METHODOLOGY OF PREPARING AN AROMATIZATION CATALYST

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Abstract
A method of preparing a fresh catalyst comprises impregnating a metal to a catalyst support to produce an impregnated catalyst, dispersing the metal in the impregnated catalyst to produce an impregnated, dispersed catalyst, contacting the impregnated, dispersed catalyst with an activating composition to produce an impregnated, dispersed, activated catalyst, and thermally treating the impregnated, dispersed, activated catalyst to produce the fresh catalyst wherein the activating composition is in the gas phase.
FIG. 1

100

Impregnating a metal to a support

110

Dispersing the metal in the support

120

Activating the metal in the support

130

Thermal Treatment

140
METHODS OF PREPARING AN AROMATIZATION CATALYST

CROSS-REFERENCE TO RELATED APPLICATION


FIELD

[0002] The present disclosure relates to aromatization of hydrocarbons with an aromatization catalyst. Specifically, the disclosure relates to methods of preparing an aromatization catalyst.

BACKGROUND

[0003] The catalytic conversion of hydrocarbons into aromatic compounds, referred to as aromatization, is an important industrial process used to produce fundamental building block chemicals on which a large portion of the chemical industry is based. The aromatization reactions may include the dehydrogenation, isomerization, and hydrocracking of hydrocarbons. These reactions are generally conducted in one or more aromatization reactors containing aromatization catalysts. These catalysts may increase the selectivity to desired aromatics, and/or the conversion rates of the reactions to the desired aromatic compounds. Given their commercial importance, an ongoing need exists for improved methods of preparing aromatization catalysts with high selectivity and conversion.

[0004] Further, the activity of these catalysts may degrade over time during their use in an aromatization process. For example, the catalysts may be poisoned by the presence of contaminants thus degrading their activities. Continued use of the catalyst may result in a catalyst that no longer efficiently catalyzes a user-desired process, termed a spent catalyst. An ongoing need exists for fresh catalysts which retain their conversion rates and/or selectivity while under aromatization conditions.

SUMMARY

[0005] Disclosed herein is a method of preparing a fresh catalyst comprises impregnating a metal to a catalyst support to produce an impregnated catalyst, dispersing the metal in the impregnated catalyst to produce an impregnated, dispersed catalyst, contacting the impregnated, dispersed catalyst with an activating composition to produce an impregnated, dispersed, activated catalyst, and thermally treating the impregnated, dispersed, activated catalyst to produce the fresh catalyst wherein the activating composition is in the gas phase.
group of zeolitic catalyst supports. Typical L-type zeolites contain mole ratios of oxides in accordance with the following formula:

\[ M_{x}OAl_{y}Si_{z}O_{2n+1}H_{2}O \]

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] In an embodiment, the catalyst support comprises a bound potassium L-type zeolite, also referred to as KL zeolite. The term “KL zeolite” as used herein refers to L-type zeolites in which the principal cation, M, incorporated in the zeolite is potassium. A KL zeolite may be cation-exchanged or impregnated with another metal-containing compound and one or more halide-containing compounds to produce a platinum-impregnated, halided zeolite or a KL supported Pt-halide zeolite catalyst. In some embodiments, the catalyst support is a bound KL zeolite.

[0015] The catalyst support may contain up to about 95 wt % of zeolite, alternatively be present in an amount of from about 60 wt % to about 95 wt % by total weight of the catalyst support, alternatively from about 70 wt % to about 92 wt %, alternatively from about 80 wt % to about 90 wt % of the catalyst support. Herein the weight percentage by total weight of the catalyst support refers to the weight percentage of the component based on the final weight of the catalyst support after all of the catalyst support preparation steps.

[0016] In an embodiment, the fresh catalyst comprises one or more catalytically active metals. Examples of such metals include without limitation Group IB transition metals and/or Group VIII transition metals of the Periodic Table such as iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, gold, silver, copper or combinations thereof. The metal or metals are added to the catalyst support by any suitable method, such as via impregnation with a solution of a metal-containing compound. Such metals may undergo an activation step, for example a change in oxidation state, prior to dispersing the metal about the catalyst support. Alternatively, such metals may be activated by contact with one or more other compounds (e.g., an activating composition), for example with one or more halide-containing compounds as described herein.

[0017] In an embodiment, the metal comprises platinum (Pt). The Pt may be added to the catalyst support by any suitable method, such as via impregnation with a solution of a Pt-containing compound. The Pt-containing compound may be any decomposable Pt-containing compound. Examples of such compounds include without limitation ammonium tetrachloroplatinate, chloroplatonic acid, diammineplatinum (II) nitrite, bis-(ethylendiamine)platinum (II) chloride, platinum (II) acetylacetonate, dichlorodiammineplatinum, platinum (II) chloride, tetraamineplatinum (II) hydroxide, tetraamineplatinum chloride, tetraamineplatinum (II) nitrate, chloroplatonic acid (IV), or combinations thereof.

[0018] In an embodiment, the metal may be present in the fresh catalyst in an amount from about 0.1 wt. % to about 50 wt. % by total weight of the fresh catalyst, alternatively from about 0.1 wt. % to about 10 wt. %, alternatively from about 0.2 wt. % to about 5 wt. %, alternatively from about 0.3 wt. % to about 3 wt. %, alternatively from about 0.3 wt. % to about 2 wt. %.

[0019] In an embodiment, the fresh catalyst comprises at least two halides. Examples of suitable halides include chloride, fluoride, bromide, iodide, or combinations thereof. In an embodiment, the catalyst comprises chloride. The halide may be added to the catalyst by any suitable method, such as via impregnation, contacting with oxygen and a halogen-containing compound, or combinations of these methods. In an embodiment, chloride may be added to the catalyst by contacting the catalyst with a dispersing composition containing a chlorine-containing compound in the presence of oxygen. In another embodiment, the chloride may be added to the catalyst by contacting the catalyst with a dispersing composition containing a chlorine-containing compound in the presence of oxygen. Such processes involving chlorine-containing compounds and oxygen are generally referred to as oxychlorination. The chlorine-containing compound may be in the solid phase, liquid phase, gas phase, or combinations thereof. Examples of chlorine-containing compounds suitable for use in this disclosure include without limitation hydrochloric acid, chlorine, carbon tetrachloride, tetrachloroethylene, chlorobenzene, methyl chloride, methylene chloride, chloroform, aliph chloride, trichloroethylene, chloramine, chlorine oxides, chlorine acids, chlorine dioxide, dichlorine monoxide, dichlorine heptoxide, chlorine acid, perchloric acid, or combinations thereof. In some embodiments, the chlorine-containing compound is hydrochloric acid, carbon tetrachloride, tetrachloroethylene, or combinations thereof.

[0020] The chlorine-containing compound may also be an organic chlorine-containing compound such as the compounds represented by the general formula NR,Cl, where R represents a hydrogen or a substituted or unsubstituted carbon chain molecule having 1 to 20 carbon atoms wherein each R may be the same or different. In an embodiment, R is methyl, ethyl, propyl, butyl, or combinations thereof. Alternatively R is methyl. Specific examples of suitable organic ammonium chlorine-containing compounds include ammonium chloride, tetramethylammonium chloride (TMAC), tetraethylammonium chloride, tetrapropylammonium chloride, tetrabutylammonium chloride, methyltriethylammonium chloride, or combinations thereof. Alternatively, the organic ammonium chlorine-containing compound is TMAC.

[0021] The organic ammonium chloride may be present in the fresh catalyst in an amount from about 0.1 wt. % to about 5 wt. % by total weight of the fresh catalyst.
weight of the fresh catalyst, alternatively from about 0.2 wt. % to about 35 wt. %, alternatively from about 0.3 wt. % to about 2 wt. %.

[0023] In an embodiment, the catalyst comprises fluoride. Fluoride may be added to the catalyst by any suitable method, such as via contacting the catalyst with a fluorine-containing compound in a process generally referred to as fluoridation. The fluorine-containing compound may be in the solid phase, liquid phase, gas phase, or combinations thereof. In an embodiment, the fluorine-containing compound is in the gas phase. Examples of fluorine-containing compounds suitable for use in this disclosure include without limitation tetramethylammonium fluoride (TMAF), ammonium fluoride (NH₄F or AF), tetrafluoroethylene, 2,2,2-trifluoroethanol (TFE), fluoride (F⁻), hydrofluoric acid (HF), or combinations thereof. In an embodiment, the fluorine-containing compound is a perfluorinated alkane, perfluorinated alcohol or mixtures thereof. Examples of perfluorinated alkanes suitable for use in this disclosure include without limitation tetrafluoroethylene, carbon tetrafluoride, carbon trifluoride, fluoromethane, hexafluoropropane, decafluorobutane, or combinations thereof. Examples of perfluorinated alcohols suitable for use in this disclosure include without limitation 2,2,2-trifluoroethanol (TFE), hexafluoroisopropanol, tetrafluoro propanol, pentafluoro propanol, hexafluorophenylpropanol, perfluorobutyl alcohol, hexafluor-2-propanol, pentfluoro-1-propanol, hexafluoro-1-propanol, 1,1,1,3,3-hexafluoro-2-propanol, 2,2,3,3,3-pentafluoro-1-propanol, and combinations thereof.

[0024] The fluorine-containing compound may be an organic ammonium halide compound and may comprise one or more compounds represented by the general formula N(R)₄X, where R represents a hydrogen or a substituted or unsubstituted carbon chain molecule having from 1 to 20 carbon atoms wherein each R may be the same or different. In an embodiment, R is methyl, ethyl, propyl, butyl, or combinations thereof. Alternatively R is a methyl. Examples of suitable organic ammonium compounds include without limitation ammonium fluoride, tetramethylammonium fluoride, tetraethylammonium fluoride, tetrabutylammonium fluoride, methyltriethylammonium fluoride, and combinations thereof.

[0025] The organic ammonium halide compound may also comprise at least one hydrofluoric acid 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 from 1 to 20 carbon atoms wherein each R may be the same or different. In an embodiment, R is methyl, ethyl, propyl, butyl, or combinations thereof. Alternatively R is a methyl. Examples of organic ammonium hydroxides suitable for use in this disclosure include tetraalkylammonium hydroxides such as tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide, tetrachloroammonium hydroxide, or combinations thereof.

[0026] Fluoride may be present in the fresh catalyst in an amount of from about 0.1 wt. % to about 10 wt. % by total weight of the fresh catalyst, alternatively from about 0.2 wt. % to about 5 wt. %, alternatively from about 0.3 wt. % to about 3 wt. %, alternatively from about 0.6 wt. % to about 2 wt. %.

[0027] In various embodiments, the catalyst comprises Pt, and chloride (Cl⁻) in an atomic ratio of Pt:Cl⁻ from about 1.0:0.1 to about 1.0:10, alternatively from about 1.0:0.2 to about 1.0:5.0, alternatively from about 1.0:0.3 to about 1.0:3.0.

[0028] FIG. 1 is a flowchart of an embodiment of a method of preparing a fresh catalyst. Referring to FIG. 1, a method of preparing a fresh catalyst may comprise a fresh catalyst support with a metal-containing compound, Block 110, both of which (i.e., catalyst and metal-containing compound) may be of type that has been described previously herein. The method may then proceed to dispersing the metal throughout the catalyst support, Block 120, to produce an impregnated dispersed catalyst. The metal may be dispersed via contact with one or more dispersing compositions. The metal may be dispersed throughout the catalyst support, in one or more layers of the catalyst support (e.g., a skin layer), about the periphery of the catalyst support, or various combinations thereof, and such dispersion may be uniform or non-uniform. The material may be further processed by activating the metal in the catalyst, Block 130, to produce an impregnated dispersed activated catalyst. In an embodiment, the metal may be activated by contact with one or more, alternatively two or more, halide-containing compounds. The method may conclude with a thermal treatment to produce the fresh catalyst, Block 140.

[0029] In an embodiment, the catalyst support may be pretreated prior to impregnating the zeolite, Block 110. In an embodiment, the catalyst support comprises KL zeolite and the metal comprises Pt. The Pt-containing compound may be of the type previously described herein. The Pt-clay catalyst containing catalyst support may be pretreated prior to impregnating the catalyst support, Block 110. For example, the catalyst support may be dried under stationary or flowing gas in a temperature range of equal to or less than about 250°C, alternatively from 0°C to about 250°C. Examples of suitable gases include hydrogen, oxygen, air, helium, nitrogen, argon, or combinations thereof. The pretreatment of the catalyst support may be carried out for a period from about 1 minute to about 100 hours, alternatively from about 0.1 hours to about 50 hours, alternatively from about 1 hour to about 24 hours. The pretreatment of the catalyst support may be performed at temperatures in a range of from about 25°C to about 1000°C, or from about 50°C to about 900°C, or from about 100°C to about 800°C, and at a pressure in a range of from about 0 psi to about 1000 psi, or from about 0 psi to about 900 psi, or from about 0 psi to about 800 psi. Hereinafter exposure of the composition to the conditions described in the pretreatment will be referred as drying the compositions.

[0030] Impregnation of the catalyst support with the metal-containing compound, Block 110, may be carried out via any method known to one of ordinary skill in the art such as incipient wetness, aqueous impregnation, organic solvent impregnation, ion exchange, or combinations thereof. In an embodiment, impregnation of a catalyst support containing KL zeolite with platinum, Block 110, may be carried out via incipient wetness impregnation with an aqueous solution of a Pt-containing compound.

[0031] After impregnation, the catalyst support impregnated with the metal-containing compound may be dried as described previously herein. In some embodiments, it may be desirable to age the impregnated catalyst. 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. In some embodiments, it may be desirable to calcine the impregnated catalyst. 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 of nitrogen of from about 1:1 to about 1:3. The calcination temperature may be maintained at temperatures equal to or less than about 600°C, alternatively from about 50°C to about 600°C, alternatively from about 160°C to about 550°C, alternatively from about 275°C to about 500°C; under pressures from ambient to about 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 were the impregnated catalyst 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.

The method may then proceed to block 120 wherein the metal deposited onto the catalyst support during the impregnation with the metal-containing compound is dispersed by contacting the impregnated catalyst with a dispersing composition to produce an impregnated dispersed catalyst. In an embodiment, the platinum associated with the KL zeolite catalyst support is dispersed by contacting the impregnated catalyst with a dispersing composition to produce an impregnated dispersed catalyst. The dispersing composition may comprise a chlorine-containing compound of the type previously described herein and oxygen. For example, the dispersing composition may comprise hydrochloric acid and oxygen. Contacting of the impregnated catalyst with a dispersing composition containing a chlorine-containing compound may be referred to as oxychlorination. In some embodiments, the dispersing composition comprises carbon tetrachloride and oxygen. In other embodiments, the dispersing composition comprises tetrachloroethylene and oxygen. Contacting of the impregnated catalyst with the dispersing composition may be carried out over a time period of from about 0.5 hour to about 50 hours, alternatively from about 1 hour to about 20 hours, alternatively from about 2 hours to about 10 hours at a temperature in the range of from about 25°C to about 1000°C, alternatively from about 50°C to about 900°C, alternatively from about 100°C to about 800°C, alternatively from about 200°C to about 400°C, alternatively from about 400°C to about 800°C. When oxygen is used, the oxygen concentration used is from about 0.01 mol % to about 20 mol %, alternatively from about 1 mol % to about 18 mol %, alternatively from about 5 mol % to about 15 mol %, alternatively from about 8 mol % to about 12 mol %. After the impregnated catalyst is dispersed by contacting the impregnated catalyst with a dispersing composition containing a chloride-containing compound and oxygen, the resulting impregnated dispersed catalyst may have chlorine levels of from about 0.1 wt. % to about 5 wt. % by total weight of the catalyst, alternatively from about 0.2 wt. % to about 3 wt. %, alternatively from about 0.3 wt. % to about 2 wt. %. After dispersion, the resultant composition is impregnated dispersed catalyst.

In an alternative embodiment, the impregnated catalyst is contacted with a dispersing composition comprising a chlorine-containing compound of the type described herein and oxygen in the presence of water. When water is used, the water to HCl mole ratio (H₂O:HCl) used is from about 0.01:1 to about 10:1, alternatively from about 0.5:1 to about 5:1, alternatively from about 1:1 to about 3:1. When chlorine-containing compounds are used other than HCl, the H₂O:HCl mole ratio is calculated based on the equivalent amount of HCl generated in the presence of the impregnated catalyst.

In an embodiment, a weak base may be included during the dispersing of the metal on the impregnated catalyst support to neutralize free acids that may be present. An example of a weak base suitable for use in this disclosure includes without limitation ethylene diamine (EDA). The Pt-impregnated Cl-containing KL zeolite may be staged as previously described herein.

The method may then proceed to block 130 wherein the impregnated, dispersed, catalysit is activated by contacting with an activating composition. In an embodiment, the Pt-impregnated Cl-containing KL zeolite is activated by contacting with an activating composition. The activating composition may be a fluoride-containing composition of the type described previously herein in the gas phase. Contacting of the impregnated dispersed catalyst with a fluoride-containing composition is referred to as fluoridation. In an embodiment, the activating composition comprises an organic ammonium halide compound. In an embodiment, the activating composition comprises TMAF. Commercially available preparations of TMAF may be used or the TMAF may be prepared as the activating composition is prepared using any suitable methods. For example, the TMAF may be prepared by mixing a tetramethylammonium hydroxide (TMAOH) with an acidic fluoride-containing compound, which may be in the gas, liquid, or solid phase such as hydrofluoric acid (HF). In another embodiment, the activating composition comprises 2,2,2-trifluoroethanol (TFE). A weak base may be included during the activation of the metal to neutralize free acids that may be present. After the impregnated dispersed catalyst is contacted with an activating composition the resultant composition is an impregnated dispersed activated catalyst. In some specific embodiments, such as fluoridation, the resultant composition is a Pt-impregnated Cl and F-containing KL zeolite. The resulting material may be dried as described previously.

The method may conclude with thermal treatment of the impregnated, dispersed, activated catalyst, block 140. In an embodiment, the thermal treatment comprises heating the resulting material at a temperature range of equal to or less than about 1000°C, alternatively from about 25°C to about 1000°C, alternatively from about 50°C to about 900°C, alternatively from about 100°C to about 800°C, alternatively from about 200°C to about 400°C, alternatively from about 400°C to about 800°C. When oxygen is used, the oxygen concentration used is from about 0.01 mol % to about 20 mol %, alternatively from about 1 mol % to about 18 mol %, alternatively from about 5 mol % to about 15 mol %, alternatively from about 8 mol % to about 12 mol %. After the impregnated catalyst is dispersed by contacting the impregnated catalyst with a dispersing composition containing a chloride-containing compound and oxygen, the resulting impregnated dispersed catalyst may have chloride levels of from about 0.1 wt. % to about 5 wt. % by total weight of the catalyst, alternatively from about 0.2 wt. % to about 3 wt. %, alternatively from about 0.3 wt. % to about 2 wt. %.
thermal treatment may be carried out utilizing stationary or flowing gas (i.e., hydrogen, oxygen, air, helium, nitrogen, argon, etc). For example, the activating may be carried out in a flowing gas comprising nitrogen and/or oxygen, air, nitrogen diluted air, or combinations thereof. The ratio of air to nitrogen may be selected by one of ordinary skill in the art to meet the needs of the process. If the thermal treatment is be carried out in the presence of oxygen, the oxygen concentration may be from about 0.001 mol% to about 20 mol% alternatively from about 0.1 mol% to about 15 mol% alternatively from about 0.2 mol% to about 10 mol%, alternatively from about 0.5 mol% to about 5 mol% alternatively from about 1 mol% to about 3 mol%. Upon completion of the process of FIG. 1, a fresh catalyst is provided and recovered.

In an embodiment, the fresh catalyst may be used in 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 fresh 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.

Examples

The invention having been generally described, the following examples are given as particular embodiments of the invention and to demonstrate the practical advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the scope of the claims to follow in any manner.

In the following examples, the catalysts used were aromatization catalysts of the type described previously herein. Specifically, the catalysts were characterized as KL zeolite containing catalyst supports having about 0.5% to about 1.5% Pt. Unless otherwise indicated, fresh catalyst samples were prepared using the following general procedure: (i) impregnating the catalyst support with Pt to form an impregnated catalyst; (ii) dispersing the Pt in the impregnated catalyst with a dispersing composition containing a chlorine-containing compound to form an impregnated dispersed catalyst; (iii) contacting the impregnated dispersed catalyst with an activating composition comprising a gas phase fluorine-containing compound to produce the impregnated dispersed activated catalyst; and (iv) thermally treated to produce the fresh catalyst, which is disclosed in detail herein.

The samples produced in the following examples were then tested for their fouling rates which correlate to their activities by $y = f(x) + \text{initial } T_{60}$, where $y$ is temperature, $f$ is the fouling rate, $x$ is time, and initial $T_{60}$ is the initial start of run temperature. The fouling rate of the catalyst samples was determined by plotting the temperature required to maintain a total yield of benzene plus toluene at 60 wt% over time at standard test conditions. The fouling rates were then determined from the calculated slope fit to the resulting temperature data. In each of the following examples the following standard test conditions were utilized, the activated catalysts were ground, sieved to about 20 to 40 mesh, and 1 gram was placed in a reactor comprising a ½ inch OD stainless steel 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 22 mL/min; a pressure of 50 psig; a H₂:Hydrocarbon mole ratio of 3:1, a liquid hourly space velocity of 9 hr⁻¹, LHSV to obtain performance data. The aliphatic hydrocarbon contained the following weight percentages of normal paraffins and isoparaffins; about 8 wt% C₈ paraffins, about 28 wt% C₁₀ paraffins, and about 62 wt% C₁₂ paraffins. The reactor effluent composition was analyzed by gas chromatography to indicate the amount of benzene and toluene. In each of the following examples the catalyst preparation procedure, preparation parameters, and/or the process conditions were evaluated by the effects observed in the final catalyst performance by determining and analyzing the catalyst fouling rates (°F/day); and the initial start of run temperature (°F) (also denoted initial $T_{60}$). Other parameters tabulated include time on-stream (hr) (also denoted TOS); and end of run temperature (°F) (denoted final $T_{60}$); and others as indicated, tabulated, and collectively referred to as the results.

Example 1

A method to generate an aromatization catalyst using a fresh catalyst by co-impregnation of a KL zeolite with low Pt loading in a gas phase in the presence of a weak base was investigated. Sample 1 was prepared by incipient wetness impregnation of 54.95 grams of a silica bound KL zeolite catalyst support which was previously calcined at about 250°C for about 2 hours. This catalyst support was impregnated with a solution prepared from 0.50 gram of tetraamminoplatinum (II) chloride (TAPC), 0.50 gram of TMAC, and 24 grams of water. The impregnated catalyst was allowed to sit at ambient conditions for about 20 hours; and was then dried for about 7 hours at ambient temperatures in flowing air. The material was then transferred to a vacuum oven and dried at ambient temperatures and about 1 mmHg of vacuum for about 48 hours, followed by drying at about 140°C, for about 16 hours at about 1 mmHg. The produced material weighed 56.3 grams. Next 31.4 grams of this material was heated treated at about 350°C for about one hour to produce an impregnated catalyst with a final weight of 32.0 grams. This impregnated catalyst was then dispersed via an oxchlorination by exposure to air (about 320 mℓ/min) and nitrogen (about 320 mℓ/min) the nitrogen having been directed through a bubbler of about 37 wt% aqueous HCl solution for about 4 hours at about 520°C, then the temperature was decreased to about 450°C for about 1 hour. The HCl bubbler was removed, and the air and nitrogen flow continued as the samples were allowed to cool to about 250°C. Next nitrogen flow of 320 cc/min was directed through a bubbler containing an about 48 wt% solution of HF. The nitrogen flow containing HF, along with air flowing at about 320 cc/min was passed over the material for about 1 hour at about 250°C before raising the temperature to about 400°C, for about 1 hour. Then the HF bubbler was removed, and the air and nitrogen flow continued as the samples were allowed to cool to ambient temperatures. The resulting impregnated, activated catalyst weighed 31.17 grams.

Sample 2 was prepared by incipient wetness impregnation of 54.95 grams of a silica bound KL zeolite catalyst support which was previously calcined at about 250°C for about 2 hours. This catalyst support was impregnated with a solution prepared from 0.50 gram of tetraamminoplatinum (II) chloride (TAPC), 0.18 gram ethylenediamine (EDA), 0.50 gram of TMAC, and 24 grams of water. The
impregnated catalyst was allowed to sit at ambient conditions for about 16 hours; and was then dried for about 7 hours at ambient temperatures in flowing air. The material was then transferred to a vacuum oven and dried at ambient temperatures and about 1 mmHg of vacuum for about 48 hours, followed by drying at about 140°C for about 16 hours at about 1 mmHg. The produced material weighed 56.3 grams. Next 41.44 grams of this material was heat treated at about 350°C for about one hour to produce an impregnated catalyst with a final weight of 42.1 grams. This impregnated catalyst was then dispersed via an oxycycloration process by exposure to air (at about 420 ml/min) and nitrogen (about 420 ml/min) the nitrogen having been done through a bubbler of an about 37 wt % aqueous HCl solution for about 4 hours at about 250°C. The nitrogen was then removed, and the air and nitrogen flow continued as the sample was allowed to cool to ambient temperatures. The resulting impregnated, activated catalyst weighed 41.20 grams.

Example 2

The effect of the oxycycloration in the preparation of catalyst samples using fresh catalyst was investigated. Specifically during preparation of the catalyst, one sample, designated Sample 4, was subjected to an oxycycloration step while a second sample, designated Sample 3, was subjected to a heat treatment instead of oxycycloration and both Samples 3 and 4 were fluorinated by a method similar to that used in Example 1.

Example 3

The effect of a heat treatment, after impregnation with the metal-containing compound (also known as a precalcination), and prior to oxycycloration was investigated by heat treating catalyst samples, designated Samples 5, 6, and 7 at temperatures of about 105°C, about 250°C, and about 400°C, respectively.

Sample 5 was prepared by incipient wetness impregnation of 54.26 grams of a silica bound KL zeolite catalyst support which was previously calcined at about 250°C for about 2 hours. This catalyst support was impregnated with a solution prepared from 0.50 gram of tetraamineplatinum (II) chloride (TAPC), 0.50 gram of TMAC, and 25 grams of water. The impregnated catalyst was allowed to sit at ambient conditions for about 2 hours; and was then dried for about 1 hour at ambient temperatures in flowing air. The material was heat treated at about 400°C for about 1 hour. The resultant material weighed 54.63 grams. This impregnated catalyst was then dispersed via an oxycycloration process via exposure to air (at about 500 ml/min) and nitrogen (about 500 ml/min) the nitrogen having been done through a bubbler of an about 37 wt % aqueous HCl solution for about 4 hours at about 520°C, then the temperature was decreased to about 530°C for about 4 hours. The HCl bubbler was then removed, and the air and nitrogen flow continued as the samples were allowed to cool to ambient temperatures. The impregnated dispersed catalyst weighed 54.63 grams. Then the performance of the catalyst samples was evaluated for the aromatization of light naphtha and the results are tabulated in Table 2. The results demonstrate that the addition of an oxycycloration step to the catalyst preparation process gave a catalyst with a fouling rate that was much lower than the catalyst prepared without the oxycycloration step.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Dispersion</th>
<th>Initial $T_{200}$ (°F)</th>
<th>TOS (hr)</th>
<th>Final $T_{200}$ (°F)</th>
<th>Fouling (F/day)</th>
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<tr>
<td>3</td>
<td>Oxychlorination</td>
<td>935</td>
<td>47</td>
<td>936</td>
<td>0.465</td>
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<td>935</td>
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<td>936</td>
<td>0.465</td>
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</table>

Example 4

The effect of the oxycycloration in the preparation of catalyst samples using fresh catalyst was investigated. Specifically during preparation of the catalyst, one sample, designated Sample 4, was subjected to an oxycycloration step while a second sample, designated Sample 3, was subjected to a heat treatment instead of oxycycloration and both Samples 3 and 4 were fluorinated by a method similar to that used in Example 1.

Table 2

The results demonstrate that the addition of an oxycycloration step to the catalyst preparation process gave a catalyst with a fouling rate that was much lower than the catalyst prepared without the oxycycloration step.

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Table 2

The results demonstrate that the addition of an oxycycloration step to the catalyst preparation process gave a catalyst with a fouling rate that was much lower than the catalyst prepared without the oxycycloration step.
grams of the impregnated dispersed catalyst was fluorinated by treatment with a nitrogen flow of about 50 cc/min was directed through a bubbler containing an about 48 wt% solution of HF. The nitrogen flow containing HF, along with air flowing at 50 cc/min was passed over the material for about 1 hour at about 250°C. Then the HF bubbler was removed, and the air and nitrogen flow continued as the samples were allowed to cool to ambient temperatures. The resulting impregnated, dispersed, activated catalyst weighed 5.03 grams.

Sample 6 was prepared by incipient wetness impregnation of 55.06 grams of a silica bound KL zeolite catalyst support which was previously calcined at about 250°C for about 2 hours. This catalyst support was impregnated with a solution prepared by diluting 10 grams of a first solution with 16 grams of water; the first solution being prepared from 1.0 gram of tetraaminoplatinum (II) chloride (TAPC), 1.0 gram of TMAC, and 18 grams of water. The impregnated catalyst was allowed to sit at ambient conditions for about 2 hours; and was then dried for about 1 hour at ambient temperatures in flowing air. The material was then treated at about 250°C for about 4 hours. The produced material weighed 55.88 grams. This impregnated catalyst was then dispersed by an oxychlorination via exposure of 5 grams of to air (at about 50 ml/min) and nitrogen (about 50 ml/min) the nitrogen having been directed through a bubbler of an about 37 wt% aqueous HCl solution for about 1 hour at about 525°C. Then the temperature was decreased to about 400°C. The HCl bubbler was then removed, and the air and nitrogen flow continued as the samples were allowed to cool to about 250°C. The material was then fluorinated by directing the nitrogen flow of about 50 cc/min through a bubbler containing an about 48 wt% solution of HF. The nitrogen flow containing HF, along with air flowing at 50 cc/min was passed over the material for about 1 hour at about 250°C. Then the HF bubbler was removed, and the air and nitrogen flow continued as the samples were allowed to cool to ambient temperatures. The resulting impregnated, dispersed, activated catalyst weighed 5.01 grams.

Sample 7 was prepared by incipient wetness impregnation of 28.5 grams of a silica bound KL zeolite catalyst support which had previously been calcined. This catalyst support was impregnated with a solution prepared by diluting 5 grams of a first solution with 7 grams of water; the first solution being prepared from 1.0 gram of tetraaminoplatinum (II) chloride (TAPC), 1.0 gram of TMAC, and 18 grams of water. The impregnated catalyst was allowed to sit at ambient conditions for about 16 hours; and was then heated at about 105°C for about 1 hour. This impregnated catalyst was then dispersed by an oxychlorination via exposure of to air (at about 250 ml/min) and nitrogen (about 250 ml/min) the nitrogen having been directed through a bubbler of an about 37 wt% aqueous HCl solution for about 2 hours at about 525°C. The HCl bubbler was then removed, and the air and nitrogen flow continued as the samples were allowed to cool to ambient temperatures. The impregnated, dispersed catalyst weighed 28.1 grams. This impregnated, dispersed catalyst (5 gram) was then fluorinated by directing a nitrogen flow of about 50 cc/min through a bubbler containing an about 48 wt% solution of HF. The nitrogen flow containing HF, along with air flowing at about 50 cc/min was passed over the material for about 1 hour at about 250°C. Then the HF bubbler was removed, and the air and nitrogen flow continued as the samples were allowed to cool to ambient temperatures. The resulting impregnated, dispersed, activated catalyst weighed 5.00 grams.

The performance of the catalyst samples was evaluated and the results are tabulated in Table 3. The results demonstrate a relationship between the precalcination temperature and the fouling rate having a minimum fouling rate over the range of precalcination temperatures.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Precalcination Temperature (°C)</th>
<th>Initial Tₜₒₜ 1/2 (F.)</th>
<th>TOS (hr)</th>
<th>Final Tₜₒₜ 1/2 (F.)</th>
<th>Fouling (F./day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>400</td>
<td>938</td>
<td>91</td>
<td>961</td>
<td>6.204</td>
</tr>
<tr>
<td>6</td>
<td>250</td>
<td>922</td>
<td>44</td>
<td>930</td>
<td>4.308</td>
</tr>
<tr>
<td>7</td>
<td>105</td>
<td>937</td>
<td>68</td>
<td>967</td>
<td>10.550</td>
</tr>
</tbody>
</table>

The effect of drying conditions of the impregnated catalyst on the fresh catalyst performance can be evaluated by comparison of Sample 6, which was vacuum dried with designated Sample 4, which was allowed to dry under ambient conditions following impregnation with the metal-containing compound. The performance of the catalyst samples was evaluated and the results are tabulated in Table 4.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Drying</th>
<th>Initial Tₜₒₜ 1/2 (F.)</th>
<th>TOS (hr)</th>
<th>Final Tₜₒₜ 1/2 (F.)</th>
<th>Fouling (F./day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Ambient</td>
<td>922</td>
<td>44</td>
<td>936</td>
<td>4.380</td>
</tr>
<tr>
<td>4</td>
<td>Vacuum</td>
<td>935</td>
<td>47</td>
<td>936</td>
<td>0.465</td>
</tr>
</tbody>
</table>

Example 4

The effect of gas phase fluoridation on the preparation of fresh catalyst was investigated. Sample 8 was prepared by incipient wetness impregnation of 25 grams of a silica bound KL zeolite catalyst support which had previously been calcined. This catalyst support was impregnated with a solution prepared from 0.67 grams of chloroplatinic acid hexahydrate (CPA), and 11.5 grams of water. The impregnated catalyst was allowed to sit at ambient conditions for about 0.5 hour. The material was then dispersed via an oxychlorination process by exposure to air (at about 200 cc/min) and nitrogen (about 200 cc/min) the nitrogen having been directed through a bubbler of an about 37 wt% aqueous HCl solution for about 5 hours at about 520°C. The HCl bubbler was then removed, and the air and nitrogen flow continued as the sample was allowed to cool to ambient temperature. The material produced weighed 24.84 grams. Next 5 grams of this material was fluorinated by impregnation with 2.5 grams of an about 20 wt% aqueous solution of TMAF. The impregnated material was allowed to sit at ambient temperature for about 16 hours, followed by a heat treatment at about 370°C for about 1 hour. The resulting impregnated, activated catalyst weighed 5.02 grams.

Samples 9-11 was prepared by incipient wetness impregnation of 25 grams of a silica bound KL zeolite catalyst support which was previously calcined. This catalyst support was impregnated with a solution prepared from 0.33 grams of chloroplatinic acid hexahydrate (CPA), and 12 grams of water. The resulting impregnated, dispersed, activated catalyst weighed 5.00 grams.
of water. The impregnated catalyst was allowed to sit at ambient conditions for about 0.5 hour. The material was then dispersed via an oxochlorination by exposure to air (at about 200 cc/min) and nitrogen (about 200 cc/min) the nitrogen having been directed through a bubbler of an about 37 wt % aqueous HCl solution for about 5 hours at about 520° C. The HCl bubbler was then removed, and the air and nitrogen flow continued as the sample was allowed to cool to ambient temperature. The material produced weighed 24.54 grams and was used to prepare Samples 9-11. Sample 9 was prepared by using 10 grams of this material and fluorinating it by exposure to air (at about 100 cc/min) and nitrogen (about 100 cc/min) the nitrogen having been directed through a bubbler of 2,2,2-trifluoroethanol (TFE) for about 1 hour at about 400° C. The TFE bubbler was then removed, and the air and nitrogen flow continued as the sample was allowed to cool to ambient temperature. Sample 10 was prepared by using 5 grams of the same material as sample 9 and fluorinating it by exposure to air (at about 50 cc/min) and nitrogen (about 50 cc/min) the nitrogen having been directed through a bubbler of 2,2,2-trifluoroethanol (TFE) for about 1 hour at about 450° C. The TFE bubbler was then removed, and the air and nitrogen flow continued as the sample was allowed to cool to ambient temperature. Sample 11 was prepared by using 5 grams of the same material as sample 9 and fluorinating it by exposure to air (at about 50 cc/min) and nitrogen (about 50 cc/min) the nitrogen having been directed through a bubbler of 2,2,2-trifluoroethanol (TFE) for about 1 hour at about 500° C. The TFE bubbler was then removed, and the air and nitrogen flow continued as the sample was allowed to cool to ambient temperature. The performance of the catalyst samples was evaluated and the results are tabulated in Table 5.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Pt (wt %)</th>
<th>Activation Composition</th>
<th>Activation Temp (°C)</th>
<th>Initial T_{90%} (F)</th>
<th>TOS (hr)</th>
<th>Final T_{90%} (F)</th>
<th>Fouling F/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>1.02</td>
<td>TMAF</td>
<td>370</td>
<td>996</td>
<td>2</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>9</td>
<td>0.51</td>
<td>TFE</td>
<td>460</td>
<td>948</td>
<td>2</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>10</td>
<td>0.51</td>
<td>TFE</td>
<td>450</td>
<td>932</td>
<td>20</td>
<td>934</td>
<td>2.773</td>
</tr>
<tr>
<td>11</td>
<td>0.51</td>
<td>TFE</td>
<td>500</td>
<td>929</td>
<td>19</td>
<td>930</td>
<td>1.121</td>
</tr>
</tbody>
</table>

The results demonstrate that catalyst prepared with TFE had a low fouling rate and that this fouling rate was reduced further when the samples were fluorinated at higher temperatures.

While embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Where numerical ranges or limitations are expressly stated, such express ranges or limitations should be understood to include iterative ranges or limitations of like magnitude falling within the expressly stated ranges or limitations (e.g., from about 1 to about 10 includes, 2, 3, 4, etc.; greater than 0.10 includes 0.11, 0.12, 0.13, etc.). For example, whenever a numerical range with a lower limit, R_l, and an upper limit, R_u, is disclosed, any number falling within the range is specifically disclosed. In particular, the following numbers within the range are specifically disclosed: R = R_l ± k*(R_u − R_l), wherein k is a variable ranging from 1 percent to 100 percent with a 1 percent increment, i.e., k is 1 percent, 2 percent, 3 percent, 4 percent, 5 percent, . . . 50 percent, 51 percent, 52 percent, . . . 95 percent, 96 percent, 97 percent, 98 percent, 99 percent, or 100 percent. Moreover, any numerical range defined by two R numbers as defined in the above is also specifically disclosed. Use of the term "optionally" with respect to any element of a claim is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the claim. Use of broader terms such as comprises, includes, having, etc. should be understood to provide support for narrower terms such as consisting of, consisting essentially of, comprised substantially of, etc.

Accordingly, the scope of protection is not limited by the description set out above but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an embodiment of the present invention. Thus, the claims are a further description and are an addition to the embodiments of the present invention. The discussion of a reference herein is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated by reference, to the extent that they provide exemplary, procedural or other details supplementary to those set forth herein.

1. A method of preparing a fresh catalyst comprising:
   Impregnating a metal to a catalyst support to produce an impregnated catalyst;
   dispersing the metal in the impregnated catalyst to produce an impregnated dispersed catalyst;
   contacting the impregnated dispersed catalyst with an activating composition to produce an impregnated dispersed activated catalyst wherein the activating composition is in the gas phase; and
   thermally treating the impregnated dispersed activated catalyst to produce the fresh catalyst.

2. The method of claim 1 wherein the catalyst support comprises an inorganic oxide.

3. The method of claim 2 wherein the inorganic oxide comprises zeolites, amorphous inorganic oxides, or combinations thereof.

4. The method of claim 2 wherein the inorganic oxide comprises an L-type zeolite.

5. The method of claim 1 wherein the metal comprises a Group VIII transition metal, Group IB transition metal, or combinations thereof.

6. The method of claim 1 wherein the metal is present in an amount of from about 0.1 wt. % to about 50 wt. % by total weight of the fresh catalyst.
7. The method of claim 1 wherein dispersing the metal in the impregnated catalyst comprises contacting the impregnated catalyst with a dispersing composition.

8. The method of claim 7 wherein the dispersing composition comprises water and a chlorine-containing compound.

9. The method of claim 8 wherein the chlorine-containing compound comprises an organic chlorine-containing compound represented by a general formula N(R)Cl, where R represents a hydrogen or a substituted or unsubstituted carbon chain molecule having 1 to 20 carbon atoms and where each R may be the same or different.

10. The method of claim 8 wherein the chlorine-containing compound comprises hydrochloric acid, chlorine, carbon tetrachloride, tetrachloroethylene, chlorobenzene, methyl chloride, methylene chloride, chloroform, allyl chloride, trichloroethylene, chloramine, chlorine oxides, chlorine acids, chlorine dioxide, dichlorine monoxide, dichlorine heptoxide, hydrochloric acid, chloric acid, perchloric acid, ammonium chloride, tetramethylammonium chloride, tetraethylammonium chloride, tetrapropylammonium chloride, tetrabutylammonium chloride, methyltriethylammonium chloride, or combinations thereof.

11. The method of claim 7 wherein the impregnated catalytic is contacted with the dispersing composition for a period of from about 1 minute to about 100 hours at a temperature of from about 25°C to about 1000°C.

12. The method of claim 1 wherein the activating composition comprises a fluorine-containing compound.

13. The method of claim 12 wherein the fluorine-containing compound comprises fluorine, hydrofluoric acid, 2,2,2-trifluoroethanol, tetrafluoroethylene, carbon tetrachloride, carbon trifluoride, fluoromethane, heptafluoropropane, decfluorobutane, hexafluoroisopropyl, tetrafluoropropyl, pentafluoropropanol, hexafluorophenylpropanol, perfluorobutyl alcohol, hexafluor-2-propanol, pentafluoro-1-propanol, tetrafluoro-1-propanol, 1,1,1,3,3,3-hexafluoro-2-propanol, 2,2,3,3,3-pentafluoro-1-propanol, or combinations thereof.

14. The method of claim 1 wherein the impregnated dispersed catalyst is contacted with the activating composition for a period of from about 1 minute to about 100 hours at a temperature of from about 25°C to about 1000°C.

15. The method of claim 1 further comprising drying the impregnated catalyst, impregnated dispersed catalyst; impregnated dispersed activated catalyst; fresh catalyst or combinations thereof at a temperature range of equal to or less than about 250°C.

16. The method of claim 1 further comprising calcining the impregnated catalyst; impregnated dispersed catalyst; impregnated dispersed activated catalyst; or combinations thereof at a temperature range of equal to or less than about 600°C.

17. The method of claim 1 wherein the impregnated dispersed catalyst is contacted with the activating composition in the presence of a weak base.

18. The method of claim 17 wherein the weak base comprises ethylenediamine.

19. The method of claim 1 wherein thermally treating the impregnated dispersed activated catalyst comprises heating at a temperature range of equal to or less than about 1000°C.

20. The method of claim 1 further comprising contacting the fresh catalyst with hydrocarbons under conditions suitable for the conversion of some portion of the hydrocarbons to aromatic products.