

REDUCTION OF ORGANIC HALIDE CONTAMINATION IN HYDROCARBON PRODUCTS

FIELD OF THE INVENTION

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The present invention relates to methods for reducing organic halide concentration in hydrocarbon products made by hydrocarbon conversion processes using ionic liquid catalysts comprising a halogen-containing acidic ionic liquids.

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BACKGROUND OF THE INVENTION

Ionic liquids are liquids that are composed entirely of ions. The so-called “low temperature” ionic liquids are generally organic salts with melting points under 100 degrees C, often even lower than room temperature. Ionic liquids may be suitable for example for use as a catalyst and as a solvent in alkylation and polymerization reactions as well as in dimerization, oligomerization, acetylation, metatheses, copolymerization, isomerization, olefin hydrogenation, hydroformylation and combinations thereof.

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One class of ionic liquids is fused salt compositions, which are molten at low temperature and are useful as catalysts, solvents and electrolytes. Such compositions are mixtures of components which are liquid at temperatures below the individual melting points of the components.

Ionic liquids can be defined as liquids whose make-up is entirely 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. The most common organic cations are ammonium cations, but phosphonium and sulphonium cations are also frequently used. Ionic liquids of pyridinium and imidazolium are perhaps the most commonly used cations. Anions include, but not limited to, BF_4^- , PF_6^- , haloaluminates such as Al_2Cl_7^- and Al_2Br_7^- , $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$, alkyl sulphates (RSO_3^-), carboxylates (RCO_2^-) and many other. The most catalytically interesting ionic liquids for acid catalysis are those derived from ammonium halides and Lewis acids (such as AlCl_3 , TiCl_4 , SnCl_4 , FeCl_3). Chloroaluminate ionic liquids are perhaps the most commonly used ionic liquid catalyst systems for acid-catalyzed reactions.

Examples of such low temperature ionic liquids or molten fused salts are the chloroaluminate salts. Alkyl imidazolium or pyridinium chlorides, for example, can be mixed with aluminum trichloride (AlCl_3) to form the fused chloroaluminate salts. The use of the fused salts of 1-alkylpyridinium chloride and aluminum trichloride as electrolytes is discussed in U.S. Patent No. 4,122,245.

Other examples of ionic liquids and their methods of preparation may also be found in U.S. Patent Nos. 5,731,101; 6,797,853 and in U.S. Patent Application Publications 2004/0077914 and 2004/0133056.

The alkylation of isobutane with butenes and ethylene in ionic liquids has been described in U.S. Patent Nos. 5,750,455; 6,028,024; and 6,235,959 and open literature

(Journal of Molecular Catalysis, 92 (1994), 155-165; "Ionic Liquids in Synthesis", P. Wasserscheid and T. Welton (eds.), Wiley-VCH Verlag, 2003, pp 275).

In general, conversion of light paraffins and light olefins to more valuable cuts is very
5 lucrative to the refining industries. This has been accomplished by alkylation of
paraffins with olefins, and by polymerization of olefins. One of the most widely used
processes in this field is the alkylation of isobutane with C₃ to C₅ olefins to make
gasoline cuts with high octane number using sulfuric and hydrofluoric acids. This
process has been used by refining industries since the 1940's. The process was driven
10 by the increasing demand for high quality and clean burning high-octane gasoline.

Alkylate gasoline is a high quality and efficient burning gasoline that constitutes
about 14% of the gasoline pool. Alkylate gasoline is typically produced by alkylating
refineries isobutane with low-end olefins (mainly butenes). Currently, alkylates are
15 produced by using HF and H₂SO₄ as catalysts. Although these catalysts have been
successfully used to economically produce the best quality alkylates, the need for
safer and more environmentally friendly catalysts systems has become an issue to the
industries involved.

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SUMMARY OF THE INVENTION

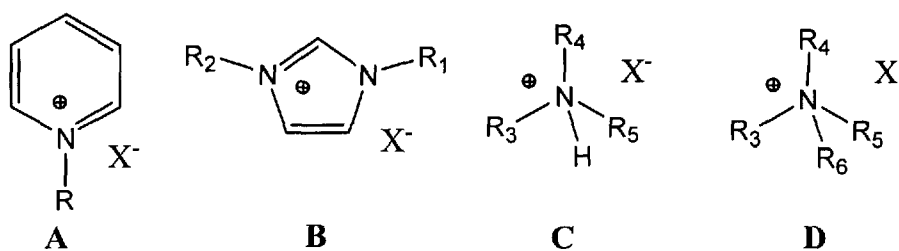
The present invention relates to methods for reducing halide concentration in a
hydrocarbon products made by a hydrocarbon conversion processes using ionic
liquid catalyst comprising a halogen-containing an acidic ionic liquid comprising: (i)

- separating at least a portion of the hydrocarbon product from the ionic liquid catalyst used in the hydrocarbon conversion process from the hydrocarbon product; (ii) contacting at least a portion of the separated hydrocarbon product with an ionic liquid catalyst having the same formula as the ionic liquid catalyst used in the hydrocarbon
- 5 conversion process; (iii) separating at least a portion of the hydrocarbon product from the ionic liquid catalyst of step (ii); and (iv) recovering at least a portion of the separated hydrocarbon product of step (iii) having a halide concentration less than the halide concentration of the hydrocarbon product of step (i).
- 10 Other aspects, features and advantages will be apparent from the description of the embodiments thereof and from the claims.

DETAILED DESCRIPTION

- 15 Hydrocarbon conversion processes using a halogen-containing acidic ionic liquid catalyst will generally produce a hydrocarbon product having an organic halide impurity content from 50 to 4000 ppm. Examples of such processes include alkylation, polymerization, dimerization, oligomerization, acetylation, metatheses, copolymerization, isomerization, olefin hydrogenation, hydroformylation and other
- 20 known processes. The presence of organic halides in such products may be undesirable. The present process can be used to reduce the organic halide concentration in such hydrocarbon products.

- The present process is being described and exemplified herein in large part by reference to alkylation processes using certain specific ionic liquid catalysts, but such description is not intended to limit the scope of the invention. The organic halide reduction processes described herein may be used for any hydrocarbon product
- 5 having an organic halide content from 50 to 4000 ppm which are made by hydrocarbon conversion processes using ionic liquid catalysts comprising halogen-containing acidic ionic liquids as will be appreciated by those persons having ordinary skill based on the teachings, descriptions and examples included herein.
- 10 In general, a strongly acidic ionic liquid is necessary for paraffin alkylation, e.g. isoparaffin alkylation. In that case, aluminum chloride, which is a strong Lewis acid in a combination with a small concentration of a Bronsted acid, is a preferred catalyst component in the ionic liquid catalyst scheme.
- 15 As noted above, the acidic ionic liquid may be any acidic ionic liquid. In one embodiment, the acidic ionic liquid is a chloroaluminate ionic liquid prepared by mixing aluminum trichloride (AlCl_3) and a hydrocarbyl substituted pyridinium halide, a hydrocarbyl substituted imidazolium halide, trialkylammonium hydrohalide or tetraalkylammonium halide to make an ionic liquid of the general formulas A, B, C
- 20 and D, respectively,



where R=H, methyl, ethyl, propyl, butyl, pentyl or hexyl group and X is a haloaluminate and preferably a chloroaluminate, and R₁ and R₂=H, methyl, ethyl, propyl, butyl, pentyl or hexyl group and where R₁ and R₂ may or may not be the same, and R₃, R₄, and R₅ and R₆=methyl, ethyl, propyl, butyl, pentyl or hexyl group and where R₃, R₄, R₅ and R₆ may or may not be the same.

The acidic ionic liquid is preferably selected from the group consisting of 1-butyl-4-methyl-pyridinium chloroaluminate, 1-butyl-pyridinium chloroaluminate, 1-butyl-3-methyl-imidazolium chloroaluminate and 1-H-pyridinium chloroaluminate. In a process according to the invention an alkyl halide may optionally be used as a promoter.

An alkyl halide is optionally added to the ionic liquid catalyst and acts to promote the alkylation by reacting with aluminum chloride to form the prerequisite cation ions in similar fashion to the Friedel-Crafts reactions. The alkyl halides that may be used include alkyl bromides, alkyl chlorides and alkyl iodides. In aspects of the invention, isopentyl halides, isobutyl halides, butyl halides, propyl halides and ethyl halides may be used. Alkyl chloride versions of these alkyl halides are preferable when chloroaluminate ionic liquids are used as the catalyst systems. Other alkyl chlorides

or halides having from 1 to 8 carbon atoms may be also used. The alkyl halides may be used alone or in combination.

A metal halide may be employed to modify the catalyst activity and selectivity. The metal halides most commonly used as inhibitors/modifiers in aluminum chloride-catalyzed olefin-isoparaffin alkylations include NaCl, LiCl, KCl, BeCl₂, CaCl₂, BaCl₂, SrCl₂, MgCl₂, PbCl₂, CuCl, ZrCl₄ and AgCl, as described by Roebuck and Evering (Ind. Eng. Chem. Prod. Res. Develop., Vol. 9, 77, 1970). Preferred metal halides are CuCl, AgCl, PbCl₂, LiCl, and ZrCl₄.

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HCl or any Bronsted acid may be employed as co-catalyst to enhance the activity of the catalyst by boosting the overall acidity of the ionic liquid-based catalyst. The use of such co-catalysts and ionic liquid catalysts is disclosed in U.S. Published Patent Application Nos. 2003/0060359 and 2004/0077914. Other co-catalysts that may be used to enhance the activity include IVB metal compounds preferably IVB metal halides such as ZrCl₄, ZrBr₄, TiCl₄, TiCl₃, TiBr₄, TiBr₃, HfCl₄, HfBr₄ as described by Hirschauer et al. in U.S. Patent No. 6,028,024.

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For example, in the process of producing alkylate hydrocarbon gasoline using haloaluminate ionic liquid catalysts, trace amounts of organic halides are found in the alkylate hydrocarbon. Removal of organic halides from gasoline is desirable to meet product specifications. Analogous results will occur, of course, when ionic liquid catalysts containing halides other than chlorides are used.

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In an aspect, the ionic liquid catalyst contains chlorides; the organic halides that contaminate the resulting product are organic chlorides. The chloride content in an alkylate hydrocarbon stream prepared using a chloroaluminate ionic liquid catalyst is generally from 50 ppm to 4000 ppm. Removal of trace organic chlorides from

5 alkylate is also desirable since organic chlorides may generate corrosive or harmful material such as HCl or dioxins during combustion.

In an embodiment, a method for reducing halide concentration in a hydrocarbon product made by a hydrocarbon conversion process using an ionic liquid catalyst

10 comprising a halogen-containing an acidic ionic liquid comprises first separating at least a portion of the hydrocarbon product from the ionic liquid catalyst used in the hydrocarbon conversion process. Then at least a portion of the separated hydrocarbon product is contacted with an ionic liquid catalyst having the same formula as the ionic liquid catalyst used in the hydrocarbon conversion process. This ionic liquid catalyst

15 may be fresh (unused) or regenerated. At least a portion of the hydrocarbon product is separated from the ionic liquid catalyst of the contacting step from which is recovered at least a portion of the separated hydrocarbon product having a halide concentration less than the halide concentration of the hydrocarbon product from the hydroconversion process. In one embodiment, the halide concentration is at least

20 30% less than the halide concentration of the hydrocarbon product of the hydroconversion process. In an aspect of that embodiment, the halide is a chloride.

In one embodiment, hydrocarbon conversion process conditions include an outlet pressure maintained at about 10 to about 250 psig and the reactor temperature

maintained about -10 to about 20 °C. The average residence time (combined volume of feeds and catalyst) is about 1-30 minutes.

Contacting can be accomplished by using various devices that provide close contact
5 of the hydrocarbon and ionic liquid catalyst. Such equipment includes, but is not limited to, in-line mixers, stirred tank reactors and nozzle mixers.

Separation of the hydrocarbon product from the ionic liquid catalyst may be accomplished by any method. Some methods and devices that are useful to achieve
10 the separation include settlers and decanters allowing enough residence time for the two phases to separate. The separator may be integral with the contactor as in a counter current extraction device or be a separate unit.

In an embodiment, the ionic liquid catalyst further comprises a co-catalyst selected
15 from the group consisting of Bronsted acids, organic halides and their mixtures thereof. The ionic liquid catalyst used for the contacting step can be a fresh (unused) catalyst or a regenerated catalyst. The ionic liquid catalyst can be a pyridinium chloroaluminate. The co-catalyst used can be butyl chloride. The hydrocarbon conversion process is selected from the group consisting of alkylation,
20 polymerization, dimerization, oligomerization, acetylation, metatheses, copolymerization, isomerization, olefin hydrogenation, hydroformylation and combinations thereof. Hydrocarbon conversion conditions for these processes are well known to persons of ordinary skill in the art.

In a second embodiment, an alkylation process comprises contacting a first hydrocarbon feed comprising at least one olefin having from 2 to 6 carbon atoms and a second hydrocarbon feed comprising at least one isoparaffin having from 3 to 6 carbon atoms with a halogen containing acidic ionic liquid catalyst under alkylation
5 conditions to produce an alkylate having an organic halide content from 50 to 4000 ppm.

At least a portion of the alkylate is separated from the ionic liquid catalyst. Then at least a portion of the separated alkylate is contacted with an ionic liquid catalyst
10 having the same formula as the ionic liquid catalyst used for production of the alkylate. At least a portion of the alkylate is separated from the ionic liquid from which at least a portion of the separated alkylate is recovered. This recovered alkylate has a halide concentration less than the halide concentration of alkylate produced by the alkylation step. In an aspect, the halide concentration in the alkylate after
15 contacting and separation is at least 30% less than the halide concentration of the alkylate as initially produced.

In an embodiment, the alkylation conditions include an outlet pressure maintained at about 30 to about 200 psig and the reactor temperature maintained about 0 to about 20
20 °C using external cooling. A molar ration of about 6:1 to about 10:1 of isobutane and olefin mixture is fed to the reactor with vigorous stirring. The average residence time (combined volume of feeds and catalyst) is about 1-30 minutes.

Contacting can be accomplished by using various devices that provide close contact of the hydrocarbon and ionic liquid catalyst. Such equipment includes, but is not limited to, in-line mixers, stirred tank reactors and nozzle mixers.

- 5 Separation of alkylate from ionic liquid catalyst may be accomplished by any method. Some methods and devices that are useful to achieve the separation include settlers and decanters allowing enough residence time for the two phases to separate. The separator may be integral with the contactor as in a counter current extraction device or be a separate unit.

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The following Examples are illustrative of the present invention, but are not intended to limit the invention in any way beyond what is contained in the claims which follow.

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EXAMPLE 1

21.9 g of N-butylpyridinium chloroaluminate ($C_5H_5NC_4H_9Al_2Cl_7$) ionic liquid catalyst having the following composition

20	Wt% Al	12.4
	Wt% Cl	56.5
	Wt% C	24.6
	Wt% H	3.2
	Wt% N	3.3

- was added to a closed container under N_2 atmosphere. Then 4.6 g of t-butyl chloride was added and the mixture was stirred for 5 minutes to produce a uniform mixture. The mixture was allowed to sit for 20 minutes to overnight

under N₂ atmosphere to determine whether the mixture would separate into the ionic liquid phase and the hydrocarbon phase. The mixture remained uniform and did not separate demonstrating that ionic liquid could be an effective absorbent for organic chloride species.

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EXAMPLE 2

(Alkylation of isobutane with C₃ – C₅ olefins using ionic liquid catalyst)

Paraffin feed containing predominantly isobutane and an olefin feed containing predominantly C₃, C₄, and C₅ olefins were obtained from a refinery. The feed

10 properties are as follows:

Table 1
Properties of Feeds for Alkylate Gasoline Synthesis

	Paraffin Feed	Olefin Feed
wt%		
C1	0.04	0.30
C2	0.05	0.05
C3	6.8	5.80
iC4	86.63	43.08
nC4	5.84	12.07
iC5	0.44	0.80
nC5	0.01	0.03
C6+	0.01	0.02
C3=	0.06	4.71
C4=	0.12	32.67
C5=	0.00	0.21
acetylene	0.00	0.01
butadiene	0.00	0.25
Sum	100.00	100.00

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C₃-C₅ olefin alkylation with isobutane was performed in a 300 cc continuously stirred tank reactor. An 8:1 molar ratio of isobutane and olefin mixture was fed to the reactor

while vigorously stirring at 1900 RPM. The ionic liquid catalyst of Example 1 was fed to the reactor via a second inlet port targeting to occupy 4-10 vol% in the reactor. The average residence time (combined volume of feeds and catalyst) was about 4-20 minutes. The outlet pressure was maintained at 50-150 psig using a backpressure
5 regulator. The reactor temperature was maintained at 0 °C using external cooling. About 100% conversion of olefin was observed, alkylate yield was nearly 200 wt% as predicted from the alkylation chemistry. The resulting alkylate gasoline had a chloride content in the range of 50-2000 ppm.

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EXAMPLE 3

(Chloride reduction in a first batch test)

A 300 mL autoclave was dried and taken into an inert atmosphere glove box. The autoclave was charged with 20 mL of ionic liquid catalyst and 200 mL of an alkylate gasoline sample containing 340 ppm chloride. The autoclave was then sealed,
15 removed from the glove box and stirred at 1500 RPM at room temperature (17 °C). The extraction (contacting) was run between 15 minutes and 60 minutes. The stirring was then stopped and the contents of the autoclave were allowed to sit and gravity separate for 3 minutes. The autoclave was then opened and the alkylate gasoline layer was collected and analyzed by X-ray fluorescence spectroscopy (XRF) and gas
20 chromatography. The XRF showed that the chloride level of the gasoline sample had been reduced as shown in Table 2. The gas chromatograph showed that the alkylate gasoline sample was not degraded during the extraction process.

Table 2
Reduction of Chloride in Alkylate Gasoline in Batch Tests #1

Contacting Time	% Chloride reduction by XRF
Starting Alkylate	0%
15 min	81%
30 min	88%
60 min	87%

- 5 The above data indicate contacting of ionic liquid with chloride containing alkylate gasoline is effective in reducing the chloride content in the gasoline.

EXAMPLE 4

(Chloride reduction in a second batch test)

- 10 A 300 mL autoclave was dried, taken into an inert-atmosphere glove box and charged with 20 grams of an alkylate gasoline sample containing 467 ppm of chloride. The autoclave was sealed and removed from the glove box. 120 grams of isobutane was then added to the autoclave. The autoclave was then stirred at 1500 RPM and heated to the extraction temperature. After the autoclave had been at the extraction
- 15 temperature for 15 minutes, 16.25 grams of ionic liquid catalyst was injected into the autoclave under 150 psi N₂ pressure (time = 0 sec). The extraction experiment was run for 15 minutes. The stirring was then stopped and the contents of the autoclave were allowed to gravity separate for 2 minutes. The autoclave was then depressurized, opened, and the hydrocarbon layer was collected. The hydrocarbon
- 20 layer was then stored at 10 °C for 12 – 16 hours to allow the isobutane to evaporate from the sample while retaining the alkylate gasoline component. The alkylate gasoline was analyzed by X-ray fluorescence spectroscopy (XRF) and gas chromatography. The XRF showed that the chloride level of the gasoline sample had

been reduced as shown in Table 3. The gas chromatograph showed that the alkylate gasoline sample was not degraded during the extraction process.

Table 3
Reduction of Chloride in Alkylate Gasoline in Batch Tests #2

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temperature	% Chloride reduction by XRF
15 °C	70%
25 °C	90%
50 °C	94%

The above data indicate contacting of ionic liquid with chloride containing alkylate gasoline is effective in reducing the chloride content in the gasoline.

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EXAMPLE 5

(Continuous Organic Chloride Removal Process)

The evaluation of a continuous organic chloride removal process was performed in a 25 cc continuously stirred tank reactor. An approximate 7:1 molar ratio of isobutane and alkylate gasoline mixture containing 305 ppm chloride was fed to the reactor while vigorously stirring at 1900 RPM. An ionic liquid catalyst was fed to the reactor via a second inlet port targeting to occupy 6 vol% of the reactor volume. The average residence time (combined volume of feeds and catalyst) was about 1 to 5 minutes. The outlet pressure was maintained at 50-75 psig using a back pressure regulator. The reactor temperature was maintained at 10 °C using an external cooling loop. The reactor effluent was then separated into 3 phases; an ionic liquid catalyst phase, a liquid hydrocarbon phase, and a gaseous hydrocarbon phase. The liquid hydrocarbons were collected and analyzed by X-ray fluorescence spectroscopy (XRF) and gas chromatography. The XRF showed that the chloride level of the gasoline

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sample had been reduced as shown in Table 4. The gas chromatograph showed that the alkylate gasoline sample was not degraded during the extraction process.

Table 4
Reduction of Chloride in a Continuous Organic Chloride Removal Process

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sample #	% Chloride reduction by XRF
1	84%
2	88%
3	89%
4	91%
5	92%
6	91%

The above data indicate contacting of ionic liquid with chloride containing alkylate gasoline is effective in reducing the chloride content in the gasoline.

- 10 There are numerous variations on the present invention which are possible in light of the teachings and supporting examples described herein. It is therefore understood that within the scope of the following claims, the invention may be practiced otherwise than as specifically described or exemplified herein.

WHAT IS CLAIMED IS:

1. A method for reducing halide concentration in a hydrocarbon product made by a hydrocarbon conversion process using an ionic liquid catalyst comprising a halogen-containing an acidic ionic liquid comprising:
 - (i) separating at least a portion of the hydrocarbon product from the ionic liquid catalyst used in the hydrocarbon conversion process from the hydrocarbon product;
 - (ii) contacting at least a portion of the separated hydrocarbon product with an ionic liquid catalyst having the same formula as the ionic liquid catalyst used in the hydrocarbon conversion process;
 - (iii) separating at least a portion of the hydrocarbon product from the ionic liquid catalyst of step (ii) ; and
 - (iv) recovering at least a portion of the separated hydrocarbon product of step (iii) having a halide concentration less than the halide concentration of the hydrocarbon product of step (i).
2. The method of claim 1, wherein the ionic liquid catalyst used for the hydrocarbon conversion process further comprises a co-catalyst selected from the group consisting of Bronsted acids, organic halides and their mixtures thereof.
3. The method of claim 1, wherein the hydrocarbon conversion process selected from the group consisting of alkylation, polymerization, dimerization,

oligomerization, acetylation, metatheses, copolymerization, isomerization, olefin hydrogenation, hydroformylation and combinations thereof.

4. The method of claim 1, wherein the ionic liquid catalyst in step (ii) is fresh catalyst.
5. The method of claim 1, wherein the ionic liquid catalyst in step (ii) is regenerated catalyst.
6. The method of claim 1, wherein the ionic liquid catalyst is a pyridinium chloroaluminate.
7. The method of claim 2, wherein the co-catalyst is butyl chloride.
8. The method of claim 1, wherein the halide is a chloride.
9. The method of claim 1, wherein the halide concentration in the recovered hydrocarbon in step (v) is at least 30% less than the halide concentration of the hydrocarbon product of step (i).
10. An alkylation process comprising:
- (i) contacting a first hydrocarbon feed comprising at least one olefin having from 2 to 6 carbon atoms and a second hydrocarbon feed comprising at least one isoparaffin having from 3 to 6 carbon atoms

- with a halogen containing acidic ionic liquid catalyst under alkylation conditions to produce an alkylate having an organic halide content from 50 to 4000 ppm;
- 5 (ii) separating at least a portion of the alkylate from the ionic liquid catalyst;
- (iii) contacting at least a portion of the separated alkylate with an ionic liquid catalyst having the same formula as the ionic liquid catalyst used for production of the alkylate in step (i);
- 10 (iv) separating at least a portion of the alkylate from the ionic liquid catalyst and
- (v) recovering at least a portion of the separated alkylate of step (iv) having a halide concentration less than the halide concentration of the alkylate of step (i).
- 15 11. The method of claim 10, wherein the ionic liquid catalyst further comprise a co-catalyst selected from the group consisting of Bronsted acids, organic halides and their mixtures thereof.
12. The method of claim 10, wherein the ionic liquid catalyst of step (iii) is fresh catalyst.
- 20 13. The method of claim 10, wherein the ionic liquid catalyst of step (iii) is regenerated catalyst.

14. The method of claim 10, wherein the ionic liquid catalyst is a pyridinium chloroaluminate.

15. The method of claim 11, wherein the co-catalyst is t-butyl chloride.

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16. The method of claim 10, wherein the alkylate product of step (v) is alkylate gasoline.

17. The method of claim 10, wherein the halide is a chloride.

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18. The method of claim 10, wherein the halide concentration in the recovered hydrocarbon in step (v) is at least 30% less than the halide concentration of the alkylate of step (i).

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