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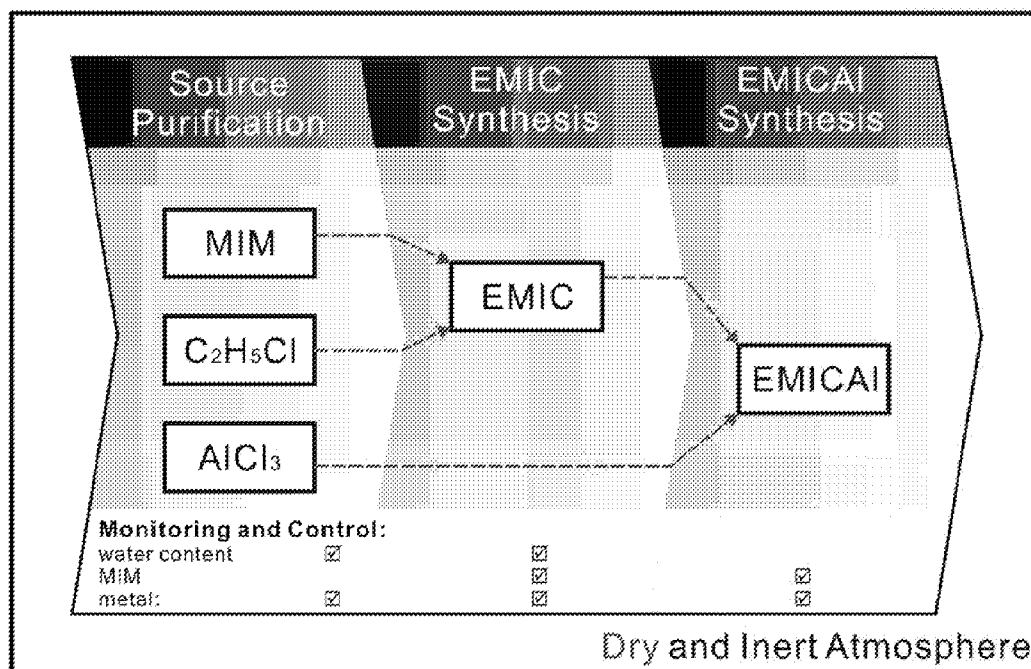
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(54) Title: PROCESS AND SYSTEM OF PREPARING ULTRA PURE IONIC LIQUIDS



(57) Abstract: A process of preparing an ionic liquid includes following steps: purifying raw materials including an alkyl imidazole, an alkyl halide and a metal halide; causing the alkyl imidazole and the alkyl halide to react with each other to produce a halide containing an object cation; and causing the halide containing the object cation to react with the metal halide to obtain the ionic liquid.

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Process and system of preparing ultra pure ionic liquids

FIELD OF INVENTION

The invention relates to a process and system for preparing ionic liquids, particularly to a process and system for preparing ultra pure ionic liquids.

BACKGROUND OF THE INVENTION

Ionic liquids are attracting a lot of attention as novel, volatile organic compound free solvent system for carrying out chemical reactions. When ionic liquids are used for carrying out chemical reactions, the purity of the ionic liquids is of great importance, because impurities can, for example, have a generally adverse effect on the course of chemical reactions. However, many ionic liquids prepared by existing processes and systems, especially these ionic liquids that are air and water sensitive, e.g. chloroaluminate ionic liquids which tend to be unstable in the presence of air or water, always can't meet high purity standards. Therefore, it is desired to provide a process and system for preparing ultra-pure ionic liquids.

Otherwise, although ionic liquids have been widely prepared and studied, many of the ionic liquid preparations and studies are performed

at laboratory scales under conditions that do not adequately represent operating conditions for full-scale industrial manufacture. Therefore, it is also desired to develop a large-scale approach to manufacture ultra-pure ionic liquids.

SUMMARY OF THE INVENTION

Embodiments of the present invention provide a process of preparing an ionic liquid. The process includes following steps: purifying an alkyl imidazole by refluxing and distillation; purifying a metal halide by sublimation; introducing an alkyl halide from a temperature controlled storage into a reactor and controlling a reaction temperature such that a reaction between the alkyl halide and the alkyl imidazole occurs in the reactor, the reaction producing a halide containing an object cation; after a predetermined portion of the alkyl imidazole in the reactor is consumed, accelerating the reaction by increasing at least one of the reaction temperature and a temperature of the alkyl halide in the temperature controlled storage; and causing the halide containing the object cation to react with the purified metal halide to obtain the ionic liquid.

Embodiments of the present invention further provide a system, which comprises a rotor-stator mixer for mixing a solid with a fluid and causing them to react to produce an ionic liquid, a reactor coupled to the rotor-stator mixer such that the ionic liquid produced by the rotor-stator

mixer can be fed into the reactor, a first reactant feeder to feed a first reactant into the reactor, a second reactant feeder to feed a second reactant into the reactor, and a mixing device to mix the ionic liquid from the rotor-stator mixer, the first reactant, and the second reactant in the reactor. The first and second reactants dissolve in the ionic liquid and react with each other to produce a product ionic liquid similar to the ionic liquid.

Embodiments of the present invention further provide a system, which comprises a rotor-stator mixer for mixing a solid reactant with a fluid reactant to produce the ionic liquid, a first feeder for feeding the solid reactant to the rotor-stator mixer, and a second feeder for feeding the fluid reactant to the rotor-stator mixer. The first feeder comprises a reservoir for storing the solid reactant and a screw motor to carry the solid reactant from the reservoir to the rotor-stator mixer. The second feeder comprises a temperature control device to maintain the fluid reactant in fluid form, and at least two feeding members to alternately feed the fluid reactant to the rotor-stator mixer.

Embodiments of the present invention further provide a process of preparing an ionic liquid. The process includes following steps: purifying an alkyl imidazole, an alkyl halide, and a metal halide; causing a reaction between the alkyl imidazole and the alkyl halide to produce a halide

containing an object cation; feeding the metal halide and the halide containing the object cation into a rotor-stator mixer; and mixing the metal halide and the halide containing the object cation to cause them to react with each other in the mixer to produce an ionic liquid.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram showing an overall production procedure of EMICAL.

FIG. 2 is a diagram showing water contents in MIM purified by different purification procedures.

FIG. 3 is a schematic diagram showing an MIM purification system.

FIG. 4 is a diagram showing purification efficiencies of AlCl_3 by different sublimation methods.

FIG. 5 is a schematic diagram showing a sublimation system and a sublimation procedure of AlCl_3 .

FIG. 6 is a schematic diagram showing an autoclave system used for synthesizing EMIC

FIG. 7 is a diagram showing an EtCl source and an autoclave of the autoclave system of FIG. 6.

FIG. 8 is a schematic diagram of an HTMX system in which AlCl_3 and EMIC are mixed and react to EMICAL.

FIG. 9 is a diagram showing an EMIC feeder of the HTMX system.

FIG. 10 is a schematic diagram of a scale-up EMICAl production system.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A system and process of the present invention are suitable to cause an alkyl imidazole to react with an alkyl halide to achieve a halide containing an object cation, and then cause the halide containing the object cation to react with a metal halide to obtain an object ionic liquid. Example of ionic liquids that can be produced by said system and process include, but are not limited to 1-ethyl-3-methylimidazolium chloride / aluminum chloride (EMIC-nAlCl_3), 1-butyl-3-methylimidazolium chloride / aluminum chloride (BMIC-nAlCl_3), 1-allyl-3-methylimidazolium chloride / aluminum chloride (AMIC-nAlCl_3), 1-ethyl-3-methylimidazolium chloride / zinc chloride (EMIC-nZnCl_2), 1-ethyl-3-methylimidazolium bromide / aluminum bromide (EMIC-nAlBr_3) and the likes.

A process and system for preparing a 1-ethyl-3-methylimidazolium chloride / aluminum chloride (EMIC-nAlCl_3) will be given in the next sections by way of nonexclusive example, wherein the 1-ethyl-3-methylimidazolium chloride / aluminum chloride is also named as 1-ethyl-3-methylimidazolium tetrachloroaluminate, and will be referred hereafter as EMICAl for short.

As shown in FIG. 1, a whole process of preparing EMICAl is divided in three main steps: source purification (raw-material purification), synthesis of 1-ethyl-3-methylimidazolium chloride (EMIC), and synthesis of EMICAl.

To obtain ultra pure products, it is important to closely monitor and significantly decrease impurities (especially water and metal impurities) during each step. A main challenge is to prevent any water to enter the system, and another major issue is to decrease metal content in the EMICAl synthesis step. To prevent water to enter the system, all processes are preferred to be operated in dry and inert atmosphere, and reactants 1-methylimidazole (MIM) and ethyl chloride (EtCl) are preferred to be dried. The metal impurities in the AlCl_3 may be removed by sublimation. Also setups for the synthesis of EMIC and EMICAl may be designed to decrease the metal content. In addition, the conversion of MIM in the EMIC synthesis step is preferred to be enhanced to reach almost 100%.

Purification of Raw Materials

As mentioned before, the first step in the synthesis of ultra pure ionic liquids is raw material purification. In this case the raw materials are MIM, EtCl, and AlCl_3 . This section will describe the detailed purification procedures for MIM and AlCl_3 . EtCl is purified in-situ in the EMIC

synthesis step.

(A) MIM Purification:

Many kinds of methods may be applied to purifying MIM. For example, a drying-distillation purification method comprises a drying procedure and a distillation procedure. In the drying procedure, MIM is dried, and then in the distillation procedure, the dried MIM is distilled.

MIM may be dried by storing MIM over CaH_2 in inert and dry atmosphere, or refluxing MIM over CaH_2 . In one embodiment, MIM is stored over 4wt% CaH_2 for 7 days in inert and dry atmosphere, and thereby the water content of the MIM can be reduced to about 300 ppm (by mass, and the water contents hereafter are all calculated by mass while metal contents are calculated by mole). In another embodiment, MIM is refluxed over 4wt% CaH_2 at 250 °C for 12 hours, and thereby the water content of the MIM can be reduced to about 65 ppm. By increasing the proportion of CaH_2 from 4wt% to 8wt%, the water content would be reduced to about 30 ppm, and by further increasing the refluxing time from 12 hours to 36 hours, the water content would be further reduced to a very low value less than 3 ppm. FIG. 2 shows decrease of water content in MIM due to optimization of drying procedure.

FIG. 3 shows a purification system 3 for carrying out a refluxing-distillation purification method comprising a refluxing procedure (for drying MIM) and a distillation procedure. There is a

three-neck round flask 311 for containing MIM in both refluxing and distillation procedures. The three-neck round flask 311 is firstly connected to refluxing devices in order to reflux MIM, and then is connected to distillation devices after refluxing is finished, in order to distill the refluxed MIM.

(a) Refluxing step: Firstly, the three-neck flask 311 and other refluxing devices are cleaned in a KOH-bath over night, rinsed and stored in 0.1 molar HCl bath for 10 minutes, and then washed with deionised water and dried at 70 °C for 3 hours. After cooling down naturally, they can be installed to form a refluxing system 31 as shown in left section of FIG. 3.

Besides the three-neck flask 311, the refluxing system 31 further comprises a stirrer 313 in the three-neck flask 311 and a heater 314 under the three-neck flask 311. One neck 315 of the three-neck flask 311 is used to add MIM and CaH_2 into the three-neck flask 311 and can be stoppered with a plug 316. A second neck 317 is connected to a tube 318 loaded with a cooler 319, and the tube 318 is connected to an over pressure valve 320 via a valve 321 for opening and closing a connection between the tube 318 and the over pressure valve 320. A third neck 323 is connected to a dry gas/vacuum switch valve 324 via a valve 325 for opening and closing a connection between the neck 323 and the switch valve 324. The dry gas/vacuum switch valve 324 is connected to a dry gas/vacuum

system and enables the neck 323 to selectively connect with a dry gas or a vacuum pump. In one embodiment, the stirrer 313 is a magnetically driven stirrer and the dry gas is argon (Ar). All connections are sealed with a small amount of grease and clipped.

Secondly, in order to remove water that covers the flask 311 and other glass wares, the refluxing system 31 is heated by vacuum/Ar technique (i.e. vacuumed and then refilled with dry argon, which two procedures are repeated for several times). During vacuuming procedure, the valve 321 is closed, the valve 325 is open, and the valve 324 is turned to the vacuum pump. During Ar refilling procedure, the valve 321 is closed, the valve 323 is open, and the valve 324 is turned to Ar line. These two procedures are repeated four times and then the refluxing system is cooled down in Ar.

Thirdly, MIM and 8wt% CaH_2 are filled into the flask 311 with continuous Ar flow. After MIM and CaH_2 are added, the neck 315 is closed by the plug 316 and then the system is vacuumed and refilled with dry Ar. In order to replace the complete atmosphere in the system, the vacuuming and refilling procedure is repeated three times.

Finally, the refluxing system is heated to 200~250 °C (measured by temperature of the heater 314) and kept on refluxing for 36 hours.

(b) Distillation step: In one embodiment, devices for distillation include three distillation flasks 331, 333 and 335 with different volumes, a

cooler 336, a distilling adapter 337, and a stop flask 339. While the refluxed MIM cools down in Ar flow, these devices are cleaned, assembled, and dried similarly as described above in the refluxing step. In assembly, the distillation flasks 331, 333 and 335 are assembled to the distilling adapter 337 via the cooler 336, and the distilling adapter 337 are provisionally connected to the stop flask 339 before the three-neck flask 311 being connected in.

After the refluxed MIM cools down, valves 321, 323 and 343 are connected to Ar line, the flask 339 is taken away from the distilling adapter 337, the tube 318 is taken away from the neck 317 of the three-neck flask 311, and then the neck 317 is connected to the distilling adapter 337 under the protection of dry Ar. Before the distillation starts, the three-neck round flask 311 and the distilling adapter 337 are insulated with an aluminum foil (not shown). The distillation flasks 331, 333 and 335, the cooler 316 and the distilling adapter 337 are vacuumed and refilled by Ar for four times while being heated with heat gun.

Distillation of MIM is carried out in vacuum at a certain temperature. In one embodiment, MIM is controlled to distill in vacuum of about 8.5×10^{-2} mbar or below at a temperature of about 35 °C. Distilled MIM is allowed into any one of the three flasks 331, 333 and 335. In one embodiment, at the beginning of distillation, the distilled MIM is allowed

into the smallest flask 335, then into the middle-volume flask 333, and finally into the largest flask 331 after the flask 333 is filled with a certain distilled MIM. The reason to operate in such a method is that the distilled MIM at the beginning may have some impurities and therefore may be unqualified. After distillation, valve 345 is connected to Ar line and the flask 331 is separated from the distilling adapter 337 with the protection of dry Ar and sealed with “parafilm”.

(B) AlCl_3 Purification:

Main impurities of AlCl_3 are hydroxides (formed with water), sulfates and metals such as Fe, Cr, Ni, Zn, Mn, Mg, Cu, Pb, etc. Sublimation in dry environment can get rid of all these impurities.

Many kinds of sublimation methods can be useful. Here three different sublimation methods are introduced for instances. In the first method, the sublimation is carried out without any additives. By this method, iron content of AlCl_3 remains pretty high whereas the other metal impurities decrease significantly. In the second method NaCl is added and in the third method NaCl and Al-powder are added. Both these two methods can reduce the metal impurities significantly, but the third method may be preferable because the addition of Al-powder certainly helps to prevent formation of iron chloride, which may be a main issue if iron content is relatively high in the raw AlCl_3 . FIG. 4 depicts purification

efficiencies of different sublimation methods. The third method is described below by way of example.

FIG. 5 depicts a system 5 and a schematic procedure of AlCl_3 sublimation. The sublimation system comprises a sublimation flask 51, a heater 52, and a cooler 53. The sublimation flask 51 is connected to a valve 55, and the valve 55 is connected to a valve 56, which is connected with a high pressure valve 57 and a vacuum/Ar switch valve 58. The vacuum/Ar switch valve 58 is connected to a vacuum/Ar system.

Firstly glassware such as the flask 51 is cleaned, assembled and dried with a heat gun in vacuum. Then AlCl_3 and additives are added into the sublimation flask 51. In one embodiment, 5 g Al powder is soaked into 100 ml 0.1 mol/l HCl aqueous solution for 2 hours in order to remove oxide layers on the top surface. The fresh Al powder is dried at 60 °C for 5 hours under Ar protection. 100 g of AlCl_3 , 3 g NaCl and 3 g Al powder are filled into a 500 ml plastic bottle and mixed by using vortex mixer at 900 rpm for 0.5 h. Then the mixture is transferred into the sublimation flask 51 under continuous Ar flow. Then the sublimation flask 51 is closed and its inside atmosphere is replaced by three times vacuuming and refilling with Ar.

In order to get rid of some organic impurities, the mixture of AlCl_3 and additives may need vacuuming pretreatment for 12 h. The pretreatment is

carried out by connecting the sublimation flask 51 to the vacuuming line and increasing the temperature of the sublimation flask 51 to 90 °C.

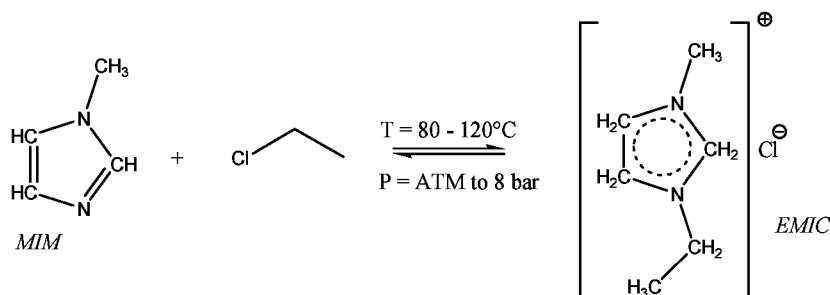
When the sublimation starts, the sublimation flask 51 is refilled with Ar and connected to the over pressure valve 57 which controls a pressure of sublimation. In one embodiment, the sublimation is carried out at 1 bar. Then the valve 55 is closed, the cooler 53 is turned on, and the temperature of the heater 52 is increased to 210 °C and kept for about 2 hours until the sublimation of AlCl_3 stops.

When the sublimation stops, the over pressure valve 57 is closed and the system 5 is allowed to cool down with continuous Ar flow.

Finally, the purified AlCl_3 is taken out in the glove box. The purified AlCl_3 is grinded using a glass mortar and screen into 20-60 mesh powders, and then added into a sample bottle, sealed with paraffin film and stored in a desiccator in Ar atmosphere and P_4O_{10} as desiccants.

Synthesis of EMIC in Autoclave System

MIM reacts with ethyl chloride to EMIC, a highly hydrophilic ionic liquid.



The synthesis of EMIC is preferably carried out in an autoclave or the like since a high pressure (e.g. 8 bar) may be reached during the reaction, and the whole process is preferably operated in dry and inert environment since a main requirement for EMIC synthesis is to be water free (less than 50 ppm water). Furthermore, a conversion of MIM is needed to be very high (e.g. 99.999%) and a total metal content is needed to be very small (e.g. below 50 ppm).

(A) Autoclave System:

FIG. 6 shows an autoclave system 6 used for synthesizing EMIC. The autoclave system 6 includes an autoclave 61, an ethyl chloride source (e.g. an EtCl storage bottle) 63 immersed in an oil bath 64, an MIM source (e.g. an MIM storage bottle) 65, and an EMIC bottle 67 for sampling EMIC, all of which are placed in a hood so that any emitted gas can be vented. The autoclave 61 is equipped with an Ar/vacuum system. Ar is dried in a cascade of silica gel, KOH, molecular sieve 4A, and 50% P₄O₁₀ in glass beads, and is then distributed together with a vacuum line in four channels in the hood. One line is permanently connected to the autoclave 61 and a second with the EtCl storage bottle 63. The other two lines are connected with the MIM source 65 and EMIC bottle 67 during sample taking, respectively.

As mentioned before, EtCl is in-situ purified in the autoclave system

6. Main impurities in EtCl are water and HCl. EtCl actually has a boiling point of 12 °C and is therefore easy to purify. In one embodiment, the raw EtCl is condensed into the storage bottle 63 for the EMIC synthesis reaction. During condensation of EtCl, the raw EtCl passes a KOH-column, which removes the HCl by forming water and KCl, then passes a column filled with P_4O_{10} and glass beads, which removes the water, and then enters into the EtCl storage bottle 63. During the EMIC synthesis, EtCl flows from the storage bottle 63 to the autoclave 61.

In one embodiment, the whole system 6 may be operated at a pressure up to 8 bar, therefore it is preferred to use 2 μ m gas filters 601, 603 and 605 after the P_4O_{10} columns to prevent contamination by the desiccant.

In order to reduce the metal content in EMIC, the inside of the autoclave 61 may be coated with a material which is inert to reactants and resultants of the EMIC synthesis reaction and is capable of withstanding the reaction temperature and pressure. In one embodiment, the inside of the autoclave 61 is "Teflon" coated.

The entire operation process of the synthesis of EMIC is described below.

(B) Preparation and Drying of the Autoclave System:

Before used, the autoclave system 6 is leak checked. In one

embodiment, the leak check includes check in vacuum and check at high pressure. Then the autoclave system 6 is dried.

(C) EtCl Feeding:

Valve V6 is closed to disconnect the EtCl source 63 from the rest of the system and the oil bath 64 is cooled to a temperature of about $-30\text{ }^{\circ}\text{C}$ at Ar flow (V7 and V14 are opened).

Before being fed with EtCl, the bottle 63 is vacuumed. During vacuuming, V14 is closed and V18 opened. Then V7 is closed and V30, V31, and V1 to V5 are opened to make raw EtCl flow through purification columns into the storage bottle 63. After a predetermined portion of EtCl condensed into the bottle 63, V1 to V5 and V30, V31 are closed.

(D) MIM Feeding:

The MIM storage bottle 65 is connected to the autoclave 61 with continuous Ar flow (V9, V12, V11, bottle valve 651, and V15 open). Then V11 is closed and V15/V19 is used to replace the atmosphere in the bottle 65 with dry Ar. V11 is opened and MIM enters the autoclave 61 under pure Ar flow. In order to control the amount of MIM, the bottle 65 is placed on a scale.

(E) EMIC Sampling:

After the EMIC bottle 67 is connected to the autoclave 61, it is

vacuumed (V17 open) and heated with a heat gun to remove water from surface of the bottle 67. Then V17 is closed and Ar is fed in (V13 is opened). This procedure is repeated 4 times.

Then the bottle 67 is kept at vacuum pressure (valve 671 is closed) and V10 slowly opened to let EMIC out. After the sample is taken, Ar is allowed to enter the bottle 67 by opening V13 and the valve 671. The silicon cover is removed under Ar flow and the bottle 67 quickly covered with a glass stop. Then the atmosphere in the bottle 67 is replaced by three times by the vacuum/Ar technique. Finally the bottle 67 is sealed with “parafilm” and ready for purification.

(F) Running the Experiment:

The Experiment is carried out in a closed system. Therefore during the experiment, all valves are closed. Only V5, V6, and V8 (for EtCl feeding) remain open. When the experiment is finished, the autoclave 61 is disconnected and cleaned.

(G) The key controlled factors:

The reaction between MIM and ethyl chloride for producing EMIC is highly exothermic. When a reaction temperature of the reaction is above 90 °C, cross products such as dimethyl- and diethyl-imidazoliumchlorid may be formed. Therefore, the reaction temperature (T1 in FIG. 7) is

preferably controlled below 90 °C (e.g. at 80 °C) as long a reaction rate is fast enough. Therefore, the autoclave 61 may be externally heated but innerly cooled. In one embodiment, the autoclave 61 is externally heated to 80 °C and innerly cooled with water. The concentration of EtCl entering the autoclave 61 is self-controlled by its partial pressure, which pressure can be controlled by temperature (T2 in FIG. 7) in the EtCl storage bottle 63. In one embodiment, the temperature T2 is controlled by an oil bath for the EtCl storage bottle 63.

During the reaction of MIM and EtCl, when a predetermined portion of MIM in the autoclave 61 is converted into EMIC, the reaction may need to be accelerated. In many cases, the predetermined portion is about 80 % or more of the MIM in the autoclave 61 before the reaction starts. The reaction can be accelerated by increasing the reaction temperature T1, by increasing the EtCl concentration by enhancing the temperature T2, or increasing both the reaction temperature T1 and the temperature T2. In one embodiment, an optimized condition is as follows:

Starting conditions:

Ratio of EtCl : MIM = 3:1;

T1 = 80 °C for 24 h;

T2 = 80 °C for 24 h;

Pressure = 4 bar

Reaction conditions after more than 90% MIM is converted into EMIC:

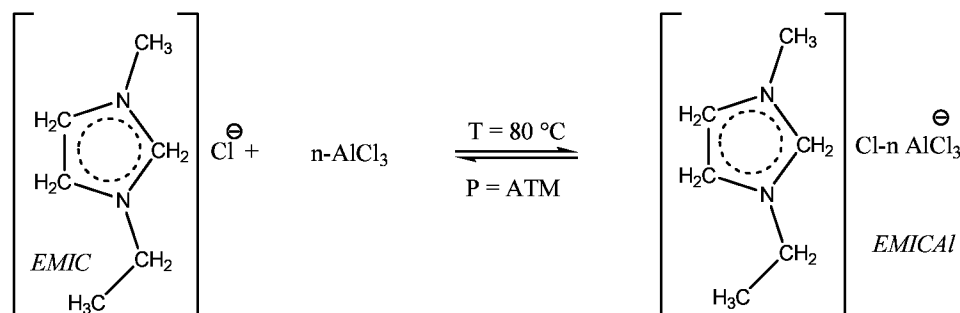
T1 = 90 °C (24 h to 72 h);

T2 = 120 °C (24 h to 72 h);

Pressure = 8 bar

Synthesis of EMICAL in HTMX

The next step is the reaction of EMIC with AlCl₃ to EMICAL.



A challenge for this reaction is to uniformly mix the solid AlCl₃ with EMIC, which is heated to a fluid form.

In one embodiment, the reaction is carried out in a rotor-stator mixer, in particular, a high-shearing force rotor-stator mixer, such as the high throughput mixer (HTMX) developed by Accelergy Corporation of Palo Alto, California. An HTMX system 8 including a said HTMX 81 (referred as mixer 81 hereafter for short) is shown in FIGs. 8 and 9.

(A) HTMX System Set-up:

Referring to FIG. 8, the mixer 81 of the HTMX system 8 comprises two substantially cylindrical members 811 and 812. Member 811, which serves as a rotor, is mounted within member 812, which serves as a stator. A space is formed between members 811 and 812 and acts as an annular reaction chamber for mixing EMIC with AlCl_3 and causing them to react to produce EMICAl. The reaction temperature may be controlled by an oil bath 813. More details of the mixer are described in Chinese Patent Application Number CN200610172190.0, which is incorporated here by reference.

The HTMX system 8 further includes a feeder 83 that feeds the solid AlCl_3 to the mixer 81. In one embodiment, the AlCl_3 powder is stored in a reservoir 831 of the feeder 83 and is slowly fed into the mixer 81 by a screw motor 832 of the feeder 83. A stirrer (not shown) placed at the end of the screw motor 832 can ensure a homogeneous flow of the solid AlCl_3 into the mixer.

In order to prevent moisture contamination, the feeder 83 is placed together with the mixer 81 in an inert/dry gas chamber 84 with a continuous dry Ar flow at a flow rate of, for example, 1 l/minute and at a pressure of, for example, 2 bar.

The HTMX system 8 further includes another feeder 85 that feeds the

EMIC in a fluid form into the mixer 81. The feeder 85 includes a reservoir 851 used to store the EMIC and two syringes 853 and 854 and used to feed the EMIC to the mixer 81. Since EMIC is solid at room temperature, all the lines for EMIC, including the reservoir 851 and syringes 853 and 854 are heated. In one embodiment, they are heated above 80°C. As shown in FIG. 9, in a first state, the syringe 853 feeds EMIC into the mixer 81, yet the syringe 854 is refilled with EMIC by increasing Ar pressure to the reservoir 851. In a second state, the syringe 853 is refilled with EMIC and the second syringe 854 feeds the EMIC into the mixer 81. These two states are repeated, and therefore a continuous EMIC feeding may be realized.

Returning to FIG. 8, the HTMX system 8 further comprises an EMICAL collecting bottle 871 and a waste bottle 872, both of which are connected with the mixer 81 and an Ar/vacuum system. There is a valve 873 switchable between the two bottles 871 and 872. The connection and disconnection procedure, respectively are carried out as described before. This method ensures that no air or moisture contacts the product EMICAL.

(B) Procedure

The whole process of EMICAL synthesis contains the following several operations: (a) cleaning and drying the whole system; (b) starting

the reaction; (c) collecting samples. A whole procedure will be described hereafter by way of example.

(a) Cleaning and Drying the Whole System

All parts of the HTMX system 8 needs to be disassembled and cleaned. They are washed first with water and acetone then dried in an oven at 120 °C for several hours. After being dried, they are assembled again.

After the reactants (EMIC and AlCl_3) are filled in their reservoirs in external glove boxes, the mixer 81 is heated to 100 °C at vacuum for 90 min. Then after at least three times of vacuum/Ar refill procedures, the HTMX system 8 is protected by continuous Ar flow with a flow rate of, for example, 1000 ml/min.

As EMIC is solid at room temperature, the EMIC reservoir 851 and the syringes 853 and 854 are heated to 120 °C to melt EMIC into a fluid and maintain it in fluid form.

(b) Starting the Reaction

Temperature of the oil bath 813, rotation speed of the mixer rotor 811, flow rate of EMIC and flow rate of AlCl_3 are set to expected values. Then EMIC is fed into the mixer 81. When EMIC flows out of the mixer 81 into the waste bottle 872, the feeder 83 starts to feed AlCl_3 into the mixer 81

such that a reaction of the EMIC and AlCl_3 starts.

(c) Collecting Samples

As soon as the HTMX system 8 runs steadily, switch the valve 873 from the waste bottle 872 to the EMICAl collecting bottle 871. After a certain amount of EMICAl is collected, the bottle 871 is removed, sealed with “parafilm”, vacuumized and stored in the glove box or in a desiccator with P_4O_{10} as desiccant.

After the reaction ends, the HTMX system needs to be disassembled and cleaned.

Scale-up system of EMICAl Production

Sometimes a larger scale EMICAl production may be needed. In one embodiment, a certain amount of EMICAl is used as a seed solvent to dissolve AlCl_3 powder and EMIC fluid or powder, and causing the AlCl_3 powder and EMIC fluid or powder to mix with each other and react with each other to produce more product EMICAl. For example, a scale-up system may be developed to use the EMICAl prepared by a mixer, such as an HTMX system, as a seed solvent to dissolve AlCl_3 powder and EMIC fluid or powder, and thereby to produce a product EMICAl similar to the EMICAl prepared by the HTMX system in a large scale, wherein “similar” used herein means the product EMICAl (EMICAl is a short for

EMIC- $n\text{AlCl}_3$ as mentioned before) may have a same or a different value of “ n ” to that of the EMICAl prepared by the HTMX system (“ n ” is a ratio between EMIC to AlCl_3 in EMICAl).

As shown in FIG. 10, the scale-up system 10 comprises an aforementioned HTMX system 101, a reactor system 102 including a reactor 103 such as an autoclave, in which a large scale EMICAl production can be carried out, an AlCl_3 feeder 104 to feed AlCl_3 into the reactor 103 and an EMIC feeder 105 to feed the EMIC into the reactor 103. The HTMX system 101 is used to prepare seed EMICAl which is fed into the reactor 103 as a solvent. The AlCl_3 feeder 104 may be similar to the feeder 83 in the HTMX system 8. The reactor system 102 may further comprise a stirrer/mixer 106 for mixing the seed EMICAl and the reactants AlCl_3 and EMIC.

By such a scale-up system 10, which is free from organic solvent, an ultra-pure product EMICAl can be manufactured in a large scale approach.

While the present invention has been illustrated and described with reference to some embodiments, the present invention is not limited to these embodiments. Those skilled in the art should recognize that various variations and modifications can be made without departing from the spirit and scope of the present invention as defined by the accompanying

claims.

CLAIMS

1. A process of preparing an ionic liquid, comprising:

purifying an alkyl imidazole by refluxing and distillation;

purifying a metal halide by sublimation;

introducing an alkyl halide from a temperature controlled storage into a first reactor and controlling a reaction temperature such that a reaction between the alkyl halide and the alkyl imidazole occurs in the first reactor, the reaction producing a halide containing an object cation;

after a predetermined portion of the alkyl imidazole in the first reactor is consumed, accelerating the reaction by increasing at least one of the reaction temperature and a temperature of the alkyl halide in the temperature controlled storage; and

causing the halide containing the object cation to react with the purified metal halide to obtain the ionic liquid.

2. The process according to claim 1, wherein the temperature of the alkyl halide in the temperature controlled storage and the reaction temperature are substantially equal when the reaction starts, and are both increased during the reaction, and wherein the temperature of the alkyl halide in the temperature controlled storage is increased to be higher than the reaction

temperature after the predetermined portion of the alkyl imidazole is consumed.

3. The process according to claim 1, wherein the predetermined portion is about 80 % of the alkyl imidazole in the first reactor before the reaction starts.

4. The process according to claim 1, wherein the alkyl imidazole is methylimidazole, the alkyl halide is selected from the group consisting of ethyl chloride, butyl chloride, allyl chloride and ethyl bromide, and the metal halide is selected from the group consisting of AlCl_3 , AlBr_3 and ZnCl_2 .

5. The process according to claim 4, wherein the methylimidazole is refluxed with 4~8wt% CaH_2 at a temperature ranged between 100~ 300 °C for above 12 hours.

6. The process according to claim 4, wherein the distillation is performed in a vacuum at a temperature of about 35 °C and a pressure less than about 8.5×10^{-2} mbar.

7. The process according to claim 1, wherein the step of causing the halide containing the object cation to react with the purified metal halide includes causing the halide containing the object cation to react with the purified metal halide in a rotor-stator mixer.

8. The process according to claim 1, further comprising feeding the metal halide, the halide containing the object cation, and the ionic liquid into a second reactor.

9. The process according to claim 8, further comprising causing the metal halide and the halide containing the object cation to dissolve in the ionic liquid and mix with each other so that the metal halide and the halide containing the object cation can react with each other to form a product ionic liquid similar to the ionic liquid.

10. A system to manufacture an ionic liquid, comprising:

a rotor-stator mixer for mixing a solid with a fluid and causing them to react to produce an ionic liquid;

a reactor coupled to the rotor-stator mixer such that the ionic liquid produced by the rotor-stator mixer can be fed into the reactor;

a first reactant feeder used to feed a first reactant into the reactor;

a second reactant feeder used to feed a second reactant into the reactor;

and

a mixing device to mix the ionic liquid from the rotor-stator mixer, the first reactant, and the second reactant in order to dissolve the first and second reactants in the ionic liquid and cause the first and second reactants to react with each other to produce a product ionic liquid similar

to the ionic liquid.

11. The system according to claim 10, wherein the rotor-stator mixer is disposed in inert gas atmosphere.

12. The system according to claim 10, wherein the first reactant feeder comprises a reservoir for storing the first reactant and a screw motor to carry the first reactant from the reservoir to the reactor.

13. A system for producing an ionic liquid, comprising
a rotor-stator mixer for mixing a solid reactant with a fluid reactant to produce the ionic liquid;

a first feeder for feeding the solid reactant to the rotor-stator mixer, the first feeder comprising a reservoir for storing the solid reactant and a screw motor to carry the solid reactant from the reservoir to the rotor-stator mixer; and

a second feeder for feeding the fluid reactant to the rotor-stator mixer, the second feeder comprising a temperature control device to maintain the fluid reactant in fluid form, the second feeder further comprising at least two feeding members to alternately feed the fluid reactant to the rotor-stator mixer.

14. The system according to claim 13, wherein the second feeder is configured to use the first feeding member to feed the fluid reactant into

the rotor-stator mixer while the second feeding member is being filled, and to use the second feeding member to feed the fluid reactant into the rotor-stator mixer while the first feeding member is being filled.

15. A process of preparing an ionic liquid, comprising:

purifying an alkyl imidazole, an alkyl halide, and a metal halide;

causing a reaction between the alkyl imidazole and the alkyl halide to produce a halide containing an object cation;

feeding the metal halide and the halide containing the object cation into a rotor-stator mixer; and

mixing the metal halide and the halide containing the object cation to cause them to react with each other in the mixer to produce an ionic liquid.

16. The process according to claim 15, wherein the purified alkyl imidazole is fed to a reactor, the purified alkyl halide is condensed in a temperature controlled storage coupled to the reactor and a concentration of the alkyl halide entering the reactor is controlled by controlling temperature in the temperature controlled storage.

17. The process according to claim 15, further comprising feeding the ionic liquid produced in the rotor-stator mixer, the metal halide and the halide containing the object cation into a reactor, mixing the ionic liquid,

the metal halide and the halide containing the object cation such that the metal halide and the halide containing the object cation dissolve in the ionic liquid and react with each other to form a product ionic liquid similar to the ionic liquid.

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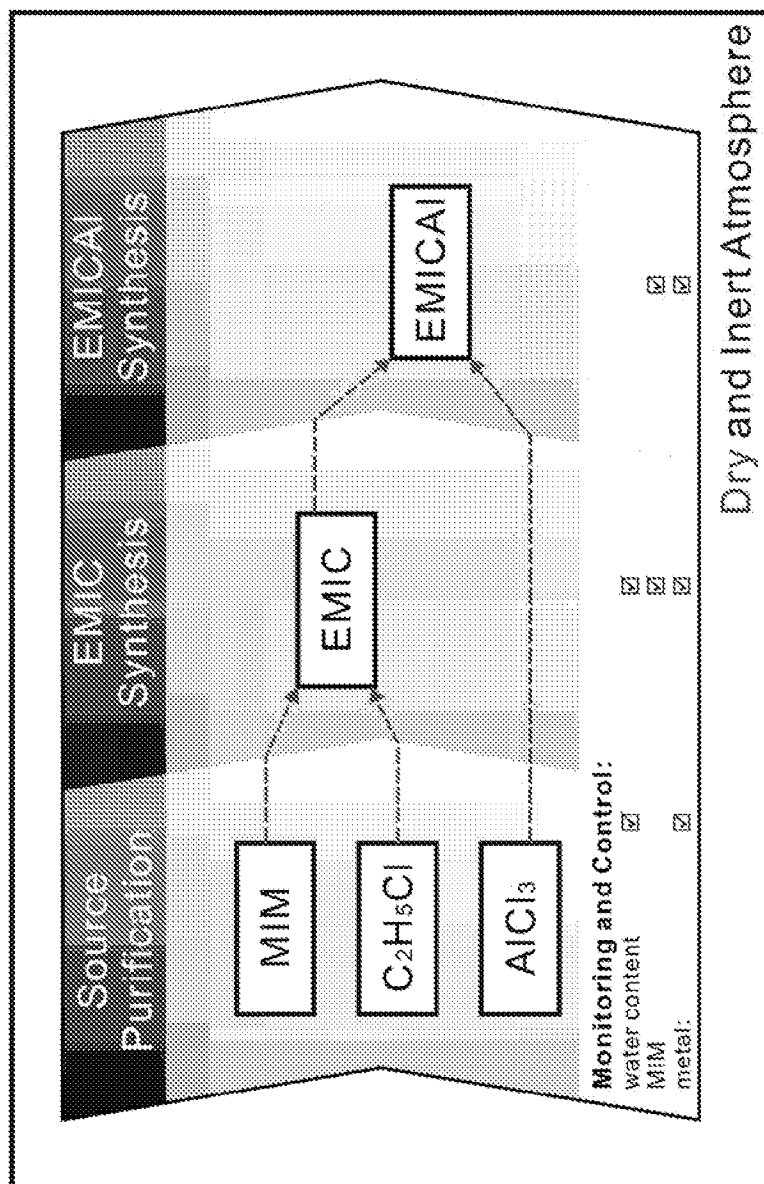


FIG. I

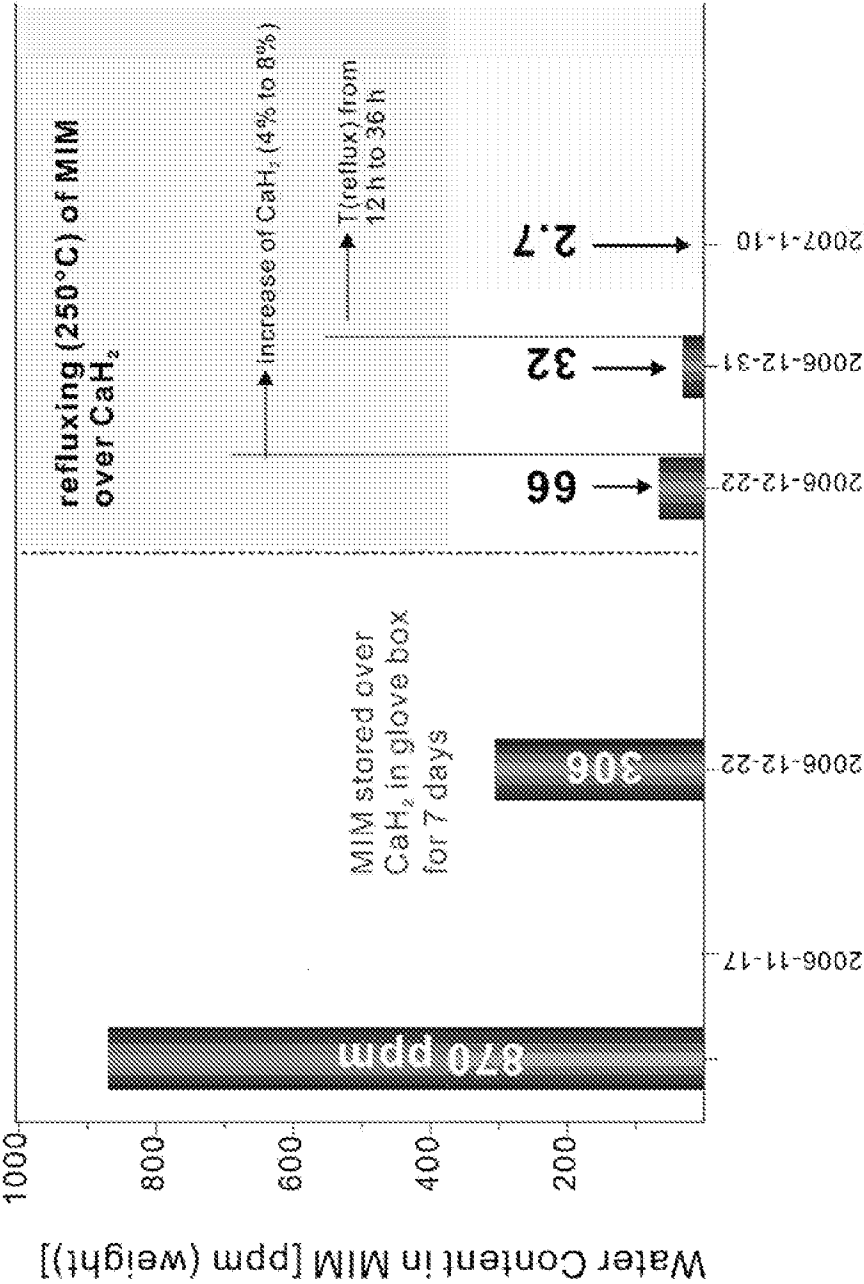


FIG. 2

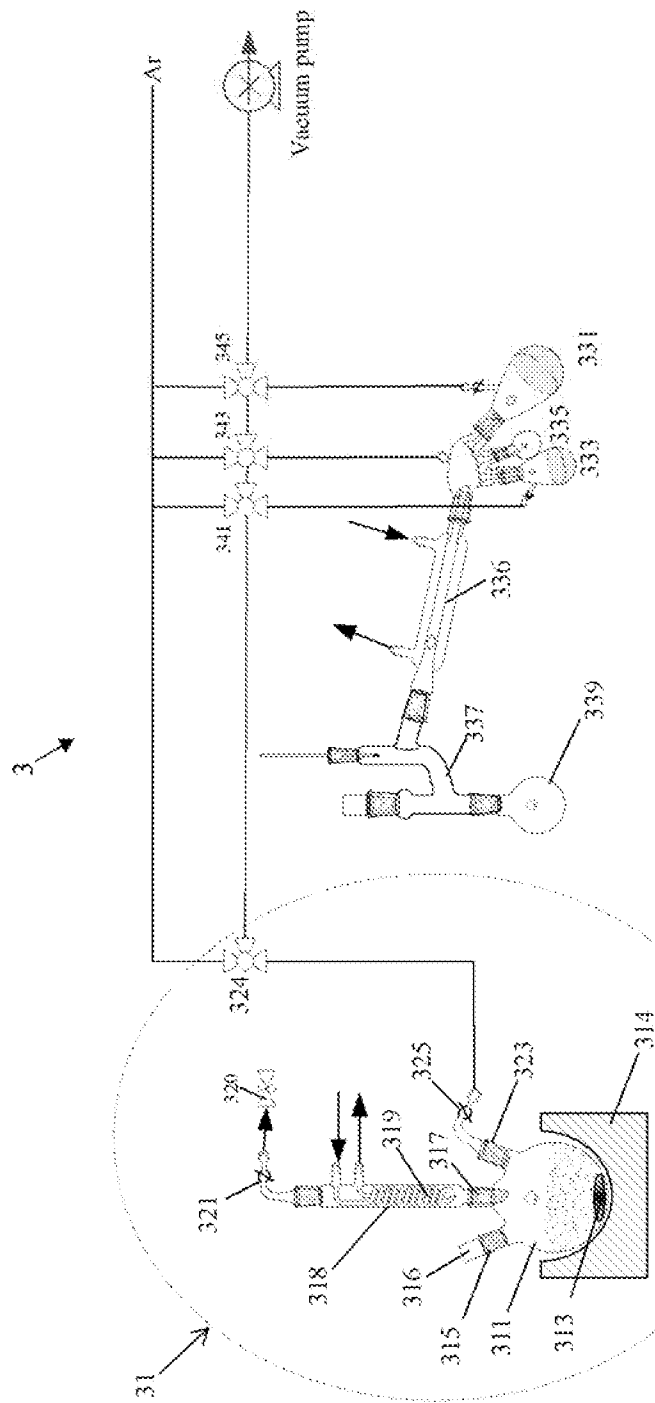


FIG. 3

-4/10-

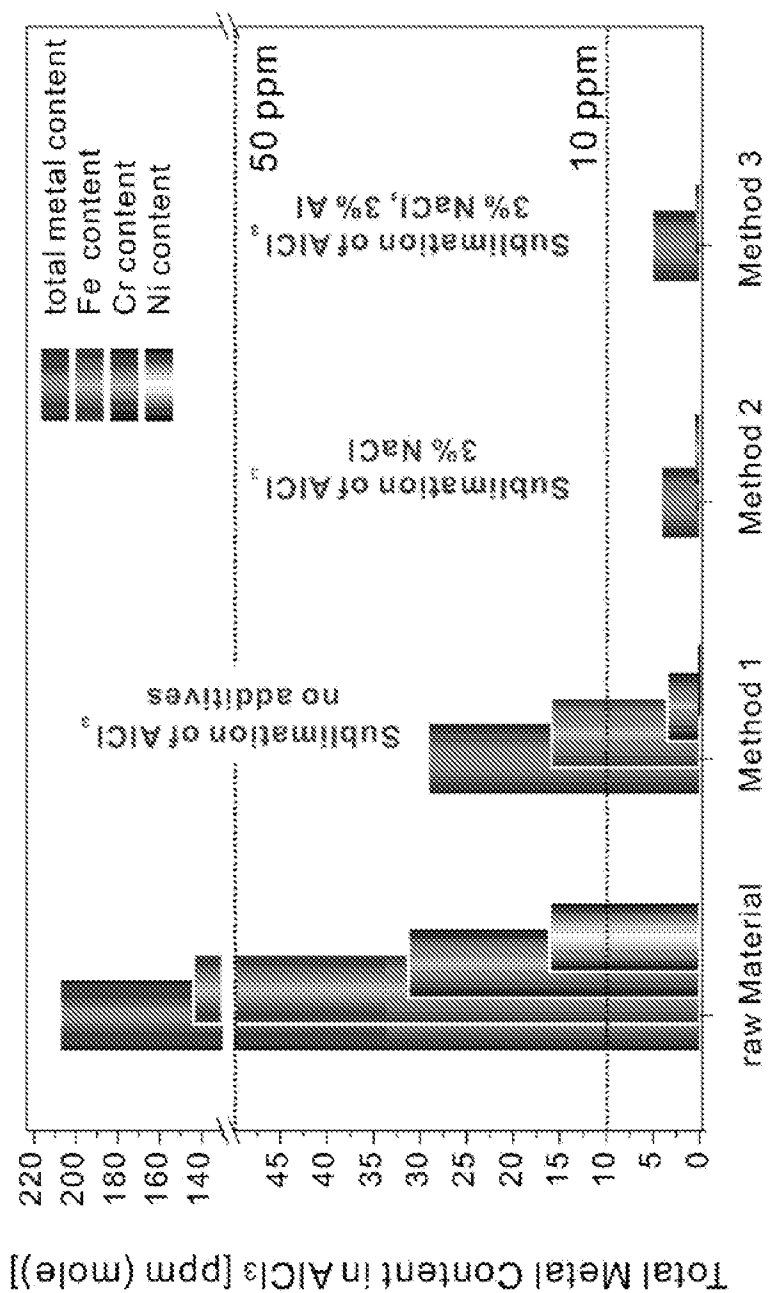


FIG. 4

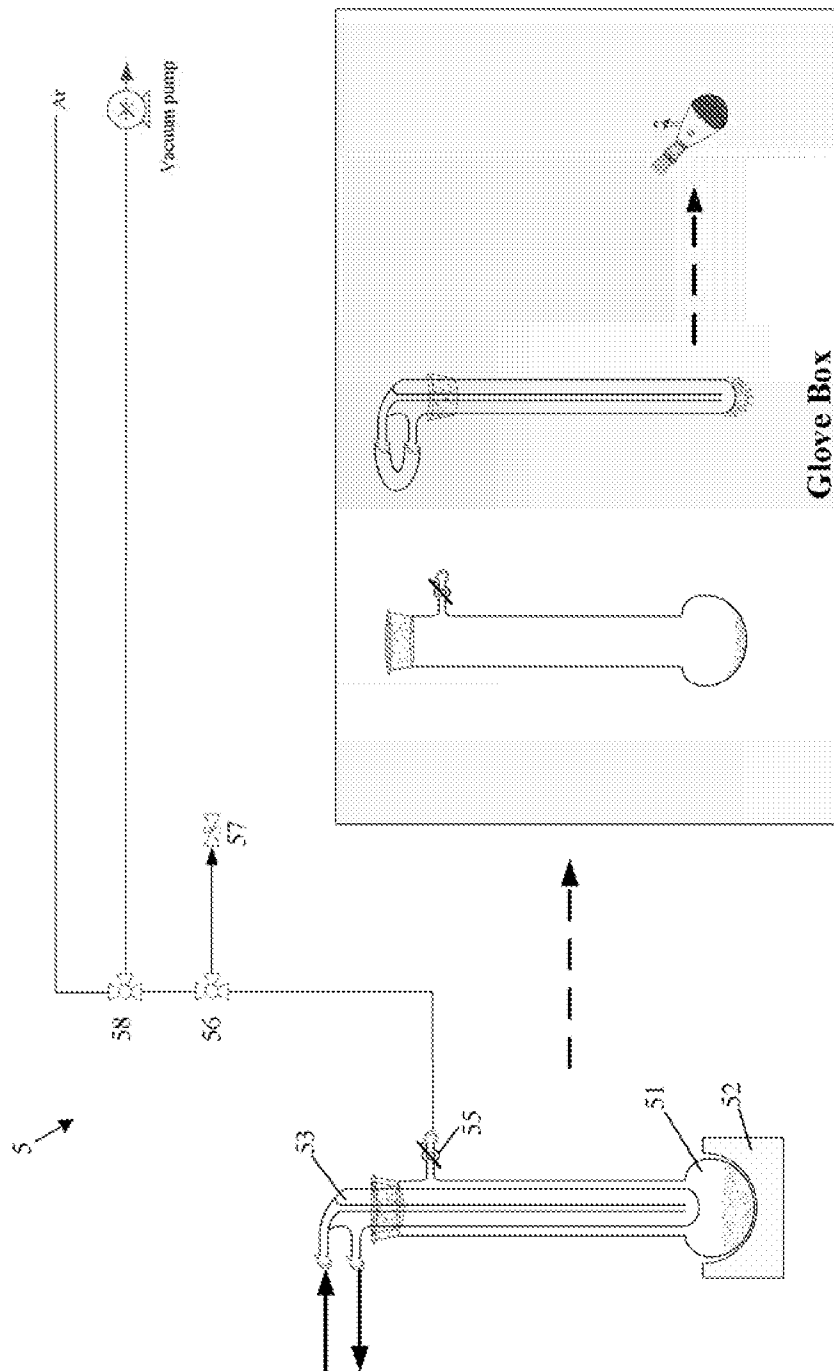


FIG. 5

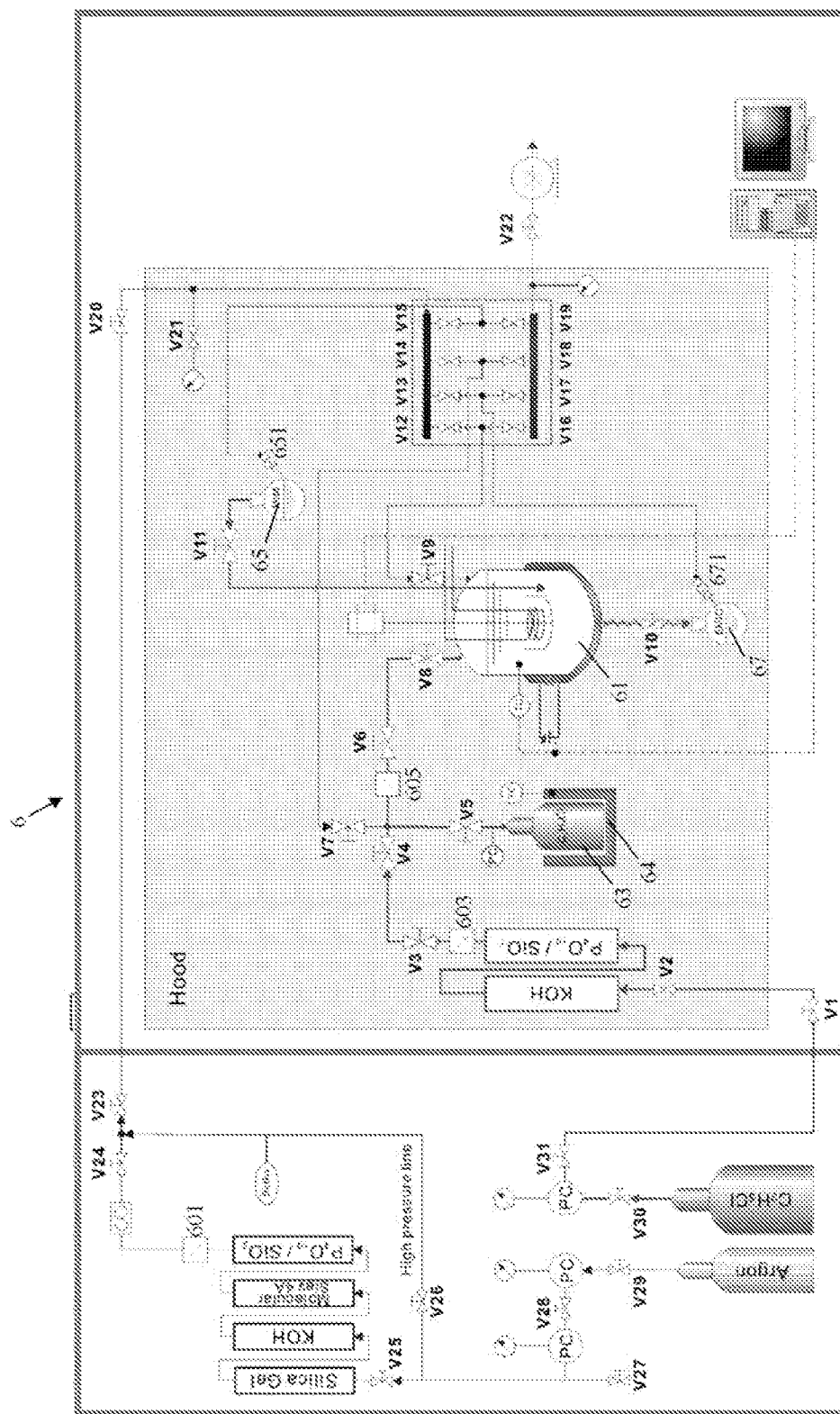


FIG. 6

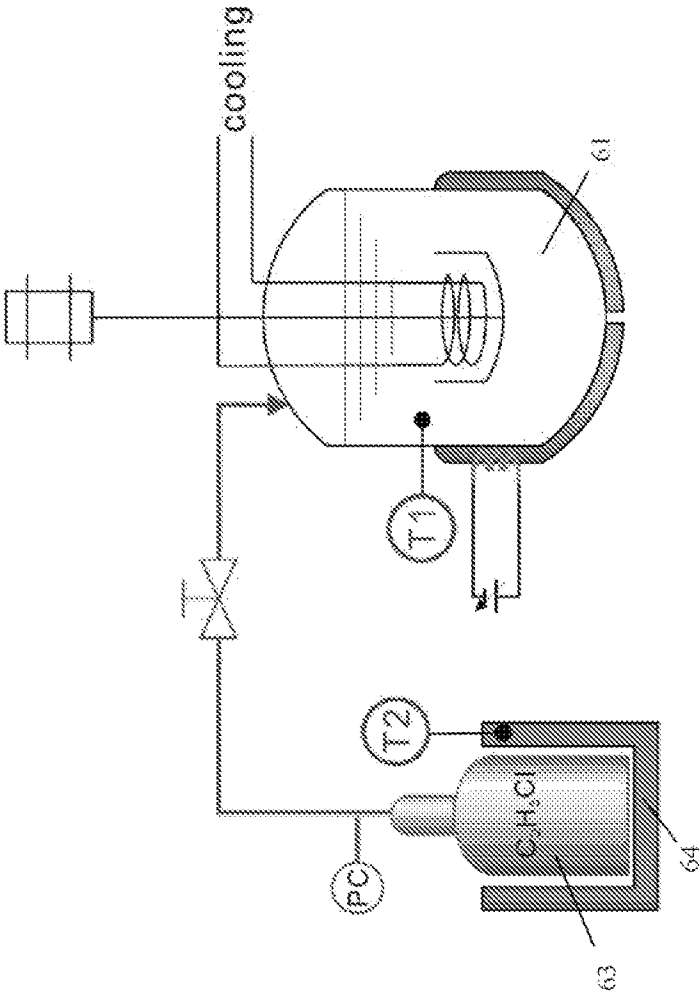


FIG. 7

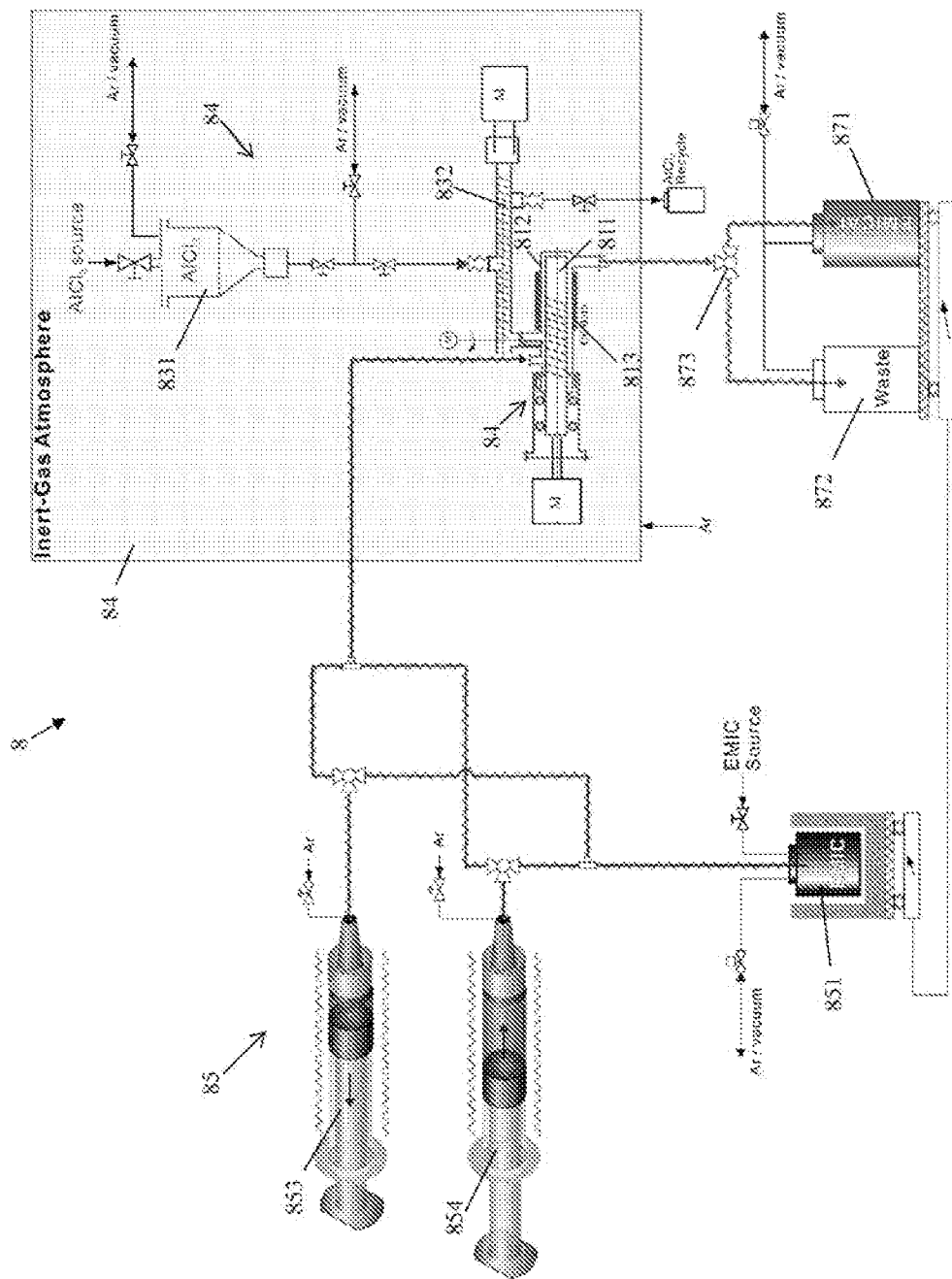


FIG. 8

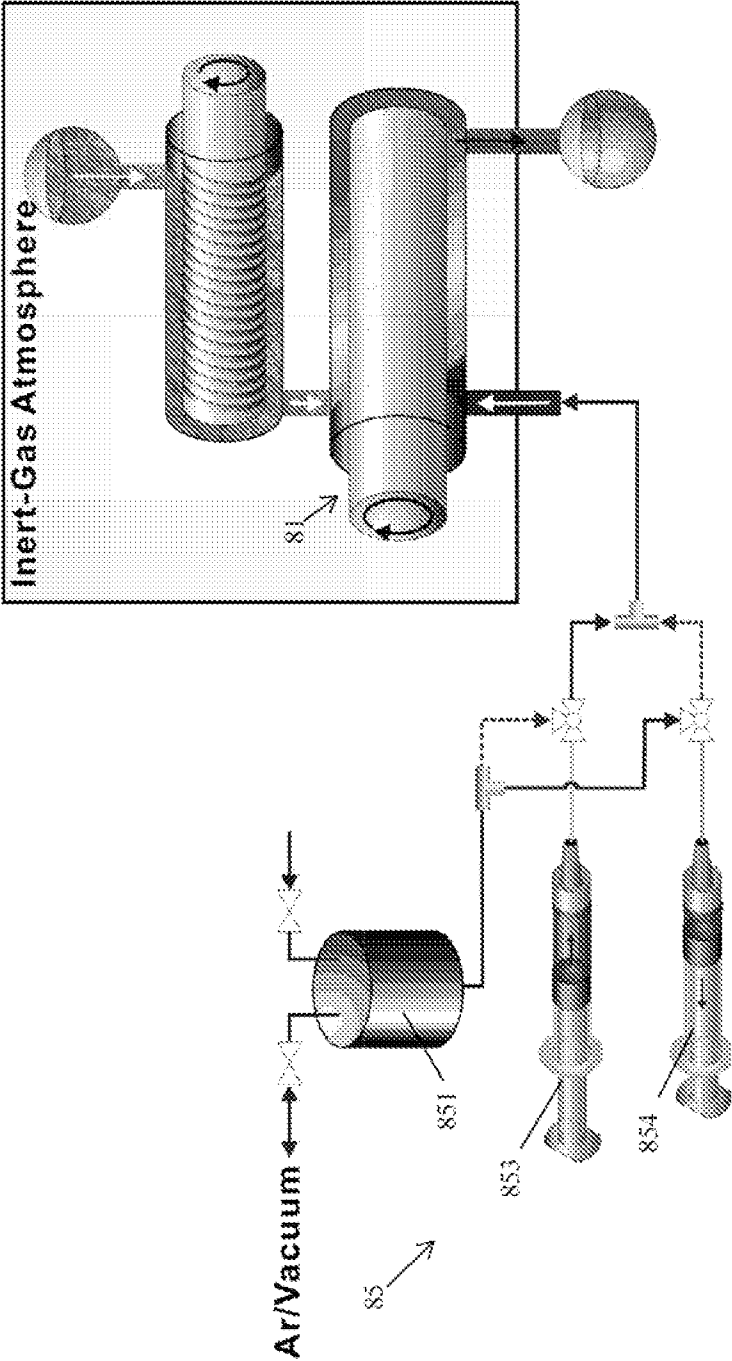


FIG. 9

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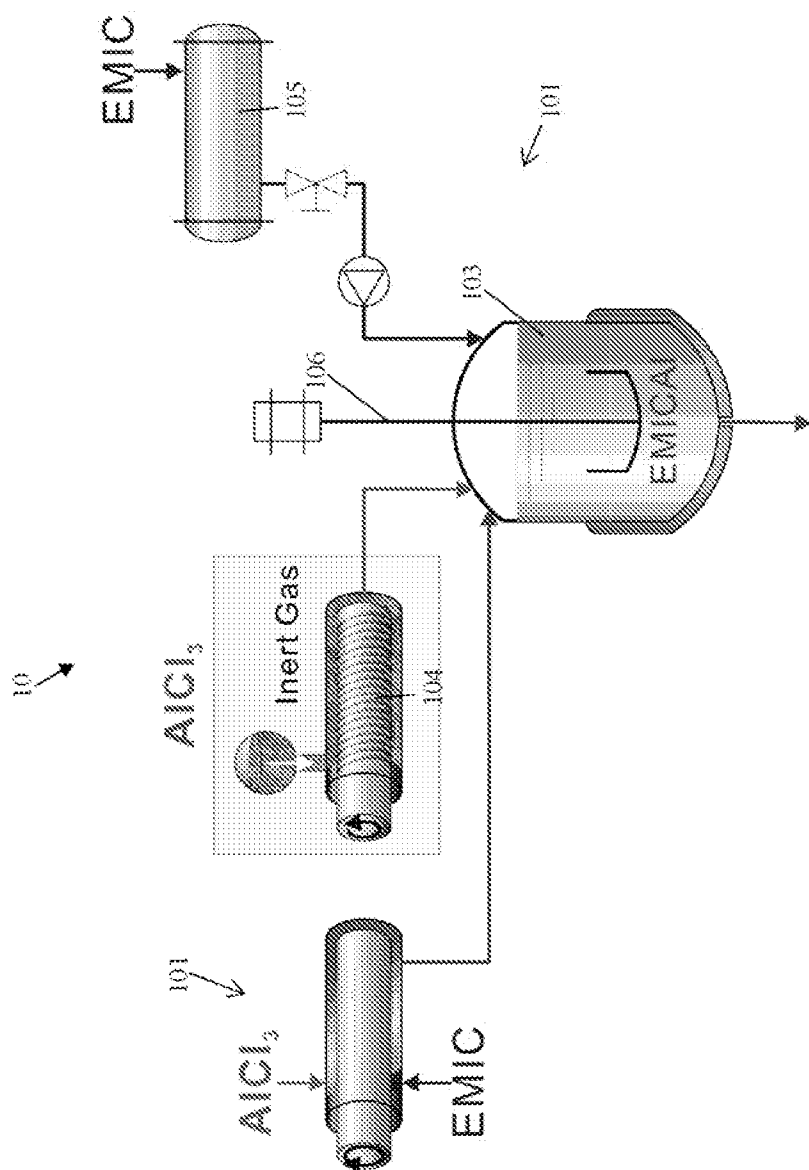


FIG. 10

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2007/070832

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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)

IPC B01J C07C C07D

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)

EPODOC, WPI, PAJ, CNPAT, CNKI (ionic liquid, molten salt, imidazole, reactor, mixer)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	XIN, Hongliang et al. Effect of Lewis Acidity and Polarizability of Imidazole-based Chloroaluminate Ionic Liquid on the Catalytic Performance for the Alkylation of Benzene. Petrochemical Technology. 2005, vol.34, No. 7, pages 617-621	1-9,15-17
X	WANG, Yuxin et al. Complex Adsorption Thiophene Sulfide using Room-temperature Aluminum Chloride-based Ionic Liquids. Journal of Petrochemical Universities. December 2004, vol.17, No. 4, pages 42-45	1-9,15-17
X	TONG, Jing et al. Thermodynamic Properties of Ionic Liquid BMIAICl ₄ . Acta Phys.-Chim. Sin. January 2006, vol.22, No. 1, pages 71-75	1-9,15-17
A	CN2267856Y(CAO, Yingjun et al.) 19 Nov. 1997(19.11.1997) the whole document	10-14

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search

13 Dec.2007(13.12.2007)

Date of mailing of the international search report

10 Jan. 2008 (10.01.2008)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2007/070832

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN1524853A(UNIV ZHEJIANG TECHNOLOGY) 01 Sep. 2004(01.09.2004) the whole document	1-9,15-17
A	EP0989134A(AKZO NOBEL NV) 29 Mar. 2000(29.03.2000) the whole document	1-9,15-17
A	KR20050028774A(KOREA ADV INST SCI & TECHNOLOGY et al.) 23 Mar. 2005(23.03.2005) the whole document	1-9,15-17
A	JP2004331521A(TOYO KASEI KOGYO CO LTD et al.) 25 Nov. 2004(25.11.2004) the whole document	1-9,15-17

PCT/CN2007/070832

Form PCT/ISA/210 (patent family annex) (April 2007)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2007/070832

CONTINUATION OF: A. CLASSIFICATION OF SUBJECT MATTER

B01J31/02(2006.01)i

C07D233/54(2006.01)i

B01J19/00(2006.01)i