

SPECIFICATION

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DESCRIPTION OF THE PRIOR ART:

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U.S. Patent no. 4,440,871 discloses crystalline microporous silicoaluminophosphates having pores which are

uniform and have nominal diameters of greater than about 3 angstroms with a chemical composition of mole fractions of silicon, aluminum and phosphorus within the pentagonal composition area defined by

5		Mole Fraction		
	x	y	z	
	A	0.01	0.47	0.52
	B	0.94	0.01	0.05
10	C	0.98	0.01	0.01
	D	0.39	0.60	0.01
	E	0.01	0.60	0.39

where x, y and z are the mole fractions of silicon, aluminum and phosphorus and ACBDE are points defining a pentagonal area of a ternary diagram as shown in Fig. 1 of U.S. Patent no. 4,440,871.

SUMMARY OF THE INVENTION

20 This invention provides a catalyst containing silicon, aluminum, phosphorus, as needed to form a silicate, aluminosilicate, aluminophosphate (AlPO) or silicoaluminophosphate (SAPO) with at least one other element selected from Group 4, Group 5, Group 13, Group 14, Group 15 and the first series transition metals in a three dimensional interconnecting crystalline tetrahedral framework. The crystalline tetrahedral framework is synthesized from an aqueous gel containing, as needed, a silica source, an aluminum source, a phosphorus source, a source for the Group 4, Group 5, 25 Group 13, Group 14, Group 15 and the first series transition 30

metal element(s) and, optionally, an organic structure-directing agent. The reaction mixture is heated to form crystals and then cooled. The crystals are separated from the synthesis liquor and are washed, dried and calcined. At least
5 one metal selected from Group 6, Group 7, Group 8, Group 9 or Group 10 is deposited on the silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate (hereinafter referred to as "deposited metal"). The catalyst may be used in a process for converting C₂-C₁₂ hydrocarbons into aromatics.

10 One example of the invention is a catalyst on which at least one Group 10 metal, such as platinum, is deposited on a medium pore zeolite having at least one element selected from Group 14 other than silicon, such as germanium, in the zeolite framework. This example includes a process for synthesizing a
15 medium pore zeolite catalyst by: a) preparing a medium pore zeolite containing at least one element selected from Group 14 other than silicon, such as germanium; b) depositing at least one metal selected from Group 10, such as platinum, on the medium pore zeolite; and c) calcining the medium pore zeolite
20 on which the Group 10 metal is deposited. This example of the invention also includes a process for the conversion of hydrocarbons of: a) contacting a hydrocarbon stream containing alkanes, olefins and mixtures thereof having 2 to 12 carbon atoms per molecule with at least one medium pore zeolite-based
25 catalyst wherein the zeolite contains germanium incorporated into the zeolite framework and wherein at least one metal

selected from Group 10, such as platinum, has been deposited on the medium pore zeolite; and b) recovering the product. Examples of medium pore zeolites are ZSM-11, ZSM-12 and ZSM-48.

Another example of the invention is a catalyst of an
5 aluminophosphate (AlPO) or silicoaluminophosphate (SAPO) with germanium incorporated into the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO) framework and, optionally, with at least one metal selected from Group 10 deposited on the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO). This
10 example includes a process for synthesizing a zeolite by preparing an aluminophosphate (AlPO) or silicoaluminophosphate (SAPO) with germanium incorporated into the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO) framework and calcining the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO)
15 aluminophosphate (AlPO) or silicoaluminophosphate (SAPO). Optionally, at least one metal selected from Group 10 is deposited on the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO), and said calcining occurs after preparation of the aluminophosphate (AlPO) or
20 silicoaluminophosphate (SAPO), before depositing at least one metal selected from Group 10 on the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO) or after depositing at least one metal selected from Group 10 on the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO). This example of the invention
25 also includes a process for the conversion of hydrocarbons of contacting a hydrocarbon stream containing alkanes, olefins and

mixtures thereof having 2 to 12 carbon atoms per molecule with at least one aluminophosphate (AlPO) or silicoaluminophosphate (SAPO)-based catalyst wherein the catalyst contains germanium incorporated into the aluminophosphate (AlPO) or
5 silicoaluminophosphate (SAPO) framework and, optionally, wherein at least one metal selected from Group 10 has been deposited on the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO) depositing at least one metal selected from Group 10 on the aluminophosphate (AlPO) or
10 silicoaluminophosphate (SAPO) and recovering the product.

Another example of the invention is a medium pore zeolite having germanium incorporated into the zeolite framework. The zeolite may have a pore structure that is one dimensional, two dimensional or three dimensional. Examples of the medium pore
15 zeolite are ZSM-11, ZSM-12 or ZSM-48. This example includes a process for synthesizing a zeolite by preparing a medium pore zeolite containing germanium in the framework of the zeolite and calcining the zeolite.

20 BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention and many of the attendant advantages thereof will be readily understood by reference to the following detailed description when considered in connection with the accompanying drawings:

25 Figure 1 (A and B) is an XRD of Pt/Ge-ZSM-5
Figure 2 is a SEM of Ge-ZSM-11 (morphology 1)

Figure 3 is an XRD of Ge-ZSM-11 (morphology 1)

Figure 4 is a SEM of Ge-ZSM-11 (morphology 2)

Figure 5 is an XRD of Ge-ZSM-11 (morphology 2)

Figure 6 is a SEM of Ge-ZSM-12

5 Figure 7 is an XRD of Ge-ZSM-12

Figure 8 is a graph of propane conversion, BTX selectivity and fuel gas selectivity for Pt/[Ge;Al]ZSM-11

Figure 9 is a graph of propane conversion, BTX selectivity and fuel gas selectivity for Pt/[Ge;Al]ZSM-48

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DETAILED DESCRIPTION OF THE INVENTION

Crystalline silicates, aluminosilicates, aluminophosphates and silicoaluminophosphates have uniform pores through which molecules can diffuse. Aluminosilicates include zeolites.

15 Examples of zeolites are MFI (ZSM-5), BEA (Beta), MWW (MCM-22), MOR (Mordenite), LTL (Zeolite L), MTT (ZSM-23), MTW (ZSM-12), TON (ZSM-22), MEL (ZSM-11), LTA (Linde Type A), CHA (chabazite), VFI (VPI-5), MSE (MCS-68), MOZ (ZSM-10), ZSM-48, MAZ (Mazzite), MEI (ZSM-18), MFS (ZSM-57), NES (NU-87), OFF
20 (Offretite), STI (Stilbite), BOG (Boggsite), ERI (Erionite), FAU (Faujasite), EUO (EU-1), FER (Ferrierite) and GME (Gemelinite). Examples of medium pore zeolites are MFI, MEL, LTL, BEA, MOR, MWW, MTT, MTW, TON, MSE, MOZ, ZSM-48, MAZ, MEI, MFS, NES, OFF, STI, BOG, ERI, FAU, EUO, FER and GME with pore
25 diameters in the range from 5 angstroms to 8 angstroms. Zeolites, including medium pore zeolites, have pore structures

that are one dimensional (1D), two dimensional (2D) or three dimensional (3D). MTW and ZSM-48 are examples of zeolites with a 1D pore structure. MEL is an example of a zeolite with a 2D pore structure. MFI and BEA are examples of zeolites with a 3D pore structure.

Crystalline silicates, aluminosilicates, aluminophosphates and silicoaluminophosphates have structures of TO_4 tetrahedra, which form a three dimensional network by sharing oxygen atoms where T represents tetravalent elements, such as silicon, trivalent elements, such as aluminum, and pentavalent elements, such as phosphorus. "Zeolite" in the present application includes aluminosilicates with open three-dimensional framework structures (without regard to the dimensional pore structure discussed above) composed of corner-sharing TO_4 tetrahedra, where T is Al or Si, but also includes tetravalent, trivalent and divalent T atoms which are able to isoelectronically replace Si and Al in the framework, e.g., germanium(4+), titanium (4+), boron (3+), gallium (3+), iron (3+), zinc (2+) and beryllium (2+). "Zeolite" is primarily a description of structure, not composition.

Silicates, aluminosilicates, aluminophosphates and silicoaluminophosphates generally crystallize from an aqueous solution. The typical technique for synthesizing silicates, aluminosilicates, aluminophosphates or silicoaluminophosphates comprises converting an aqueous gel of a silica source, an aluminum source and a phosphorus source, as needed, to crystals

by a hydrothermal process, employing a dissolution/recrystallization mechanism. The reaction medium may also contain an organic structure-directing agent which is incorporated in the microporous space of the crystalline network during crystallization, thus controlling the construction of the network and assisting to stabilize the structure through the interactions with the silicon, aluminum or phosphorus components. The solids content of the gel ranges from about 5% to about 25%. In one embodiment of the invention the solids content ranges from about 10% to about 20%.

The aqueous gel contains, in addition to the silica source, the aluminum source, the phosphorus source, as needed, and the optional organic structure-directing agent, a source of at least one other element from Group 4, Group 5, Group 13, Group 14, Group 15 or the first series transition metals to be incorporated into the framework of the silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate.

Examples of the silica source are silicon oxide or silica (SiO_2) which is available in various forms, such as silica sol, commercially available as Ludox AS-40TM, precipitated silica, commercially available as Ultrasil VN3SPTM and fumed silica, commercially available as Aerosil 200TM.

Examples of the aluminum source are sodium aluminate, aluminum nitrate, aluminum sulfate, aluminum hydroxide and pseudoboehmite.

Examples of the phosphorus source are orthophosphoric acid, triethylphosphate and sodium metaphosphate.

Examples of the source of Group 4, Group 5, Group 13, Group 14, Group 15 and the first series transition metals are
5 oxides, chlorides, sulfates, alkoxides, fluorides, nitrates and oxalates.

Examples of the structure-directing agent are organic amine and quaternary ammonium compounds and salts and cations thereof, such as tetra n-propyl ammonium hydroxide, tetra n-
10 propyl ammonium bromide and tetra n-propyl ammonium chloride, tetraethyl ammonium hydroxide, hexamethyleneimine, 1,4-di(1'4'-diazabicyclo[2.2.2]octane)butane hydroxide, morpholine, cyclohexylamine and diethylethanolamine, N,N'-diisopropyl imidazolium cation, tetrabutylammonium compounds,
15 di-n-propylamine (DPA), tripropylamine, triethylamine (TEA), triethanolamine, piperidine, 2-methylpyridine, N,N-dimethylbenzylamine, N,N-diethylethanolamine, dicyclohexylamine, N,N-dimethylethanolamine, choline cation, N,N'-dimethylpiperazine, 1,4-diazabicyclo(2,2,2)octane,
20 N',N',N,N-tetramethyl-(1,6)hexanediamine, N-methyldiethanolamine, N-methyl-ethanolamine, N-methyl piperidine, 3-methyl-piperidine, N-methylcyclohexylamine, 3-methylpyridine, 4-methyl-pyridine, quinuclidine, N,N'-dimethyl-1,4-diazabicyclo(2,2,2) octane ion; di-n-butylamine,
25 neopentylamine, di-n-pentylamine, isopropylamine, t-butylamine, ethylenediamine, pyrrolidine, 2-imidazolidone, a N-

benzyl-1,4-diazabicyclo[2.2.2]octane cation, a 1-[1-(4-chlorophenyl)-cyclopropylmethyl]-1-ethyl-pyrrolidinium or 1-ethyl-1-(1-phenyl-cyclopropylmethyl)-pyrrolidinium cation and mixture thereof. Specific examples of structure directing agents are tetraethyl ammonium bromide; 1, 8-diaminooctane; 1, 6-hexanediamine; tetramethylammonium chloride; tetraethylammonium bromide; tetrabutylammonium bromide. Other specific examples of structure directing agents are tetrapropylammonium hydroxide (or bromide) for Ge-ZSM-5; tetrabutylammonium bromide for ZSM-11 and Ge-ZSM-11; tetraethylammonium hydroxide for ZSM-12, Ge-ZSM-12, Al-Beta and Ge-Al-Beta and 1, 6 - Hexanediamine for ZSM-48 and Ge-ZSM-48.

The reaction may also utilize an acid as a reagent. The acid may be a Bronsted acid or a Lewis acid. Examples without limitation of an acid useful in the present invention are sulfuric acid, acetic acid, nitric acid, phosphoric acid, hydrochloric acid, hydrofluoric acid, oxalic acid or formic acid. One example of the pH of the reaction mixture for zeolites is from about 9 to about 13. Another example of the pH of the reaction mixture for zeolites is from about 9.5 to about 12.5. Other examples of the pH of the reaction mixture are about 9.2 for Ge-ZSM-5; 11.2 to 12.6 for Ge-ZSM-11; 12.4 for Ge-ZSM-12 and 13.8 for Ge-Al-Beta. One example of the pH of the reaction mixture for aluminophosphate (AlPO) or silicoaluminophosphate (SAPO) is about 3 to about 9. Another

example of the pH of the reaction mixture for aluminophosphate (AlPO) or silicoaluminophosphate (SAPO) is about 4 to about 8.

The reaction mixture may sit statically or may be stirred about 600 rpm for one to seven days and heated to a temperature of about 100°C to about 200°C to form crystals. In one embodiment of the invention the temperature range was from about 135°C to about 180°C. The reaction mixture is cooled to room temperature in a range from 15 to 60 minutes at a rate of from about 3°C to 10°C per minute. The crystals are separated from the synthesis liquor. The liquid portion of the synthesis liquor may be removed by filtration, evaporation, spray drying or any other means for removing water from the crystals. The crystals are washed with water and then dried and calcined.

The silicates are essentially aluminum-free but may contain aluminum and other impurities up to 500 ppm.

The aluminosilicates may have a silicon to aluminum atomic ratio (Si:Al) greater than 2:1. In one embodiment of the present invention, the silicon to aluminum atomic ratio is in the range from 15:1 to 200:1. In another embodiment of the present invention, the silicon to aluminum atomic ratio is in the range from 18:1 to 100:1.

The aluminophosphates may have an aluminum to phosphorus atomic ratio (Al:P) in the range from about 0.8:1 to about 1.2:1 as disclosed in U.S. Patent no. 4,310,440, hereby incorporated by reference.

The silicoaluminophosphates may have a silicon to aluminum to phosphorus atomic ratio represented by $(S_xAl_yP_z)O_2$ where "x", "y" and "z" represent the mole fractions of silicon, aluminum and phosphorus respectively, present as tetrahedral oxides, said mole fractions being such that they are within the pentagonal compositional area defined by points ABCD and E of a ternary diagram with values represented in the table below:

Mole Fraction			
	x	y	z
A	0.01	0.47	0.52
B	0.94	0.01	0.05
C	0.98	0.01	0.01
D	0.39	0.60	0.01
E	0.01	0.60	0.39

as disclosed in U.S. Patent no. 4,440,871, hereby incorporated by reference.

The amount of Group 4, Group 5, Group 13, Group 14, Group 15 and the first series transition metals present in the crystalline framework is in the range from 0.1 wt.% to 25 wt.%.

In one embodiment of the present invention, this range is from 0.1 wt.% to 10 wt.%. In another embodiment of the present invention, this range is from 0.1 wt.% to 5 wt.%.

The silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate has average pore size in the range from 2 angstroms to 20 angstroms, i.e., microporous.

At least one metal selected from Group 6, Group 7, Group 8, Group 9 or Group 10 is deposited on the silicate,

aluminosilicate, aluminophosphate or silicoaluminophosphate ("deposited metal"). The metal is deposited not only on the surface of the silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate but also in the pores and channels which occur in the silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate. The metal is deposited on the silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate by any known method of depositing a metal on a silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate. Typical methods of depositing a metal on a silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate are ion exchange and impregnation. In one embodiment of the present invention, the metal is present in the range from 0.05% to 3% by weight. In another embodiment of the present invention, the metal is present in the range from 0.1% to 2% by weight. In another embodiment of the present invention, the metal is present in the range from 0.2 to 1.5% by weight.

However, for silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate-based catalysts on which metals have been deposited, the process temperatures and catalyst regeneration temperatures cause the metal to "sinter", i.e., agglomeration of the metal particles resulting in an increase of metal particle size on the surface of the zeolite and a decrease of metal surface area, causing a loss of catalyst performance, specifically catalyst performance, e.g., activity

and/or selectivity.

Without the present invention and its claims being limited by theory, it is believed that certain elements in the framework and certain metals deposited on the silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate associate to resist sintering of the deposited metal. U.S. Patent no. 6,784,333 discloses and claims an aluminum-silicon-germanium zeolite on which platinum has been deposited for use in a process for the aromatization of hydrocarbons. The presence of germanium in the framework of the zeolite and the presence of platinum deposited on the zeolite apparently results in higher selectivity for benzene, toluene and xylenes (BTX) which remains essentially constant over a significant time on stream. Without the invention of U. S. Patent no. 6,784,333 and its claims being limited by theory, it may be that the germanium in the framework and the platinum deposited on the zeolite associate such that the platinum remains dispersed and sintering is reduced. The association of certain elements in the framework and certain deposited metals may be present for zeolites other than ZSM-5 as disclosed in U. S. Patent no. 6,784,333. Other zeolites may be synthesized with germanium in the framework and platinum deposited on the zeolite to form Pt/Ge-zeolite catalysts.

Besides germanium, there may be other elements in the crystalline framework which associate with platinum or other deposited metals. Elements in the crystalline framework may be

selected from Group 4, Group 5, Group 13, Group 14, Group 15 and the first series transition metals of the Periodic Table of Elements. Specific examples of these elements are germanium, boron, gallium, indium, tin, titanium, zirconium, vanadium, chromium, iron, niobium and phosphorus. One or more elements may be in the crystalline framework.

Besides platinum, there may be other deposited metals which associate with germanium or other elements in the crystalline framework. Deposited metals may be selected from Group 6, Group 7, Group 8, Group 9 and Group 10 of the Periodic Table of Elements. Specific examples of the deposited metal are platinum, molybdenum, rhenium, nickel, ruthenium, rhodium, palladium, osmium and iridium. One or more metals, such as bimetallics, e.g., Pt/Sn, Pt/Ge, Pt/Pb or metal/ metal oxide combinations, e.g. Pt/GeO₂, may be deposited.

The crystalline framework of which these elements from Group 4, Group 5, Group 13, Group 14, Group 15 and the first series transition metals are part and on which metals selected from Group 6, Group 7, Group 8, Group 9 and Group 10 are deposited need not be limited to a zeolite but may be any microporous silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate.

Before or after deposition of the metal, the silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate may be bound by oxides or phosphates of magnesium, aluminum, titanium, zirconium, thorium, silicon, boron or mixtures

thereof. The process steps of binding and depositing metal can occur in any order. Binding may occur before or after metal deposition.

The catalyst may be calcined at different stages in the synthesis. The silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate may be calcined to remove the organic structure-directing agent. This calcination is at a temperature of about 300°C to about 1000°C or about 300°C to about 750°C for a time sufficient to remove essentially all of any structure-directing agent, e.g., one to six hours or about four hours. One example of calcination is at 550°C for ten hours. Calcination may occur after binding. This calcination is at a temperature in the range of from about 300°C to about 1000°C for a time in the range of from about one hour to about 24 hours. Calcination may also occur after metal deposition to fix the metal. This calcination should not exceed a temperature of 500°C and may be at a temperature of about 200°C to about 500°C for a time in the range of from about 0.5 hour to about 24 hours. These calcinations need not be separate but may be combined to accomplish more than one purpose. When the silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate is calcined, it may be bound or unbound and it may have metal deposited on it or not.

The catalyst, bound or unbound, will have porosity in addition to the uniform porosity of the silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate.

For an unbound catalyst, the average pore size of the catalyst can vary for bound and unbound catalyst and is in the range from 2 angstroms to 100 angstroms. In one embodiment of the present invention, the average pore size is in the range from 5
5 angstroms to 50 angstroms. In another embodiment of the present invention, the average pore size is in the microporous range from 5 angstroms to 20 angstroms. For a bound catalyst, the average pore size of the catalyst may vary from 5 angstroms up to 100 microns.

10 Some catalysts used for hydrocarbon conversion are susceptible to sulfur poisoning. However, for some catalysts used for hydrocarbon conversion, modest amounts of sulfur, such as about 0 to 200 ppm in the feed, are acceptable and sometimes preferred. The catalyst may also be pretreated with sulfur. A
15 standard sulfurization method that is well known in the art consists in heating in the presence of a sulfur compound, such as hydrogen sulfide, or a mixture of a sulfur compound and an inert gas, such as hydrogen or nitrogen, to a temperature of between 150 and 800°C. Non-limiting examples of sulfur compounds
20 are H₂S, an organosulfide compound, such as dimethyl disulfide or DMSO (dimethyl sulfoxide), or C_nH_{2n+2}S or C_nH_{2n+2}S₂, where n = 1-20. In one embodiment of the present invention, the temperature is between 250 and 600°C.

The catalyst may contain a reaction product, such as a
25 sulfide of the deposited metal, that is formed by contacting

the catalyst with sulfur or a sulfur compound. In one embodiment of the present invention, the amount of sulfur on the catalyst is in the range of from 10 ppm to 0.1 wt.%.

The catalyst may also contain elements other than sulfur, such as tin, germanium or lead. These elements would be present in the range of from 1:1 to 1:100 as a ratio of the deposited metal to tin, germanium or lead. These elements may be added to the catalyst by wet impregnation, chemical vapor deposition or other methods known in the art.

The silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate-based catalyst which contains at least one element selected from Group 4, Group 5, Group 13, Group 14, Group 15 and the first series transition metals isomorphously incorporated into the zeolite framework and at least one metal selected from Group 6, Group 7, Group 8, Group 9 and Group 10 deposited on the zeolite can be used in a process for conversion of hydrocarbon streams containing C₂-C₁₂ alkanes, olefins or mixtures thereof, which may be straight, branched, cyclic or mixtures thereof, into aromatics.

The zeolite may be base-exchanged with an alkali metal or alkaline earth metal, such as cesium, potassium, sodium, rubidium, barium, calcium, magnesium and mixtures thereof, to reduce acidity and form a non-acidic zeolite. A non-acidic zeolite has substantially all of its cationic sites of exchange, e.g., those typically associated with aluminum, occupied by nonhydrogen cationic species, e.g., alkali or

alkaline earth metals. These cationic sites are often responsible for cracking of hydrocarbons into undesired products. A zeolite may be non-acidic by exchange with a base or, for meaning and purposes of the present invention, by having a low aluminum content, i.e., having aluminum content of no more than 0.4wt%. The base-exchange may occur before or after the noble metal is deposited. Such a base-exchanged catalyst may be used to convert C₆-C₁₂ alkanes, such as might be obtained from natural gas condensate, light naphtha, raffinate from aromatics extraction and other refinery or chemical processes, to aromatics, such as benzene, ethyl benzene, toluene and xylenes. Base-exchange may take place during synthesis of the zeolite with an alkali metal or alkaline earth metal being added as a component of the reaction mixture or may take place with a crystalline zeolite before or after deposition of the noble metal. The zeolite is base-exchanged to the extent that most or all of the cations associated with aluminum are alkali metal or alkaline earth metal. An example of a monovalent base:aluminum molar ratio in the zeolite after base exchange is at least about 0.9. For a divalent or trivalent base, the molar ratio would be half (0.45) or a third (0.3) as that for a monovalent base, respectively, and for mixtures of monovalent, divalent and trivalent bases, the above molar ratios would be apportioned by their respective content in the mixture.

Examples of hydrocarbon conversion processes for which this catalyst can be used are:

(A) The catalytic cracking of a naphtha feed to produce light olefins. Typical reaction conditions include from about 500°C to about 750°C, pressures of subatmospheric or atmospheric, generally ranging up to about 10 atmospheres (gauge) and catalyst residence time (volume of the catalyst/feed rate) from about 10 milliseconds to about 10 seconds.

(B) The catalytic cracking of high molecular weight hydrocarbons to lower weight hydrocarbons. Typical reaction conditions for catalytic cracking include temperatures of from about 400°C to about 700°C, pressures of from about 0.1 atmosphere (bar) to about 30 atmospheres, and weight hourly space velocities of from about 0.1 to about 100 hr⁻¹.

(C) The transalkylation of aromatic hydrocarbons in the presence of polyalkylaromatic hydrocarbons. Typical reaction conditions include a temperature of from about 200°C to about 500°C, a pressure of from about atmospheric to about 200 atmospheres, a weight hourly space velocity of from about 1 to about 100 hr⁻¹ and an aromatic hydrocarbon/polyalkylaromatic hydrocarbon mole ratio of from about 1/1 to about 16/1.

(D) The isomerization of aromatic (e.g., xylene) feedstock components. Typical reaction conditions for such include a temperature of from about 230°C to about 510°C, a pressure of from about 0.5 atmospheres to about 50 atmospheres, a weight hourly space velocity of from about 0.1 to about 200 hr⁻¹ and a

hydrogen/hydrocarbon mole ratio of from about 0 to about 100.

(E) The dewaxing of hydrocarbons by selectively removing straight chain paraffins. The reaction conditions are dependent in large measure on the feed used and upon the
5 desired pour point. Typical reaction conditions include a temperature between about 200°C and 450°C, a pressure up to 3,000 psig and a liquid hourly space velocity from 0.1 to 20 hr⁻¹.

(F) The alkylation of aromatic hydrocarbons, e.g., benzene and
10 alkylbenzenes, in the presence of an alkylating agent, e.g., olefins, formaldehyde, alkyl halides and alcohols having 1 to about 20 carbon atoms. Typical reaction conditions include a temperature of from about 100°C to about 500°C, a pressure of from about atmospheric to about 200 atmospheres, a weight
15 hourly space velocity of from about 1 hr⁻¹ to about 100 hr⁻¹ and an aromatic hydrocarbon/alkylating agent mole ratio of from about 1/11 to about 20/1.

(G) The alkylation of aromatic hydrocarbons, e.g., benzene, with long chain olefins, e.g., C₁₄ olefin. Typical reaction
20 conditions include a temperature of from about 50°C to about 200°C, a pressure of from about atmospheric to about 200 atmospheres, a weight hourly space velocity of from about 2 hr⁻¹ to about 2000 hr⁻¹ and an aromatic hydrocarbon/olefin mole ratio of from about 1/1 to about 20/1. The resulting products
25 from the reaction are long chain alkyl aromatics which when subsequently sulfonated have particular application as

synthetic detergents.

(H) The alkylation of aromatic hydrocarbons with light olefins to provide short chain alkyl aromatic compounds, e.g., the alkylation of benzene with propylene to provide cumene.

5 Typical reaction conditions include a temperature of from about 10°C to about 200°C, a pressure of from about 1 to about 30 atmospheres, and an aromatic hydrocarbon weight hourly space velocity (WHSV) of from 1 hr⁻¹ to about 50 hr⁻¹.

10 (I) The hydrocracking of heavy petroleum feedstocks, cyclic stocks, and other hydrocrack charge stocks. The zeolite-bound high silica zeolite will contain an effective amount of at least one hydrogenation component of the type employed in hydrocracking catalysts.

15 (J) The alkylation of a reformat containing substantial quantities of benzene and toluene with fuel gas containing short chain olefins (e.g., ethylene and propylene) to produce mono- and dialkylates. Preferred reaction conditions include temperatures from about 100°C to about 250°C, a pressure of from about 100 to about 800 psig, a WHSV -olefin from about 20 0.4 hr⁻¹ to about 0.8 hr⁻¹, a WHSV -reformat of from about 1 hr⁻¹ to about 2 hr⁻¹ and, optionally, a gas recycle from about 1.5 to 2.5 vol/vol fuel gas feed.

25 (K) The alkylation of aromatic hydrocarbons, e.g., benzene, toluene, xylene, and naphthalene, with long chain olefins, e.g., C₁₄ olefin, to produce alkylated aromatic lube base stocks. Typical reaction conditions include temperatures from

about 100°C to about 400°C and pressures from about 50 to 450 psig.

(L) The alkylation of phenols with olefins or equivalent alcohols to provide long chain alkyl phenols. Typical reaction conditions include temperatures from about 100°C to about 250°C, pressures from about 1 to 300 psig and total WHSV of from about 2 hr⁻¹ to about 10 hr⁻¹.

(M) The conversion of light paraffins to olefins and/or aromatics. Typical reaction conditions include temperatures from about 425°C to about 760°C and pressures from about 10 to about 2000 psig.

(N) The conversion of light olefins to gasoline, distillate and lube range hydrocarbons. Typical reaction conditions include temperatures of from about 175°C to about 500°C and a pressure of from about 10 to about 2000 psig.

(O) Two-stage hydrocracking for upgrading hydrocarbon streams having initial boiling points above about 200°C to premium distillate and gasoline boiling range products or as feed to further fuels or chemicals processing steps. The first stage can be the zeolite-bound high silica zeolite comprising one or more catalytically active substances, e.g., a Group 8 metal, and the effluent from the first stage would be reacted in a second stage using a second zeolite, e.g., zeolite Beta, comprising one or more catalytically active substances, e.g., a Group 8 metal, as the catalyst. Typical reaction conditions include temperatures from about 315°C to about 455°C, a

pressure from about 400 to about 2500 psig, hydrogen circulation of from about 1000 to about 10,000 SCF/bbl and a liquid hourly space velocity (LHSV) of from about 0.1 to 10 hr⁻¹.

5 (P) A combination hydrocracking/dewaxing process in the presence of the zeolite-bound high silica zeolite comprising a hydrogenation component and a zeolite such as zeolite Beta. Typical reaction conditions include temperatures from about 350°C to about 400°C, pressures from about 1400 to about 1500
10 psig, LHSV from about 0.4 to about 0.6 hr⁻¹ and a hydrogen circulation from about 3000 to about 5000 SCF/bbl.

(Q) The reaction of alcohols with olefins to provide mixed ethers, e.g., the reaction of methanol with isobutene and/or isopentene to provide methyl-t-butyl ether (MTBE) and/or t-
15 amyl methyl ether (TAME). Typical conversion conditions include temperatures from about 20°C to about 200°C, pressures from 2 to about 200 atm, WHSV (gram-olefin per hour·gram-zeolite) from about 0.1 hr⁻¹ to about 200 hr⁻¹ and an alcohol to olefin molar feed ratio from about 0.1/1 to about 5/1.

20 (R) The disproportionation of aromatics, e.g. the disproportionation of toluene to make benzene and xylenes. Typical reaction conditions include a temperature of from about 200°C to about 760°C, a pressure of from about atmospheric to about 60 atmosphere (bar), and a WHSV of from
25 about 0.1 hr⁻¹ to about 30 hr⁻¹.

(S) The conversion of naphtha (e.g., C₆-C₁₀) and similar

mixtures to highly aromatic mixtures. Thus, normal and slightly branched chained hydrocarbons, preferably having a boiling range above about 40°C, and less than about 200°C, can be converted to products having a substantially higher octane
5 aromatics content by contacting the hydrocarbon feed with the zeolite at a temperature in the range of from about 400°C to 600°C, preferably 480°C to 550°C at pressures ranging from atmospheric to 40 bar, and liquid hourly space velocities (LHSV) ranging from 0.1 to 15 hr⁻¹.

10 (T) The adsorption of alkyl aromatic compounds for the purpose of separating various isomers of the compounds.

(U) The conversion of oxygenates, e.g., alcohols, such as methanol, or ethers, such as dimethylether, or mixtures thereof to hydrocarbons including olefins and aromatics with
15 reaction conditions including a temperature of from about 275°C to about 600°C, a pressure of from about 0.5 atmosphere to about 50 atmospheres and a liquid hourly space velocity of from about 0.1 to about 100.

(V) The oligomerization of straight and branched chain olefins
20 having from about 2 to about 5 carbon atoms. The oligomers which are the products of the process are medium to heavy olefins which are useful for both fuels, i.e., gasoline or a gasoline blending stock, and chemicals. The oligomerization process is generally carried out by contacting the olefin
25 feedstock in a gaseous state with a zeolite-bound high silica zeolite at a temperature in the range of from about 250°C to

about 800°C, a LHSV of from about 0.2 to about 50 and a hydrocarbon partial pressure of from about 0.1 to about 50 atmospheres. Temperatures below about 250°C may be used to oligomerize the feedstock when the feedstock is in the liquid phase when contacting the zeolite-bound high silica zeolite catalyst. Thus, when the olefin feedstock contacts the catalyst in the liquid phase, temperatures of from about 10°C to about 250°C can be used.

(W) The conversion of C₂ unsaturated hydrocarbons (ethylene and/or acetylene) to aliphatic C₆₋₁₂ aldehydes and converting said aldehydes to the corresponding C₆₋₁₂ alcohols, acids, or esters.

(X) The desulfurization of FCC (fluid catalytic cracking) feed streams. The desulfurization process is generally carried out at a temperature ranging from 100°C to about 600°C, preferably from about 200°C to about 500°C, and more preferably from about 260°C to about 400°C, at a pressure ranging from 0 to about 2000 psig, preferably from about 60 to about 1000 psig, and more preferably from about 60 to about 500 psig, at a LHSV ranging from 1 to 10 h⁻¹. The hydrocarbon mixtures which can be desulfurized according to the process of the present invention contain more than 150 ppm of sulfur, e.g., hydrocarbon mixtures with a sulfur content higher than 1000 ppm, even higher than 10000 ppm.

The invention having been generally described, the following examples are given as particular embodiments of the

invention and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims to follow in any manner.

5

Example 1

Synthesis of Ge-ZSM-5

Chemicals used:

Ludox AS-40 colloidal silica SiO_2 ; 40 wt. % suspension in
10 water; Aldrich;

Sodium hydroxide NaOH , 50 wt. % solution in water; Sigma-Aldrich;

Germanium dioxide GeO_2 ; Germanium Corporation of America GTAH
68002;

15 Sodium aluminate NaAlO_2 (23.6 wt. % Al_2O_3 ; 19.4 wt. % Na_2O ; 57.0 wt. % H_2O); Southern Ionics;

Tetrapropylammonium hydroxide $(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{NOH}$, 40 wt. % solution
in water; SACHEM;

Acetic acid $\text{CH}_3\text{CO}_2\text{H}$, 99.7%; Aldrich.

20

Solution 1.

15.84 grams of sodium hydroxide solution were mixed with
131.25 grams of D.I. water. 7.11 grams of GeO_2 were dissolved
in the solution with stirring.

25

Solution 2.

3.84 grams of sodium aluminate were mixed with 153.9 grams of D.I. water.

5 Solution 1 was poured into 150 grams of Ludox AS-40 with vigorous gel stirring for 10 minutes. Then Solution 2 was introduced and gel was stirred for 15 minutes. Tetrapropylammonium hydroxide (105.42 grams) was added to the mixture and gel was stirred for about one hour. 23.32 grams
10 of acetic acid was added to the gel with continuous stirring. pH of gel after ten minutes of stirring was 9.25. Crystallization was made in 1L stainless steel autoclave at 160°C with stirring (300 rpm) for 36 hours. Zeolite was filtered and washed with D.I. water. Zeolite was dried at 90°C
15 overnight and was calcined at 550°C for 10 hours in oven forced with air.

XRF analysis results are: 0.244 wt. % Na; 41.04 wt. % Si; 0.73 wt. % Al; 5.67% Ge.

XRD analysis confirmed formation of ZSM-5 structure.

20

Pt/CsGeZSM-5

15 grams of laboratory prepared GeZSM-5 was washed with 350 ml of aqueous CsNO₃ (0.5M) then filtered. The filtrate was then rewashed 3 more times with 0.5M CsNO₃ and rinsed with
25 distilled H₂O on the final filtering. The zeolite powder was then calcined for 3 hours at 280°C in air.

Incipient wetness impregnation was carried out by adding drop wise a solution of 0.0408 g $\text{Pt}(\text{NH}_2)_4(\text{NO}_3)_2$ dissolved in .8150 g of deionized water to 1.99 grams of the Cs-exchanged GeZSM-5. The material was dried for 1 hour in a 110°C drying oven then calcined in air at 280°C for 3 hours.

Elemental analysis gave 41.0 wt% Si, 0.71 wt% Al, 5.27 wt% Cs, 4.13 wt% Ge and 0.96 wt% Pt.

XRD analysis confirmed formation of ZSM-5 structure (Figure 1, A and B)

The catalyst powder was pressed and sized to 20-40 mesh. 0.25 cm³ (0.123 g) of the sized catalyst was mixed with 1.75 ml of inert quartz chips and was pretreated at 460°C for 1 hour in flowing H₂. Catalytic testing was then started.

Catalyst particles, mixed with inert quartz chips, were loaded into a ¼" OD plug flow reactor. n-hexane was vaporized into a stream of flowing hydrogen at a temperature of approximately 150°C. This gas mixture was passed through the reactor at a LHSV of 8.6 hr⁻¹, the reactor being maintained at a temperature of 515°C by an external heating jacket. The reaction products were analyzed by gas chromatography. Products ranging in size from methane to dimethylnaphthalene were observed. A variety of C₆ isomerization products were observed, including isohexanes (e.g., 2-methylpentane) and olefins (e.g. 1-hexene.) For the purposes of calculating conversion and selectivity, these C₆ products were considered to be unreacted. The selectivities reported are calculated as

the sum of benzene, toluene, xylenes, and ethylbenzene produced divided by the total amount of all benzene, C1-C5, and C7+ materials recovered. These selectivities are presented on a molar C6 basis.

5

catalyst	X ₁₀	S ₁₀
Pt/CsGeZSM-5	24	88

Performance of ZSM-5 catalysts for n-hexane aromatization.

10 T = 515°C, LHSV = 8.6 hr⁻¹, H₂/n-hexane feed ratio = 0.75. Conversion and aromatics selectivity measured after 10 hours on stream.

Example 2

15 Synthesis of Ge-ZSM-11 (morphology 1)

Chemicals used:

Sodium aluminate (Al₂O₃-23.6%; Na₂O-19.4 %; H₂O-57%); Southern Ionics;

Sodium hydroxide, >98%, Aldrich;

20 Tetrabutylammonium bromide, 98%; Sigma-Aldrich;

Ludox HS-30; colloidal silica, 30% suspension in water; Sigma-Aldrich;

Germanium (IV) oxide GeO₂, Germanium Corporation of America GTAH 68002.

25 1.7 grams of sodium aluminate and 2.817 grams of sodium hydroxide were dissolved in 136.0 grams of D.I. water. 28.16 grams of tetrabutylammonium bromide were added and dissolved

in the solution. 2.8452 grams of germanium oxide were dissolved in the solution. Colloidal silica Ludox HS-30 (80 grams) was introduced into solution with stirring for about 15 minutes. pH of gel was 12.61. Crystallization was made in
5 300ml stainless steel autoclave at 150°C for 144 hours with stirring (200 rpm).

Material was filtered and washed with D.I water. Material was dried overnight at 90°C, sieved 40 mesh size and calcined at 550°C for 10 hours in a furnace with forced air flow.

10 XRF analysis data for sample: 42.50 wt. % Si; 0.99 wt. % Al; 1.177 wt. % Na; 2.81 wt. % Ge.

A SEM of Ge-ZSM-11 (morphology 1) is shown in Figure 2.

XRD analysis confirmed formation of ZSM-11 structure by comparison with published pattern for ZSM-11 in references
15 such as "Collection of Simulated XRD Powder Patterns for Zeolites", 5th edition, M.M.J. Treacy & J. B. Higgins, Amsterdam: Elsevier (2007). See Figure 3.

Synthesis of 1%Pt/CsGeZSM-11

20 4 grams of laboratory prepared GeZSM-11 (morphology 1) was washed with 200 ml of aqueous CsNO₃ (0.5M) then filtered. The filtrate was then rewashed 3 more times with 0.5M CsNO₃ and rinsed with distilled H₂O on the final filtering. The
25 zeolite powder was then calcined for 3 hours at 280°C in air.

Incipient wetness impregnation was carried out by adding drop wise a solution of 0.0396 g Pt(NH₂)₄(NO₃)₂ dissolved in

1.962 g of deionized water to 1.962 grams of the Cs-exchanged ZSM-11. The material was dried for 1 hour in a 110°C drying oven then calcined in air at 280°C for 3 hours. Elemental analysis is shown below.

5 The catalyst powder was pressed and sized to 20-40 mesh. 0.25 cm³ (0.124 g) of the sized catalyst was mixed with 1.75 ml of inert quartz chips and was pretreated at 460°C for 1 hour in flowing H₂. Catalytic testing was then started.

10

Example 3

Synthesis of Ge-ZSM-11 (morphology 2)

Chemicals used:

15 Aluminum sulfate hydrate Al₂(SO₄)₃ · x H₂O, 99.998%; Aldrich;
Potassium hydroxide, >90%; Sigma-Aldrich;
1, 8-Diaminooctane, 98%; Aldrich;
Ludox HS-30; colloidal silica, 30% suspension in water; Sigma-Aldrich;
20 Germanium (IV) oxide, Germanium Corporation of America GTAH 68002;
Sulfuric acid, 95-98%; Sigma-Aldrich.

25 7.2 grams of aluminum sulfate hydrate was dissolved in 544 grams of D.I. water. Potassium hydroxide (16 grams) was dissolved in the solution. 6.83 grams of germanium oxide were dissolved in the same solution. 64 grams of 1, 8-

diaminooctane were added into solution and dissolved with stirring. Colloidal silica Ludox HS-30 (192 grams) was introduced gradually into solution with stirring. White gel was formed. Gel was stirred for about 1 hour. Then 10 ml of sulfuric acid were added gradually with vigorous solution stirring. pH of gel was about 11.

Crystallization was made in 1L stainless steel autoclave at 160°C for 120 hours with stirring (200 rpm). Material was filtered and washed with D.I water. Material was dried overnight at 90°C, sieved to 40 mesh size and calcined at 550°C for 10 hours in the furnace with forced air flow.

XRF analysis data for sample: 40.80 wt. % Si; 1.12 wt. % Al; 1.06 wt. % K; 5.52 wt. % Ge.

A SEM of Ge-ZSM-11 (morphology 2) is shown in Figure 4.

XRD analysis confirmed formation of ZSM-11 structure by comparison with published pattern for ZSM-11 in references such as "Collection of Simulated XRD Powder Patterns for Zeolites", 5th edition, M.M.J. Treacy & J. B. Higgins, Amsterdam: Elsevier (2007). See Figure 5.

Synthesis of 1%Pt/CsGeZSM-11

3 grams of laboratory prepared GeZSM-11 (morphology 2) was washed with 150 ml of aqueous CsNO₃ (0.5M) then filtered. The filtrate was then rewashed 3 more times with 0.5M CsNO₃ and rinsed with distilled H₂O on the final filtering. The zeolite powder was then calcined for 3 hours at 280°C in air.

Incipient wetness impregnation was carried out by adding

drop wise a solution of 0.0398 g $\text{Pt}(\text{NH}_2)_4(\text{NO}_3)_2$ dissolved in 1.00g of deionized water to 2.002 grams of the Cs-exchanged ZSM-11. The material was dried for 1 hour in a 110°C drying oven then calcined in air at 280°C for 3 hours. Elemental analysis is shown below.

The catalyst powder was pressed and sized to 20-40 mesh. 0.25 cm³ (0.129 g) of the sized catalyst was mixed with 1.75 ml of inert quartz chips and was pretreated at 460°C for 1 hour in flowing H₂. Catalytic testing was then started.

Elemental analyses for Pt/CsGeZSM-11 catalysts as tested

catalyst	Si	Al	Ge	Cs	Na	Pt
Pt/CsGeZSM-11 morphology 1	41.63%	0.96%	0.90%	8.68%	0.07%	0.98%
Pt/CsGeZSM-11 morphology 2	42.14%	1.06%	0.82%	8.74%	0.0%	0.97%

Catalyst particles, mixed with inert quartz chips, were loaded into a ¼" OD plug flow reactor. n-hexane was vaporized into a stream of flowing hydrogen at a temperature of approximately 150°C. This gas mixture was passed through the reactor at a LHSV of 8.6 hr⁻¹, the reactor being maintained at a temperature of 515°C by an external heating jacket. The reaction products were analyzed by gas chromatography. Products ranging in size from methane to dimethylnaphthalene

were observed. A variety of C6 isomerization products were observed, including isohexanes (e.g., 2-methylpentane) and olefins (e.g. 1-hexene.) For the purposes of calculating conversion and selectivity, these C6 products were considered to be unreacted. The selectivities reported are calculated as the sum of benzene, toluene, xylenes, and ethylbenzene produced divided by the total amount of all benzene, C1-C5, and C7+ materials recovered. These selectivities are presented on a molar C6 basis.

catalyst	comments	added	X ₁₀	S ₁₀
Pt/CsGeZSM-11	morphology 1	0.90% Ge	11	89
Pt/CsGeZSM-11	morphology 2	0.82% Ge	16	89

Performance of ZSM-11 catalysts for n-hexane aromatization.

T = 515°C, LHSV = 8.6 hr⁻¹, H₂/n-hexane feed ratio = 0.75. Conversion and aromatics selectivity measured after 10 hours on stream.

Example 4

Synthesis of Ge-ZSM-12

Chemicals used:

Sodium hydroxide NaOH, 50% solution in water, Aldrich;

Sodium aluminate NaAlO₂ (23.6 wt. % Al₂O₃; 19.4 wt. % Na₂O; 57.0 wt. % H₂O); Southern Ionics;

Germanium dioxide GeO₂; Germanium Corporation of America GTAH

68002;

Tetraethylammonium hydroxide $(\text{CH}_2\text{CH}_2)_4\text{NOH}$; 35% w/w aq. soln.;

Alfa-Aesar;

Ludox HS-30 SiO_2 colloidal silica (30 wt. %); Sigma-Aldrich.

5

2.0042 grams of sodium hydroxide, 1.6808 grams of sodium aluminate and 26.29 grams of tetraethylammonium hydroxide were mixed in 25.00 grams of D.I. water. 3.0648 grams of germanium
10 dioxide were dissolved in this solution.

100 grams of silica source Ludox HS-30 were added to solution gradually with stirring. Stirring continued for one hour. Viscous gel was formed.

Crystallization was done at 160°C for about 6 days in
15 Teflon lined 300 ml reactor in static regime. After crystallization $\text{pH}=12.01$. Material was filtered and washed with D.I. water. Material was dried at 90°C , sieved 40 mesh size, and calcined at 600°C for 10 hours.

A SEM of Ge-ZSM-12 is shown in Figure 6.

20 XRF analysis results are: 0.793 wt. % Na; 43.97 wt. % Si; 0.69 wt. % Al; 3.28 wt. % Ge.

XRD analysis confirmed formation of ZSM-12 structure (Figure 7).

25

Pt/CsGeZSM-12

3.22 grams of laboratory prepared GeZSM-12 (361-032) was washed with 150 ml of aqueous CsNO₃ (0.5M) then filtered. The filtrate was then rewashed 3 more times with 0.5M CsNO₃ and
5 rinsed with distilled H₂O on the final filtering. The zeolite powder was then calcined for 3 hours at 280°C in air.

Incipient wetness impregnation was carried out by adding drop wise a solution of 0.0410 g Pt(NH₂)₄(NO₃)₂ dissolved in
10 1.04 g of deionized water to 2.012 grams of the Cs-exchanged GeZSM-12. The material was dried for 1 hour in a 110°C drying oven then calcined in air at 280°C for 3 hours. Elemental analysis gave 42.95 wt % Si, 5.83 wt % Cs, 0.70 wt % Al, 1.60 wt % Ge, and 0.80 wt% Pt.

15 The catalyst powder was pressed and sized to 20-40 mesh. 0.25 cm³ (0.127 g) of the sized catalyst was mixed with 1.75 ml of inert quartz chips and was pretreated at 460°C for 1 hour in flowing H₂. Catalytic testing was then started.

20 Catalyst particles, mixed with inert quartz chips, were loaded into a ¼" OD plug flow reactor. n-hexane was vaporized into a stream of flowing hydrogen at a temperature of approximately 150°C. This gas mixture was passed through the reactor at a LHSV of 8.6 hr⁻¹, the reactor being maintained at
25 a temperature of 515°C by an external heating jacket. The reaction products were analyzed by gas chromatography.

Products ranging in size from methane to dimethylnaphthalene were observed. A variety of C6 isomerization products were observed, including isohexanes (e.g., 2-methylpentane) and olefins (e.g. 1-hexene.) For the purposes of calculating conversion and selectivity, these C6 products were considered to be unreacted. The selectivities reported are calculated as the sum of benzene, toluene, xylenes, and ethylbenzene produced divided by the total amount of all benzene, C1-C5, and C7+ materials recovered. These selectivities are presented on a molar C6 basis.

Catalyst	X ₁₀	S ₁₀
Pt/CsGeZSM-12	16	87

Performance of ZSM-5 catalysts for n-hexane aromatization.

T = 515°C, LHSV = 8.6 hr⁻¹, H₂/n-hexane feed ratio = 0.75. Conversion and aromatics selectivity measured after 10 hours on stream.

Example 5

Pt/Ge-ZSM-11

Chemicals used:

Aluminum sulfate hydrate Al₂(SO₄)₃ · x H₂O, 99.998%; Aldrich;

Potassium hydroxide KOH; >90%; Sigma-Aldrich;

1, 8-Diaminooctane NH₂(CH₂)₈NH₂, 98%; Aldrich;

Ludox HS-30 colloidal silica, 30% suspension in water; Sigma-

Aldrich;

Germanium (1V) oxide GeO_2 , Germanium Corporation of America
GTAH 68002;

Sulfuric acid H_2SO_4 ; 95-98%; Sigma-Aldrich.

5

7.2 grams of aluminum sulfate hydrate was dissolved in
544 grams of D.I. water. Potassium hydroxide (16 grams) was
dissolved in the solution. 6.83 grams of germanium oxide were
dissolved in the same solution. 64 grams of 1, 8-
10 diaminoctane were added into solution and dissolved with
stirring. Colloidal silica Ludox HS-30 (192 grams) was
introduced gradually into solution with stirring. Gel was
formed and stirred for about 1 hour. Then 10 ml of sulfuric
acid were added gradually with vigorous solution stirring. pH
15 of gel was about 11.

Crystallization was made in 1L stainless steel autoclave
at 160°C for 120 hours with stirring (200 rpm). Material was
filtered and washed with D.I water. Material was dried
overnight at 90°C, sieved to 40 mesh size and calcined at 550°C
20 for 10 hours in the furnace with forced air flow.

XRF analysis data for sample: 0.518 wt. % Na; 40.80 wt. % Si;
1.12 wt. % Al; 1.06 wt. % K; 5.52 wt. % Ge.

Ge-ZSM-11 zeolite was bound with silica at 50/50 wt.
Bound zeolite was dried at 90°C and calcined at 550°C for 6
25 hours. Material was crushed and sieved to 20/40 mesh size.
Then ion-exchange with ammonium was made by sample treatment

with 0.5M NH_4NO_3 at 60°C in three steps. Sample was rinsed with D.I. water, dried at 90°C and calcined at 550°C for 6 hours.

Platinum was introduced into catalyst by ion-exchange with 0.005M $(\text{NH}_2)_4\text{Pt}(\text{NO}_3)_2$ at 60°C. After rinsing with D.I. water catalyst was dried at 60°C overnight and calcined in air at 300°C for 5.5 hours.

XRF analysis results are: 0.045 wt. % Na; 45.77 wt. % Si; 0.53 wt. % Al; 0.89 wt. % Ge; 0.36 wt. % Pt; K was not detected.

10 Example 6

Pt/Ge-ZSM-48

Chemicals used:

Sodium hydroxide NaOH, 50% solution in water; Sigma-Aldrich; Hi-Sil®233 SiO_2 , hydrated amorphous silica; PPG Industries, Inc.;

1, 6-Diaminohexane $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$; 98+%, Alfa-Aesar;

Ethanol $\text{CH}_3\text{CH}_2\text{OH}$; 94-96%; Alfa-Aesar;

Germanium (IV) oxide GeO_2 , Germanium Corporation of America GTAH 68002.

4.5597 grams of sodium hydroxide solution was added to 40 grams of D.I. water. Germanium oxide (2.2846 g) was introduced and dissolved. 363.86 grams of D.I. water was added to solution. 38.5 grams of silica source Hi-Sil®233 was introduced with stirring. Mixture was stirred for about 10 minutes. Then 1, 6- diaminohexane (28 grams) was added to mixture and

stirring was continuous overnight. 9.1 grams of ethanol was added with stirring. pH of mixture was 11.74.

Crystallization was done at 160°C for 4 days in 1L stainless steel autoclave with stirring (300 rpm.).

5 Material was filtered and washed with D.I water. Material was dried overnight at 90°C, sieved to 40 mesh size and calcined at 600°C for 10 hours in the furnace with forced air flow.

XRF analysis data for sample: 0.428 wt. % Na; 45.38 wt. % Si;
10 0.30 wt. % Al; 1.01 wt. % Ge.

Ge-ZSM-48 zeolite was bound with silica at 50/50 wt. Bound zeolite was dried at 90°C and calcined at 550°C for 6 hours. Material was crushed and sieved to 20/40 mesh size. Then ion-exchange with ammonium was made by sample treatment
15 with 0.5M NH_4NO_3 at 60°C in three steps. Sample was rinsed with D.I. water, dried at 90°C and calcined at 550°C for 6 hours.

Platinum was introduced into catalyst by ion-exchange with 0.005M $(\text{NH}_2)_4\text{Pt}(\text{NO}_3)_2$ at 60°C. After rinsing with D.I. water catalyst was dried at 60°C overnight and calcined in air
20 at 300°C for 5.5 hours.

XRF analysis results are: 0.055 wt. % Na; 46.43 wt. % Si; 0.17 wt. % Al; 0.19 wt. % Ge; 0.12 wt. % Pt.

All catalysts were tested in a stainless steel tube at
25 500°C using 34 cc/min propane at 22 psig total pressure. The products were analyzed by on-line sampling to a gas

chromatograph where all hydrocarbon components with carbon numbers between 1 and 10 were quantitatively determined. Results for yield [fraction of BTX (benzene, toluene, xylenes) in product] and conversion (portion of propane converted) are shown in the graphs below.

Numerous modifications and variations of the present invention are possible in light of the above teachings. It is to be understood that, within the scope of the appended claims, the invention may be practiced other than as specifically described.

WHAT IS CLAIMED AS NEW AND DESIRED TO BE SECURED BY LETTER OF PATENT OF THE UNITED STATES OF AMERICA IS:

1. A catalyst for conversion of hydrocarbons comprising:
 - a) a medium pore zeolite having germanium incorporated into the zeolite framework and
 - b) at least one metal selected from Group 10 deposited on the medium pore zeolite.
2. The catalyst of Claim 1 wherein the metal deposited on the medium pore zeolite is platinum.
3. The catalyst of Claim 1 wherein the zeolite is non-acidic.
4. The catalyst of Claim 1 wherein the zeolite has a one dimensional pore structure.
5. The catalyst of Claim 1 wherein the zeolite has a two dimensional pore structure.
6. The catalyst of Claim 1 wherein the zeolite has a three dimensional pore structure.
7. The catalyst of Claim 1 wherein the zeolite is MFI, MEL, LTL, BEA, MOR, MWW, MTT, MTW, TON, MSE, MOZ, ZSM-48, MAZ, MEI, MFS, NES, OFF, STI, BOG, ERI, FAU, EUO, FER or GME.

8. A process for synthesizing a medium pore zeolite catalyst comprising:

- a) preparing a medium pore zeolite containing germanium in the framework of the zeolite;
- b) depositing at least one metal selected from Group 10 on the medium pore zeolite; and
- c) calcining the medium pore zeolite during preparation of the zeolite or before or after depositing the Group 10 metal is deposited.

9. The process of Claim 8 wherein the metal deposited on the medium pore is platinum.

10. The process of Claim 8 wherein the zeolite is base-exchanged with an alkali metal or alkaline earth metal to make the zeolite non-acidic.

11. The process of Claim 10 wherein the zeolite is base-exchanged with cesium, potassium, sodium, rubidium, barium, calcium, magnesium or mixtures thereof.

12. The process of Claim 8 wherein the zeolite has a one dimensional pore structure.

13. The process of Claim 8 wherein the zeolite has a two dimensional pore structure.

14. The process of Claim 8 wherein the zeolite has a three dimensional pore structure.

15. The process of Claim 8 wherein the zeolite is MFI, MEL, LTL, BEA, MOR, MWW, MTW, MTT, TON, MSE, MOZ, ZSM-48, MAZ, MEI, MFS, NES, OFF, STI, BOG, ERI, FAU, EUO, FER or GME.

16. A process for the conversion of hydrocarbons comprising:
a) contacting a hydrocarbon stream containing alkanes, olefins or mixtures thereof having 2 to 12 carbon atoms per molecule with at least one medium pore zeolite-based catalyst wherein the zeolite contains germanium incorporated into the zeolite framework and wherein at least one metal selected from Group 10 has been deposited on the medium pore zeolite; and
b) recovering the product.

17. The process of Claim 16 wherein the metal deposited on the medium pore is platinum.

18. The process of Claim 16 wherein the zeolite is non-acidic.

19. The process of Claim 16 wherein the alkanes or the olefins are straight, branched, cyclic or mixtures thereof.

20. The process of Claim 16 wherein the zeolite has a one dimensional pore structure.

21. The process of Claim 16 wherein the zeolite has a two dimensional pore structure.

22. The process of Claim 16 wherein the zeolite has a three dimensional pore structure.

23. The process of Claim 16 wherein zeolite is MFI, MEL, LTL, BEA, MOR, MWW, MTW, MTT, TON, MSE, MOZ, ZSM-48, MAZ, MEI, MFS, NES, OFF, STI, BOG, ERI, FAU, EUO, FER or GME.

24. A zeolite comprising:

a medium pore zeolite having germanium incorporated into the zeolite framework.

25. The zeolite of Claim 24 wherein the zeolite has a one dimensional pore structure.

26. The zeolite of Claim 24 wherein the zeolite has a two dimensional pore structure.

27. The zeolite of Claim 24 wherein the zeolite has a three dimensional pore structure.

28. The zeolite of Claim 24 wherein the medium pore zeolite is MFI, MEL, LTL, BEA, MOR, MWW, MTT, MTW, TON, MSE, MOZ, ZSM-48, MAZ, MEI, MFS, NES, OFF, STI, BOG, ERI, FAU, EUO, FER or GME.

29. A process for synthesizing a zeolite comprising:

- a) preparing a medium pore zeolite containing germanium in the framework of the zeolite;
- b) calcining the zeolite.

30. The process of Claim 29 wherein the zeolite is one dimensional pore structure.

31. The process of Claim 29 wherein the zeolite is two dimensional pore structure.

32. The process of Claim 29 wherein the zeolite is three dimensional pore structure.

33. The process of Claim 29 wherein the medium pore zeolite is MFI, MEL, LTL, BEA, MOR, MWW, MTT, MTW, TON, MSE, MOZ, ZSM-48, MAZ, MEI, MFS, NES, OFF, STI, BOG, ERI, FAU, EUO, FER or GME.

34. A catalyst for conversion of hydrocarbons comprising:
an aluminophosphate (AlPO) or silicoaluminophosphate (SAPO)
with germanium incorporated into the aluminophosphate (AlPO) or

silicoaluminophosphate (SAPO) framework.

35. The catalyst of Claim 34 wherein at least one metal selected from Group 10 deposited on the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO).

36. A process for synthesizing a catalyst comprising:

- a) preparing an aluminophosphate (AlPO) or silicoaluminophosphate (SAPO) with germanium incorporated into the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO) framework; and
- b) calcining the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO) aluminophosphate (AlPO) or silicoaluminophosphate (SAPO).

37. The process of Claim 36 additionally comprising depositing at least one metal selected from Group 10 on the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO); and said calcining occurring after preparation of the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO), before depositing at least one metal selected from Group 10 on the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO) or after depositing at least one metal selected from Group 10 on the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO).

38. A process for the conversion of hydrocarbons comprising:

a) contacting a hydrocarbon stream containing alkanes, olefins or mixtures thereof having 2 to 12 carbon atoms per molecule with at least one aluminophosphate (AlPO) or silicoaluminophosphate (SAPO)-based catalyst wherein the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO) contains germanium incorporated into the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO) framework; and

b) recovering the product.

39. The process of Claim 38 wherein the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO) has at least one metal selected from Group 10 on the aluminophosphate (AlPO) or silicoaluminophosphate (SAPO).