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(54) Title: CATALYST FOR CONVERSION OF HYDROCARBONS, PROCESS OF MAKING AND PROCESS OF USING THEREOF - INCORPORATION-1

(57) Abstract: This invention is for a catalyst for conversion of hydrocarbons. The catalyst contains a zeolite having germanium and at least one selected from the group consisting of tin and boron incorporated into the zeolite framework and at least one metal selected from Group 10 deposited on the zeolite. The catalyst is prepared by synthesizing a zeolite having germanium and at least one selected from the group consisting of tin and boron incorporated into the zeolite framework; depositing the metal; and calcining after preparation of the zeolite and before or after depositing the metal. The catalyst may be used in a process for the conversion of hydrocarbons, such as propane to aromatics, by contacting the catalyst with alkanes having 2 to 12 carbon atoms per molecule and recovering the product.

WO 2008/147543 A1

CATALYST FOR CONVERSION OF HYDROCARBONS, PROCESS OF MAKING AND PROCESS OF USING THEREOF - INCORPORATION-1

SPECIFICATION

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION: This invention relates to a catalyst for hydrocarbon conversion, e.g., a catalyst for the aromatization of alkanes, olefins and mixtures thereof having two to twelve carbon atoms per molecule. The catalyst is a microporous silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate on which a metal has been deposited.

DESCRIPTION OF THE PRIOR ART:

Crystalline silicates, aluminosilicates, aluminophosphates and silicoaluminophosphates are known catalysts for hydrocarbon conversion and may contain other metals. An aluminosilicate such as zeolite may include not only aluminum and silicon but other trivalent elements which replace aluminum and other tetravalent elements which replace silicon. Also, other elements may be deposited on the silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate.

U.S. Patent no. 4,310,440 discloses crystalline aluminophosphates having a framework structure with chemical composition in mole ratios of 1 Al_2O_3:1.0±0.2 P_2O_5 and being microporous with uniform pores of nominal diameters from about 3 to about 10 angstroms.

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

	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

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

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, Group 13, Group 14, Group 15 and the first series transition 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 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 C_2-C_{12} hydrocarbons into aromatics.

One example of the invention is a catalyst on which at least one Group 10 metal, such as platinum, is deposited on a zeolite having at least two elements selected from Group 13 or Group 14, such as germanium and either tin or boron, in the zeolite framework. This example includes a process for synthesizing a zeolite by: a) preparing a zeolite having at least two elements selected from Group 13 or Group 14, such as germanium and either tin or boron, in the zeolite framework; b) depositing at least one metal selected from Group 10 on the zeolite; and c) calcining the zeolite, said calcining occuring after preparation of the zeolite, before depositing at least one metal selected from Group 10 on the zeolite or after depositing at least one metal selected from Group 10 on the zeolite. 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 zeolite-based catalyst wherein the zeolite has at least two elements selected from Group 13 or Group 14, such as germanium and either tin or boron, in the zeolite framework and wherein at least one metal selected from Group 10 has been deposited on the zeolite; and b) recovering the product. Another example of the invention is a catalyst on which at least one Group 10 metal, such as platinum, is deposited on a zeolite having at least one element selected from Group 13 or Group 14, such as boron, in the zeolite framework. This example includes a process for synthesizing a zeolite by: a) preparing a zeolite having boron incorporated into the zeolite framework; b) depositing at least one metal selected from Group 10 on the zeolite; and c) calcining the zeolite on which at least one metal selected from Group 10 is deposited, said calcining occuring after preparation of the zeolite, before depositing at least one metal selected from Group 10 on the zeolite or after depositing at least one metal selected from Group 10 on the zeolite. This example of the invention 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 zeolite-based catalyst wherein boron is incorporated into the zeolite framework and wherein at least one metal selected from Group 10 has been deposited on the zeolite and recovering the product.

Another example of the invention is a ZSM-5 zeolite having germanium and at least one selected from the group consisting of tin and boron incorporated into the zeolite framework. This example also includes a process for synthesizing a zeolite by preparing a ZSM-5 zeolite containing germanium and at least one selected from the group consisting of tin and boron incorporated into the zeolite framework and calcining the zeolite.

DETAILED DESCRIPTION OF THE INVENTION

Crystalline silicates, aluminosilicates, aluminophosphates and silicoaluminophosphates have uniform pores through which molecules can diffuse. Aluminosilicates include zeolites. 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) and MEL (ZSM-11).

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 composed of corner-sharing TO_4 tetrahedra, where T is Al or Si, but also includes tetravalent, trivalent and divalent T atoms which 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 aqueous gel contains in addition to the silica source, the aluminum source, the phosphorus source, as needed, and the optional organic structure-directing agent, and 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-40™, precipitated silica, commercially available as Ultrasil VN3SP ™ and fumed silica, commercially available as Aerosil 200™.

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

Examples of the phosphorus source are phosphoric acid (85 wt%), P_2O_5, 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 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-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, 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, N',N',N,N-tetramethyl-(1,6)hexanediamine, Nmethyldiethanolamine, 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, neopentylamine, di-n-pentylamine, isopropylamine, t-butyl-amine, 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)-pyrrolidium cation and mixtures thereof.

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.

The reaction mixture is stirred and heated to a temperature of about 100°C to about 200°C to form crystals. The reaction mixture is cooled to room temperature. 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 liquid, e.g., 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, impregnation and vapor deposition. 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.

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. Specific examples of elements in the framework are germanium and at least one selected from the group consisting of tin and boron.

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/GeO_2, 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. For example, there may be a first calcination of the silicate, aluminosilicate, aluminophosphate or silicoaluminophosphate to remove the organic structure-directing agent followed by metal deposition and subsequent calcinations at lower temperatures. The calcination to remove the organic structure-directing agent 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. Calcination can occur in an environment of oxygen, nitrogen, hydrogen, water vapor, helium and mixtures thereof.

The catalyst, bound and 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 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.

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 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 are H_2S, an organosulfide compound, such as dimethyl disulfide or DMSO (dimethyl sulfoxide), or $C_nH_{2n+2}S$ or $C_nH_{2n+2}S_2$, 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 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 C_2-C_{12} alkanes, olefins or mixture 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 by having a low aluminum content. The base-exchange may occur before or after the noble metal is deposited. Such a base-exchanged catalyst may be used to convert C_6-C_{12} 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.

Depending on the element incorporated into the zeolite framework, the zeolite may be non-acidic without base-exchange, e.g., boron, germanium or tin in an aluminum-free zeolite. "Aluminum-free" has a meaning of having aluminum content of no more than 0.4wt%.

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 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 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 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., C_{14} olefin. Typical reaction 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 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. 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}.

(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.

(J) The alkylation of a reformate 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 0.4 hr^{-1} to about 0.8 hr^{1}, a WHSV-reformate 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.

(K) The alkylation of aromatic hydrocarbons, e.g., benzene, toluene, xylene, and naphthalene, with long chain olefins, e.g., C_{14} 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}.

(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 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-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 per 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.

(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 about 0.1 hr^{-1} to about 30 hr^{-1}.

(S) The conversion of naphtha (e.g., C_6-C_{10}) 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 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}.

(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 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 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 feedstock in a gaseous phase 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 C_2 unsaturated hydrocarbons (ethylene and/or acetylene) to aliphatic C_{6-12} aldehydes and converting said aldehydes to the corresponding C_{6-12} 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.

Example 1:

Synthesis of Sn-Ge-ZSM-5

Chemicals used:

Tin (II) chloride dihydrate, $SnCl_2 * 2H_2O$, 98%; Sigma-Aldrich;
Sodium hydroxide solution, 50% in water; Sigma-Aldrich;
Germanium oxide GeO_2, 99.99%; Germanium Corporation of America,

GTAH 68002;

Sodium aluminate (23.6% Al_2O_3; 19.4% Na_2O; 57.0% H_2O); Southern Ionics;

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

Tetrapropylammonium bromide TPABr, 98%; Alfa-Aesar;

Acetic acid, 99.7%; Aldrich.

Solution #1. 2.21 grams of tin chloride dihydrate were dissolved in 55 grams of D.I. water. 25.98 grams of sodium hydroxide solution were added to the same solution with stirring. 1.0462 grams of GeO_2 were dissolved in solution also.

Solution #2. 3.84 grams of sodium aluminate were homogenized in 50 grams of D.I. water.

Solution #3. 28.12 grams of TPABr were dissolved in 100 grams of D.I. water.

Solution # 1 was added to 150 grams of Ludox AS-40 with gel formation. Stirring was made for 10 minutes. Then solution #2 was introduced to gel. Gel was stirred for 15 minutes. Then solution #3 was added to gel and stirring was continued for 60 minutes.

15.97 grams of acetic acid were added gradually with gel stirring. Gel pH was measured in 30 minutes after acid addition (pH=10.59).

Crystallization was made in 1L stainless steel autoclave at 160°C for 4 days with stirring (200 rpm).

Material was washed and filtered with D.I. water, dried at 90°C, sieved to 40 mesh size and calcined at 550°C for 10 hours.

XRF analysis results are: 0.686 wt. % Na; 42.38 wt. % Si; 0.75 wt. % Al; 1.52 wt. % Sn; 0.96 wt. % Ge.

Identified as ZSM-5 by XRD.

Synthesis of 1%Pt/CsGeSnZSM-5

3.8 grams of laboratory prepared SnGeZSM-5 was washed with 200 ml of aqueous CsNO3 (0.5M) then filtered. The filtrate was then rewashed 3 more times with 0.5M $CsNO_3$ and rinsed with deionized 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 0.0432 g $Pt(NH_2)_4(NO_3)_2$ dissolved in 0.9327 g of deionized water to 2.047 grams of the Cs-exchanged SnGeZSM-5. The material was dried for 1 hour in a 110°C drying oven then calcined at 280°C for 3 hours. Elemental analysis gave 41.74 wt % Si, 0.73 wt % Al, 0.85 wt % Ge, 2.25 wt % Sn, 6.34 wt % Cs and 0.80 wt % Pt.

The catalyst powder was pressed and sized to 20-40 mesh. 0.25 cm^3 (0.128 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.

Example 2:

Synthesis of Ge-B-ZSM-5

Chemicals used:

Boric acid H3BO3; 99.99%; Aldrich;

Sodium hydroxide NaOH; >98%; Aldrich;

Tetrapropylammonium bromide $(CH_3(CH_2)_2)4NBr$; 98%;Alfa-Aesar;

Germanium dioxide GeO_2;Germanium Corporation of America GTAH 68002;

Ludox HS-30 SiO_2, colloidal silica, 30% suspension in water; Sigma-Aldrich.

2.304 grams of sodium hydroxide were dissolved in 184 grams of D.I. water. 0.96 gram of boric acid and then 28.96 grams of tetrapropylammonium bromide were dissolved in the same solution with stirring. 1.2527 grams of germanium dioxide were dissolved gradually with stirring. Gel was formed after 35.2 grams of Ludox HS-30 were introduced into solution. Gel was stirred for about 15 minutes (pH=12.76).

Crystallization was made in stainless steel 300 ml autoclave at 165°C for 5 days with stirring (100 rpm). Analysis results are: 41.6 wt. % Si; 0.41 wt. % B; 0.83 wt. % Ge.

Identified as ZSM-5 by XRD.

Synthesis of 1%Pt/CsBGeZSM-5

2.4 grams of laboratory prepared BGeZSM-5 was washed with 150 ml of aqueous $CsNO_3$ (0.5M) then filtered. The filtrate was then rewashed 3 more times with 0.5M $CsNO_3$ and rinsed with deionized 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 0.0310 g $Pt(NH_2)_4(NO3)_2$ dissolved in 0.7637 g of deionized water to 1.509 grams of the Cs-exchanged BGeZSM-5. The material was dried for 1 hour in a 110°C drying oven then calcined at 280°C for 3 hours. Elemental analysis gave 42.85 wt % Si, 0.63 wt % Ge, 0.256 wt % B, 6.24 wt % Cs, and 0.74 wt% Pt.

The catalyst powder was pressed and sized to 20-40 mesh. 0.25 cm3 (0.130 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.

Example 3:

Synthesis of B-ZSM-5

<u>Chemicals used:</u>

Boric acid H_3BO_3; 99.99%; Aldrich;

Sodium hydroxide NaOH; >98%; Aldrich;

Tetrapropylammonium bromide $(CH_3(CH_2)_2)_4NBr$; 98%;Alfa-Aesar;

Ludox HS-30 SiO_2, colloidal silica, 30% suspension in water; Sigma-Aldrich.

2.88 grams of sodium hydroxide were dissolved in 230 grams of D.I. water. Then 1.2 grams of boric acid and then 36.20 grams of tetrapropylammonium bromide were dissolved in the same solution with stirring. Light gel was formed after 44.0 grams of silica source Ludox HS-30 were introduced.

Crystallization was made in a one liter stainless steel autoclave at 165°C for 5 days with stirring (100 rpm). Analysis results are: 42.7 wt. % Si; 0.411 wt. % B. Identified as ZSM-5 by XRD.

Synthesis of 1%Pt/BZSM-5

Incipient wetness impregnation was carried out by adding drop wise a solution of 0.0402 g $Pt(NH_2)_4(NO_3)_2$ dissolved in 0.9925 g of deionized water to 2.011 grams of laboratory prepared BZSM-5. The material was dried for 1 hour in a 110°C drying oven then calcined at 280°C for 3 hours. Elemental analysis gave 44.99 wt % Si, 0.682 wt % Na, and 0.94 wt% Pt. Boron content was not measured.

The catalyst powder was pressed and sized to 20-40 mesh. 0.25 cm3 (0.128 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.

Example 4:

Synthesis of 1%Pt/CsBZSM-5

2.7 grams of laboratory prepared BZSM-5 was washed with 150 ml of aqueous $CsNO_3$ (0.5M) then filtered. The filtrate was then rewashed 3 more times with 0.5M $CsNO_3$ and rinsed with deionized 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 0.0402 g $Pt(NH_2)_4(NO_3)_2$ dissolved in 0.9925 g of deionized water to 2.019 grams of the Cs-exchanged BZSM-5. The material was dried for 1 hour in a 110°C drying oven then calcined at 280°C for 3 hours. Elemental analysis gave 44.06 wt % Si, 0.234wt % B, 5.74 wt % Cs, and 0.86 wt% Pt.

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.

Example 5:

Synthesis of B-Al-ZSM-5

Chemicals used:

Boric acid H3BO3; 99.99%; Aldrich;

Sodium hydroxide NaOH; >98%; Aldrich;

Sodium aluminate $NaAlO_2$ (23.6 wt. % Al_2O_3; 19.4 wt. % Na_2O; 57 wt. % H_2O); Southern Ionics.

Tetrapropylammonium bromide $(CH_3(CH_2)_2)_4NBr$; 98%;Alfa-Aesar; Ludox HS-30 SiO_2, colloidal silica, 30% suspension in water; Sigma-Aldrich.

3.7939 grams of sodium hydroxide were dissolved in 345 grams of D.I. water. 1.8 grams of boric acid were dissolved in the same solution. Then sodium aluminate (1.3582 grams) was added and then 54.3 grams of tetrapropylammonium bromide were dissolved in the same solution with stirring. Silica source Ludox HS-30 (66.0 grams) was introduced into the solution with gel formation. Gel was stirred for 10-15 minutes (pH=13.03). Crystallization was made in 1L stainless steel autoclave at 165°C for 5 days with stirring (100 rpm).

Analysis results are: 37.5 wt. % Si; 0.248 wt. % B; 0.97 wt. % Al.

Identified as ZSM-5 by XRD.

Synthesis of 1%Pt/CsBZSM-5

2.7 grams of laboratory prepared BZSM-5 was washed with 150 ml of aqueous CsNO3 (0.5M) then filtered. The filtrate was then rewashed 3 more times with 0.5M $CsNO_3$ and rinsed with deionized 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 0.0409 g $Pt(NH_2)_4(NO_3)_2$ dissolved in 0.9257 g of deionized water to 2.054 grams of the Cs-exchanged

BZSM-5. The material was dried for 1 hour in a 110°C drying oven then calcined at 280°C for 3 hours. Elemental analysis gave 42.11 wt % Si, 0.126 wt % Al, 0.90 wt % B, 9.13 wt % Cs, and 0.68 wt%.

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.

Example 6:

Synthesis of Ge-B-ZSM-5

Chemicals used:

Boric acid H_3BO_3; 99.99%; Aldrich;

Sodium hydroxide NaOH; >98%; Aldrich;

Tetrapropylammonium bromide $(CH_3(CH_2)_2)4NBr$; 98%;Alfa-Aesar;

Germanium dioxide GeO2;Germanium Corporation of America GTAH 68002;

Ludox HS-30 SiO_2, colloidal silica, 30% suspension in water; Sigma-Aldrich.

2.304 grams of sodium hydroxide were dissolved in 184 grams of D.I. water. 0.96 gram of boric acid and then 28.96 grams of tetrapropylammonium bromide were dissolved in the same solution with stirring. 1.2527 grams of germanium dioxide were dissolved gradually with stirring. Gel was formed after 35.2 grams of Ludox HS-30 were introduced into solution. Gel was stirred for about 15 minutes (pH=12.76).

Crystallization was made in stainless steel 300 ml autoclave at 165°C for 5 days with stirring (100 rpm).

Analysis results are: 41.6 wt. % Si; 0.41 wt. % B; 0.83 wt. % Ge.

Identified as ZSM-5 by XRD.

1%Pt/GeBZSM-5

Incipient wetness impregnation was carried out by adding drop wise a solution of 0.0412 g $Pt(NH_2)_4(NO_3)_2$ dissolved in 0.96 grams of deionized water to 2.003 grams of laboratory prepared GeBZSM-5. The material was dried for 1 hour in a 110°C drying oven then calcined in air at 280°C for 3 hours.

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 H_2. Catalytic testing was then started.

Catalyst Testing

All catalysts were tested according to the same procedure. 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 C_6 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.

Example	catalyst	Si/Al_2	Sn, Ge, B in final catalyst	X_{25}	S_{25}
1	Pt/CsSnGeZSM-5	110	2.3% Sn, 0.85% Ge	11	86
2	Pt/CsBGeZSM-5	∞	0.29% B, 0.63% Ge	35	75
3	Pt/BZSM-5	∞	0.41% B	43	78
4	Pt/CsBZSM-5	∞	0.25% B	51	87
5	Pt/CsBZSM-5	90	0.14% B	45	72
6	Pt/BGeZSM-5	∞	0.41% B, 0.63% Ge	24	91

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 zeolite having germanium and at least one element selected from the group consisting of tin and boron incorporated into the zeolite framework and

b) at least one metal selected from Group 10 deposited on the zeolite.

2. The catalyst of Claim 1 wherein the metal deposited on the zeolite is platinum.

3. The catalyst of Claim 1 wherein the zeolite is MFI (ZSM-5).

4. The catalyst of Claim 1 wherein the zeolite is non-acidic.

5. A process for synthesizing a zeolite comprising:

a) preparing a zeolite having germanium and at least one selected from the group consisting of tin and boron incorporated into the zeolite framework;

b) depositing at least one metal selected from Group 10 on the zeolite; and

c) calcining the zeolite, said calcining occuring after preparation of the zeolite, before depositing at least one metal selected from Group 10 on the zeolite or after depositing at least one metal selected from Group 10 on the zeolite.

6. The process of Claim 5 wherein the metal deposited on the zeolite is platinum.

7. The process of Claim 5 wherein the zeolite is MFI (ZSM-5).

8. The process of Claim 5 wherein the zeolite is base-exchanged with an alkali metal or alkaline earth metal to make the zeolite non-acidic.

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

10. The process of Claim 9 wherein the metal deposited on the zeolite is platinum.

11. The process of Claim 9 wherein the zeolite is MFI (ZSM-5).

12. The process of Claim 9 wherein the zeolite is non-acidic.

13. The process of Claim 9 wherein the alkanes or the olefins are straight, branched, cyclic or mixtures thereof.

14. A catalyst for conversion of hydrocarbons comprising:
a) a zeolite having boron incorporated into the zeolite framework and
b) at least one metal selected from Group 10 deposited on the zeolite.

15. The catalyst of Claim 14 wherein the metal deposited on the zeolite is platinum.

16. The catalyst of Claim 14 wherein the zeolite is MFI (ZSM-5).

17. The catalyst of Claim 14 wherein the zeolite is aluminum-free.

18. The catalyst of Claim 14 wherein the zeolite is base-exchanged with an alkali metal or alkaline earth metal to make the zeolite non-acidic.

19. A process for synthesizing a zeolite comprising:
a) preparing a zeolite having boron incorporated into the zeolite framework;

b) depositing at least one metal selected from Group 10 on the zeolite; and

c) calcining the zeolite after preparation of the zeolite, before depositing at least one metal selected from Group 10 on the zeolite or after depositing at least one metal selected from Group 10 on the zeolite.

20. The process of Claim 19 wherein the metal deposited on the zeolite is platinum.

21. The process of Claim 19 wherein the zeolite is MFI (ZSM-5).

22. The process of Claim 21 wherein the zeolite is aluminum-free.

23. The process of Claim 19 wherein the zeolite is base-exchanged with an alkali metal or alkaline earth metal to make the zeolite non-acidic.

24. 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 zeolite-based catalyst wherein the catalyst contains boron incorporated into the zeolite framework and wherein at least one metal selected from Group 10 has been deposited on the zeolite; and

b) recovering the product.

25. The process of Claim 24 wherein the metal deposited on the zeolite is platinum.

26. The process of Claim 24 wherein the zeolite is MFI (ZSM-5).

27. The process of Claim 24 wherein the zeolite is aluminum-free.

28. The process of Claim 24 wherein the alkanes or the olefins are straight, branched, cyclic, or mixtures thereof.

29. The process of Claim 24 wherein the zeolite is base-exchanged with an alkali metal or alkaline earth metal to make the zeolite non-acidic.

30. A zeolite comprising:

a ZSM-5 zeolite having germanium and at least one selected from the group consisting of tin and boron incorporated into the zeolite framework.

31. A process for synthesizing a zeolite comprising:

a) preparing a ZSM-5 zeolite containing germanium and at least one selected from the group consisting of tin and boron incorporated into the zeolite framework;

b) calcining the zeolite.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 08/06631

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01J 29/04 (2008.04)
USPC - 502/60, 77
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC - 502/60, 77

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 502/$

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST(USPT,PGPB,EPAB,JPAB); Google Patents; Google
Search Terms Used: zeolite aluminum free ZSM MFI incorporate framework Groups 10 13 14 conversion hydrocarbon non acidic base exchange boron platinum germanium

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2005/0158238 A1 (TATSUMI et al.) 21 July 2005 (21.07.2005) entire document especially paras [0050], [0060], [0061]	1-31
Y	US 2005/0274647 A1 (BOEHMER et al.) 15 December 2005 (15.12.2005) entire document especially paras [0013], [0014], [0034], [0056]	1-29
Y	US 2005/0197515 A1 (JUTTU et al.) 8 September 2005 (08.09.2005); paras [0021]	3, 7, 11, 16, 17, 21, 22, 26, 27, 30 and 31
Y	US 4,962,250 A (DESSAU et al.) 9 October 1990 (09.10.1990); col 3, ln 40-45	4 and 12
Y	4,830,732 A (MOHR et al.) 16 May 1989 (16.05.1989); col 6, ln 41-48	8, 18, 23 and 29

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 7 August 2008 (07.08.2008)	Date of mailing of the international search report 15 AUG 2008
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774