The Application of Ionic Liquid Composite Materials in Denitrification from Flue Gas

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ABSTRACT

In this paper, ionic liquid BMIMPF6 was synthesized and characterized by IR and \(^1\)H NMR, and the properties, such as melting point, density, viscosity conductivity and the solubility with common solvents were detected. The NO\(_2\) solubility in composite materials composed of ionic liquid and organic base was also discussed, the absorption process was optimized and the absorption mechanism was speculated. The results showed that the purity of ionic liquid is 99\% by \(^1\)H NMR. The properties of ionic liquid are basically identical with literature reported data. Under the optimum experimental conditions, the composite material composed of the ionic liquid and the organic alkali showed a high NO\(_2\) absorption amount of 0.311gNO\(_2\)/g ionic liquid composite material, and the absorption process is a physical and chemical process. The ionic liquid composite material can be recycled for 4 times, and the absorption effect is basically unchanged.

INTRODUCTION

Ionic liquid (IL) as a kind of green media, has become the focus and frontier of the international scientific research, and attracted the attention and concern of chemists. Ionic liquid refers to the room temperature or low temperature of liquid salt, composed of nitrogen, phosphorus and other components of the organic cations and organic or inorganic anions etc. compared with traditional organic solvent, has a series of outstanding advantages: steam pressure, difficult volatile, colorless, tasteless, has a wide range of thermal stability and better chemical stability; the solubility of inorganic substances, water, organic matter and polymer can be adjusted by changing the cation anion. At present, ionic liquid has been widely used in many fields, such as organic synthesis, extraction and separation, electrochemistry, nano materials, clean fuels, environmental science and so on[1]. Ionic liquids have good prospects for development in the field of environmental pollution control, especially the huge potential in the field of prevention and control of atmospheric pollution. On the one hand, the vapor pressure of ionic liquids is very small, not easy to volatilize, is regarded as an ideal alternative to traditional
organic solvent, and the expansion of the application of ionic liquids and the research of the deep, reduce the traditional organic solvent usage will reduce air pollution from the source. On the other hand, ionic liquids have the advantages of adjustable design, people can synthesize ionic liquids with specific functions according to their need, especially can be used in the selective absorption of gas pollutants. Application of ionic liquids in air pollution control is divided into two aspects: atmospheric pollution source control and end control of air pollution, the former mainly includes the desulfurization of fuel oil and alternative volatile organic solvents, the latter mainly includes removing the SO2 in flue gas, H2S, and volatile organic compounds (VOC). Research on ionic liquids as extraction agent to remove the harmful components in the fuel has just started, there is still a need for more detailed research into many aspects: one is the function of the ionic liquid in the aspect of environmental pollution control needs to be further extended, a lot of research in the adsorption and removal of SO2 and CO2, and the removal of nitrogen in the source is relatively two types of ionic liquids is less; two is the type of ionic liquids to be further expanded, whether in the field of environmental pollution control or in other areas, the current use of imidazolium based ionic liquids. So, the research and development of novel structure, performance, ideal ionic liquids, or their composite materials and other materials, the kinds of ionic liquids for extension number and promote its application has important practical significance[2].

The absorption of NO2 by ionic liquids has been reported in some literature. Guo et al. Studied the absorption of NO and NO2 in flue gas by [CPL][TBAX] ionic liquids[3]. The results showed that the amount of substance ratio of 2:1 CPL - TBAX at 25 ℃ to 90 ℃ can absorb NO and NO2 in great quantities, and the order of absorption from large to small is bromine > fluorine > chlorine. 5 ℃, the amount of substance ratio of 2:1 CPL - TBAB mole fraction of NO and NO2 solubility were 0.170 mol/L and 0.809 mol/L. No chemical reactions in the absorption process, NO and NO2 to maintain the molecular state. At high temperature, the amount of catalyst can be reduced, and the ionic liquid can be reused several times. Due to the use of physical methods of nitrogen removal is safe, the caprolactam - four Butyl Ammonium Bromide ionic liquid absorption of NO and NO2 has broad prospects. Gao et al. [4] in a single tower equipment complete desulfurization denitration at the same time, tower height decreased significantly, without catalyst, low cost, the removal efficiency of nitrogen oxides and sulfides in the exhaust were more than 85% and 98%. The ionic liquid used were guanidine salts, alcohol amine, amine or quaternary amines and heterocyclic compounds. The gas flow is 6000 m3/h, the sulfur oxide content is 1194 mg/m3, the content of nitrogen oxide is 687 mg/m3 denitration absorbent and gas flow rate is 3 L/m3, the absorption under normal pressure, the temperature is 53℃, the absorption liquid can be directly recycled, avoid the two separation, improve economic efficiency. The advantages of the method are that the equipment is simple and easy to use, and the utility model is also suitable for the transformation of the existing wet desulfurization equipment. Compared with the existing technology, cover an area of an area small, fixed investment and operating costs significantly reduced. In addition, the sulfide and nitrogen oxides are absorbed by the absorbing liquid, and the corresponding product is obtained, which can be directly recycled and utilized, and the separation of the two times is reduced, and the economic value is high. In this paper, we study the absorption effect of a kind of ionic liquid composite on NO2, and provide
experimental basis and technical support for the practical application of ionic liquid in flue gas denitrification.

EXPERIMENT

Major Instruments And Reagents

98-1-B type electronic electric heating sleeve, SHD- III circulating water multipurpose vacuum pump, RE-2000 rotary evaporator, JJ300 precision electronic balance, FTS-135 Fourier infrared spectrometer, Brucker Equinox 55 spectrometer, UV-2550 ultraviolet spectrometer, BA-500 nuclear magnetic resonance spectrometer, Brucker Avance 500 spectrometer in CDCl3(TMS as the internal standard). Main reagent: Concentrated nitric acid, copper bromide, N-methyl imidazole, six sodium fluoride, three ethylamine. All the starting materials were commercially available in generally 99% or higher purity and used without further purification.

Preparation Of Ionic Liquid [Bmim]PF₆

The ionic liquid was prepared according to the previously published reports and fully characterized by IR and NMR. N-methylimidazole(1mol) and 1-butyl bromide(1mol) were added in 100mL heptane and the mixture was stirred for 12 h at 80°C. The reaction mixture was washed with heptane, dried under reduced pressure and then Sodium hexafluorophosphate (1mol) in 500mL water was added, the mixture was then stirred for 12 h at room temperature. The upper water phase was removed, and the low phase was washed several times with water and pure [BMim]PF₆ (1-butyl-3-methylimidazolium hexafluorophosphate) was obtained as a colorless liquid with a nearly quantitative yield.

Absorption Of NO2 In Ionic Liquid Organic Alkali Composites

Accurate weighed 1- butyl -3- methylimidazolium hexafluorophosphate (BMIMPF6 ) 3.11g and 3.13g in tri-n-butylamine were mixed at room temperature to obtain the BMIMPF6 ionic liquid composite material. The ionic liquid composite material was transferred into a 25 ml three mouth flask which was immersed in a constant temperature water bath pot. Open the separatory funnel, NO2 gas generated by the reaction of nitric acid and copper powder. Control the gas producing speed bubbled into three bottles in ionic liquid composite material. Fully mixing for NO2 dissolves. Every 10 min with precision of 0.01 g of electronic balance recording an ionic liquid absorption. Stop the experiment until absorption reaches equilibrium. The ratio of the absorption of NO2 and the quality of ionic liquid were calculated as the mass fraction of absorption, parallel determination of 3 times, take the average. According to the quality of absorbed dose calculated molar absorption fraction.
RESULTS AND DISCUSSION

Characterization And Determination Of Ionic Liquids

| Table 1. Properties of [Bmim]PF6 ionic liquid. |
|---------------------------------------------|
| Literature data | mp(℃) | ρ(g/cm³) | η(30℃,cp) | σ(s/m) | Water content |
| -61 | 1.37 | 312 | 1.46s/m | 360ppm |
| Detected data | -60 | 1.37 | 310 | 1.47 | <0.01% |

Solubility

- Water: immiscible
- Methanol: miscible
- Acetone: miscible
- Methyl acetate: partly miscible
- Ethyl ether: immiscible

The characterized results confirmed the structure of BMIMPF6. IR,δ/cm⁻¹: 3171, 3125(aromatic νC-H), 2966, 2939, 2878(aliphatic νC-H), 1573, 1468(aromatic C=C) 1170(aliphatic C-H), 1468, 1387(aliphatic MeC-H), 838 (νP-F). ¹H-NMR (400MHz CDCl₃)(δ, ×10⁻⁶): 8.68(1H, s, NCHN), 7.45(1H, m, CH₃NCHCHN), 7.26(1H, m, CH₃NCHCHN), 4.19(2H, t, NCH₂(CH₂)CH₃), 3.83(3H, s, NCH₃), 1.64(2H, m, NCH₂CH₂CH₃), 1.28(2H, m, N(CH₂)₂CH₂CH₃), 0.86(3H, t, N(CH₂)₃CH₃).

The results of the determination of the ionic liquid density viscosity, melting point, solubility and so on are shown in table 1. The purity of ionic liquid is 99% by ¹H NMR, which is consistent with the results reported in the literature. It can be applied to the follow-up research process. The solubility tests of [Bmim]PF6 ionic liquid with common solvents were shown in Table 1, from where we can see that it is miscible in high polar solvents such as ketones and alcohols, whereas it is partly miscible or immiscible in moderate or weak polar solvents such as methyl acetate and ether. It always contains trace amount of water although it is immiscible in water. The literature reported properties of [Bmim]PF6 such as melting point, density, viscosity, conductivity were also listed in Table 1, which showed that it is a promising green alternative solvent in electrochemical process for its excellent properties such as high conductivity, low viscosity and wide liquid range.

Absorption of NO₂

It is found that imidazolium ionic liquids have a certain ability to absorb NO₂ gas, but the higher viscosity of ionic liquids (for example,BMIMBF₄, 25 ℃ and 110.308 cp)[5]. In order to reduce the viscosity of the ionic liquid and further improve the absorption of NO₂ gas, we have studied a series of organic alkali and ionic liquid composite absorption system, after a lot of experiments, we found that the imidazole ionic liquid and N- alkyl imidazole organic alkali prepared by an ionic liquid composite material not only has high absorption capacity, but also has obvious synergistic absorption effect. The uptake should be greater than the absorption effect is the sum of linear superposition of single components. The absorption decreases with the increase of temperature, which means that it is beneficial for the absorption process at low temperature, and it is suitable for the absorption of NO₂ at high temperature. Through the NMR analysis of the absorbed ionic liquids, it is known that the absorption process is a physical and chemical process.

At 25 ℃, the absorption amount of the composite material composed of BMIMPF6- ethylamine was 0.311g NO₂/g ionic liquid composite material, 1- butyl
-3- methyl imidazole (BMIMP6) N- methyl imidazole 0.242g NO2/g ionic liquid composite.

**Recycling Analysis**

The imidazole ionic liquid composite material which absorb NO2 is installed in the distillation bottle, and the water pump is distilled under pressure (4.5 kPa) at a temperature of 100℃, weigh the absorption bottle every ten minutes until the constant weight. Quantitative recovery of imidazole ionic liquid composite materials, continue to apply to the next absorption process, The process was carried out for 4 times, and the NO2 removal rate was kept above 99% in the ionic liquid composite, and the recovered ionic liquid composite remained constant for NO2 absorption.

**Compared With The Literature**

By comparison, 25℃ mole fraction solubility of NO2 gas in caprolactam four butyl bromide ionic liquid as high as 0.809, equivalent to 0.355g NO2/g ionic liquid, close to the absorption effect. The group also reported that the viscosity of ionic liquids in 50 ℃ for 1500 cp, as the NO2 gas absorption agent, the higher the viscosity of the means of high energy consumption. It shows that the ionic liquid composite prepared in this paper has a good application prospect.

**CONCLUSION**

In this paper, a class of imidazolium ionic liquids were synthesized, the density and viscosity of the melt were measured. The application of the composite material with organic base in the absorption of NO2 was discussed. The results showed that the absorption and the effect were good. The main advantages are as follows: in the wide temperature range, the ionic liquid composite is in liquid state, which is beneficial to the gas absorption and mass transfer. The viscosity of the ionic liquid composite at 25 ℃ is generally less than 20cp, and the lower viscosity means lower energy consumption, which makes the absorption and desorption process easy to realize continuous operation. Before and after the use of ionic liquid composite materials are in liquid state, so that the absorption and desorption process is easy to achieve continuous operation. How to guarantee the absorption effect, reduce the cost of the absorption process of ionic liquid, absorption of nitrogen oxide ionic liquid, how to carry out the separation and reuse of NO2, to avoid the two pollution, further research is needed to improve the utilization rate of resources.

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