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(54) Title: IMPROVED CATALYST COMPOSITION USEFUL FOR CONVERSION OF NON-AROMATIC HYDROCARBONS TO AROMATICS AND LIGHT OLEFINS

(57) Abstract

A novel zeolite catalyst comprising an acid treated zeolite impregnated with zinc and at least one other metal selected from the group consisting of Group 4B, Group 6B, Group 3A, Group 4A and Group 5A of the periodic table of elements, a method of making such zeolite catalyst, and the use thereof for converting paraffin hydrocarbons to olefins and aromatics with a low rate of coke formation during such conversion.

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IMPROVED CATALYST COMPOSITION USEFUL FOR CONVERSION OF NON-AROMATIC HYDROCARBONS TO AROMATICS AND LIGHT OLEFINS

The invention relates to an improved process for converting non-aromatic hydrocarbons in the presence of an improved zeolite material to aromatic and lower olefin hydrocarbons preferably with a low rate of coke formation during the conversion of such hydrocarbons in the presence of such improved zeolite material.

It is known to catalytically crack non-aromatic gasoline boiling range hydrocarbons (in particular paraffin and olefins) to lower olefins (such as ethylene and propylene) and aromatic hydrocarbons (such as benzene, toluene, and xylenes) in the presence of catalysts which contain a zeolite (such as ZSM-5), as is described in an article by N.Y. Chen et al in Industrial & Engineering Chemistry Process Design and Development, Volume 25, 1986, pages 151-155. The reaction product of this catalytic cracking process contains a multitude of hydrocarbons such as unconverted C_5+ alkanes, lower alkanes (methane, ethane, propane), lower alkenes (ethylene and propylene), C_6-C_8 aromatic hydrocarbons (benzene, toluene, xylenes, and ethylbenzene), and C_9+ aromatic hydrocarbons. Depending upon the relative market prices of the individual reaction products, it can be desirable to increase the yield of certain of the more valuable products relative to the others.

One concern with the use of zeolite catalysts in the conversion of hydrocarbons to aromatic hydrocarbons and lower olefins is the excessive production of coke during the conversion reaction. Coke formed during the zeolite catalyzed aromatization of hydrocarbons tends to cause catalyst deactivation. It is desirable to improve processes for the aromatization of hydrocarbons and the formation of lower olefins from hydrocarbons by minimizing the amount of coke formed during such processes. It is also desirable to have a zeolite catalyst that is useful in producing significant quantities of the aromatic and olefin conversion products.

It is an object of this invention to at least partially convert hydrocarbons to ethylene, propylene and BTX (benzene, toluene, xylene and ethylbenzene) aromatics.

A yet further object of this invention is to provide an improved zeolite material which when used in the conversion of hydrocarbons results in less coke formation than alternative zeolite materials.

A still further object of this invention is to provide an improved zeolite material that gives an improved yield of lower olefins and BTX aromatics when utilized in the conversion of hydrocarbons.

Another object of this invention is to provide hydrocarbon conversion processes which have an acceptably low coke production rate and/or which produces a conversion product containing suitable quantities of olefins and BTX aromatics.

Another further object of this invention is to provide a method for making an improved zeolite material having such desirable properties as providing for lower coke production and favorable production of olefins and BTX aromatics when used in the conversion of hydrocarbons.

One of the inventive processes provides for the conversion of non-aromatic hydrocarbons to aromatic hydrocarbons and lower olefins by contacting under conversion conditions a hydrocarbon feed with an impregnated acid treated zeolite comprising an acid treated zeolite having incorporated therein zinc and at least one other metal from the group consisting of Group 4B, Group 6B, Group 3A, Group 4A and Group 5A of the periodic table of elements.

Another embodiment of the invention is a novel composition used in the conversion of hydrocarbons. The novel composition comprises an acid treated zeolite impregnated with zinc and at least one other metal selected from the group consisting of Group 4B, Group 6B, Group 3A, Group 4A and Group 5A of the periodic table of elements. The novel composition may be made by incorporating zinc and at least one other metal from the group consisting of Group 4B, Group 6B, Group 3A, Group 4A and Group 5A of the periodic table of elements into an acid treated zeolite to thereby provide an impregnated acid treated zeolite.

Other objects and advantages of the invention will become apparent from the detailed description and the appended claims.

The inventive composition includes a zeolite starting material that has been treated with an acid to thereby provide an acid treated zeolite. The inventive composition further contains zinc and at least one other metal or element selected from the group consisting of Group 4B, Group 6B, Group 3A, Group 4A and Group 5A of the periodic table of elements. It is understood herein that any reference to the other metal in addition to zinc contained in the inventive composition will be an element from the Group 4B elements including Titanium (Ti), Zirconium (Zr), and Hafnium (Hf); Group 6B elements including Chromium (Cr), Molybdenum (Mo), Tungsten (W); Group 3A elements including Boron (B), Aluminum (Al), Gallium (Ga), Indium (In), Thallium (Tl); Group 4A elements including Silicon (Si), Germanium (Ge), Tin (Sn) and Lead (Pb); Group 5A elements including Phosphorous (P), Arsenic (As), Antimony (Sb), and Bismuth (Bi). Some of the foregoing listed elements may not be considered by those skilled in the art to be a metal by the conventional meaning of such term, but, as the term is used within this description and in the claims, any references to metals will include zinc and those elements listed above.

An important, if not critical, aspect of the invention is the requirement that the composition be dual metal promoted with zinc as the first or primary metal and the at least one other metal as the second or secondary metal. A further important aspect of the inventive composition is for the starting zeolite material, which is being modified to provide the inventive composition having the desirable properties as earlier described herein, to be treated with an acid to give an acid treated zeolite. The acid treated zeolite is further modified by the incorporation of the two metal promoters of zinc and at least one other metal.

Any suitable means or method can be used to treat the zeolite starting material with acid. It is preferred for the zeolite to be soaked with an acid solution by any suitable means known in the art for contacting the zeolite with such acid solution. The acid solution used to treat the zeolite can be a solution of any acid that suitably provides for the leaching of aluminum atoms from the zeolite particles. Preferably, the acid concentration in this solution is about 1-10 equivalents per liter. Examples of such suitable acids include sulfuric, phosphoric, nitric and hydrochloric. The preferred acid solution is aqueous hydrochloric acid. The zeolite is soaked in the acid solution (preferably at a temperature of about 50-100°C) for a period upwardly to about 15 hours, but, preferably from 0.1 hour to 12 hours. After soaking, the resultant acid treated zeolite is washed free of the acid and then can be dried or calcined, or both.

The zeolite starting material used in the composition of the invention can be any zeolite which is effective in the conversion of non-aromatics to aromatics when contacted under suitable reaction conditions with non-aromatic hydrocarbons. Preferably, the zeolite has a constraint index (as defined in U.S. Patent 4,097,367, which is incorporated herein by reference) in the range of about 0.4 to about 12, preferably about 2-9. Generally, the molar ratio of SiO_2 to Al_2O_3 in the crystalline framework of the zeolite is at least about 5:1 and can range up to infinity. Preferably the molar ratio of SiO_2 to Al_2O_3 in the zeolite framework is about 8:1 to about 200:1, more preferably about 12:1 to about 100:1. Preferred zeolites include ZSM-5, ZSM-8, ZSM-11, ZSM-12, ZSM-35, ZSM-38, and mixtures thereof. Some of these zeolites are also known as “MFI” or “Pentasil” zeolites. The presently more preferred zeolite is ZSM-5.

The inventive composition further includes, in addition to the acid leached zeolite, zinc and at least one other metal. These metals may be incorporated into the acid leached zeolite by any suitable means or method known in the art for incorporating metallic elements into a substrate material. A preferred method is the use of any standard incipient wetness technique for impregnating the acid leached zeolite substrate with the metal promoters. The preferred method uses a liquid impregnation solution containing the desirable concentrations of zinc and other metals so as to ultimately provide the final inventive composition having the required concentration of metals.

It is particularly desirable to use for the impregnation of the acid treated zeolite aqueous solutions of one or more of the metal promoters that are incorporated into the acid treated zeolite. The acid treated zeolite may be impregnated with the metal promoters described herein simultaneously or sequentially, or both, provided the acid treated zeolite ultimately contains zinc and the at least one other metal. The preferred impregnation solution is an aqueous solution formed by dissolving a salt of the metal in question in water. However, it is acceptable to use somewhat of an acidic solution to aid in the dissolution of the metal salt. It is most preferred for the acid treated zeolite to be co-impregnated with the zinc and the at least one other metal promoter by use of a solution containing a first salt of zinc and a second salt of at least one other metal promoter as described herein.

The other metal promoter, or secondary metal, as earlier noted, includes those metals or elements selected from the group consisting of Group 4B elements, Group 6B elements, Group 3A elements, Group 4A elements and Group 5A elements. Among these, the preferred metals include Ti, Zr, Cr, Mo, W, B, Al, Si, Ge, Sn, Pb, P, As and Sb. The most preferred secondary metals include Ti, Cr, Mo, B, Si, and P.

The amounts of the primary metal promoter of zinc and the secondary metal promoter incorporated or impregnated into the acid treated zeolite should be such as to give concentrations effective in providing the desirable properties of favorable aromatics and olefin conversion yields with low coke production when the inventive composition is employed in the conversion of a hydrocarbon feed. Generally, the atomic ratio of the secondary metal to zinc in the impregnated acid treated zeolite is in the range of from about 0.1:1 to about 10:1. A preferred atomic ratio of secondary metal to zinc in the impregnated acid treated zeolite is in the range of from about 0.2:1 to about 5:1 and, most preferably, the atomic ratio is in the range of from 0.5:1 to 3:1.

The weight percent of zinc present in the impregnated acid treated zeolite is generally in the range upwardly to about 10 weight percent of the impregnated acid treated zeolite. The preferred concentration of zinc in the impregnated acid treated zeolite is in the range of from about 0.05 to about 8 weight percent and, most preferably, from 0.1 to 6 weight percent. The secondary metal should generally be present in the impregnated acid treated zeolite in the range upwardly to about 15 weight percent. Preferably, the concentration of secondary metal is in the range of from about 0.1 to about 12 weight percent and, most preferably, from 0.2 to 10 weight percent.

It is theorized that the unique properties of the inventive composition described herein result from the zinc component of the double metal promoted acid treated zeolite providing an increased activity toward the production of aromatics and olefins in the conversion of a hydrocarbon feed. However, this increased activity toward the production of aromatics and olefin conversion products also results in an undesirable increase in coke production. To offset this propensity for increased coke production caused by the presence of zinc, the secondary metal is added as a coke suppressant. The secondary metal, however, does not have a significant negative impact on the yield of conversion products and may even promote the production of such conversion products. Thus, the dual metal promoted acid treated zeolite provides for an improved olefin and aromatic conversion product yield with a low coke production rate.

The inventive compositions described herein can also contain an inorganic binder (also called matrix material) preferably selected from the group consisting of alumina, silica, alumina-silica, aluminum phosphate, clays (such as bentonite), and mixtures thereof. The content of the impregnated acid treated zeolite component of the mixture of impregnated acid treated zeolite and inorganic binder is about 1-99 (preferably about 5-80) weight-%, and the content of the above-listed inorganic binders in the mixture of impregnated acid treated zeolite and inorganic binder is about 1-50 weight-%. Generally, the impregnated acid treated zeolite and inorganic binder components are compounded and subsequently shaped (such as by pelletizing, extruding or tableting). Generally, the surface area of the compounded composition is about 50-700 m^2/g, and its particle size is about 1-10 mm.

The impregnated acid treated zeolite can be subjected to a first heat treating step whereby it is exposed by any suitable method known in the art to an atmosphere of a first gas under temperature and pressure conditions and for a period of time that suitably provide a first heat treated material. The first gas used in the first heat treatment of the impregnated acid treated zeolite can be selected from the group consisting of inert gases (for example, nitrogen, helium and argon gases), reducing gases (for example, carbon monoxide and hydrogen gases), air, oxygen and steam. The preferred first gas is selected from the group consisting of air, oxygen, nitrogen, steam and mixtures thereof. Most preferably, the first gas is selected from the group consisting of air, oxygen, nitrogen and mixtures of one or two thereof.

The first heat treatment may be conducted at any pressure and temperature conditions that suitably provide the first heat treated material. Generally, the first heat treatment may be conducted at a pressure from below atmospheric upwardly to about 1000 pounds per square inch absolute (psia). More typical pressures, however, are in the range of from about atmospheric to about 100 psia. The first heat treatment temperature is generally in the range of from about 30°C to about 400°C. Preferably, this temperature range is from about 40°C to about 300°C and, most preferably, the first heat treatment temperature is in the range of from 50°C to 200°C.

The time period for conducting the first heat treatment step must be sufficient to provide a substantially dry, i.e., free of water, material. Generally, the period for exposing the impregnated acid treated zeolite to the atmosphere of the first gas at appropriate temperature conditions can range from about 0.1 hour to about 30 hours. Preferably, the first heat treatment step is conducted for a period of from about 0.25 hour to about 25 hours and, most preferably, from 0.5 hour to 20 hours.

The first heat treated material can undergo a second heat treatment step in which it is exposed by any suitable method known in the art to an atmosphere of a second gas under temperature and pressure conditions and for a period of time such that a second heat treated material having the desirable properties as referred to herein is obtained.

The second gas used in the second heat treatment of the first heat treated material can be selected from the group consisting of inert gases (for example, nitrogen, helium and argon gases), reducing gases (for example, carbon monoxide and hydrogen gases), air, oxygen and steam. The preferred second gas is selected from the group consisting of air, oxygen, nitrogen, steam and mixtures thereof. Most preferably, the second gas is steam.

The second heat treatment may be conducted at any pressure and temperature conditions that suitably provide the second heat treated material. Generally, the second heat treatment may be conducted at a pressure from below atmospheric upwardly to about 3000 psia. More typical pressures, however, are in the range of from about atmospheric to about 2500 psia. The second heat treatment temperature is generally in the range of from about 100°C to about 1500°C. Preferably, this temperature range is from about 200°C to about 1300°C and, most preferably, the second heat treatment temperature is in the range of from 400°C to

1200°C. When steam is used in the second heat treatment step, it is preferred for it to be superheated and not saturated.

The time period for conducting the second heat treatment step must be sufficient to provide a second heat treated material having the desirable properties of good catalytic activity and resistance to coke formation. Generally, the period for exposing the first heat treated material to the atmosphere of the second gas at the appropriate temperature and pressure conditions can be in the range of from about 0.1 hour to about 20 hours. Preferably, the second heat treatment step is conducted for a period of from about 0.25 hour to about 18 hours and, most preferably, from 0.5 hour to 15 hours.

Any suitable hydrocarbon feedstock which comprises paraffins (alkanes) and/or olefins (alkenes) and/or naphthenes (cycloalkanes), wherein each of these hydrocarbons contains 2-16 carbon atoms per molecule can be used as the feed to be contacted with the inventive compositions under suitable process conditions for obtaining a reaction product comprising lower alkenes containing 2-5 carbon atoms per molecule and aromatic hydrocarbons. Frequently, these feedstocks also contain aromatic hydrocarbons. Non-limiting examples of suitable, available feedstocks include gasolines from catalytic oil cracking (e.g., FCC and hydrocracking) processes, pyrolysis gasolines from thermal hydrocarbon (e.g., ethane, propane, and naphtha) cracking processes, naphthas, gas oils, reformates, straight-run gasoline and the like. The preferred feed is a gasoline-boiling range hydrocarbon feedstock suitable for use as at least a gasoline blend stock generally having a boiling range of about 30-210°C. Generally, the content of paraffins exceeds the combined content of olefins, naphthenes and aromatics (if present).

The hydrocarbon feed stream can be contacted by any suitable manner with the inventive compositions described herein contained within a reaction zone. The contacting step can be operated as a batch process step or, preferably, as a continuous process step. In the latter operation, a solid catalyst bed or a moving catalyst bed or a fluidized catalyst bed can be employed. Any of these operational modes have advantages and disadvantages, and those skilled in the art can select the one most suitable for a particular feed and catalyst.

The contacting step is preferably carried out within a conversion reaction zone, wherein is contained the inventive composition, and under reaction conditions that suitably promote the formation of olefins, preferably light olefins, and aromatics, preferably BTX, from at least a portion of the hydrocarbons of the hydrocarbon feed. The reaction temperature of the contacting step is more particularly in the range of from about 400°C to about 800°C, preferably, from about 450°C to about 750°C and, most preferably, from 500°C to 700°C. The contacting pressure can range from subatmospheric pressure upwardly to about 500 psia, preferably, from about atmospheric to about to about 450 psia and, most preferably, from 20 psia to 400 psia.

The flow rate at which the hydrocarbon feed is charged to the conversion reaction zone is such as to provide a weight hourly space velocity ("WHSV") in the range of from exceeding 0 hour^{-1} upwardly to about 1000 hour^{-1}. The term "weight hourly space velocity", as used herein, shall mean the numerical ratio of the rate at which a hydrocarbon feed is charged to the conversion reaction zone in pounds per hour divided by the pounds of catalyst contained in the conversion reaction zone to which the hydrocarbon is charged. The preferred WHSV of the feed to the conversion reaction zone or contacting zone can be in the range of from about 0.25 hour^{-1} to about 250 hour^{-1} and, most preferably, from 0.5 hour^{-1} to 100 hour^{-1}.

The following examples are presented to further illustrate this invention and are not to be construed as unduly limiting its scope.

EXAMPLE I

This example illustrates the preparation of several catalysts which were subsequently tested as catalysts in the conversion of a gasoline sample, which had been produced in a commercial fluidized catalytic cracking unit (FCC), to aromatics.

ACID LEACHED ZEOLITE

A commercially available ZSM-5 catalyst (provided by United Catalysts Inc., Louisville, KY, under product designation "T-4480" was treated by acid leaching. To acid leach the catalyst, it was soaked in an aqueous HCl solution, having a concentration of 38 weight percent HCl (approximately 6N), for two hours at a constant temperature of about 90°C. After soaking, the catalyst was separated from the acid solution and thoroughly washed with water and dried. The acid soaked, washed and dried catalyst was calcined at a temperature of about 525°C for four hours.

CATALYST A

A 10.83 gram quantity of above-described acid leached ZSM-5 catalyst was impregnated by an incipient wetness technique with an 8.3 gram quantity of a solution containing 2 parts by weight zinc chloride ($ZnCl_2$), 18 parts by weight ethanol and 20 parts by weight tetraethoxysilane (TEOS). The impregnation solution had an atomic ratio of silicon to zinc of 6.6. This impregnated, acid leached zeolite was then dried in air at a temperature of 125°C for 16 hours followed by treatment in a steam atmosphere for 6 hours at 650°C. The steam treated material was then exposed to a helium gas atmosphere at a temperature of 525°C for 2 hours. The final product contained 1.653 weight percent zinc and 4.72 weight percent silicon.

CATALYST B

A 10.00 gram quantity of the above described acid leached zeolite material was impregnated with a 12.50 gram quantity of a solution containing 1.50 parts by weight hydrated zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$), 4.10 parts by weight hydrated chromium nitrate ($Cr(NO_3)_3{\cdot}9H_2O$), and 6.90 parts by weight water. The impregnation solution had an atomic ratio of chromium to zinc of 2. This impregnated, acid leached zeolite was then dried in air at 125°C for 16 hours followed by treatment in a steam atmosphere for 6 hours at 650°C. The steam treated material was then exposed to a helium gas atmosphere at a temperature of 538°C for 2 hours. The final product contained 3.0 weight percent zinc and 4.8 weight percent chromium.

CATALYST C

A 10.00 gram quantity of the above described acid leached zeolite material was impregnated with an 8.43 gram quantity of a solution containing 10 parts by weight hydrated zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$), 6 parts by weight hydrated ammonium molybdate ($(NH_4)_6Mo_7O_{24}{\cdot}6H_2O$), and 84 parts by weight water. The impregnation solution had an atomic ratio of molybdenum to zinc of 1.011. The impregnated, acid leached zeolite was then dried in air at 125°C for 16 hours followed by treatment in a steam atmosphere for 6 hours at 650°C. The final product contained 1.822 weight percent zinc and 2.703 weight percent molybdenum.

CATALYST D

A 10.00 gram quantity of the above described acid leached zeolite material was impregnated with a 8.0 gram quantity of a solution containing 5.4 parts by weight hydrated zinc nitrate ($Zn(NO_3)_2 \cdot H_2O$), 2.25 parts by weight hydrogen borate (H_3BO_3), and 42.35 parts by weight water. The impregnation solution had an atomic ratio of boron to zinc of 2.005. The impregnated, acid-leached zeolite was then dried in air at 125°C for 16 hours followed by treatment in a steam atmosphere for 2 hours at 650°C. The final product contained 1.851 weight percent zinc and 0.614 weight percent molybdenum.

CATALYST E

A 10.00 gram quantity of the above-described acid-leached zeolite material was impregnated with 9.24 gram quantity of a solution containing 4 parts by weight titanium tetrachloride ($TiCl_4$), 2.8 parts by weight zinc chloride ($ZnCl_2$), and 93.2 parts by weight of an aqueous solution of HCl containing 7.40 weight percent HCl. The impregnation solution had an atomic ratio of titanium to zinc of 1.026. The impregnated, acid-leached zeolite was then dried in air at 125°C for 16 hours followed by treatment in a steam atmosphere for 6 hours at 650°C. The steam treated material is then exposed to a helium gas atmosphere at a temperature of 538°C for 2 hours. The final product contained 1.224 weight percent zinc and 0.920 weight percent titanium.

CATALYST F

A 10.00 gram quantity of the above-described acid-leached zeolite material was impregnated with an 8.98 gram quantity of a solution containing 6.00 parts by weight hydrated zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$), 2.00 parts by weight of an 85 weight percent aqueous phosphoric acid (H_3PO_4) solution, and 32.00 parts by weight water. The impregnation solution had an atomic ratio of phosphorous to zinc of 0.86. The impregnated, acid-leached zeolite was then dried followed by treatment with steam for 6 hours at 650°C and then with helium for 2 hours at 525°C. The final product contained 2.823 weight percent zinc and 1.151 weight percent phosphorous.

CATALYST G

A 16.27 gram quantity of the above-described acid-leached zeolite material was impregnated with a 13.86 gram quantity of a 15 weight percent aqueous solution of hydrated zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$). The impregnated, acid-leached zeolite was dried in air at 125°C for 16 hours followed by treatment with steam for 6 hours at 625°C. The steam treated material was then exposed to a helium gas atmosphere at a temperature in the range of 625°C to 538°C for a period of 6 hours. The final product contained 2.700 weight percent zinc.

CATALYST H

A 20.00 gram calcined sample of the above-described ZSM-5 catalyst (not acid leached) was impregnated with an 11.83 gram quantity of a 15 weight percent aqueous solution of hydrated zinc nitrate. This impregnated, calcined zeolite was then air dried followed by treatment in a steam for 6 hours at 625°C. The steam treated material was then exposed to a helium gas atmosphere at a temperature of 538°C for 6 hours. The final product contained 1.899 weight percent zinc.

EXAMPLE II

This example illustrates the use of the zeolite materials described in Example I as catalysts in the conversion of a gasoline feed to benzene, toluene and xylenes (BTX) and lower olefins (ethylene, propylene).

For each of the test runs, a 5.0 g sample of the catalyst materials described in Example I was placed into a stainless steel tube reactor (length: about 18 inches; inner diameter: about 0.5 inch). Gasoline boiling range feedstock from a catalytic cracking unit of a refinery was passed through the reactor at a flow rate of about 14 ml/hour, at a temperature of about 600°C and at atmospheric pressure (about 0 psig). The formed reaction product exited the reactor tube and passed through several ice-cooled traps. The liquid portion remained in these traps and was weighed, whereas the volume of the gaseous portion which exited the traps was measured in a “wet test meter”. Liquid and gaseous product samples (collected at hourly intervals) were analyzed by means of a gas chromatograph. Results of eight test runs for Catalysts A through H are summarized in Table I. All test data were obtained after 8 hours on stream.

Table I

Catalyst	Description of Promoter	BTX Yield	Light Olefin Yield*	Sum of BTX and olefin	Ratio of olefin to BTX	Percent Coke	Comment
A (Invention)	Zinc and Silicon	45	23	68	0.51	0.7	Low coke, good olefin/BTX ratio and olefin + BTX yield
B (Invention)	Zinc and Chromium	40.9	19.8	60.7	0.48	1.0	Low coke, good olefin/BTX ratio and olefin + BTX yield
C (Invention)	Zinc and Molybedenum	34.0	26.6	60.6	0.66	1.0	Low coke, good olefin/BTX ratio and olefin + BTX yield
D (Invention)	Zinc and Boron	38.5	20.0	58.5	0.52	0.3	Low coke, good olefin/BTX ratio and olefin + BTX yield
E (Invention)	Zinc and Titanium	50	14.6	64.6	0.29	0.7	Low coke, good BTX yield
F (Invention)	Zinc and Phosphorus	54	15	69	0.28	0.7	Low coke, good olefin + BTX yield
G (Invention)	Zinc only, acid leached zeolite	40	13	53	0.33	0.6	Low BTX and olefin yield
H (Control)	Zinc only, zeolite is not acid leached	38	20	58	0.52	2.7	High coke, low BTX yield

*Ethylene + Propylene

The test data presented in Table 1 show that the inventive catalysts exhibited considerably less coking (which results in excessive catalyst deactivation) than Control Catalyst H and yielded more BTX and olefin and a greater ratio of olefin to BTX than Control Catalyst G. The improvement in catalyst performance is believed to be due to the dual metallic promoted acid leached zeolite. The dual metal promoter is zinc in combination with another metal.

It is also noted that the non-acid leached zeolite containing only zinc produces a significant amount of coke with a somewhat reasonable yield of BTX and olefin. The acid leached zeolite containing only zinc lowers the coke production rate, but it also undesirably reduces the olefin to BTX ratio and yield of BTX and olefin. The use of the secondary metals, in combination with zinc, suppresses coke formation while also enhancing the yield of BTX and olefins and in most cases improving the ratio of olefin to BTX in the product.

Reasonable variations, modifications, and adaptations can be made within the scope of the disclosure and the appended claims without departing from the scope of this invention.

CLAIMS

1. A catalyst composition comprising an acid treated zeolite and further comprising zinc and at least one other element from Group 4B, Group 6B, Group 3A, Group 4A or Group 5A of the periodic table of elements.

2. A composition according to claim 1, wherein the zinc is present in the range upwardly to about 10 weight percent and said at least one other element is present in the range upwardly to about 15 weight percent.

3. A composition according to claim 2, wherein the atomic ratio of the at least one other element to zinc is in the range of from about 0.1:1 to about 10:1.

4. A composition according to claim 2, wherein the zinc is present in the range from about 0.05 to about 8 weight percent and said at least one other element present in the range from about 0.1 to about 12 weight percent.

5. A composition according to claim 4, wherein the atomic ratio of said at least one other element to zinc is in the range of from about 0.2:1 to about 5:1 weight percent.

6. A composition according to claim 4, wherein the zinc is present in the range from 0.1 to 6 weight percent and said at least one other element is present in the range from 0.2 to 10 weight percent.

7. A composition according to claim 6, wherein the atomic ratio of said at least one other element to zinc is in the range of from 0.5:1 to 3:1.

8. A composition according to claim 1, which has undergone a first heat treatment whereby said composition is contacted with a first gas under high temperature conditions to thereby provide a first heat treated material.

9. A composition according to claim 8, wherein said first heat treated material has undergone a second heat treatment whereby said first heat treated material is further contacted with a second gas under high temperature conditions to thereby provide a second heat treated material.

10. A composition according to claim 9, wherein said first gas and said second gas are individually an inert gas, a reducing gas, air, oxygen, steam or a mixture of any two or more of said gases.

11. A composition according to claim 9, wherein said first heat treatment is conducted at a temperature in the range of from about 30°C. to about 400°C. and

for a time period of from about 0.1 hour to about 30 hours.

12. A composition according to claim 9, wherein said second heat treatment is conducted at a temperature in the range of from about 400°C. to about 1200°C. and for a time period of from about 0.1 hour to about 12 hours.

13. A composition according to claim 1, wherein the acid-treated zeolite has been impregnated with said zinc and said at least one other element.

14. A composition according to claim 13, wherein the impregnation of said acid treated zeolite includes contacting said acid treated zeolite with a solution containing a first salt of said zinc and a second salt of said at least one other metal.

15. A composition according to claim 1, wherein said at least one other element is titanium, chromium, molybdenum, boron, silicon or phosphorus.

16. A process for the conversion of hydrocarbons which comprises contacting under conversion conditions a hydrocarbon feed with a composition according to any one of the preceding claims, wherein a conversion product includes aromatics and olefins.

17. A process according to claim 16, wherein said hydrocarbon feed comprises hydrocarbon containing 2-16 carbon atoms per molecule.

18. A process according to claim 16, wherein said conversion conditions include a reaction temperature in the range of from about 400°C. to about 800°C. and a contacting pressure in the range of from subatmospheric pressure upwardly to about 500 psia.

19. A process according to claim 18, wherein said conversion conditions further include a charge rate of said hydrocarbon feed such that the weight hourly space velocity is in the range of from exceeding 0 hour^{-1} upwardly to about 1000 hour^{-1}.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/07400

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B01J 23/00, 23/02, 29/04, 29/06, 21/00; C07C 4/12, 15/00
US CL :Please See Extra Sheet.
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)

U.S. : 502/61, 64, 71, 77, 306, 307, 340, 341, 342, 343; 585/407, 418, 486

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS
search terms: zinc, titanium, chrominum, molybdenum, boron, phosphorus

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,490,569 A (CHU et al) 25 Dec 1984, the abstract, col. 1, line 51 through col. 3, line 10, col. 8, lines 1-55, col. 10, lines 18-33, col. 11, line 1 through col. 12 , line 50.	1-19
P, X	US 5,686,374 A (NAKAOKA) 11 November 1997, the abstract, col. 1, line 51 through col. 2, line 25, col. 3, line 8 through col. 4, line 20; col. 3, lines 54-62; examples.	1-15

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"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
"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)	"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
"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	"&"	document member of the same patent family

Date of the actual completion of the international search

22 MAY 1998

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER:
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502/61, 64, 71, 77, 306, 307, 340, 341, 342, 343; 585/407, 418, 486