06	4
29.33	3.05	3
29.82	2.99	10
30.11	2.97	7
30.47	2.93	1
31.15	2.87	1
31.63	2.83	1
32.19	2.78	1
32.71	2.74	2
33.36	2.69	1
33.69	2.66	1
33.92	2.64	2
34.30	2.61	1
34.59	2.59	2
35.00	2.56	2
35.63	2.52	2
36.00	2.49	3
36.23	2.48	2
36.61	2.45	1
37.18	2.42	2
37.50	2.40	2
38.20	2.36	1
38.65	2.33	1
40.43	2.23	1
40.97	2.20	1
41.40	2.18	1
41.72	2.16	1
42.50	2.13	<1
42.85	2.11	1
43.20	2.10	1
43.61	2.08	1
45.02	2.01	6

Table 8 Contd.

2θ	d(A)	I/I$_o$
45.48	1.99	5
45.92	1.98	1
46.44	1.96	1
47.35	1.92	2
48.43	1.88	1
48.80	1.87	1
49.52	1.84	<1
49.82	1.83	1
50.20	1.82	<1
50.90	1.79	<1
51.24	1.78	<1
51.62	1.77	1
51.93	1.76	1
52.20	1.75	1
53.25	1.72	<1
53.65	1.71	1
54.98	1.67	3
55.25	1.66	1
55.50	1.66	1
55.75	1.65	1
56.55	1.63	1
56.90	1.62	<1
57.22	1.61	1
58.45	1.58	<1
59.00	1.57	1

Example 7

Same as Example 1 except that 1.5 gm of $Zn_2B_6O_{11}$ and 25 gm of tetraethylammonium bromide were used to replace the chromium compound and the tetrapropylammonium bromide, respectively.

Table 9

2θ	d(A)	I/I$_o$
7.91	11.2	100
8.78	10.1	54
9.05	9.8	17
9.80	9.0	1
10.97	8.07	1
11.85	7.47	1
12.47	7.10	<1
13.18	6.72	4
13.92	6.36	6
14.74	6.01	10
14.95	5.93	1
15.50	5.72	4
15.87	5.58	6
16.42	5.40	1
16.59	5.34	1
17.25	5.14	1
17.60	5.04	3
17.80	4.98	3
18.15	4.89	1
18.80	4.72	1
19.21	4.62	2
19.80	4.48	4
20.33	4.37	3
20.83	4.26	5
21.74	4.09	1
22.23	4.00	2
22.58	3.94	1
23.05	3.86	77

Table 9 Contd.

2θ	d(A)	I/I_o
23.30	3.82	23
23.70	3.75	14
23.94	3.72	36
24.32	3.66	10
24.53	3.63	10
24.75	3.60	3
25.50	3.49	5
25.76	3.46	5
25.92	3.44	5
26.18	3.40	2
26.53	3.36	5
26.94	3.31	5
27.37	3.26	3
27.58	3.23	1
28.08	3.18	1
28.33	3.15	3
28.53	3.13	1
29.18	3.06	5
29.36	3.04	5
29.87	2.99	13
30.18	2.96	6
30.53	2.93	1
31.18	2.87	2
31.43	2.85	1
31.70	2.82	1
32.10	2.79	1
32.73	2.74	3
33.38	2.68	1
33.72	2.66	1
33.92	2.64	1
34.30	2.61	2
34.55	2.60	2
35.04	2.56	2
35.64	2.52	3
36.08	2.49	3
36.28	2.48	1
36.55	2.46	1
36.79	2.44	1
37.17	2.42	2
37.38	2.41	1
37.58	2.39	1
38.20	2.36	1
38.63	2.33	1
38.83	2.32	1
39.17	2.30	1
40.38	2.23	1
40.58	2.22	1
41.02	2.20	1
41.37	2.18	1
41.65	2.17	1
42.43	2.13	1
42.82	2.11	1
43.11	2.10	1
43.53	2.08	1
45.02	2.01	8
45.53	1.99	5
45.95	1.98	1
46.39	1.96	1
46.65	1.95	1
49.90	1.83	1
50.30	1.81	<1
50.95	1.79	1

Table 9 Contd.

2θ	d(A)	I/I$_o$
51.28	1.78	1
51.70	1.77	1
51.95	1.76	1
52.26	1.75	1
54.92	1.67	4
55.13	1.67	2
55.73	1.65	1
56.52	1.63	1
56.67	1.62	1
57.25	1.61	1
58.40	1.58	1
59.03	1.56	1

Example 8

Same as Example 1, but using 3.97 gm of molybdic acid (H_2MoO_4) to replace the chromium compound.

Table 10

2θ	d(A)	I/I$_o$
7.90	11.2	100
8.79	10.1	55
9.10	9.7	12
9.83	9.0	1
11.02	8.03	1
11.80	7.50	1
12.50	7.08	1
13.20	6.71	7
13.90	6.37	10
14.78	5.99	17
15.08	5.87	2
15.52	5.71	7
15.90	5.57	11
16.50	5.37	3
17.25	5.14	2
17.60	5.04	5
17.82	4.98	5
18.13	4.89	1
18.90	4.70	1
19.22	4.62	4
19.87	4.47	1
20.38	4.36	7
20.83	4.26	7
21.25	4.18	1
21.78	4.08	3
22.17	4.01	4
22.69	3.92	3
23.07	3.86	57
23.35	3.81	25
23.68	3.76	17
23.92	3.72	34
24.30	3.66	11
24.51	3.63	10
24.77	3.59	4
25.53	3.47	4
25.79	3.45	5
26.20	3.40	3
26.57	3.35	4
26.91	3.31	6
27.37	3.26	3
27.69	3.22	1

Table 10 Contd.

2θ	d(A)	I/I_o
28.10	3.18	1
28.39	3.14	1
29.20	3.06	3
29.41	3.04	3
29.88	2.99	10
30.18	2.96	5
30.52	2.93	1
31.21	2.87	1
31.60	2.83	<1
32.17	2.78	1
32.77	2.73	2
33.42	2.68	1
33.72	2.66	1
34.32	2.61	2
34.68	2.59	1
35.07	2.56	2
35.67	2.52	2
36.08	2.49	3
36.33	2.47	2
36.65	2.45	1
37.20	2.42	2
37.55	2.40	<1
38.32	2.35	1
38.63	2.33	<1
39.26	2.29	2
40.50	2.23	1
40.93	2.20	1
41.25	2.19	1
41.60	2.17	1
42.51	2.13	<1
42.90	2.11	<1
43.20	2.10	1
43.57	2.08	1
45.07	2.01	6
45.53	1.99	5
46.50	1.95	2
47.48	1.92	2
48.53	1.88	2
48.89	1.86	1
49.62	1.84	1
49.97	1.82	1
50.35	1.81	<1
50.90	1.79	<1
51.33	1.78	<1
51.61	1.77	1
51.90	1.76	1
52.27	1.75	1
53.35	1.72	<1
53.68	1.71	<1
54.25	1.69	1
54.92	1.67	2
55.20	1.66	2
55.73	1.65	1
56.10	1.65	<1
56.55	1.63	1
56.85	1.62	<1
57.25	1.61	<1

Table 10 Contd.

58.45	1.58	<1
59.09	1.56	<1

Example 9

This was made similarly to Example 1, except that 5 gm of silver acetate replaced the chromium compound. The X-ray analysis showed it to have a pattern similar to the previous Examples.

Example 10

This was made as shown in Example 1 except that 35 gm of HCl was used instead of sulfuric acid and 5 gm of $HgCl_2$ was used instead of the chromium compound. The X-ray analysis showed it to have a pattern similar to the previous Examples.

Example 11

This was also made like Example 1, except that 5 gm of H_6TeO_6 was used instead of the chromium compound. The X-ray analysis showed it to have a pattern similar to the previous Examples.

Employing the catalyst of this invention containing a hydrogenation component, heavy petroleum residual stocks, cycle stocks, and other hydrocrackable charge stocks can be hydrocracked at temperatures between 400°F and 825°F using molar ratios of hydrogen to hydrocarbon charge in the range between 2 and 80. The pressure employed will vary between 10 and 2,500 psig and the liquid hourly space velocity between 0.1 and 10.

Employing the catalyst of this invention for catalytic cracking, hydrocarbon cracking stocks can be cracked at a liquid hourly space velocity between about 0.5 and 50, a temperature between about 550°F and 1100°F, a pressure between about sub-atmospheric and several hundred atmospheres.

Employing a catalytically active form of the zeolites of this invention containing a hydrogenation component, reforming stocks can be reformed employing a temperature between 700°F and 1000°F. The pressure can be between 100 and 1000 psig, but is preferably between 200 and 700 psig. The liquid hourly space velocity is generally between 0.1 and 10, preferably between 0.5 and 4 and the hydrogen to hydrocarbon mole ratio is generally between 1 and 20, preferably between 4 and 12.

The catalyst can also be used for hydroisomerization of normal paraffins, when provided with a hydrogenation component, e.g., platinum. Hydroisomerization is carried out at a temperature between 200 and 700°F, preferably 300 to 550°F, with a liquid hourly space velocity between 0.01 and 2, preferably between 0.25 and 0.50 employing hydrogen such that the hydrogen to hydrocarbon mole ratio is between 1:1 and 5:1. Additionally, the catalyst can be used for olefin isomerization employing temperatures between 30°F and 500°F, and for methanol and dimethylether conversion.

Other reactions which can be accomplished employing the catalyst of this invention containing a metal, e.g. platinum include hydrogenation-dehydrogenation reactions and desulfurization and hydrocarbon oxidation reactions.

The products were tested in several of the conversion processes mentioned above. The results follow:

Evaluation of Products

Toluene Disproportionation

Table 11 summarizes data obtained using various samples of the hydrogen form of the zeolite in toluene conversion. The runs were made at 600 psig, 3.5 WHSV and a H_2-hydrocarbon (H_2/HC) ratio of 2/1, except where different conditions are noted. The hydrogen form was obtained by the procedure of Example 1.

Table 11

Metal Used in Synthesis	*Temp., °F*	*Wt. % Toluene Conversion*
Pt (Example 2)	850	31.8
V (Example 6)	900	14.0
Mo (Example 8)	900	14.7
Cr (Exmple 1)	1100 (10 WHSV)	16.9

Hydrocracking

Table 12 shows the results obtained in converting 224°F—365°F Buffalo Naphtha using the hydrogen form of the zeolite at 900° and 1000°F. Conversion was at 100 psig, 5 WHSV and a H_2/HC of 3/1. The naphtha had the characteristics shown in the table. The hydrogen form of the zeolite was obtained as per the description hereinabove.

Table 12

Metal Used in Synthesis	Temp., °F	Wt. % Conv.	Wt. % C_1—C_5	Aromatics Made Gm/100 Gm Charge	C_1—C_5 Made Conv.	Aromatics Made Conv.
Pt	900	57.3	44.8	10.3	78.2	18.0
Ru	900	46.0	28.6	14.5	62.2	31.5
Cr	900	35.5	21.8	10.8	61.6	30.6
In	1000	15.6	2.5	2.7	43.8	47.9

224°—365°F Buffalo Naphtha, Wt. %

C_6's	0.8
Benzene	0.1
C_7's	20.1
Toluene	3.2
C_8's	31.8
C_8Ar	9.5
C_9^+	29.1
C_9^+Ar	5.0

Reaction of Methanol

Vaporized methanol was passed over the hydrogen form of the zeolite prepared using platinum. The conditions and results are shown in Table 13.

Table 13

Temp, °F	PSIG	H_2/HC	CO+	~H_2O	Wt % CH_4 of HC	Wt % Cl+	Wt % Ar Made	Wt % $C_2^=$ of HC	p-Xyl Sel.	Conv..
751	50	2/1	0	60	<1	40	4	11	42	100
702	50	2/1	0.3	53	<1	45	7	15	52	99

Xylene Isomerization

The same zeolite used for the test summarized in Table 13 was tested for xylene isomerization activity.

Table 14

680°F, 200 Psig, 5 WHSV and 4/1 H_2/Hc

Fractions Obtained	Wt. %	% Xylene	Charge
C_1—C_5	0.1		
Benzene	2.1		0.1
Toluene	0.2		0.1
EB	16.1		20.9
p-Xyl.	19.1	24.5	2.8
m-Xyl.	41.6	53.3	51.3
o-Xyl.	17.4	22.2	24.5
C_9+Ar	3.4		0.3

The charge set forth in Table 15 was passed over the same catalyst used as per Tables 13 and 14 at the conditions specified. A summary of results is shown in the table.

Table 15

Temp, °F	1000°F	
PSIG	0	
H_2	0	
WHSV	1	
Product Distribution, Wt. %		*Charge-Light Woodhaven Reformate*
C_1	3.6	
C_2's	13.8	
C_3's	19.2	
C_4's	4.9	
C_5's	0	0.2
C_6's	0.5	25.9
C_7's	0.2	25.1
C_6H_6	11.8	8.6
C_8's	0	7.6

Table 15 (cont'd.)

Tol	33.5	32.1
C_8Ar	9.6	0.5
C_9+Ar	2.9	
New Aromatics Make, g/100 g Charge	16.6	
Wt. % of Aromatics Made/Conv.	28.7	

Claims

1. A crystalline aluminosilicate zeolite composition having, in the anhydrous state, a formula in terms of mole ratios of oxides as follows:

$$[R_2O, M'_{2/n}O]_W : [Al_2O_3]_X : [SiO_2]_Y : [M''_{2/n}O]_Z$$

wherein W/X is from >0.5 to <3, X/Y is >20 and Z/X is from >zero to <~100, R is a nitrogen containing cation, M' is a metal from Group IA of the Periodic Table, M'' is a metal selected from the group consisting of indium, boron, ruthenium, platinum, chromium, rare earth, vanadium, palladium, molybdenum, mercury, tellurium, silver and a mixture of such metals, and n is the valence of the metal, said composition having the X-ray diffraction pattern substantially as set forth in Table 1 of the specification.

2. The composition of claim 1 wherein R is a tetraalkylammonium cation in which the alkyl contains from 2 to 5 carbon atoms.

3. The composition of claim 1 wherein R and/or M' has been replaced by cations selected from the group consisting of alkylammonium, metal, ammonium, hydrogen and mixtures thereof.

4. The product resulting from thermally treating the composition of claim 3 at a temperature above 500°F.

5. The composition of claim 1 wherein M' is sodium.

6. The composition of claim 1 wherein M'' is selected from the group consisting of chromium, ruthenium, platinum, indium, cerium, vanadium, boron, molybdenum, mercury, tellurium and silver.

7. The composition of claim 6 wherein M' is chromium.

8. The composition of claim 6 wherein M'' is ruthenium.

9. The composition of claim 6 wherein M'' is platinum.

10. The composition of claim 6 wherein M'' is indium.

11. The composition of claim 6 wherein M'' is cerium.

12. The composition of claim 6 wherein M'' is vanadium.

13. The composition of claim 6 wherein M'' is boron.

14. The composition of claim 6 wherein M'' is molybdenum.

15. The composition of claim 6 wherein M'' is mercury.

16. The composition of claim 6 wherein M'' is tellurium.

17. The composition of claim 6 wherein M'' is silver.

18. The composition of claim 1 in which the SiO_2 to Al_2O_3 ratio is from greater than about 35 to about 3000.

19. A process for converting an organic charge under conversion conditions comprising passing said charge over a crystalline aluminosilicate zeolite composition having, in the anhydrous state, a formula in terms of mole ratios of oxides as follows:

$$[R_2O, M'_{2/n}O]_W : [Al_2O_3]_X : [SiO_2]_Y : [M''_{2/n}O]_Z$$

wherein W/X is from >0.5 to <3, Y/Z is >20 and Z/X is from >zero to <~100, R is a nitrogen cation, M' is a metal from Group IA of the Periodic Table, M'' is a metal selected from the group consisting of indium, boron, ruthenium, platinum, chromium, rare earth, vanadium, palladium, molybdenum, mercury, tellurium, silver and a mixture of such metals, and n is the valence of the metal, said composition having the X-ray diffraction pattern substantially as set forth in Table 1 of the specification.

20. The process of claim 19 wherein in the composition R is a tetraalkylammonium cation, the alkyl containing 2 to 5 carbon atoms.

21. The process of claim 19 in which the composition used has been thermally treated.

22. The process of claim 19 wherein the composition used is the product resulting from replacing R and/or M' by cations selected from the group consisting of alkylammonium, metal, ammonium, hydrogen and mixtures thereof and thermally treating the material at a temperature above 500°F.

23. The process of claim 19 wherein in said composition M' is sodium.

24. The process of claim 19 wherein said composition M'' is selected from the group consisting

of chromium, ruthenium, platinum, indium, cerium, vanadium, boron, molybdenum, mercury, tellurium, and silver.

25. The process of claim 24 wherein said composition M″ is chromium.

26. The process of claim 24 wherein in said composition M″ is ruthenium.

27. The process of claim 24 wherein in said composition M″ is platinum.

28. The process of claim 24 wherein in said composition M″ is indium.

29. The process of claim 24 wherein in said composition M″ is cerium.

30. The process of claim 24 wherein in said composition M″ is vanadium

31. The process of claim 24 wherein in said composition M″ is boron.

32. The process of claim 24 wherein in said composition M″ is molybdenum.

33. The process of claim 24 wherein in said composition M″ is mercury.

34. The process of claim 24 wherein in said composition M″ is tellurium.

35. The process of claim 24 wherein in said composition M″ is silver.

36. The process of claim 19 in which the SiO_2 to Al_2O_3 ratio in said zeolite is from greater than about 35 to about 3000.

37. A method of preparing a crystalline aluminosilicate zeolite is defined in claim 1 which comprises preparing a reaction mixture comprising sources of tetraalkylammonium compound, silica, alumina, alkali metal and M″, the mixture having the following mole ratios of oxides or % of total moles of oxides:

	Broad	*Preferred*	*Most Preferred*
OH^-/SiO_2	0.07—1.0	0.1—0.8	0.2—0.75
$R_4N^+/(R_4N^+ + Na^+)$	0.2—0.95	0.3—0.9	0.4—0.9
H_2O/OH^-	10—300	10—300	10—300
SiO_2/Al_2O_3	50—3000	70—1000	70—500
Other metal Oxide (% of total oxides)	1×10^{-6}—1.0	1×10^{-5}—0.1	1×10^{-5}—0.01

wherein R is a nitrogen cation, heating the mixture until crystals having the characteristic X-ray diffraction pattern of ZSM-5, as set forth in Table 1, are formed and ion exchanging and calcining same.

38. The method of claim 37 wherein M″ is chromium.

39. The method of claim 37 wherein M″ is ruthenium.

40. The method of claim 37 wherein M″ is platinum.

41. The method of claim 37 wherein M″ is indium.

42. The method of claim 37 wherein M″ is cerium.

43. The method of claim 37 wherein M″ is vanadium.

44. The method of claim 37 wherein M″ is boron.

45. The method of claim 37 wherein M″ is molybdenum.

46. The method of claim 37 wherein M″ is mercury.

47. The method of claim 37 wherein M″ is tellurium.

48. The method of claim 37 wherein M″ is silver.

49. A zeolite composition according to Claim 1 substantially as described in the foregoing Examples.

50. A method of preparing a zeolite as defined in Claim 1 substantially as described in the foregoing Examples.

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