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(71) Applicant (for all designated States except US):
CHEVRON PHILLIPS CHEMICAL COMPANY,
LP [US/US]; 10001 Six Pines Drive, The Woodlands, TX
77380 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **WU, An-Hsiang**
[US/US]; 4723 Brook Shadow Drive, Kingwood, TX
77345 (US).

(74) Agents: **CONLEY ROSE, P.C.** et al.; 5700 Granite Park-
way, Suite 330, Plano, TX 75024 (US).

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(54) Title: AROMATIZATION CATALYST AND METHODS OF MAKING AND USING SAME

(57) Abstract: A method of making a catalyst composition, comprising impregnating a large pore zeolite support with a platinum precursor and at least one organic ammonium halide precursor. In an embodiment, the ammonium halide precursor is represented by the formula N(R)₄X, where X is a halide and R is a substituted or unsubstituted carbon chain molecule having 1-20 carbon atoms wherein each R may be the same or different. In an embodiment, the ammonium halide precursor comprises at least one acid halide and at least one ammonium hydroxide represented by the formula N(R')₄OH, where R' is hydrogen or a substituted or unsubstituted carbon chain molecule having 1-20 carbon atoms wherein each R' may be the same or different. A process for aromatizing a hydro-carbon using said catalyst composition.



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AROMATIZATION CATALYST AND METHODS OF MAKING AND USING SAME

FIELD OF THE INVENTION

[0001] The present invention relates to an aromatization catalyst and associated methods of making and using same, wherein the catalyst comprises a large pore zeolite support impregnated with a platinum precursor and at least one organic ammonium halide precursor.

BACKGROUND

[0002] Large pore zeolite catalysts are useful to dehydrocyclize aliphatic hydrocarbons to produce aromatic hydrocarbons. For example, large pore catalysts are useful for reforming petroleum naphtha (e.g., C₆-C₈) into benzene, toluene, and xylenes. Examples of such aromatization catalysts include large pore zeolite supports impregnated with a mixture of tetraamineplatinum chloride, ammonium chloride (NH₄Cl) and ammonium fluoride (NH₄F). Due to the commercial importance of such catalysts, an ongoing need exists from improved aromatization catalysts and methods of making and using same.

SUMMARY OF THE INVENTION

[0003] Disclosed herein is a method of making a catalyst composition, comprising impregnating a large pore zeolite support with a platinum precursor and at least one organic ammonium halide precursor. In an embodiment, the ammonium halide precursor is represented by the formula N(R)₄X, where X is a halide and R is a substituted or unsubstituted carbon chain molecule having 1-20 carbon atoms wherein each R may be the same or different. In an embodiment, the ammonium halide precursor comprises at least one acid halide and at least one ammonium hydroxide represented by the formula N(R')₄OH, where R' is hydrogen or a substituted or unsubstituted carbon chain molecule having 1-20 carbon atoms wherein each R' may be the same or different. In an embodiment the organic ammonium halide precursor comprises (a) a compound represented by the formula N(R)₄X, where X is a halide and where R represents a hydrogen or a substituted or unsubstituted carbon chain molecule having 1-20 carbons wherein each R may be the same or different and (b) at least one acid halide and at least one ammonium

hydroxide represented by the formula $N(R')_4OH$, where R' is hydrogen or a substituted or unsubstituted carbon chain molecule having 1-20 carbon atoms wherein each R' may be the same or different.

[0004] Disclosed herein is a process for aromatizing a hydrocarbon, comprising contacting hydrocarbons with a catalyst under suitable reaction conditions for aromatizing the hydrocarbons, wherein the catalyst is formed by a process comprising impregnating a large pore zeolite support with a platinum precursor and at least one organic ammonium halide precursor.

[0005] Other aspects and features of the invention will become apparent from review of the detailed description and the claims.

DETAILED DESCRIPTION OF THE INVENTION

[0006] In an embodiment, the organic ammonium halide precursor comprises one or more compounds represented by the formula $N(R)_4X$, where X is a halide and where R represents a hydrogen or a substituted or unsubstituted carbon chain molecule having 1-20 carbons wherein each R may be the same or different. In an embodiment, R is selected from the group consisting of methyl, ethyl, propyl, butyl, and combinations thereof, more specifically methyl. Examples of suitable organic ammonium precursor is represented by the formula $N(R)_4X$ include tetraalkylammonium halides such as tetramethylammonium chloride, tetramethylammonium fluoride, tetraethylammonium chloride, tetraethylammonium fluoride, tetrapropylammonium chloride, tetrapropylammonium fluoride, tetrabutylammonium chloride, tetrabutylammonium fluoride, methyltriethylammonium chloride, methyltriethylammonium fluoride, and combinations thereof.

[0007] In an embodiment, the organic ammonium halide precursor comprises at least one acid halide and at least one ammonium hydroxide represented by the formula $N(R')_4OH$, where R' is hydrogen or a substituted or unsubstituted carbon chain molecule having 1-20 carbon atoms wherein each R' may be the same or different. In an embodiment, R' is selected from the group consisting of methyl, ethyl, propyl, butyl, and combinations thereof, more specifically methyl. Examples of suitable ammonium hydroxide represented by the formula $N(R')_4OH$ include ammonium hydroxide, tetraalkylammonium hydroxides such as tetramethylammonium hydroxide, tetraethylammonium hydroxide,

tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, and combinations thereof. Examples of suitable acid halides include HCl, HF, HBr, HI, or combinations thereof.

[0008] In an embodiment the organic ammonium halide precursor comprises (a) as described previously, a compound represented by the formula $N(R)_4X$, where X is a halide and where R represents a hydrogen or a substituted or unsubstituted carbon chain molecule having 1-20 carbons wherein each R may be the same or different and (b) as described previously, at least one acid halide and at least one ammonium hydroxide represented by the formula $N(R')_4OH$, where R' is hydrogen or a substituted or unsubstituted carbon chain molecule having 1-20 carbon atoms wherein each R' may be the same or different.

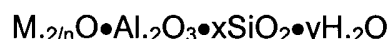
[0009] The halide precursor may further comprise an ammonium halide such as ammonium chloride, ammonium fluoride, or both in various combinations with the organic ammonium halide precursor compounds described previously. More specifically, ammonium chloride, ammonium fluoride, or both may be used with (a) as described previously, a compound represented by the formula $N(R)_4X$, where X is a halide and where R represents a hydrogen or a substituted or unsubstituted carbon chain molecule having 1-20 carbons wherein each R may be the same or different and/or (b) as described previously, at least one acid halide and at least one organic ammonium hydroxide represented by the formula $N(R')_4OH$, where R' is a substituted or unsubstituted carbon chain molecule having 1-20 carbon atoms wherein each R' may be the same or different. For example, a first fluoride or chloride precursor can be introduced as a tetraalkylammonium halide with a second fluoride or chloride precursor introduced as an ammonium halide. In an embodiment, tetraalkylammonium chloride is used with ammonium fluoride.

[0010] Supports for aromatization catalysts can generally include any inorganic oxide. These inorganic oxides include bound large pore aluminosilicates (zeolites), amorphous inorganic oxides and mixtures thereof. Large pore aluminosilicates include, but are not limited to, L-zeolite, Y-zeolite, mordenite and the like. Amorphous inorganic oxides include, but are not limited to, aluminum oxide, silicon oxide and titania. Suitable bonding agents for the inorganic oxides include, but are not limited to, silica, alumina, clays, titania and magnesium oxide.

[0011] Zeolite materials, both natural and synthetic, are known to have catalytic properties for many hydrocarbon processes. Zeolites typically are ordered porous crystalline aluminosilicates having structure with cavities and channels interconnected by channels. The cavities and channels throughout the crystalline material generally can be of a size to allow selective separation of hydrocarbons.

[0012] The term "zeolite" generally refers to a particular group of hydrated, crystalline metal aluminosilicates. These zeolites exhibit a network of SiO_4 and AlO_4 tetrahedra in which aluminum and silicon atoms are crosslinked in a three-dimensional framework by sharing oxygen atoms. In the framework, the ratio of oxygen atoms to the total of aluminum and silicon atoms is equal to 2. The framework exhibits a negative electrovalence which typically is balanced by the inclusion of cations within the crystal such as metals, alkali metals, alkaline earth metals or hydrogen.

[0013] L-type zeolite catalysts are a sub-group of zeolitic catalysts. Typical L-type zeolites contain mole ratios of oxides in accordance with the following formula:



wherein "M" designates at least one exchangeable cation such as barium, calcium, cerium, lithium, magnesium, potassium, sodium, strontium, and zinc as well as non-metallic cations like hydronium and ammonium ions which may be replaced by other exchangeable cations without causing a substantial alteration of the basic crystal structure of the L-type zeolite. The "n" in the formula represents the valence of "M", "x" is 2 or greater; and "y" is the number of water molecules contained in the channels or interconnected voids with the zeolite.

[0014] Bound potassium L-type zeolites, or KL zeolites, have been found to be particularly desirable. The term KL zeolite as used herein refers to L-type zeolites in which the principal cation M incorporated in the zeolite is potassium. As used in this application, a KL zeolite is one that has not been significantly cation-exchanged or impregnated with another metal unless the term KL zeolite is preceded by a modifier such as "platinum-impregnated" or the zeolite explicitly is referred to as a "KL supported Pt zeolite catalyst."

[0015] The platinum precursor can be any decomposable platinum compound. Examples of such compounds include, but are not limited to, ammonium tetrachloroplatinate, chloroplatinic acid, diammineplatinum (II) nitrite, bis-

(ethylenediamine)platinum (II) chloride, platinum (II) acetylacetonate, dichlorodiammine platinum, platinum (II) chloride, tetraammineplatinum (II) hydroxide, tetraammineplatinum chloride, and tetraammineplatinum (II) nitrate.

[0016] In an embodiment, a method for making an aromatization catalyst composition comprises the following steps: (1) predrying large pore zeolite support; (2) treating the zeolite support by impregnating the support with platinum and halide precursors; (3) optionally aging the impregnated support; (4) optionally drying the support; and (5) calcining the support.

[0017] Prior to impregnation, the zeolite support typically is dried under flowing or stationary gas selected from the group consisting of hydrogen, oxygen, air, helium, nitrogen, argon, and mixtures thereof. As an example, in some cases the gas can be air, and the drying can be performed from about 1 minute to about 20 hours and at a temperature from about 100° to about 600° C. Impregnation of the halide and platinum precursors into the zeolite support may be performed by any suitable method as known to those skilled in the art, such as insipient wetness.

[0018] In some embodiments, it may be desirable to age the impregnated catalyst support. This aging can be performed at temperatures from about subambient to about 200°C, at pressures from about ambient to about 500 psig for periods of time from about 1 minute to about 10 days and under conditions where the impregnated solid is stationary or moving. Ambient conditions are defined as environmental temperature at atmospheric pressure.

[0019] In some embodiments, it may be desirable to dry the impregnated catalyst support. The drying generally occurs in the presence of a gas, which can be air, oxygen, nitrogen, hydrogen, or any inert gas, or mixtures thereof. As an example, it may be desirable to dry the impregnated catalyst in the presence of a gas comprising nitrogen and/or oxygen, for example enriched air or diluted air, such that it contains from about 0.1 vol % to about 100 vol % nitrogen, alternatively from about 0.1 vol % to about 60 vol % nitrogen, alternatively from about 0.1 vol % to about 30 vol % nitrogen. In an embodiment, the gas is a mixture of air and nitrogen. This drying can be performed at temperatures from about 0° to about 300°C, alternatively from about 25° to about 250°C, alternatively from about 50° to about 200°C, and at pressures from about 0.01 mmHg to about 500 psig, alternatively from about 0.01 mmHg to about 50 psig, alternatively from about 0.01 mmHg to about 5 psig,

alternatively at subambient pressure, also referred to as vacuum drying; for periods of time from about 1 minute to about 20 hours; under conditions where the gas is stationary or moving; and under conditions where the impregnated solid is either stationary or moving. During the drying step, the temperature can be optionally increased from ambient temperature to the desired drying temperature in a controlled manner, preferably through a series of temperature increases followed by temperature hold periods. The drying step may be carried out in any suitable drying equipment, for example a rotary drier.

[0020] In some embodiments, it may be desirable to calcine the impregnated catalyst support. The calcination generally occurs in the presence of a gas, which can be air, oxygen, nitrogen, hydrogen, or any inert gas, or mixtures thereof. As an example, it may be desirable to calcine in the presence of a gas comprising nitrogen and/or oxygen, for example enriched air or diluted air, such that it contains from about 0.1 vol % to about 100 vol % oxygen, alternatively from about 1 vol % to about 80 vol % oxygen, alternatively from about 5 vol % to about 60 vol % oxygen. In an embodiment, the gas is a mixture of air and nitrogen, for example having a volume ratio air to nitrogen of from about 1:1 to about 1:3. The calcination step can be performed at temperatures from about 50° to about 600°C, alternatively from about 160° to about 550°C, alternatively from about 275° to about 500°C; under pressures from ambient to 500 psig; for periods of time from about 1 minute to about 100 hours; under conditions where the gas is stationary or moving; and under conditions where the impregnated catalyst support is stationary or moving. During the calcination step, the temperature is increased from ambient temperature in a controlled manner, preferably through a series of temperature increases followed by temperature hold periods. The calcining step may be carried out in any suitable calcining equipment, for example a rotary calciner or a belt conveyed calciner.

[0021] In an embodiment, a KL-zeolite supported platinum aromatization catalyst is prepared by impregnating a KL-zeolite-support with tetramethylammonium chloride (TMAC), and/or tetramethylammonium fluoride (TMAF), and tetraamineplatinum chloride (TAPC); and calcinating the impregnated zeolite. In an embodiment, a KL-zeolite supported platinum aromatization catalyst is prepared by impregnating a KL-zeolite-support with ammonium fluoride, tetramethylammonium

chloride (TMAC), and tetraamineplatinum chloride (TAPC); and calcinating the impregnated zeolite.

[0022] In another aspect, the invention provides a process for reforming a hydrocarbon, for example aromatization, isomerization, dehydrogenation, and combinations thereof. For example, such a process could include contacting a hydrocarbon stream with a catalyst as described herein under suitable reaction conditions for aromatization of hydrocarbons, for example a temperature in the range of about 800° F to about 1050° F. In an embodiment, hydrogen is recovered as a product from the reforming process. In an embodiment, the catalyst comprises a composition made according to one of the methods described herein.

[0023] In some embodiments, it may be desirable to provide a catalyst having less than about 1.3 wt% chlorine, alternatively less than about 1.0 wt% chlorine, alternatively less than about 0.5 wt% chlorine. In other embodiments, it may be desirable to provide a catalyst having less than about 1.3 wt% fluorine, alternatively less than about 1.0 wt% fluorine, alternatively less than about 0.5 wt% fluorine. Similarly, in other embodiments, it may be desirable to provide a catalyst having less than about 1.0 wt% platinum, alternatively less than about 0.6 wt% platinum, alternatively from about 0.2 to about 0.7 wt% platinum. In various embodiments, the atomic ratio of Pt : F : Cl in the catalyst is from about 1-0.5 : 3.3-1.7 : 10-5, respectively. As an example, the amount of fluorine, chlorine, and/or platinum in the catalyst can be controlled by controlling the amount of the respective precursors in the impregnation treatment.

[0024] In various embodiments, the catalyst composition comprises less than or equal to about 1 wt% platinum and has a T_{60} temperature of less than about 960°F and/or a deactivation rate of less than about 2.4 °F/day, alternatively a T_{60} temperature of less than about 935°F and/or a deactivation rate of less than about 1.5 °F/day.

[0025] In various embodiments, the catalyst composition comprises less than or equal to about 0.5 wt% platinum and has a T_{60} temperature of less than about 1010°F and/or a deactivation rate of less than about 36 °F/day, alternatively a T_{60} temperature of less than about 965°F and/or a deactivation rate of less than about 3.5 °F/day, alternatively a T_{60} temperature of less than about 935°F and/or a deactivation rate of less than about 1.2 °F/day.

[0026] In various embodiments, the catalyst composition comprises less than or equal to about 0.3 wt% platinum and has a T_{60} temperature of less than about 972°F and/or a deactivation rate of less than about 11.4 °F/day, alternatively a T_{60} temperature of less than about 950°F and/or a deactivation rate of less than about 1.5 °F/day, alternatively a T_{60} temperature of less than about 935°F and/or a deactivation rate of less than about 1.2 °F/day. The T_{60} temperature is defined as the temperature for a given feedstock at which the sum of the benzene wt% and toluene wt% in the reactor effluent is 60 wt%. Once this conversion rate is achieved at T_{60} , the deactivation rate is defined as a degree increase in temperature per day to maintain this conversion rate.

EXAMPLES

[0027] In each of the following examples, the prepared catalysts were ground, sieved to 20-40 mesh, and placed in a reactor comprising a metal reactor vessel in a temperature controlled furnace. After reducing the catalyst under flowing hydrogen, a feed stream of aliphatic hydrocarbon and hydrogen was introduced to the reactor vessel at a feed rate of 22mL/min and a pressure of 50 psig to obtain performance data. The reactor effluent composition was analyzed by gas chromatography to indicate the amount of benzene and toluene.

[0028] The catalysts prepared in accordance with Examples 1-11 below illustrate effects of varying the amount of platinum impregnated into the KL-zeolite catalyst when compared to Aromax® II catalyst. Under the present invention, significantly lower T_{60} values and deactivation rates can be obtained by preparing KL supported Pt zeolite catalysts using TMAF in place of NH_4F and using a tetraalkylammonium chloride in place of NH_4Cl . The results are summarized in Table 1.

Example 1

[0029] A platinum-impregnated KL-zeolite catalyst containing 1.0 wt% platinum is prepared in the following manner. An impregnating mixture of 0.10g TAPC, 0.45g TMAF, 0.10g TMAC and 2.50g water is formed and added to a container containing 5.0g of a silica bound KL-zeolite extrudates that has been calcined for 2 hours at 538°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours at 95°C. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C (ramp rate is 0.5°C/min) and then calcined at 300°C for another 2 hours (ramp

rate is 0.25°C/min). The resultant catalyst contains 1.07 wt% Pt, 1.02 wt% Cl and 1.0 wt% F.

Example 2 (comparison)

[0030] A platinum-impregnated KL-zeolite catalyst containing 0.5 wt% platinum is prepared in the following manner. An impregnating mixture of 0.05g TAPC, 0.10g NH₄F, and 0.05g NH₄Cl is formed and added to a container containing 5.0g of a silica bound KL-zeolite predried for 2 hours at 538°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours at 95°C. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C (ramp rate is 0.5°C/min) and then calcined at 300°C for another 2 hours (ramp rate is 0.25°C/min). The resulting catalyst contains 0.55 wt% Pt, 0.5 wt% Cl and 1.0 wt% F.

Example 3

[0031] A platinum-impregnated KL-zeolite catalyst containing 0.5 wt% platinum is prepared in the following manner. An impregnating mixture of 0.05g TAPC, 0.45g TMAF, 0.10g TMAC and 2.50g water is formed and added to a container containing 5.0g of a KL-zeolite predried for 2 hours at 538°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours at 95°C. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C (ramp rate is 0.5°C/min) and then calcined at 300°C for another 2 hours (ramp rate is 0.25°C/min). The resulting catalyst contains 0.54 wt% Pt, 0.83 wt% Cl and 1.0 wt% F.

Example 4 (comparison)

[0032] A platinum-impregnated KL-zeolite catalyst containing 0.3 wt% platinum is prepared in the following manner. An impregnating mixture of 0.10g TAPC, 0.40g NH₄F, and 0.8g NH₄Cl (0.8% aqueous solution) is formed and added to a container containing 5.0g of a KL-zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours ambient temperature. The impregnated KL-zeolite is dried in a vacuum for four hours at 170°C and then calcined at 350°C for 2 hours. The resulting catalyst contains 0.30 wt% Pt, 0.34 wt% Cl and 1.1 wt% F.

Example 5

[0033] A platinum-impregnated KL-zeolite catalyst containing 0.3 wt% platinum is prepared in the following manner. An impregnating mixture of 0.10g TAPC, 0.40g NH₄F, and 0.14g TMAC is formed and added to a container containing 18.23g of a

KL-zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours ambient temperature. The impregnated KL-zeolite is dried in a vacuum for four hours at 170°C and then calcined at 350°C for 2 hours. The resulting catalyst contains 0.30 wt% Pt, 0.32 wt% Cl and 1.12 wt% F.

Example 6

[0034] A platinum-impregnated KL-zeolite catalyst containing 0.3 wt% platinum is prepared in the following manner. An impregnating mixture of 0.10g TAPC, 1.78g TMAF, 0.10g TMAC and 6.90g water is formed and added to a container containing 18.23g of a KL-zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for 2 hours. The resulting catalyst contains 0.30 wt% Pt, 0.30 wt% Cl and 1.12 wt% F.

Example 7

[0035] A platinum-impregnated KL-zeolite catalyst containing 0.3 wt% platinum is prepared in the following manner. An impregnating mixture of 0.10g TAPC, 1.84g TMAF, and 7g NH₄Cl is formed and added to a container containing 18.23g of a KL-zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for 2 hours. The resulting catalyst contains 0.30 wt% Pt, 0.31 wt% Cl and 1.15 wt% F.

Example 8

[0036] A platinum-impregnated KL-zeolite catalyst containing 0.29 wt% platinum is prepared in the following manner. An impregnating mixture of 0.1g TAPC, 1.60g TMAF and 0.11g TMAC is formed and added to a container containing 18.22g of a KL-zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for 2 hours. The resulting catalyst contains 0.29 wt% Pt, 0.30 wt% Cl and 1.00 wt% F.

Example 9

[0037] A platinum-impregnated KL-zeolite catalyst containing 0.3 wt% platinum is prepared in the following manner. An impregnating mixture of 0.10g TAPC, 2.05g TMAF and 0.10g TMAC is formed and added to a container containing 18.25g of a KL-zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for 2 hours. The resulting catalyst contains 0.30 wt% Pt, 0.30 wt% Cl and 1.28 wt% F.

Example 10

[0038] A platinum-impregnated KL-zeolite catalyst containing 0.3 wt% platinum is prepared in the following manner. An impregnating mixture of 0.10g TAPC, 1.75g TMAF, 0.18g tetraethylammonium chloride (TEAC) and 6.50g water is formed and added to a container containing 18.24g of a KL-zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 16 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for 2 hours. The resulting catalyst contains 0.30 wt% Pt, 0.32 wt% Cl and 1.09 wt% F.

Example 11

[0039] A platinum-impregnated KL-zeolite catalyst containing 0.3 wt% platinum is prepared in the following manner. An impregnating mixture of 0.10g TAPC, 1.75g TMAF, 0.30g tetrabutylammonium chloride (TBAC) and 6.50g water is formed and added to a container containing 18.29g of a KL-zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for 2 hours. The resulting catalyst contains 0.30 wt% Pt, 0.32 wt% Cl and 1.09 wt% F.

TABLE 1

Example	Pt (wt%)	Pt Source	Fluorine Precursor	Chlorine Precursor	Initial T ₆₀ *	Deactivation Rate (°F/day)
Aromax II (comparison)	1.0%	TAPC	NH ₄ F	NH ₄ Cl	935	1.416
1	1.0%	TAPC	TMAF	TMAC	911	1.486

2 (comparison)	0.5%	TAPC	NH ₄ F	NH ₄ Cl	981	36.211
3	0.5%	TAPC	TMAF	TMAC	933	3.441
4 (comparison)	0.3%	TAPC	NH ₄ F	NH ₄ Cl	961	11.416
5	0.3%	TAPC	NH ₄ F	TMAC	979	8.99
6	0.3%	TAPC	TMAF	TMAC	933	1.28
7	0.3%	TAPC	TMAF	NH ₄ Cl	937	5.07
8	0.29%	TAPC	TMAF	TMAC	940	7.28
9	0.3%	TAPC	TMAF	TMAC	951	16.79
10	0.3%	TAPC	TMAF	TEAC	945	6.85
11	0.3%	TAPC	TMAF	TBAC	933	0.67

* Temperature (°F) at which the sum of the benzene wt% and toluene wt% in the reactor effluent is 60 wt%.

[0040] The results in Table 1 demonstrate that the substitution of TMAF and TMAC for NH₄F and NH₄Cl, respectively, significantly decreases the deactivation rate and/or the T₆₀ value. Example 1 used an impregnation comprising TAPC, TMAC and TMAF and produced a 1.0 wt% Pt. When compared to the Aromax® II catalyst, there was a 24° F reduction in the T₆₀ value. By reducing the amount of platinum from 1.0 wt% to 0.5 wt%, as shown in the comparison of Examples 2 and 3, the catalyst made using TAPC, NH₄F and NH₄Cl (Example 2) had a 75° F increase in the T₆₀ value and a significant increase in the deactivation rate when compared to the Aromax® II catalyst which contained 1 wt% platinum.

[0041] While the catalyst containing 0.5 wt% platinum made by using TAPC, TMAF and TMAC (Example 3) did not show improvement over the Aromax® II catalyst with respect to the T₆₀ value or the deactivation rate, the catalyst was a significant improvement over Example 2 which is an Aromax® II type catalyst, but containing 0.5 wt% platinum.

[0042] Examples 4 and 6 show the differences between Aromax® II catalyst and an Aromax® II type catalyst containing 0.3 wt% platinum and a catalyst prepared using TAPC, TMAF and TMAC containing 0.3 wt% platinum. The Aromax® II type catalyst (Example 4) showed a significant increase in the T₆₀ value and in the deactivation rate when compared to the Aromax® II catalyst (comparison) and a platinum-impregnated KL-zeolite catalyst of the invention made in accordance with Example 6.

[0043] Example 4 and 5 show the differences between an Aromax® II type catalyst containing 0.3 wt% platinum and a catalyst prepared using TAPC, NH₄F,

and TMAF containing 0.3 wt% platinum. The Aromax® II type catalyst (Example 4) showed a significant increase in the deactivation rate when compared to the platinum-impregnated KL-zeolite catalyst of the invention made in accordance with Example 5.

[0044] Examples 7-11 show improved T_{60} values and lower deactivation rates than comparative Example 4 when TMAF was substituted for NH_4F . Examples 8 and 9 show the effects of fluorine and chlorine loading, as shown in more detail below.

[0045] Examples 3, 12, 13, and 14 in Table 2 illustrate effects on T_{60} value and the deactivation rate when the amount of chlorine in the catalyst is varied. Examples 12, 13, and 14 were prepared as follows:

Example 12

[0046] A platinum KL-zeolite containing 0.5 wt% platinum is prepared in the following manner. An impregnating mixture of 0.05g TAPC, 0.45g TMAF, 0.02g TMAF and 2.0g water is formed and added to a container containing 5.0g of a KL-zeolite predried for 2 hours at 538°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 300°C for another 2 hours.

Example 13

[0047] A platinum KL-zeolite containing 0.5 wt% platinum is prepared in the following manner. An impregnating mixture of 0.05g TAPC, 0.45g TMAF, 0.05g TMAF and 2.0g water is formed and added to a container containing 5.0g of a KL-zeolite predried for 2 hours at 538°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 300°C for another 2 hours.

Example 14

[0048] A platinum KL-zeolite containing 0.5 wt% platinum is prepared in the following manner. An impregnating mixture of 0.05g TAPC, 0.45g TMAF, and 2.0g water is formed and added to a container containing 5.0g of a KL-zeolite predried for 2 hours at 538°C. The mixture is impregnated into the KL-zeolite and then allowed

to stand for 20 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 300°C for another 2 hours.

TABLE 2

Example	Platinum wt %	Fluorine wt %	Chlorine wt %	Initial T ₆₀ [*]	Deactivation Rate (°F/day)
12	0.5	1.0	0.3	908	1.442
13	0.5	1.0	0.5	930	3.608
14	0.5	1.0	0.2	933	-0.456
3	0.5	1.0	0.8	933	3.441
2	0.5	1.0 (NH ₄ F)	0.5 (NH ₄ Cl)	981	36.211

* Temperature (°F) at which the sum of the benzene wt% and toluene wt% in the reactor effluent is 60 wt%.

[0049] Table 2 is a comparison of changes in the chlorine content of catalyst prepared using TAPC, TMAF and TMAC. The results demonstrate a progressively lower deactivation rate and T₆₀ value as chlorine levels are reduced. Example 2 demonstrates that a poor T₆₀ value and deactivation rate are obtained when the impregnate comprises NH₄F and NH₄Cl instead of TMAF and TMAC.

[0050] Examples 15-23 (in addition to Examples 6-11) set forth procedures for preparing KL supported Pt zeolite aromatization catalysts containing about 0.3 wt% platinum. The catalysts produced have varying amounts of fluorine and chlorine.

Example 15

[0051] A platinum KL-zeolite containing 0.3 wt% platinum is prepared in the following manner. An impregnating mixture of 0.05g TAPC, 0.08g TMAF and 4.5g water is formed and added to a container containing 9.26g of a KL-zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for another 2 hours.

Example 16

[0052] A platinum KL-zeolite containing 0.3 wt% platinum is prepared in the following manner. An impregnating mixture of 0.16g TAPC, 2.55g TMAF, 8.0g TMAC and 7.0g water is formed and added to a container containing 29.50g of a KL-

zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for another 2 hours.

Example 17

[0053] A platinum KL-zeolite containing 0.3 wt% platinum is prepared in the following manner. An impregnating mixture of 0.10g TAPC, 1.28g TMAF, 0.07g TMAC and 7.0g water is formed and added to a container containing 18.26g of a KL-zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for another 2 hours.

Example 18

[0054] A platinum KL-zeolite containing 0.3 wt% platinum is prepared in the following manner. An impregnating mixture of 0.10g TAPC, 1.60g TMAF, 0.07g TMAC and 7.0g water is formed and added to a container containing 18.24g of a KL-zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 68 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for another 2 hours.

Example 19

[0055] A platinum KL-zeolite containing 0.3 wt% platinum is prepared in the following manner. An impregnating mixture of 0.05g TAPC, 0.80g TMAF, 0.049g TMAC and 4.5g water is formed and added to a container containing 9.26g of a KL-zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for another 2 hours.

Example 20

[0056] A platinum KL-zeolite containing 0.3 wt% platinum is prepared in the following manner. An impregnating mixture of 0.10g TAPC, 1.78g TMAF, 0.07g TMAC and 7.0g water is formed and added to a container containing 18.23g of a KL-zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite

and then allowed to stand for 20 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for another 2 hours.

Example 21

[0057] A platinum KL-zeolite containing 0.3 wt% platinum is prepared in the following manner. An impregnating mixture of 0.10g TAPC, 1.92g TMAF, 0.07g TMAC and 7.0g water is formed and added to a container containing 18.24g of a KL-zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for another 2 hours.

Example 22

[0058] A platinum KL-zeolite containing 0.3 wt% platinum is prepared in the following manner. An impregnating mixture of 0.50g TAPC, 0.82g TMAF, 0.06g TMAC and 4.0g water is formed and added to a container containing 9.11g of a KL-zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for another 2 hours.

Example 23

[0059] A platinum KL-zeolite containing 0.3 wt% platinum is prepared in the following manner. An impregnating mixture of 0.05g TAPC, 0.82g TMAF, 0.10g TMAC and 4.0g water is formed and added to a container containing 9.11g of a KL-zeolite that has been baked for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for another 2 hours.

[0060] The T_{60} and deactivation rate data for the catalysts prepared in accordance with Examples 15 - 23 as well as Examples 6 - 11 are summarized in Table 3.

TABLE 3

Example	Platinum wt%	Fluorine wt%	Chlorine wt%	Initial T ₆₀ *	Deactivation Rate (°F/day)
15	0.30	1.00	0.11	980	0.51
16	0.30	1.00	0.18	929	0.76
17	0.30	0.80	0.23	928	0.79
18	0.30	1.00	0.23	949	0.37
19	0.30	0.99	0.23	943	0.18
20	0.30	1.12	0.23	948	1.29
21	0.30	1.21	0.23	934	0.03
22	0.30	1.02	0.32	930	-0.006
6	0.30	1.12	0.30	933	-0.59
7	0.30	1.15	0.31	937	5.07
8	0.29	1.00	0.30	940	7.28
9	0.30	1.28	0.30	951	16.79
10	0.30	1.09	0.32	945	6.85
11	0.30	1.09	0.32	933	0.67
23	0.31	1.04	0.49	946	0.44

* Temperature (°F) at which the sum of the benzene wt% and toluene wt% in the reactor effluent is 60 wt%.

[0061] The results of Table 3 show that satisfactory T₆₀ values and low deactivation rates can be obtained from a low-platinum load catalyst formed by using the TAPC, TMAF and TMAc impregnate (Examples 16-23) to prepare the catalyst on a KL-zeolite support. The results show further that when TMAF is used in place of NH₄F, the catalyst has lower T₆₀ values and lower deactivation rates than catalysts containing 0.3 wt.% and 0.5 wt.% platinum prepared using an impregnate containing TAPC, NH₄F and NH₄Cl. See comparative Examples 2 and 4 in Table 1.

[0062] Table 4 is a comparison of changes in the fluorine impregnating agent used to prepare the catalyst.

Example 24

[0063] A platinum KL-zeolite containing 1.0 wt% platinum is prepared in the following manner. An impregnating mixture of 0.20g TAPC and 4.5g water is formed and added to a container containing 10.0g of a KL-zeolite predried for 2 hours at 538°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 16 hours at 75°C and then 2 hours at 170°C. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 300°C for another 2 hours.

Example 25

[0064] A platinum KL-zeolite containing 1.0 wt% platinum is prepared in the following manner. An impregnating mixture of 0.20g TAPC, 0.10g ammonium chloride and 4.8g water is formed and added to a container containing 10.0g of a KL-zeolite predried for 2 hours at 538°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 10 hours at 95°C. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 160°C and then calcined at 300°C for another 2 hours.

Example 26

[0065] A platinum KL-zeolite containing 1.0 wt% platinum is prepared in the following manner. An impregnating mixture of 0.20g TAPC, 0.20g TMAC and 4.8g water is formed and added to a container containing 10.0g of a KL-zeolite predried for 2 hours at 538°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 16 hours at 95°C, and then 2 hours at 160°C. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 300°C for another 2 hours.

Example 27

[0066] A platinum KL-zeolite containing 1.0 wt% platinum is prepared in the following manner. An impregnating mixture of 0.20g TAPC, 0.15g ammonium chloride, 0.2g ammonium fluoride and 4.5g water is formed and added to a container containing 10.0g of a KL-zeolite predried for 2 hours at 538°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 16 hours at 70°C. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 300°C for another 2 hours.

Example 28

[0067] A platinum KL-zeolite containing 1.0 wt% platinum is prepared in the following manner. An impregnating mixture of 0.10g TAPC, 0.1g ammonium fluoride, 0.10g TMAC and 2.4g water is formed and added to a container containing 5.0g of a KL-zeolite predried for 2 hours at 538°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 20 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for another 2 hours.

[0068] The T_{60} and deactivation rate data for the catalysts prepared in accordance with Examples 24 - 28 is summarized in Table 4.

TABLE 4

Example	Pt (wt%)	Pt Source	Fluorine Precursor	Chlorine Precursor	Initial T ₆₀ *	Deactivation Rate (°F/day)
24	1.0	TAPC	None	None	930	14.86
25	1.0	TAPC	None	NH ₄ Cl	965	26.697
26	1.0	TAPC	None	TMAC	933	38.444
27	1.0	TAPC	NH ₄ F	NH ₄ Cl	935	2.472
28	1.0	TAPC	NH ₄ F	TMAC	920	0.250

* Temperature (°F) at which the sum of the benzene wt% and toluene wt% in the reactor effluent is 60 wt%.

[0069] The results of Table 4 show that satisfactory T₆₀ values and low deactivation rates can be obtained by using a TAPC, TMAC and ammonium fluoride impregnate to prepare the catalyst on a KL-zeolite support (Example 28). Conversely, where no fluorine impregnate was used (Examples 24-26), or where ammonium fluoride was used in conjunction with ammonium chloride (Example 27), the resulting T₆₀ and deactivation rates were undesirably higher.

[0070] In addition to the methods described in the Examples above, the catalysts of the present invention can be prepared by impregnating a suitable catalytic substrate with TAPC with hydrogen fluoride (HF), hydrogen chloride (HCl) and an organic or inorganic hydroxide represented by the formula N(R)₄OH, where R represents hydrogen or a substituted or unsubstituted carbon chain molecule having 1-20 carbon atoms.

Example 29

[0071] A platinum KL-zeolite containing 0.5 wt% platinum is prepared in the following manner. An impregnating mixture of 0.10g TAPC, 1.50g HF, 0.64g HCl, 0.83g ammonium hydroxide and 2.0g water is formed and added to a container containing 10.97g of a KL-zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 16 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for another 2 hours.

Example 30

[0072] A platinum KL-zeolite containing 0.5 wt% platinum is prepared in the following manner. An impregnating mixture of 0.10g TAPC, 1.50g HF, 0.64g HCl, 2.45g tetramethylammonium hydroxide and 0.50g water is formed and added to a container containing 10.96g of a KL-zeolite predried for 2 hours at 250°C. The

mixture is impregnated into the KL-zeolite and then allowed to stand for 16 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for another 2 hours.

Example 31

[0073] A platinum KL-zeolite containing 0.5 wt% platinum is prepared in the following manner. An impregnating mixture of 0.10g TAPC, 1.50g HF, 0.64g HCl and 2.8g tetraethylammonium hydroxide is formed and added to a container containing 10.96g of a KL-zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 16 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for another 2 hours.

Example 32

[0074] A platinum KL-zeolite containing 0.5 wt% platinum is prepared in the following manner. An impregnating mixture of 0.10g TAPC, 1.50g HF, 0.64g HCl and 6.8g tetrapropylammonium hydroxide is formed and added to a container containing 10.93g of a KL-zeolite predried for 2 hours at 250°C. The mixture is impregnated into the KL-zeolite and then allowed to stand for 16 hours at ambient temperature. The impregnated KL-zeolite is dried in a vacuum for 2 hours at 170°C and then calcined at 350°C for another 2 hours.

[0075] The results of Examples 29-32 are summarized in Table 5. This table shows that low loading catalysts containing 0.5 wt% platinum, 1.03 wt% fluorine and 0.39 wt% chlorine prepared using TAPC, HF, HCl and ammonium hydroxide or a tetraalkylammonium hydroxide result in low fouling rates.

TABLE 5

Example	Platinum wt%	Fluorine wt%	Chlorine wt%	Ammonium Compound	Initial T ₆₀ *	Deactivation Rate (°F/day)
29	0.50	1.03	0.39	NH ₄ OH	963	0.331
30	0.50	1.03	0.39	(CH ₃) ₄ NOH	917	0.095
31	0.50	1.03	0.39	(C ₂ H ₅) ₄ NOH	931	0.131
32	0.50	1.03	0.39	(C ₃ H ₇) ₄ NOH	918	-0.174

* Temperature (°F) at which the sum of the benzene wt% and toluene wt% in the reactor effluent is 60 wt%.

[0076] While the foregoing discussion is intended to provide a detailed illustration of certain embodiments of the invention, it will be appreciated that additional

embodiments are also possible under the claims provided herein. It will also be appreciated that numerical values and ranges are presented in approximate form such that small or inconsequential deviations from such values are intended to be within the scope of the values and ranges presented.

CLAIMS

The following is claimed:

1. A method of making a catalyst composition, comprising:
impregnating a large pore zeolite support with a platinum precursor and at least one organic ammonium halide precursor.
2. The method of claim 1 wherein the ammonium halide precursor is represented by the formula $N(R)_4X$, where X is a halide and R is a substituted or unsubstituted carbon chain molecule having 1-20 carbon atoms wherein each R may be the same or different.
3. The method of claim 2 wherein the large pore zeolite is an L-type zeolite.
4. The method of claim 2 wherein the large pore zeolite is a potassium L-type zeolite.
5. The method of claim 2 wherein R is an alkyl.
6. The method of claim 2 wherein R is selected from the group consisting of methyl, ethyl, propyl, butyl, and combinations thereof.
7. The method of claim 2 wherein R is methyl.
8. The method of claim 2 wherein X is selected from the group consisting of F, Cl, Br, I, and combinations thereof.
9. The method of claim 6 wherein X is selected from the group consisting of F, Cl, Br, I, and combinations thereof.
10. The method of claim 2 wherein X is F.
11. The method of claim 2 wherein X is Cl.
12. The method of claim 2 wherein the halide precursor is tetramethylammonium chloride.
13. The method of claim 2 wherein the halide precursor is tetramethylammonium fluoride.
14. The method of claim 12 wherein the halide precursor further comprises tetramethylammonium fluoride.
15. The method of claim 2 wherein the halide precursor further comprises ammonium chloride.
16. The method of claim 12 wherein the halide precursor further comprises ammonium chloride.

17. The method of claim 13 wherein the halide precursor further comprises ammonium chloride.
18. The method of claim 14 wherein the halide precursor further comprises ammonium chloride.
19. The method of claim 2 wherein the halide precursor further comprises ammonium fluoride.
20. The method of claim 12 wherein the halide precursor further comprises ammonium fluoride.
21. The method of claim 13 wherein the halide precursor further comprises ammonium fluoride.
22. The method of claim 14 wherein the halide precursor further comprises ammonium fluoride.
23. The method of claim 15 wherein the halide precursor further comprises ammonium fluoride.
24. The method of claim 16 wherein the halide precursor further comprises ammonium fluoride.
25. The method of claim 17 wherein the halide precursor further comprises ammonium fluoride.
26. The method of claim 18 wherein the halide precursor further comprises ammonium fluoride.
27. The method of claim 2, wherein the platinum precursor is selected from the group consisting of ammonium tetrachloroplatinate, chloroplatinic acid, diammineplatinum (II) nitrite, bis (ethylenediamine)platinum (II) chloride, platinum (II) acetylacetonate, dichlorodiammine platinum, platinum (II) chloride, tetraammineplatinum (II) hydroxide, tetraammineplatinum (II) nitrate, and combinations thereof.
28. The method of claim 2 wherein the platinum precursor is tetraamineplatinum chloride.
29. The method of claim 12 wherein the platinum precursor is tetraamineplatinum chloride.

30. The method of claim 13 wherein the platinum precursor is tetraamineplatinum chloride.
31. The method of claim 14 wherein the platinum precursor is tetraamineplatinum chloride.
32. The method of claim 16 wherein the platinum precursor is tetraamineplatinum chloride.
33. The method of claim 17 wherein the platinum precursor is tetraamineplatinum chloride.
34. The method of claim 18 wherein the platinum precursor is tetraamineplatinum chloride.
35. The method of claim 20 wherein the platinum precursor is tetraamineplatinum chloride.
36. The method of claim 21 wherein the platinum precursor is tetraamineplatinum chloride.
37. The method of claim 22 wherein the platinum precursor is tetraamineplatinum chloride.
38. The method of claim 23 wherein the platinum precursor is tetraamineplatinum chloride.
39. The method of claim 24 wherein the platinum precursor is tetraamineplatinum chloride.
40. The method of claim 25 wherein the platinum precursor is tetraamineplatinum chloride.
41. The method of claim 26 wherein the platinum precursor is tetraamineplatinum chloride.
42. The method of claim 1 wherein the ammonium halide precursor comprises at least one acid halide and at least one ammonium hydroxide represented by the formula $N(R')_4OH$, where R' is hydrogen or a substituted or unsubstituted carbon chain molecule having 1-20 carbon atoms wherein each R' may be the same or different.
43. The method of claim 42 wherein the large pore zeolite is an L-type zeolite.
44. The method of claim 42 wherein the large pore zeolite is a potassium L-type zeolite.

45. The method of claim 42 wherein R' is an alkyl.
46. The method of claim 42 wherein R' is selected from the group consisting of methyl, ethyl, propyl, butyl, and combinations thereof.
47. The method of claim 42 wherein R' is methyl.
48. The method of claim 42 wherein the acid halide is HCl, HF, HBr, HI, or combinations thereof.
49. The method of claim 46 wherein the acid halide is HCl, HF, or both.
50. The method of claim 47 wherein the acid halide is HCl.
51. The method of claim 47 wherein the acid halide is HF.
52. The method of claim 42 wherein the halide precursor further comprises ammonium chloride, ammonium fluoride, or both.
53. The method of claim 49 wherein the halide precursor further comprises ammonium chloride, ammonium fluoride, or both.
54. The method of claim 43 wherein the platinum precursor is selected from the group consisting of ammonium tetrachloroplatinate, chloroplatinic acid, diammineplatinum (II) nitrite, bis (ethylenediamine)platinum (II) chloride, platinum (II) acetylacetonate, dichlorodiammine platinum, platinum (II) chloride, tetraammineplatinum (II) hydroxide, tetraammineplatinum (II) nitrate, and combinations thereof.
55. The method of claim 42 wherein the platinum precursor is tetraamineplatinum chloride.
56. The method of claim 48 wherein the platinum precursor is tetraamineplatinum chloride.
57. The method of claim 49 wherein the platinum precursor is tetraamineplatinum chloride.
58. The method of claim 50 wherein the platinum precursor is tetraamineplatinum chloride.
59. The method of claim 51 wherein the platinum precursor is tetraamineplatinum chloride.
60. The method of claim 53 wherein the platinum precursor is tetraamineplatinum chloride.

61. The method of claim 2 wherein the ammonium halide precursor further comprises at least one acid halide and at least one ammonium hydroxide represented by the formula $N(R')_4OH$, where R' is hydrogen or a substituted or unsubstituted carbon chain molecule having 1-20 carbon atoms wherein each R' may be the same or different.
62. The method of claim 61 wherein the large pore zeolite is a potassium L-type zeolite.
63. The method of claim 61 wherein each R and R' are selected from the group consisting of methyl, ethyl, propyl, butyl, and combinations thereof.
64. The method of claim 61 wherein X is selected from the group consisting of F , Cl , Br , I , and combinations thereof.
65. The method of claim 61 wherein the acid halide is HCl , HF , or both.
66. The method of claim 61 wherein the halide precursor further comprises ammonium chloride, ammonium fluoride, or both.
67. The method of claim 61 wherein the platinum precursor is selected from the group consisting of ammonium tetrachloroplatinate, chloroplatinic acid, diammineplatinum (II) nitrite, bis (ethylenediamine)platinum (II) chloride, platinum (II) acetylacetonate, dichlorodiammine platinum, platinum (II) chloride, tetraammineplatinum (II) hydroxide, tetraammineplatinum chloride, tetraammineplatinum (II) nitrate, and combinations thereof.
68. The method of claim 2, wherein the catalyst comprises less than about 1.3 wt% chlorine.
69. The method of claim 42, wherein the catalyst comprises less than about 1.3 wt% chlorine.
70. The method of claim 2, wherein the catalyst comprises less than about 1.3 wt% fluorine.
71. The method of claim 42, wherein the catalyst comprises less than about 1.3 wt% fluorine.
72. The method of claim 2, wherein the catalyst comprises less than about 1.3 wt% chlorine and less than about 1.3 wt% fluorine.

73. The method of claim 42, wherein the catalyst comprises less than about 1.3 wt% chlorine and less than about 1.3 wt% fluorine.
74. The method of claim 2, wherein the catalyst comprises platinum in the range of about 0.2 wt% to about 0.7 wt%.
75. The method of claim 42, wherein the catalyst comprises platinum in the range of about 0.2 wt% to about 0.7 wt%.
76. The method of claim 2, wherein the catalyst comprises less than about 0.6 wt% platinum, less than about 1.3 wt% chlorine, and less than about 1.3 wt% fluorine.
77. The method of claim 42, wherein the catalyst comprises less than about 0.6 wt% platinum, less than about 1.3 wt% chlorine, and less than about 1.3 wt% fluorine.
78. The process of claim 1 wherein the catalyst has a deactivation rate of less than about 2.4 °F/day and a T_{60} of about 875 to about 975 °F.
79. The process of claim 2 wherein the catalyst has a deactivation rate of less than about 2.4 °F/day and a T_{60} of about 875 to about 975 °F.
80. The process of claim 42 wherein the catalyst has a deactivation rate of less than about 2.4 °F/day and a T_{60} of about 875 to about 975 °F.
81. The process of claim 61 wherein the catalyst has a deactivation rate of less than about 2.4 °F/day and a T_{60} of about 875 to about 975 °F.
82. A method of making a catalyst composition, comprising:
impregnating a large pore zeolite support with a platinum precursor; at least one acid halide; and at least one organic ammonium hydroxide represented by the formula $N(R')_4OH$, where R' is a substituted or unsubstituted carbon chain molecule having 1-20 carbon atoms wherein each R' may be the same or different.
83. A method of making a catalyst composition, comprising:
impregnating a large pore zeolite support with a platinum precursor and at least one organic ammonium halide precursor represented by the formula $N(R)_4X$, where X is a halide and R is a substituted or unsubstituted carbon chain molecule having 1-20 carbon atoms wherein each R may be the same or different.
84. A composition made according to the method of claim 1.
85. A process for reforming a hydrocarbon, comprising:

contacting hydrocarbons with a catalyst under suitable reaction conditions for aromatizing the hydrocarbons, wherein the catalyst is formed by a process comprising impregnating a large pore zeolite support with a platinum precursor and at least one organic ammonium halide precursor.

86. The process of claim 85 wherein the catalyst has a deactivation rate of less than about 2.4 °F/day and a T_{60} of about 875 to about 975 °F.
87. The process of claim 85 further comprising recovering hydrogen.
88. The process of claim 82 further comprising vacuum drying the impregnated catalyst support.
89. The process of claim 83 further comprising vacuum drying the impregnated catalyst support.
90. The process of claim 82 further comprising calcining the impregnated catalyst support in air having a diluted oxygen content.
91. The process of claim 83 further comprising calcining the impregnated catalyst support in air having a diluted oxygen content.
92. The process of claim 88 further comprising calcining the impregnated catalyst support in air having a diluted oxygen content.
93. The process of claim 89 further comprising calcining the impregnated catalyst support in air having a diluted oxygen content.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/014848

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J29/62 B01J37/02 C10G35/00

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)

IPC 7 B01J C10G

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 practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 912 072 A (PERSAUD LALCHAN ET AL) 27 March 1990 (1990-03-27) column 2, line 25 - column 3, line 45; claims; examples; tables -----	1-93
X	US 5 461 016 A (GALPERIN LEONID B ET AL) 24 October 1995 (1995-10-24) column 2, line 58 - column 8, line 60; claims; examples; tables -----	1-93
Y	US 6 063 724 A (JACOBS GARY ET AL) 16 May 2000 (2000-05-16) column 2, line 64 - column 6, line 55; claims; examples; tables -----	1-93
Y	US 6 406 614 B1 (CHEUNG TIN-TACK PETER ET AL) 18 June 2002 (2002-06-18) column 2, line 5 - column 4, line 18; claims; examples; tables -----	1-93

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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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)

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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

17 September 2004

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

de Cauwer, R

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2004/014848

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			CA 2391295 A1	28-06-2001
			EP 1259320 A1	27-11-2002
			JP 2003517925 T	03-06-2003
			WO 0145841 A1	28-06-2001