

DOCUMENT MADE AVAILABLE UNDER THE PATENT COOPERATION TREATY (PCT)

International application number:	PCT/IB2017/057674
International filing date:	06 December 2017 (06.12.2017)
Document type:	Certified copy of priority document
Document details:	Country/Office: IN
	Number: 201621042124
	Filing date: 09 December 2016 (09.12.2016)
Date of receipt at the International Bureau:	19 January 2018 (19.01.2018)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a),(b) or (b-bis)

IBI/57679



INTELLECTUAL
PROPERTY INDIA

PATENTS | DESIGNS | TRADE MARKS
GEOGRAPHICAL INDICATIONS

बौद्धिक संपदा भारत

एकस्व अभिकल्प व्यापार चिह्न

भौगोलिक उपदर्शन



सत्यमेव जयते

भारत सरकार

GOVERNMENT OF INDIA

वाणिज्य एवं उद्योग मंत्रालय

MINISTRY OF COMMERCE & INDUSTRY

पेटेंट कार्यालय

THE PATENT OFFICE

जिस किसी से संबन्धित हो
TO WHOMSOEVER IT MAY CONCERN

मैं, अधोहस्ताक्षरी जो पेटेंट अधिनियम, 1970 की धारा 73(3) के तहत महानियंत्रक एकस्व, अभिकल्प एवं व्यापार चिह्न की ओर से प्रमाणपत्र हस्ताक्षर व जारी करने के लिए प्राधिकृत अधिकारी हूँ, एतद्वारा यह प्रमाणित करता(ती) हूँ कि निम्नलिखित पेटेंट आवेदन के संबंध में फाइल दस्तावेज(जों) की सही प्रतिलिपि इसके साथ संलग्न है:

I, the undersigned, being an officer duly authorized to sign and issue the certificate on behalf of the Controller General of Patents, Designs and Trademarks in accordance with the provisions of Section 73(3) of the Patents Act, 1970, hereby certify that annexed hereto is a True Copy of the document(s) as filed in connection with the following Patent Application:

- क) आवेदन संख्या / a) Application Number: 201621042124
ख) फाइल करने की तारीख / b) Date of Filing: 09/12/2016
ग) अनुरोधित दस्तावेज(जों) का नाम / c) Name of the document(s) requested:

Provisional Specification filed on 09/12/2016.

यह प्रमाणपत्र पेटेंट अधिनियम, 1970 की धारा 147(1) के अधीन मुझमें निहित शक्तियों के तहत जारी किया गया है।

This certificate is issued under the powers vested in me U/S 147(1) of The Patents Act, 1970.

दिनांक / Dated this 05th day of Jan. 2018


(VIJAY T. DOYE)

सहायक नियंत्रक पेटेंट व डिजाइन/ Assistant Controller of Patents and Designs

(प्राधिकृत हस्ताक्षरी/ Authorized Signatory)

FORM 2

THE PATENTS ACT, 1970

(39 of 1970)

AND

THE PATENTS RULES, 2003

PROVISIONAL

SPECIFICATION

(See Section 10; Rule 13)

REGENERATION OF SPENT IONIC LIQUIDS

RELIANCE INDUSTRIES LIMITED

an Indian company of

3rd Floor, Maker Chambers-IV

222, Nariman Point, Mumbai – 400021

Maharashtra, India.

THE FOLLOWING SPECIFICATION DESCRIBES THE INVENTION.

FIELD

The present disclosure relates to regeneration of spent ionic liquids.

DEFINITIONS

As used in the present disclosure, the following terms are generally intended to have the meaning as set forth below, except to the extent that the context in which they are
5 used indicates otherwise.

Used Ionic liquid: The term “Used Ionic Liquid” or spent ionic liquid or de-activated ionic liquid refers to ionic liquid that has been used in a process and is currently in a de-activated form.

Clathrate: The term “clathrate” refers to a compound in which molecules of one
10 component are physically trapped within the crystal structure of another.

Metallate: The term “metallate” refers to any complex anion containing a metal ligated to several atoms or small groups.

Eutectic: The term “eutectic” refers to a mixture of substances (in fixed proportions) that melts and freezes at a single temperature that is lower than the melting points of
15 the separate constituents or of any other mixture of them.

BACKGROUND

An ionic liquid (IL) is a salt in the liquid state. Ionic liquids have different applications in various fields. Ionic liquids are powerful solvents and electrically conducting fluids (electrolytes). Salts that are liquid at near-ambient temperature are
20 important for electric battery applications, and are considered as sealants due to their very low vapor pressure. Ionic liquids are used as catalysts in the production of a number of commercially important products. Recently, ionic liquids have found application as biological reaction media.

However, ionic liquids are susceptible to contamination by other chemical compounds. Halogen based ionic liquids, such as alkyl pyridinium, imidazolium, phosphonium, and ammonium, are deactivated due to the presence of unsaturated hydrocarbons, polymers, tar, etc. The formation of complex with ionic liquids or the
5 entrapment of the ionic liquids in tar or the contaminating compound present in the reaction mixture is responsible for the deactivation of the ionic liquids. Also, valuable chemicals need to be recovered for better economic and minimum waste generation.

Various attempts have been made to regenerate the deactivated ionic liquids. Used
10 acidic chloroaluminate ionic liquid catalyst can be regenerated by contacting the used chloroaluminate ionic liquid catalyst and hydrogen with a metal/homogeneous/supported hydrogenation catalyst in a reaction zone under hydrogenation conditions for sufficient time period as to increase the activity of the ionic liquid catalyst. Another method involves the use of iso-paraffin with bronsted
15 acid for regeneration of the used ionic liquid catalyst under alkylation by keeping them in contact for sufficient time to obtain ionic liquid with enhanced catalytic activity. Regeneration of chloroaluminate based ionic liquid which are deactivated due to the presence of conjunct polymers, by contacting the used ionic liquid catalyst with aluminium metal in the presence of hydrogen to remove the conjunct polymers
20 by hydrogenation is also known. Attempts have been made to regenerate ionic liquid by combining the used ionic liquid with a metal and/or hydrocarbon solvents in a regeneration zone under hydrogenation conditions, the process can be carried out in a reactive extraction column. Another method involves the addition of cationic part of ionic liquid and inert hydrocarbon ranging from C₅-C₈ for regeneration of
25 chloroaluminate ionic liquids. Regeneration of used ionic liquids and removal of metal halide by addition of ammonium halide has been attempted. Secondary alcohol has been used for the regeneraion of chloroaluminate based ionic liquid by the formation of an adduct between the secondary alcohol and the aluminium chloride.

Regenerate ionic liquid catalyst by using a moving bed reactor comprising a slurry of ionic liquid and aluminium metal in combination with solvent and hydrogen has also been attempted.

5 However, the afore-stated methods provide only a partial recovery of the ionic liquids. Further, at some point of time, the ionic liquids has to be disposed. Since, ionic liquids are acidic in nature, the only available way is to treat with a base in the presence of water, which results in huge aqueous effluent and solid waste.

Therefore, there is felt a need to provide a process for treating used ionic liquids that mitigates the drawbacks mentioned hereinabove.

10 OBJECTS

Some of the objects of the present disclosure, which at least one embodiment herein satisfies, are as follows:

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

15 Another object of the present disclosure is to provide a method for treating a halo-metallate ionic liquid/deep eutectic mixture.

Still another object of the present disclosure is to provide a method for treating a halo-metallate ionic liquid/deep eutectic mixture which was used in a Friedel-Crafts reaction, acylation, or reaction involving use of chloroaluminate ionic liquids.

20 Yet another object of the present disclosure is to provide a method for separation of desired hydrocarbon from mother liquor obtained after treating the spent ionic liquid.

Still another object of the present disclosure is to provide a method flow for treating the spent ionic liquid such that there is no liquid effluent generated.

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

5 The present disclosure relates to a method for regenerating spent ionic liquid catalyst. The method involves mixing the spent ionic liquid catalyst with a fluid medium followed by addition of water to obtain a reaction slurry comprising precipitate of the spent ionic liquid catalyst. The reaction slurry is filtered to obtain separated precipitate and filtrate. The separated precipitate can be dried at a
10 temperature in the range of 60 °C to 120 °C to obtain the regenerated ionic liquid. Typically, the ionic liquid is an halo-metallic based ionic liquid selected from the group consisting of chloroaluminate ionic liquid, imidazolium based chloroaluminate, phosphonium based chloroaluminate, pyridinium based chloroaluminate and combinations thereof. In an embodiment, the chloroaluminate
15 ionic liquid is a clathrate of benzene and $\text{Al}(\text{OH})_3:\text{AlCl}_3$, wherein the ratio of $\text{Al}(\text{OH})_3:\text{AlCl}_3$ is in the range of 1:2 to 1:3.5, and the benzene in the mixture is in the range of 5 wt% to 50 wt%.

Typically, the fluid medium can be selected from the group consisting of primary aldehydes, secondary aldehydes, ketones, esters and combinations thereof and the
20 ratio of the fluid medium to the ionic liquid can be in the range of 1:1 to 10:1 by volume. The ratio of the fluid medium to water can be in the range of 20:1 to 5:1 by weight. In one embodiment, the filtrate is distilled to separate the fluid medium which can be recycled and reused.

BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWING

25 The present disclosure will now be described with the help of the accompanying drawing, in which:

Figures 1 illustrates a flowchart depicting the method for recovery of spent ionic liquid in accordance with the present disclosure.

DETAILED DESCRIPTION

5 In an aspect of the present disclosure, there is provided a method for treating spent ionic liquids.

Typically, the ionic liquid can be halo-metallic based ionic liquid/deep eutectic mixture, such as chloroaluminate ionic liquid.

10 In one embodiment of the present disclosure, the chloroaluminate ionic liquid is a clathrate between benzene and $\text{Al}(\text{OH})_3:\text{AlCl}_3$. Typically, the ratio of $\text{Al}(\text{OH})_3:\text{AlCl}_3$ is in the range of 1:2 to 1:3.5, while the benzene in the mixture is in the range of 5 wt% to 50 wt%.

15 Alternatively, the ionic liquids can be selected from the group consisting of imidazolium or phosphonium or pyridinium or ammonium or substituted amine based chloroaluminates and combinations thereof. The ionic liquids can be a clathrate or in a non-clathrate form. Further, benzene can be present along with the ionic liquids.

Typically, the molar ratio of cation to AlCl_3 in the ionic liquids can be in the range of 1:10.

20 Still further, the ionic liquid can be in adduct form or Lewis acid or Bronsted acid form; may or may not be in presence of an aromatic fluid medium. When an aromatic fluid medium is present with the ionic liquid, the proportion of the aromatic fluid medium in the mixture can be in the range of 5 wt% to 50 wt %.

Initially, the spent/de-activated ionic liquid is mixed with a fluid medium which completely solubilizes the spent ionic liquid along with tar and polymers, followed

by the addition of stoichiometric quantity of water resulting in a reaction slurry comprising the precipitate of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ along with other solid materials which are used initially to prepare the catalyst.

Typically, the fluid medium can be selected from the group consisting of primary
5 aldehydes, secondary aldehydes, ketones, esters and combinations thereof.

The ratio of the fluid medium to the ionic liquid can be in the range of 1:1 to 10:1 by volume and the ratio of fluid medium to water can be in the range of 20:1 to 5:1 by weight.

The reaction slurry is then subjected to filtration to separate the solids followed by
10 drying.

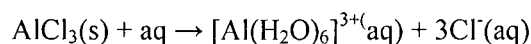
In an embodiment of the present disclosure, when imidazolium or phosphonium or pyridinium based chloroaluminates based ionic liquids are to be regenerated, solvent extraction can be carried out in order to recover the active material from the mixture of solids obtained after drying.

15 Typically, the solvent used for the extraction of active material can be selected from the group consisting of water, dichloromethane, acetonitrile, methyl tert butyl ketone, primary alcohol, secondary alcohol, ketone, aldehyde, and ether.

The key component in the halo-metallic based ionic liquid is AlCl_3 . Since, aluminium chloride is at the border of ionic and covalent, anhydrous AlCl_3 behaves
20 as covalent. Although the bond is between a metal and a non-metal, it is highly covalent. This is so because Al^{3+} has a high polarizing power due to its high charge and small size. It can easily polarize the electron cloud of Cl^- . Therefore it has a high degree of co-valency.

A fluid medium, which is polar in nature, such as acetone is also a covalent solvent,
25 so dissolves covalent molecules like Anhydrous AlCl_3 . If aluminium chloride is

dissolved in a large amount of water the solution is acidic, but this has nothing to do with formation of hydrochloric acid. The solution contains hydrated aluminium ions and chloride ions:



- 5 However, this hex-aqua complex ion behaves exactly like ions of similar type formed from transition metals; the small, highly charged metal ion polarizes (withdraws electron density from) the water molecules that are attached to the aluminium ion through dative covalent bonds. This makes the hydrogen atoms d+ and susceptible to attack from solvent water, which is acting as a base. The complex ion is deprotonated, causing the solution to be acidic from the formation of hydroxonium ions H_3O^+ :
- 10



- The moment spent catalyst is added to the acetone-water system, the spent catalyst (containing AlCl_3 , $\text{Al}(\text{OH})_3$, benzene and tar) will disassociate and gives hydrated AlCl_3 , $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, is undoubtedly an ionic solid, containing the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ cation. Since, the acetone-water system is highly polarized, tar along with benzene remains in the soluble form.
- 15

- Figure-1** illustrates a flowchart depicting the method for recovery of spent ionic liquid. The process can be operational in either batch or semi-continuous or continuous mode. **(101)** represents mixer; the pre-mixer can be either a stirred vessel or static mixer or jet mixer or pump mixer; **(102, 106)** represent filter; **(104)** represents distillation column; **(105)** represents extractor; **(108)** represents solvent evaporator/dryer
- 20

- The filter can be selected from the group consisting of centrifuge filter, pressure nutsche filter, agitated nutsche filter, vacuum filter, belt filter and combinations
- 25

thereof. In another embodiment a filter-dryer combination, such as agitated nutsche filter dryer, (103, 107) (evaporator/dryer) can be used. The filter-dryer combination can be one of single effect, multiple effect dryer, tray-dryer, agitated thin film dryer, paddle dryer, and combinations thereof.

- 5 The distillation column can be selected from the group consisting of single stage tray column, multi stage tray column, packed column, falling film evaporator, agitated thin film evaporator, and combinations thereof.

The extractor can be selected from the group consisting of single stage, multistage, co-current, counter current, stirred vessel, and extraction column.

- 10 The evaporator can be selected from the group consisting of single effect evaporator, multiple effect evaporator, agitated thin film evaporator, and combinations thereof.

- The whole process can be operated in batch or semi-continuous or continuous mode. stream 1 containing spent halo-metallic based ionic liquid which is to be disposed can be directly send to mixer (101) where it is mixed with suitable fluid medium-water system in stream 2 and 3, respectively. Alternately there can be another pre-mixer for separately mixing the stream 1 and 2, followed by mixing with stream 3 in mixer (101). The residence time inside the mixer can be in the range of 5 minutes to 60 minutes for complete precipitation of hexahydrate.
- 15

- The slurry mass from reactor (101) is sent into filter (102) via stream 5. The solids are washed with excess fluid medium (via stream 4) to remove the traces of tar, if any.
- 20

- The solids retained on the filter (102) are sent to evaporator or dryer (103) through stream 6 where the solids are dried. The drying is typically carried out in the temperature range of 60 °C to 120 °C. The drying can be carried out at atmospheric or under vacuum or combination of both. The filtrate obtained from (102) is sent
- 25

through stream 7 to distillation column (104) to distill out solvent and recycle as such via stream 9, leaving behind tar & polymers as residue (stream 10). Stream 8 is the solid containing hexahydrate.

5 In case of imidazolium or phosphonium or pyridinium based chloroaluminates, the active material also precipitates out along with hexahydrate which needs to be recovered. The dried solid obtained from the drier (103) via stream 8 is sent to extractor (105), where it is mixed with the fluid medium coming from stream 11 in order to separate the active material from the solid mixture. The extractor outlet is sent through stream 12 to filter (106) where hexahydrate is separated and sent to
10 dryer (107) via stream 13. The mother liquor from filter (106) is sent to evaporator (108) via stream 14 to separate solvent via stream 16 and solids via steam 17 which is an active material in the catalyst. The evaporated solvent from dryer (107) and also from evaporator (108) is recycled back to extractor (105) via stream 15 and 16, respectively.

15 The present disclosure is further described in light of the following laboratory scale experiments 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 and the results obtained can be extrapolated to industrial/commercial scale.

20 **Experimental Details**

Experiment-1: Alkylation reaction to obtain spent catalyst

25 250 liters per hour (LPH) of benzene was mixed with 3.6 LPH of fresh catalyst consisting of clathrate of chloroaluminate (contains 50 % benzene by weight and Al (OH)₃: AlCl₃ in 1:3 mole ratio) in a static mixer, this stream was passed through another static mixer where it was mixed with 500 LPH of hydrocarbon stream containing 12 % C₁₀-C₁₄ olefins and 88 % paraffins. All the streams were maintained

at 47 °C. The outlet stream was then passed through a settler having a residence time of 20 minutes. The upper hydrocarbon layer was further processed while the bottom spent catalyst layer was collected separately in a container for regeneration. The conversion of olefin was found to be 99.7 %. The bottom spent catalyst layer was kept aside in a closed container.

Experiment-2: Treatment of ionic liquid catalyst using acetone-water system

100 g of spent catalyst layer obtained from Experiment -1 was mixed with 440 g of acetone-water mixture with stoichiometric amount of water to form hexahydrate in a 1000 ml round bottom (RB) flask kept under an overhead stirrer. The solid immediately precipitated out leaving behind the liquid containing acetone and other tar and hydrocarbons that were present in the spent catalyst layer. The slurry was then filtered, dried to get dry solids containing hexahydrate AlCl_3 along $\text{Al}(\text{OH})_3$. The filtrate was distilled off to recover acetone leaving behind the tar and hydrocarbons. This acetone can be recycled as such.

Experiment-3: Treatment of ionic liquid catalyst using methyl acetate-water system

100 g of spent catalyst layer obtained from Experiment -1 was mixed with 465 g of methyl acetate-water mixture with stoichiometric amount of water to form hexahydrate in a 1000 ml RB flask kept under an overhead stirrer. The solid immediately precipitated out leaving behind the liquid containing acetone and other tar and hydrocarbons that are were present in the spent catalyst layer. The slurry was then filtered, dried to get dry solids containing hexahydrate AlCl_3 along $\text{Al}(\text{OH})_3$. The filtrate was distilled off to recover methyl acetate leaving behind the tar and hydrocarbons. This methyl acetate can be recycled as such.

25

Experiment-4: Trans-alkylation of spent catalyst

750 ml of heavier alkyl benzene was mixed with 750 ml of benzene in a 2 liter RB flask equipped with an over-head stirrer. At 80 °C, 255 g of spent catalyst layer obtained from Experiment-1 was charged and stirred for 2 hours. After 2 hours, the mixture was cooled to 45 °C and the layers were separated. The bottom catalyst layer was used for further treatment.

Experiment-5:

100 g of spent catalyst layer obtained from Experiment-4 was mixed with 440 g of acetone-water mixture with stoichiometric amount of water to form hexahydrate in a 1000 ml RB flask kept under an overhead stirrer. The solid immediately precipitated out leaving behind the liquid containing acetone and other tar and hydrocarbons that are were present in the spent catalyst layer. The slurry was then filtered, dried to get dry solids containing hexahydrate AlCl_3 along $\text{Al}(\text{OH})_3$. The filtrate was distilled off to recover acetone leaving behind the tar and hydrocarbons. This acetone can be recycled as such.

The method of the present disclosure can be applied to regenerate spent ionic liquid catalyst using a fluid medium without generating aqueous effluent. Further, the contaminations present in the ionic liquid, such as tar and hydrocarbon can be recovered as a by-product. Further, metals such as gallium (Ga) and Indium (In) can be recovered from the mixture of the spent ionic liquid, which makes the method of the present disclosure cost effective.

TECHNICAL ADVANCEMENTS

The present disclosure described herein above has several technical advantages including, but not limited to, the realization of a method for regenerating spent ionic liquid catalyst. The method avoids the generation of aqueous effluent and also 5 impurities present in the ionic liquid can be recovered as solid material and hence makes the method economical.

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 10 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 invention to achieve one or more of the desired objects or results. While certain embodiments of the inventions have been described, these embodiments have been 15 presented by way of example only, and are not intended to limit the scope of the inventions. Variations or modifications to the formulation of this invention, within the scope of the invention, may occur to those skilled in the art upon reviewing the disclosure herein. Such variations or modifications are well within the spirit of this invention.

20 The numerical values given for various physical parameters, dimensions and quantities are only approximate values and it is envisaged that the values higher than the numerical value assigned to the physical parameters, dimensions and quantities fall within the scope of the invention unless there is a statement in the specification to the contrary.

25 While considerable emphasis has been placed herein on the specific features of the preferred embodiment, it will be appreciated that many additional features can be

added and that many changes can be made in the preferred embodiment without departing from the principles of the disclosure. These and other changes in the preferred embodiment 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
5 foregoing descriptive matter is to be interpreted merely as illustrative of the disclosure and not as a limitation.

Dated 9th day of December, 2016



MOHAN DEWAN
10 OF R. K DEWAN &CO
APPLICANT'S PATENT ATTORNEY

NAME: RELIANCE INDUSTRIES LIMITED

ONE SHEET

NO : 201621.....

PROVISIONAL SPECIFICATION

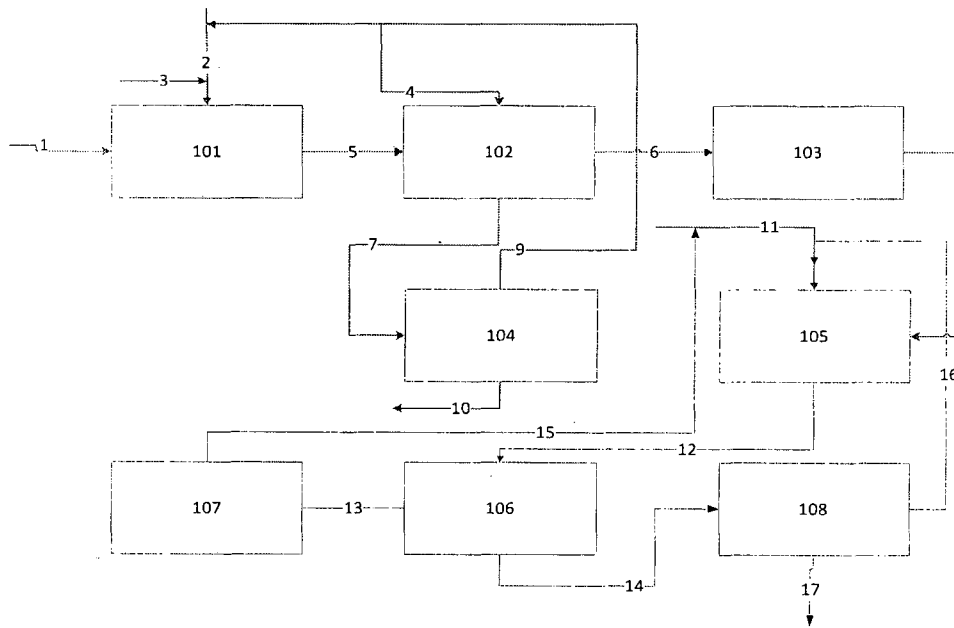


Figure 1

MOHAN DEWAN
OF R. K. DEWAN & CO.
APPLICANT'S PATENT ATTORNEY