

A PROCESS FOR HYDROCARBON CONVERSION USING, A METHOD TO MAKE, AND COMPOSITIONS OF, AN ACID CATALYST

This application is related to co-filed patent applications titled “An Ionic Liquid Catalyst Having a High Molar Ratio of Aluminum to Nitrogen,” and “Process to Make a Liquid Catalyst Having a High Molar Ratio of Aluminum to Nitrogen,” herein incorporated by reference in their entireties.

FIELD OF THE INVENTION

This invention is directed to a process for hydrocarbon conversion using an acid catalyst with high wt% conjunct polymer; a method to make a catalyst having greater than 15 wt% conjunct polymer that is effective for catalyzing a reaction; and acid catalyst compositions.

DETAILED DESCRIPTION OF THE INVENTION

In one embodiment, a process for hydrocarbon conversion, comprising: contacting a hydrocarbon with an acid catalyst containing greater than 15 wt% conjunct polymer is provided; wherein the acid catalyst has a molar ratio of Al to a heteroatom selected from the group of N, P, O, S, and combinations thereof greater than 2.0; and wherein the hydrocarbon is converted during the contacting.

In another embodiment, a method to make a catalyst is provided, comprising: mixing aluminum chloride in the presence of a hydrocarbon solvent and an organic chloride and optionally an ionic liquid; whereby the resulting acidic ionic liquid catalyst has greater than 15 wt% conjunct polymer and has a molar ratio of Al to a heteroatom selected from the group consisting of N, P, O, S, and combinations thereof greater than 2.0. The resulting ionic liquid catalyst is effective for catalyzing a reaction.

Additionally, there is provided an acid catalyst composition, comprising greater than 15 wt% conjunct polymer and having a molar ratio of Al to a heteroatom selected from the group consisting of N, P, O, S, and combinations

thereof greater than 2.0. The catalyst is effective for a conversion of a hydrocarbon.

Also, an acid hydroconversion catalyst is provided, comprising greater than 15 wt% halide-containing conjunct polymer and a Lewis acid; wherein
5 less than 0.1 wt% solid precipitates from the catalyst when it is held for three hours or longer at 25°C or below.

Definitions:

The term “comprising” means including the elements or steps that are
10 identified following that term, but any such elements or steps are not exhaustive, and an embodiment may include other elements or steps.

The term “effective for catalyzing a reaction” means that a commercially sufficient amount of a hydrocarbon is converted by a reaction. The term “effective for conversion of a hydrocarbon” also means a
15 commercially sufficient amount of the hydrocarbon is converted. For example, in an isoparaffin/olefin alkylation this could be greater than 75 wt% conversion of an olefin, greater than 85 wt% conversion of an olefin, greater than 95 wt% conversion of an olefin, or up to 100 wt% conversion of an olefin. The commercially significant amount can vary substantially depending on the
20 hydrocarbon being converted and the value of the converted product that is produced.

The term conjunct polymer was first used by Pines and Ipatieff to distinguish these polymeric molecules from typical polymers. Unlike typical polymers which are compounds formed from repeating units of smaller
25 molecules by controlled or semi-controlled polymerizations, “conjunct polymers” are “pseudo-polymeric” compounds formed asymmetrically from two or more reacting units by concurrent acid-catalyzed transformations including polymerization, alkylation, cyclization, additions, eliminations and hydride transfer reactions. Consequently, the produced “pseudo-polymeric”
30 may include a large number of compounds with varying structures and substitution patterns. The skeletal structures of “conjunct polymers”, therefore, range from the very simple linear molecules to very complex multi-feature molecules.

Some examples of the likely polymeric species in conjunct polymers were reported by Miron et al. (Journal of Chemical and Engineering Data, 1963), and Pines (Chem. Tech, 1982). Conjunct polymers are also commonly known to those in the refining industry as "red oils" due to their reddish-amber color or "acid-soluble oils" due to their high uptake in the catalyst phase where paraffinic products and hydrocarbons with low olefinicity and low functional groups are usually immiscible in the catalyst phase. In this application, the term "conjunct polymers" also includes ASOs (acid-soluble-oils), red oils, and C12+ polyalkylates.

In one embodiment the acid catalyst is a solid. Examples of solid acid catalysts are supported catalysts, supported Lewis acid catalysts, H-form zeolites, mass sulfated zirconia catalysts, zirconium oxide catalysts, solid phosphoric acid catalysts, crystalline tin oxide, supported sulfonic acids, and heteropoly acids.

In one embodiment the acid catalyst is a liquid. Examples of liquid catalysts are sulfuric acid or hydrofluoric acid. In another embodiment the liquid acid catalyst is an ionic liquid catalyst.

Ionic Liquid Catalyst:

"Ionic liquids" are liquids whose make-up is comprised of ions as a combination of cations and anions. The most common ionic liquids are those prepared from organic-based cations and inorganic or organic anions. Ionic liquid catalysts are used in a wide variety of reactions, including Friedel-Crafts reactions.

The ionic liquid catalyst is composed of at least two components which form a complex. To be effective at alkylation the ionic liquid catalyst is acidic. The ionic liquid catalyst comprises a first component and a second component. The first component of the catalyst will typically comprise a Lewis acid compound selected from components such as Lewis acid compounds of Group 13 metals, including aluminum halides, alkyl aluminum halide, gallium halide, and alkyl gallium halide (see International Union of Pure and Applied Chemistry (IUPAC), version 3, October 2005, for Group 13 metals of the periodic table). Other Lewis acid compounds besides those of Group 13

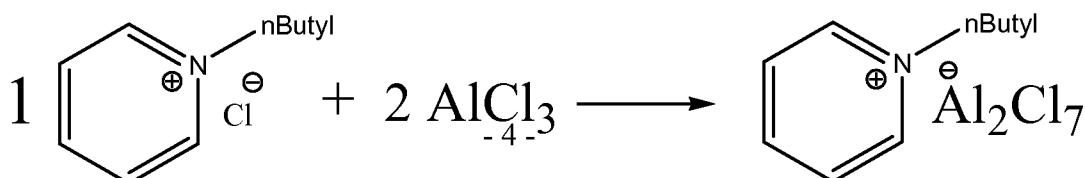
metals may also be used. In one embodiment the first component is aluminum halide or alkyl aluminum halide. For example, aluminum trichloride (AlCl_3) may be used as the first component for preparing the ionic liquid catalyst.

The second component making up the ionic liquid catalyst is an organic salt or mixture of salts. These salts may be characterized by the general formula Q^+A^- , wherein Q^+ is an ammonium, phosphonium, boronium, oxonium, iodonium, or sulfonium cation and A^- is a negatively charged ion such as Cl^- , Br^- , ClO_4^- , NO_3^- , BF_4^- , BCl_4^- , PF_6^- , SbF_6^- , AlCl_4^- , Al_2Cl_7^- , $\text{Al}_3\text{Cl}_{10}^-$, ArF_6^- , TaF_6^- , CuCl_2^- , FeCl_3^- , SO_3CF_3^- , SO_3C_7^- , and 3-sulfurtrioxyphenyl. In one embodiment the second component is selected from those having quaternary ammonium halides containing one or more alkyl moieties having from about 1 to about 9 carbon atoms, such as, for example, trimethylammonium hydrochloride, methyltributylammonium, 1-butylpyridinium, or alkyl substituted imidazolium halides, such as for example, 1-ethyl-3-methyl-imidazolium chloride.

In one embodiment the ionic liquid catalyst is a quaternary ammonium chloroaluminate ionic liquid having the general formula $\text{RR}'\text{R}''\text{N}^+\text{H}^+\text{Al}_2\text{Cl}_7^-$, wherein RR' and R'' are alkyl groups containing 1 to 12 carbons. Examples of quaternary ammonium chloroaluminate ionic liquid salts are an N-alkylpyridinium chloroaluminate, an N-alkyl-alkylpyridinium chloroaluminate, a pyridinium hydrogen chloroaluminate, an alkyl pyridinium hydrogen chloroaluminate, a di-alkyl-imidazolium chloroaluminate, a tetra-alkylammonium chloroaluminate, a tri-alkyl-ammonium hydrogen chloroaluminate, or a mixture thereof.

The presence of the first component should give the ionic liquid a Lewis or Franklin acidic character. Generally, the greater the mole ratio of the first component to the second component, the greater is the acidity of the ionic liquid mixture.

For example, a typical reaction mixture to prepare n-butyl pyridinium chloroaluminate ionic liquid salt is shown below:



The molar ratio of Al to the heteroatom is greater than 2.0 when the acid catalyst is held at a temperature at or below 25°C for at least two hours.

5 In different embodiments the molar ratio of Al to the heteroatom is about 5 or greater, about 10 or greater, about 50 or greater, or even greater than 100. In some embodiments there is little or no heteroatom, so the molar ratio of Al to the heteroatom can be about 10 to about 1000, or even higher.

The acid catalyst comprises greater than 15 wt% conjunct polymer.

10 The high level of conjunct polymer in the catalyst increases the catalyst's capacity to uptake acids, such as AlCl_3 . In different embodiments the acid catalyst comprises greater than 20 wt% conjunct polymer, greater than 25 wt% conjunct polymer, greater than 30 wt% conjunct polymer, greater than 40 wt% conjunct polymer, or greater than 50 wt% conjunct polymer.

15 The contacting may occur at any temperature known to produce good hydrocarbon conversion. These temperatures can range from about -20°C up to about 500°C. For isoparaffin/olefin alkylation using an ionic liquid catalyst the temperature can range from about -20°C up to about 200°C. In different embodiments the temperature can be from -10°C to 100°C, from 0°C to 50°C,
20 or below 25°C.

In one embodiment the acid catalyst is made with reagents having no nitrogen-containing compounds.

In another embodiment the acid catalyst is made from at least one conjunct polymer and a Lewis acid. AlCl_3 is one example of a useful Lewis
25 acid. In yet another embodiment the acid catalyst is made from at least one conjunct polymer, AlCl_3 , and hydrogen chloride. The conjunct polymer can comprise a halide. Examples of halides are fluorine, chlorine, bromine, iodine, and combinations thereof.

The level of conjunct polymer in the acid catalyst is determined by
30 hydrolysis of known weights of the catalyst. An example of a suitable test method is described in Example 3 of commonly assigned U.S. Patent Publication Number US20070142213A1. Conjunct polymers can be recovered from the acid catalyst by means of hydrolysis. The hydrolysis recovery methods employ procedures that lead to complete recovery of the conjunct

polymers and are generally used for analytical and characterization purposes because it results in the destruction of the catalyst. Hydrolysis of the acid catalyst is done, for example, by stirring the spent catalyst in the presence of excess amount of water followed by extraction with low boiling hydrocarbon solvents such as pentane or hexane. In the hydrolysis process, the catalyst salt and other salts formed during hydrolysis go into the aqueous layer while conjunct polymers go into the organic solvent. The low boiling solvent containing the conjunct polymers are concentrated on a rotary evaporator under vacuum and moderate temperature to remove the extractant, leaving behind the high boiling residual oils (conjunct polymers) which are collected and analyzed. The low boiling extractants can be also removed by distillation methods.

In one embodiment, the conjunct polymer is extractable. The conjunct polymer may be extracted during a catalyst regeneration process, such as by treatment of the catalyst with aluminum metal or with aluminum metal and hydrogen chloride. Examples of methods for regenerating ionic liquid catalysts are taught in U.S. Patent Publications US20070142215A1, US20070142213A1, US20070142676A1, US20070142214A1, US20070142216A1, US20070142211A1, US20070142217A1, US20070142218A1, US20070249485 A1, and in U.S. Patent Applications 11/960319, filed December 19, 2007; 12/003577, filed December 28, 2007; 12/003578, filed December 28, 2007; 12/099486, filed April 8, 2008; and 61/118215, filed November 26, 2008.

One advantage of the acid catalyst having a molar ratio of Al to a heteroatom selected from the group of N, P, O, S, and combinations thereof greater than 2.0 is its ability to continue to function effectively to convert the hydrocarbon, without becoming significantly deactivated by conjunct polymer. In this embodiment the acid catalyst can be used continuously without having to be removed from the reactor for regeneration for more than 7 days, more than 25 days, or more than 50 days. In this embodiment the acid catalyst may be regenerated in part, such that only a portion of the acid catalyst is regenerated at a time and the hydrocarbon conversion process does not need to be interrupted. For example, a slip stream of the acid catalyst effluent can be regenerated and recycled to the hydrocarbon conversion reactor. In one

embodiment the level of the conjunct polymer is maintained within the desired range by partial regeneration in a continuous hydrocarbon conversion process.

Examples of hydrocarbon conversions are alkylation, isomerization,
5 hydrocracking, polymerization, dimerization, oligomerization, acylation, metathesis, copolymerization, hydroformylation, dehalogenation, dehydration, and combinations thereof. In one embodiment the hydrocarbon conversion is isoparaffin/olefin alkylation. Examples of ionic liquid catalysts and their use for isoparaffin/olefin alkylation are taught, for example, in U.S. Patent
10 Numbers 7,432,408 and 7,432,409, 7,285,698, and U.S. Patent Application Number 12/184069, filed July 31, 2008. In another embodiment the conversion of a hydrocarbon is alkylation of paraffins, alkylation of aromatics, or combinations thereof.

In some embodiments the acid catalyst comprising greater than 15 wt%
15 conjunct catalyst remains liquid, and does not precipitate significant amounts of solids when it is held for extended periods of time at 25°C. For example, in one embodiment the Lewis acid remains soluble in the acid catalyst, such that less than 0.5 wt%, less than 0.1 wt%, less than 0.05 wt%, less than 0.01 wt%, or zero wt% of the Lewis acid or other solid precipitates out of the liquid
20 catalyst when it is held for three hours or longer at 25°C. This provides a significant technical advantage over other ionic liquid catalysts that precipitate out solids during use.

The time the catalyst can be held at a temperature at or below 25°C can be fairly lengthy. In general, the time is for greater than a minute, but it
25 can be much longer, such as for greater than 5 minutes, for at least two hours, three hours or longer, more than 7 days up to two weeks, more than 50 days, several months, or even up to a year.

Any term, abbreviation or shorthand not defined is understood to have the ordinary meaning used by a person skilled in the art at the time the
30 application is filed. The singular forms “a,” “an,” and “the,” include plural references unless expressly and unequivocally limited to one instance.

All of the publications, patents and patent applications cited in this application are herein incorporated by reference in their entirety to the same extent as if the disclosure of each individual publication, patent application or

patent was specifically and individually indicated to be incorporated by reference in its entirety.

This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to make and use the invention. Many modifications of the exemplary embodiments of the invention disclosed above will readily occur to those skilled in the art. Accordingly, the invention is to be construed as including all structure and methods that fall within the scope of the appended claims.

EXAMPLES

Example 1:

An ionic liquid catalyst based on n-butyl pyridinium chloroaluminate, having a molar ratio of Al to N of about 5 was prepared and tested as follows: 10.8 g (81 mmoles) of AlCl_3 was combined with 5.0 ml (15 mmoles) of n-butyl pyridinium chloroaluminate ionic liquid salt in 30 ml isopentane. 20 ml (180 mmoles) t-butyl chloride was added over a period of 15 minutes. As the reaction proceeded, the hydrocarbon solution boiled and the temperature dropped to about 2 to 5 °C. After the t-butyl chloride addition ended, the temperature started to climb back up. Most of the added AlCl_3 was dissolved, although a small amount still remained undissolved. An additional 10 ml isopentane was added and a GC sample revealed that the hydrocarbon phases consisted of a mixture of saturated isoalkanes predominantly in the C5 to C7 range. After stirring over the weekend, almost all the AlCl_3 was dissolved, and the acid catalyst phase contained 24.6 wt% conjunct polymer.

5 ml of the conjunct polymer, prepared above, was cooled to 0°C. At t=0 min., 25 ml of a cold (0°C) solution of 3.6% 2-pentene in isopentane was added and the mixture was stirred on an ice bath. GC samples of the hydrocarbon phase showed slow olefin conversion. After 15 minutes, about 33 wt% of the olefin was converted. Following the addition of 30 ml gaseous hydrogen chloride (1.2 mmoles) the reaction rate increased dramatically. After an additional 3 minutes, 100% of the olefin was converted. The

hydrocarbon phase showed that the olefin conversion was to predominantly C8 to C10 isoalkanes.

Example 2:

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A liquid acid catalyst made entirely of conjunct polymer, and having no heteroatom-containing compounds containing N, S, O, or P, was prepared and tested. This liquid acid catalyst had a molar ratio of Al to heteroatom selected from N, S, O, P, or combinations thereof much greater than 100.

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14.2 g (106 mmol) AlCl_3 was slurried up in 30 ml isopentane at room temperature in a flask. 45 ml (38 g, 410 mmol) t-butyl chloride was added gradually over about half an hour. Gas evolution was observed. The temperature of the slurry in the flask dropped during addition. Without being bound by theory, it is expected that the temperature drop was caused by evaporating hydrogen chloride and the formation of isobutene in the reaction. After the complete addition of the t-butyl chloride, the flask was allowed to warm back up to room temperature. At this point the flask contained a clear brown somewhat viscous liquid with a very small amount of clear hydrocarbon phase on top. The yield of the clear brown somewhat viscous liquid was 31.9 g. The clear brown somewhat viscous liquid was analyzed and was found to contain 43.5 wt% conjunct polymer. This clear brown somewhat viscous liquid was a conjunct polymer based ionic liquid. Laboratory experience has shown that the conjunct polymer prepared in this manner does not to any significant extent differ from the conjunct polymer formed in ionic liquid catalyzed isobutane alkylation.

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5 ml of the conjunct polymer based ionic liquid described above was saturated with hydrogen chloride at 1 atm pressure and reacted with 25 ml of 5% 2-pentene in isopentane at 0°C as described in Example 3. After 1.5 minutes the olefin conversion was 74 wt%, and after 3 minutes more than 98 wt% of the olefin was converted. The reaction product contained a substantial amount of C9-C11 alkylate. Initially, in this experiment, much of the reacted olefin was converted to a mixture of 2- and 3-pentyl chloride, which subsequently reacted to form the final alkylate product.

Example 3:

Two alkylation experiments using different ionic liquid catalysts were run on the same feed, at the same temperature, and for the same length of time. The feed was isopentane and 2-pentenenes; the temperature was 0°C; and the time was 6 minutes. In one experiment the alkylation catalyst was n-butyl pyridinium heptachlorodialuminate. In the second experiment the alkylation catalyst was the same conjunct polymer acid catalyst as described in Example 2 (ASO.HAl₂Cl₇). The reaction products were collected and analyzed by GC. The GC results are shown below.

Ionic Liquid:	NBuPyAL ₂ CL ₇ (Reference)	ASO.HAl ₂ Cl ₇ Example 2
Reaction Conditions:	6 min, 0°C	6 min, 0°C
C6	15.44	22.85
C7	4.07	11.47
C8	3.35	5.79
C9	10.45	12.68
C10	33.36	32.10
C11+	33.33	15.11

The yields and selectivity of the products were similar between the two experiments. Although the n-butyl pyridinium heptachlorodialuminate hydrocarbon conversion gave a slightly heavier product in this particular experiment, this can be controlled by the adjustment of the hydrogen chloride level during the reaction. The adjustment of the hydrogen chloride level to control product selectivity is described in U.S. Patent Application No. 12/233,481, filed September 17, 2008.

WHAT IS CLAIMED IS:

1. A process for hydrocarbon conversion, comprising: contacting a hydrocarbon with an acid catalyst containing greater than 15 wt% conjunct polymer; wherein the acid catalyst has a molar ratio of Al to a heteroatom selected from the group of N, P, O, S, and combinations thereof greater than 2.0; and wherein the hydrocarbon is converted during the contacting.
2. The process of claim 1, wherein the acid catalyst comprises an ionic liquid catalyst.
3. The process of claim 2, wherein the ionic liquid catalyst is a quaternary ammonium chloroaluminate.
4. The process of claim 1, wherein the heteroatom is N.
5. The process of claim 1, wherein the molar ratio is about 5 or greater.
6. The process of claim 1, wherein the acid catalyst comprises greater than 20 wt% conjunct polymer.
7. The process of claim 1, wherein the contacting occurs at a temperature below 25°C.
8. The process of claim 1, wherein the acid catalyst is made from at least one conjunct polymer and a Lewis acid.
9. The process of claim 1, wherein the conjunct polymer comprises a halide.
10. A method to make a catalyst, comprising: mixing aluminum chloride in the presence of a hydrocarbon solvent and an organic chloride and optionally an ionic liquid to make an acidic ionic liquid catalyst; whereby the acidic ionic liquid catalyst has greater than 15 wt% conjunct polymer and a molar ratio of Al to a heteroatom selected from the group consisting of N, P, O, S, and combinations thereof greater than 2.0; and wherein the acidic ionic liquid catalyst is effective for catalyzing a reaction.
11. The method of claim 10, wherein the acidic ionic liquid catalyst comprises a quaternary ammonium chloroaluminate.
12. The method of claim 10, wherein the acidic ionic liquid catalyst has greater than 20 wt% conjunct polymer.
13. An acid catalyst composition, comprising greater than 15 wt% conjunct polymer and having a molar ratio of Al to a heteroatom selected from the

group consisting of N, P, O, S, and combinations thereof greater than 2.0;
wherein the catalyst is effective for a conversion of a hydrocarbon.

14. The acid catalyst of claim 13, comprising greater than 20 wt% conjunct polymer.
- 5 15. The acid catalyst of claim 13, having a molar ratio of about 5 or greater.
16. The acid catalyst of claim 13, additionally comprising a quaternary ammonium ionic liquid salt.
17. The acid catalyst of claim 13, wherein the conversion is alkylation of paraffins, alkylation of aromatics, or combinations thereof.
- 10 18. An acid hydroconversion catalyst, comprising greater than 15 wt% halide-containing conjunct polymer, and a Lewis acid; wherein less than 0.1 wt% solid precipitates from the catalyst when it is held for three hours or longer at 25°C or below.