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(54) **Title:** REGENERATION OF DEACTIVATED IONIC LIQUIDS

(57) **Abstract:** The present disclosure relates to a process for separating the cationic and anionic components from an ionic liquid deactivated by at least one deactivating agent. The process includes reacting the deactivated ionic liquid with tetraethoxysilane to convert the anionic component of the ionic liquid into the form of a gel; thereby freeing the anionic component of the deactivating agent(s). The cationic component of the ionic liquid is also subsequently freed from the deactivating agent(s) and recovered for further combining with an anionic component for reuse. The gellified-anionic component may also be used for various applications such as a catalyst or as a filler.



REGENERATION OF DEACTIVATED IONIC LIQUIDS

FIELD OF THE DISCLOSURE

The present disclosure relates to ionic liquids. Particularly, the present disclosure relates to a process for the regeneration of deactivated ionic liquids by separating its cationic and anionic components.

BACKGROUND

Ionic compounds, as the name suggests, are compounds comprising cations and anions. Typically, they consist of salts having melting point below 100 °C. Ionic liquids are known to be used in various applications such as catalysts, solvents and electrolytes in processes such as alkylation, polymerization, dimerization, oligomerization, acetylation, metatheses and copolymerization. For instance, United States Patent No. 7432408 recites a method for alkylation of isoparaffin and C₂-C₅ olefins using ionic liquids such as 1-butyl-4-methyl-pyridinium chloroaluminate (BMP), 1-butyl-pyridinium chloroaluminate (BP), 1-butyl-3-methyl-imidazolium chloroaluminate (BMIM) and 1-H-pyridinium chloroaluminate (HP) as the catalyst. United States Patent No. 7495144 also suggests a method for alkylation of isoparaffin and C₂-C₅ olefins using a composite ionic liquid catalyst, wherein the ionic liquid is a mixture of acid ionic liquids such as 1-butyl-4-methyl-pyridinium chloroaluminate (BMP), 1-butyl-pyridinium chloroaluminate (BP), 1-butyl-3-methyl-imidazolium chloroaluminate (BMIM) and 1-H-pyridinium chloroaluminate (HP) and metal halides such as AlCl₃.

Ammonium, phosphonium, sulphonium, pyridinium and imidazolium are some of the commonly used cations; whereas BF₄⁻, PF₆⁻, haloaluminates such as Al₂Cl₇⁻ and Al₂Br₇⁻, [(CF₃SO₂)₂N]⁻, alkyl sulphates (RSO₃⁻), carboxylates (RCO₂⁻) are some of the commonly used anions in ionic liquids. However, when the haloaluminate containing ionic liquids are used in any of the afore-stated reactions, they get

deactivated due to various chemical entities present in the reaction such as hydrocarbons, conjunct polymers and water. Thus, upon the completion of the reaction, the ionic liquids, due to their deactivated state, are incapable of being reused for other reactions. Replenishing the stock becomes imperative; however the expensive nature of the chemical results in an exponential increase in the processing cost. Moreover, as the used ionic liquids have to be discarded, tremendous amount of waste is generated and valuable reagents get wasted.

Attempts have been made to facilitate the regeneration and reuse of ionic liquids. United States Patent Application No. 20100160145 recites a process for recycling ionic liquid catalyst that employs a secondary alcohol to achieve this. WO 2010062902 also describes a process for recycling ionic liquids. However, the process of WO 2010062902 facilitates this by removing aluminum trichloride from the ionic liquid by way of cooling or cooling and seeding the ionic liquid to precipitate out the aluminum trichloride.

The techniques that have been used for the regeneration of ionic liquids are, however, associated with certain disadvantages such as use of expensive reagents and time-consuming processes. The present disclosure, therefore, provides a process for the regeneration of ionic liquids which acts as an alternative to the conventionally known processes. Not only is the process cost effective as compared to the conventional process, but it also generates certain reaction products that may be effectively harnessed.

OBJECTS

Some of the objects of the present disclosure, of which at least one embodiment is adapted to provide, are described herein below:

It is an object of the present disclosure to provide a process for the regeneration of deactivated ionic liquids.

It is another object of the present disclosure to provide a process for the regeneration of deactivated ionic liquids and for the separation of its cationic and anionic components.

It is yet another object of the present disclosure to provide a process for the regeneration of deactivated ionic liquids, which is economical and environment friendly.

It is still another object of the present disclosure to ameliorate one or more problems of the prior art or to at least provide a useful alternative.

Other objects and advantages of the present disclosure will be more apparent from the following description which is not intended to limit the scope of the present disclosure.

SUMMARY

The present disclosure provides a process for separating the cationic and anionic components from an ionic liquid deactivated by at least one deactivating agent; said process comprising the following steps:

- a. reacting said ionic liquid with tetraethoxysilane, in the presence of a first solvent and a pH adjusting agent, at a temperature ranging from 40 °C to 90 °C, at a stirring speed ranging from 50 to 500 rpm, at pH ranging from 9-13 and at atmospheric pressure to obtain a bi-phasic mixture comprising:
 - i. a gel phase comprising a reaction product of said anionic component and tetraethoxysilane; and
 - ii. a solvent phase comprising said cationic component and said deactivating agent(s);
- b. separating said gel phase from said bi-phasic mixture to yield said solvent phase comprising said cationic component and said deactivating agent(s);

- c. extracting said deactivating agent(s) from said solvent phase by using a second solvent to obtain a cationic component devoid of said deactivating agent(s); and
- d. recovering said cationic component.

The cationic component can be a hetero-cyclic cationic component selected from the group consisting of 1-butyl-3-methyl imidazolium bromide, 1-butyl-3-methyl imidazolium chloride, 1-butyl-4-methylpyridinium chloride and 1-butyl-4-methylpyridinium bromide; said anionic component can be aluminum chloride; said deactivating agent can be at least one selected from the group consisting of conjunct polymer(s), polymers, tar, hydrocarbons and moisture and said gel phase comprises aluminosilicate.

DETAILED DESCRIPTION

The disclosure will now be described with reference to the accompanying embodiments which do not limit the scope and ambit of the disclosure. The description provided is purely by way of example and illustration.

The embodiments herein and the various features and advantageous details thereof are explained with reference to the non-limiting embodiments in the following description. Descriptions of well-known components and processing techniques are omitted so as to not unnecessarily obscure the embodiments herein. The examples used herein are intended merely to facilitate an understanding of ways in which the embodiments herein may be practiced and to further enable those of skill in the art to practice the embodiments herein. Accordingly, the examples should not be construed as limiting the scope of the embodiments herein.

The description of the specific embodiments will so fully reveal the general nature of the embodiments herein that others can, by applying current knowledge, readily modify and/or adapt for various applications such specific embodiments without departing from the generic concept, and, therefore, such adaptations and modifications should and are intended to be comprehended within the meaning and range of

equivalents of the disclosed embodiments. It is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation. Therefore, while the embodiments herein have been described in terms of preferred embodiments, those skilled in the art will recognize that the embodiments herein can be practiced with modification within the spirit and scope of the embodiments as described herein.

Ionic liquids are used as catalysts, solvents and electrolytes in different reactions such as polymerization and alkylation. As the completion of these processes nears, the ionic liquids get deactivated due to different chemical entities such as conjunct polymers and hydrocarbons; thereby obviating their reuse. The present disclosure provides a process for the regeneration of used, deactivated ionic liquids that may be regenerated and reused for different applications. The deactivating agent(s) of the present disclosure is selected from the group consisting of conjunct polymer(s), polymers, tar, hydrocarbons and moisture. The process of the present disclosure achieves the regeneration of the ionic liquids by effecting the separation of its cationic and anionic components from the deactivating agent(s). Typically, the cationic component of the present disclosure is a heterocyclic cationic component and is selected from the group consisting of 1-butyl-3-methyl imidazolium bromide, 1-butyl-3-methyl imidazolium chloride, 1-butyl-4-methylpyridinium chloride and 1-butyl-4-methylpyridinium bromide and the anionic component is aluminum chloride.

The present process initially includes reacting the deactivated ionic liquid with tetraethoxysilane in the presence of a first solvent. Aluminum chloride present as the anionic component in the ionic liquid reacts with silicone present in the tetraethoxysilane to form aluminosilicate. Typically, the aluminosilicate is in the form of a gel formed with the first solvent. The process of gel formation between aluminum chloride and tetraethoxysilane brings about the release of the deactivating agent(s) from the anionic component. Furthermore, as the binding between the anionic part and cationic part is broken, the cationic part gets free. Therefore, the bi-phasic mixture that results after the first step comprises the gellified aluminosilicate as one phase and the

solvent phase that includes cationic component and the deactivating agent(s) both dissolved in the first solvent, as the second phase. Typically, the first solvent is at least one selected from the group consisting of ethanol, methanol and water where water is used for hydrolysis of tetraethoxysilane. The present step is carried out in the presence of at least one pH adjusting agent selected from the group consisting of carbonates or hydroxides such as sodium carbonate and sodium hydroxide. The pH range is maintained in the range of 9-13 as a decrease in the pH of the solution promotes the formation of amorphous aluminosilicates.

Subsequently, the gel phase is separated and recovered from the bi-phasic mixture to leave behind the solvent phase containing the cationic component and the deactivating agent(s). The separated gel phase may further be processed to obtain purified aluminosilicates that may be used for different applications. The solvent phase that remains after the separation of the aluminosilicates is then distilled to remove the first solvent and the slurry that results is treated with a second solvent to extract the deactivating agent(s). Typically, the second solvent is at least one selected from the group consisting of ethyl acetate, toluene and xylene.

Once, the deactivating agent(s) are separated, the cationic component is recovered and purified by extracting in solvents such as dichloromethane (DCM) which renders it ready to be combined with another anionic component for use as a fresh ionic liquid.

It is evident from the description presented herein above that the present process causes the regeneration and recycling of ionic liquids by recovering the deactivated cationic and anionic components. The separated anionic component, in the form of a gel obtained according to the present process, can prove to be valuable for use as a catalyst; filler in paper, rubber and paint industry and as a coagulant for the removal of heavy metals from waste water. Thus, the process of the present disclosure effectively reuses the deactivated ionic liquid which would earlier have been discarded; thereby making the process economical and environment friendly.

The present disclosure is further described in light of the experiments provided herein below which are set forth for illustration purpose only and not to be construed for limiting the scope of the disclosure. These laboratory scale experiments can be scaled up to industrial/commercial scale.

Example 1: Process for the separation of the cationic and anionic components

Preparation of fresh ionic liquid catalyst (1-Butyl-3-methylimidazolium bromide + aluminum chloride)

The setup consisted of a 5 L three necked round bottom (RB) flask fitted with an overhead stirrer and placed in an ice bath at 0-5 °C. The flask was clamped to provide stability under stirring. The whole assembly was kept under nitrogen atmosphere. 680 g of 1-Butyl-3-methylimidazolium bromide, [BMIM]Br, was weighed and carefully charged into the flask through a funnel. The stirrer was started at slow speed. Then 830 g of aluminum chloride, AlCl₃, was weighed and added slowly into the flask. The charging of AlCl₃ was completed in 1.5 hours after which the mixture was stirred for 2 hours to mix the raw materials properly. The final catalyst was closed tightly under nitrogen conditions.

Separation of the cationic and anionic components from the fresh ionic liquid catalyst

100 g of the fresh ionic liquid catalyst prepared herein above was taken in a RB flask and 343.5 g of tetraethyl orthosilicate was slowly added to it accompanied by stirring. To this mixture, 119 g of water and 250 ml of ethanol was added. A small amount of sodium hydroxide (NaOH) was also added to maintain the pH between 12 and 13. The reaction mixture was heated at 90 °C for 3 hours which resulted in the formation of an aluminosilicate gel with ethanol. Water and ethanol were removed by filtration and the solid aluminosilicates were dried in an oven to give a yield of 170 g. The aqueous/alcoholic layer was distilled to get 70 g slurry. The remaining solid was extracted with 250 ml of dichloromethane (DCM), subsequent to which 150 ml of the DCM layer was evaporated to give 21 g of BMIMBr.

Preparation of deactivated ionic liquid catalyst (Alkylation using the ionic liquid catalyst prepared herein above)

9.2 liters of paraffin stream containing 10-15% C₁₀ to C₁₄ olefins and 3.6 liters of benzene were added into a 25.0 liter round bottom reactor kept inside a heating mantle. The agitator was started and heating coils were switched on. When the mixture attained the temperature of 45 °C, 0.13 kg of the afore-stated fresh catalyst was charged and stirred for 10 minutes. After 10 minutes the hydrocarbon and the catalyst layers were separated and the bottom catalyst layer was recycled back with the same quantities of fresh olefin stream and benzene.

Separation of the cationic and anionic components from the deactivated catalyst (Aluminosilicate: Si/Al = 4)

100 g of the afore-mentioned deactivated ionic liquid was taken in a RB flask to which 343.5 g of tetraethyl orthosilicate was slowly added with stirring followed by addition of 119 g of water and 250 ml of ethanol. Small amounts of NaOH were added to the solution to adjust the pH between 12 and 13. The reaction mixture was heated at 80 °C for 3 hours which resulted in the formation of an aluminosilicate gel with ethanol. The gel was soaked in 25 ml of water followed by crushing. The ethanol was removed by distillation and then was washed with ethyl acetate to remove the organic impurities. The water was then removed by filtration. The solid aluminosilicates were dried in an oven to give a yield of 170 g. The aqueous layer was distilled to get 260 ml of aqueous solution and 70 g of solid. The solid was added to the solid obtained from ethanol and extracted with 250 ml of dichloromethane (DCM) after which the DCM layer was evaporated (150 ml) to get 21 g of BMIMBr.

Separation of the cationic and anionic components from the deactivated catalyst (Aluminosilicate: Si/Al = 8)

100 g of the afore-stated deactivated ionic liquid was taken in a RB flask to which 687.3 g of tetraethyl orthosilicate was slowly added with stirring followed by addition of 237.5 g of water and 250 ml of ethanol. Small amounts of NaOH were added to the solution to adjust the pH between 12 and 13. The reaction mixture was heated at 80 °C

for 3 hours which formed the aluminosilicate gel with ethanol. The gel was soaked in 500 ml of water followed by crushing. The ethanol was removed by distillation and then was washed with ethyl acetate to remove the organic impurities. The water was then removed by filtration. The solid aluminosilicates were dried in an oven to give a yield of 300 g. The aqueous layer was distilled to get 450 ml of aqueous solution and 80 g of solid. The solid was added to the solid obtained from ethanol and extracted with 250 ml of dichloromethane (DCM) after which the DCM layer was evaporated (200 ml) to get 23 g of BMIMBr.

Inference:

The process of the present disclosure for separating the cationic and anionic components from ionic liquids can be successfully applied for deactivated ionic liquids.

Throughout this specification the word “comprise”, or variations such as “comprises” or “comprising”, will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

The use of the expression “at least” or “at least one” suggests the use of one or more elements or ingredients or quantities, as the use may be in the embodiment of the disclosure to achieve one or more of the desired objects or results.

Any discussion of documents, acts, materials, devices, articles or the like that has been included in this specification is solely for the purpose of providing a context for the disclosure. It is not to be taken as an admission that any or all of these matters form a part of the prior art base or were common general knowledge in the field relevant to the disclosure as it existed anywhere before the priority date of this application.

The numerical values mentioned for the various physical parameters, dimensions or quantities are only approximations and it is envisaged that the values higher/lower than the numerical values assigned to the parameters, dimensions or quantities fall

within the scope of the disclosure, unless there is a statement in the specification specific to the contrary.

While considerable emphasis has been placed herein on the components and component parts of the preferred embodiments, it will be appreciated that many embodiments can be made and that many changes can be made in the preferred embodiments without departing from the principles of the disclosure. These and other changes in the preferred embodiment as well as other embodiments of the disclosure will be apparent to those skilled in the art from the disclosure herein, whereby it is to be distinctly understood that the foregoing descriptive matter is to be interpreted merely as illustrative of the disclosure and not as a limitation.

TECHNICAL ADVANTAGES AND ECONOMIC SIGNIFICANCE

- The process of the present disclosure recovers the used, deactivated ionic liquid, which can be further reused for different applications.
- The process of the present disclosure saves undue waste of valuable chemicals; thereby reducing the environmental hazards.
- The expenditure on purchasing fresh ionic liquid catalyst for every single application is reduced.
- The gellified anionic component obtained as a result of the process of the present disclosure may find further applications in areas such as catalysts; filler in paper, rubber and paint industry and as a coagulant for the removal of heavy metals from waste water; thereby increasing the process profitability.

CLAIMS:

1. A process for separating the cationic and anionic components from an ionic liquid deactivated by at least one deactivating agent; said process comprising the following steps:
 - a. reacting said deactivated ionic liquid with tetraethoxysilane, in the presence of a first solvent and a pH adjusting agent, at a temperature ranging from 40 °C to 90 °C, at a stirring speed ranging from 50 to 500 rpm, at pH ranging from 9-13 and at atmospheric pressure to obtain a bi-phasic mixture comprising:
 - i. a gel phase comprising a reaction product of said anionic component and tetraethoxysilane; and
 - ii. a solvent phase comprising said cationic component and said deactivating agent(s);
 - b. separating said gel phase from said bi-phasic mixture to yield said solvent phase comprising said cationic component and said deactivating agent(s);
 - c. extracting said deactivating agent(s) from said solvent phase by using a second solvent to obtain a cationic component devoid of said deactivating agent(s); and
 - d. recovering said cationic component.
2. The process as claimed in claim 1, wherein said cationic component is a heterocyclic cationic component.
3. The process as claimed in claim 2, wherein said heterocyclic cationic component is at least one selected from the group consisting of 1-butyl-3-

methyl imidazolium bromide, 1-butyl-3-methyl imidazolium chloride, 1-butyl-4-methylpyridinium chloride and 1-butyl-4-methylpyridinium bromide.

4. The process as claimed in claim 1, wherein said anionic component is a metal chloride.
5. The process as claimed in claim 1, wherein said anionic component is aluminum chloride.
6. The process as claimed in claim 1, wherein said deactivating agent is at least one selected from the group consisting of conjunct polymer(s), polymers, tar, hydrocarbons and moisture.
7. The process as claimed in claim 1, wherein said first solvent is at least one selected from the group consisting of water, ethanol and methanol.
8. The process as claimed in claim 1, wherein said pH adjusting agent is at least one selected from the group consisting of hydroxides or carbonates like sodium hydroxide and sodium carbonate.
9. The process as claimed in claim 1, wherein said gel phase comprises aluminosilicate.
10. The process as claimed in claim 1, wherein said second solvent is at least one selected from the group consisting of ethyl acetate, xylene and toluene.

INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER
C02F1/58, C02F1/52 Version=2015.01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C02F

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

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

IPO INTERNAL DATABASE, PATSEER

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 20100160145 A1, 24 June 2010, CHEVRON CORPORATION, See abstract, example, para 25, para 26 and claims 1-26.	1-10
A	US 20100130799 A1, 27 May 2010, CHEVRON U.S.A. INC., See abstract and claim 1-10.	1-10

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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INTERNATIONAL SEARCH REPORT
Information on patent family members

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Citation	Pub.Date	Family	Pub.Date
US 20100160145 A1	24-06-2010	WO 2010075224 A2	01-07-2010
		WO 2010075224 A3	30-09-2010
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