

Absorption of nitric oxide in simulated flue gas by a metallic functional ionic liquid

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ABSTRACT

Nitric oxide (NO) is one of the main air pollutants threatening human health and environment, but it is also an important intermediate for the production of nitric acid. In this work, a metallic functional ionic liquid (IL) [Bmim]₂FeCl₄ was designed and applied to efficiently and reversibly absorb NO in a simulated flue gas. The effects of absorption time, temperature, and NO concentration on the absorption in the IL were investigated. The results indicated that the absorption capacity of NO by the IL increased as temperature decreased and NO concentration increased. The absorption capacity of NO with a concentration of 0.2% by the IL was high up to 0.205 mol NO per mol IL at 30 °C, and the absorbed NO could be desorbed from the IL at 80 °C. The regeneration experiments demonstrated that the IL could be reused, and its absorption capacity did not vary in four absorption/desorption cycles. The absorption mechanism of NO by the IL was studied by FT-IR, and the result indicated that there was a chemical interaction between Fe²⁺ and NO, and Fe²⁺ was the absorptive active species.

1. Introduction

Nitrogen oxides (NO_x) are major air pollutants of fossil fuel-fired flue gas, which lead to acid rain, photochemical smog and ash haze of particulate matter of 2.5 μm or less in diameter (PM_{2.5}) [1–5]. The major constituent of NO_x in flue gas is nitric oxide (NO) that has a very low solubility in aqueous solutions and therefore is hard to be removed [6]. On the other hand, NO is an important intermediate for the production of nitric acid in the chemical industry. Consequently, the study on renewable and efficient absorbents for absorption and recovery of NO is important to our society.

At present, the major industrial techniques to control the emission of NO_x in flue gas include selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) [7–9]. But these technologies cannot recover NO from flue gas. Moreover, they are facing the problems of high removal temperatures, catalyst's poison caused by K, Ca, Na and As, and frequent changes of catalyst, resulting in high cost [10]. Compared with above dry denitration, wet denitration also draws much attention, due to its advantages of low cost and simple equipment. However, the absorption capacities of NO in aqueous solutions are very low. To enhance the absorption capacity of NO in aqueous solutions, researchers have experimented with adding additives [11,12]. The additives added in aqueous solutions and the enhancement of NO

removal were first studied in 1970s [13]. Due to the presence of a diatomic free radical, NO can easily combine with transition metals. Hence, abundant absorbents containing transition metals were designed and applied for NO capture. Among these absorbents, Fe^{II}-EDTA gained much attention due to its high absorption capacity for NO. For example, Ma et al. [14] reported that the absorption capacity of Fe^{II}-EDTA in aqueous solution was about 0.043 mol NO per mol Fe^{II}-EDTA. This absorbent was also demonstrated to have a rapid absorption rate of NO [15]. Nevertheless, all ferrous-contained absorbents reported in the literature had to be dissolved in water, but the solubility of these ferrous absorbents in aqueous solution was quite low [16,17]. If we could design an absorbent containing ferrous ions that is liquid at room temperature, the absorption efficiency can be enhanced.

Ionic liquids (ILs), low-melting molten salts entirely composed of ions, are widely used for desulfurization and decarbonization of flue gas due to their benign properties, such as negligible vapor pressure, high thermal stability [18,19], unflammability [20], low volatility [21,22], chemical stability, wide liquid temperature range and tunable properties [23]. In 2002, Bates et al. [24] reported the first functional IL for capturing CO₂ by introducing amino groups into alkyl side chain on the cation ring of imidazolium-based ILs. As a result, the IL could absorb CO₂ with an absorption capacity of about 0.5 mol CO₂/mol IL at ambient pressure. After two years, Han et al. [25] reported the first

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functional IL 1,1,3,3-tetramethylguaninium lactate ([TMG][La]) for capturing SO_2 , and its absorption capacity of SO_2 was about 0.98 mol SO_2 per mol IL for capturing 8% SO_2 in N_2 . Later, the absorption of acidic gases by ILs entered a fast development period. However, there have been few reports about capturing NO, one of the main pollutants in flue gas, by ILs. In 2016, Wang et al. [26] reported the first functional IL trihexyl(tetradecyl) phosphonium tetraazole ([P₆₆₆₁₄][Tetz]) for capturing NO, but the IL was difficult to synthesize and had a low absorption rate and high desorption residue.

If ferrous ion is introduced into ILs, a kind of metallic functional ILs with ferrous ion can be synthesized. It is then possible to greatly increase the concentration of ferrous ions in a solution, and improve the efficiency of ferrous absorbents. In this work, a ferrous ion-contained functional IL ([Bmim]₂FeCl₄) was synthesized and applied to capture NO. The results indicated that the IL can both keep a fast NO absorption rate by ferrous ion and overcome difficult desorption shortcomings for the functional IL [P₆₆₆₁₄][Tetz].

2. Experimental

2.1. Materials

NO (99.8%) and N_2 (99.999%) were obtained from Beijing Haipu Gas Co., Ltd. Beijing, China. Simulated flue gases with different NO concentrations (0.2% and 0.4%) were obtained by mixing NO and N_2 together in a 40 dm³ high-pressure cylinder. Iron (II) chloride anhydrous (FeCl₂, 99.5% in purity) was purchased from Alfa Aesar (China) Chemicals Co. Ltd., Beijing, China. 1-n-Butyl-3-methylimidazolium chloride ([Bmim]Cl, 97% in purity) was obtained from Yuanye Bio-Technology Co. Ltd., Shanghai, China.

2.2. Preparation of IL

The IL [Bmim]₂FeCl₄ was prepared by directly mixing FeCl₂ and [Bmim]Cl together at a mole ratio of 1:2, and stirring at 50 °C for 24 h.

2.3. Absorption and desorption of NO in IL

The process of NO absorption and desorption was performed under ambient pressure. An amount of IL (about 2.0 g) was charged in a glass tube with a length of 100 mm and an inner diameter of 15 mm. Simulated flue gas with a flow rate of 100 cm³/min was bubbled through the IL in the tube which was immersed in a constant-temperature water bath. The amount of absorbed NO was determined by measuring the weight of the tube using an electronic balance with an accuracy of ± 0.1 mg, before and after absorption.

The NO-absorbed IL was regenerated by bubbling pure N_2 at 80 °C through the IL. In a typical experiment of desorption of NO, N_2 of 100 cm³/min at atmospheric pressure was bubbled through about 2.0 g NO-absorbed IL in a tube, which was immersed in a constant-temperature oil bath. The temperatures of the water bath and oil bath had uncertainties within 0.5 °C. The amounts of NO during absorption and desorption were determined at regular intervals using the balance.

2.4. Raman, FT-IR and TG analyses

Raman spectra of the IL was recorded from 100 to 4500 cm⁻¹ on the LabRAM ARAMIS Raman Spectrometer (HORIBA Jobin Yvon) with a 532 nm argon ion laser for excitation. FT-IR spectra of the original IL, NO-absorbed IL and NO-desorbed IL were recorded on a Fourier transform spectrometer (Nicolet 6700, USA) with wavenumbers from 400 to 4000 cm⁻¹. A thermogravimetric analyzer (Henven, China, TGA/HCT-1) was used to determine the thermal decomposition temperatures. It was run in a nitrogen atmosphere at a heating rate of 10 °C/min.

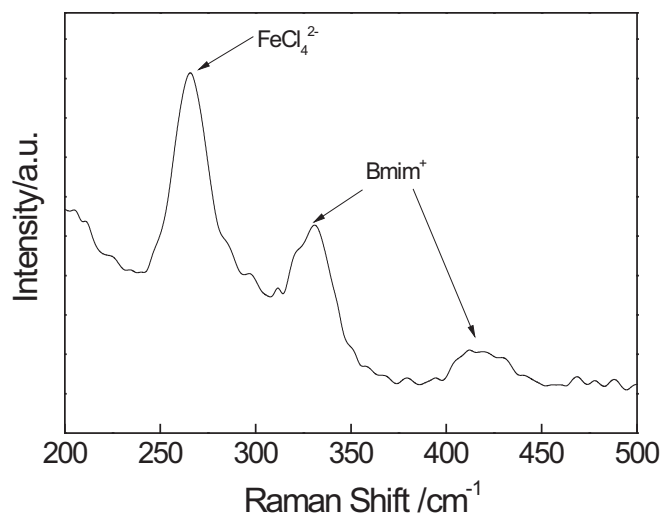


Fig. 1. Raman spectrum of the synthesized IL [Bmim]₂FeCl₄.

3. Results and discussion

3.1. Characterization of the synthesized IL

Fig. 1 shows the Raman spectrum of the synthesized IL [Bmim]₂FeCl₄. The large peak at 265 cm⁻¹ is most likely the vibration of FeCl₄²⁻. This assignment is consistent with the literature, the feature is reported at 266 cm⁻¹ in the solid [(CH₃CH₂)₄N]₂FeCl₄ [27]. The peaks at 325 cm⁻¹ and 415 cm⁻¹ are both assigned to [Bmim]⁺ cation, as reported in the literature [28]. The results indicate that the IL synthesized in this work is [Bmim]₂FeCl₄.

The TGA result showed the IL decomposed at 300 °C, suggesting that the IL has good thermal stability.

3.2. Absorption of NO in IL

The absorption of NO at temperatures of 20, 30 and 40 °C is shown in Fig. 2. It can be seen from Fig. 2 that the absorption amounts of NO increase almost linearly with time at the initial stage and then the absorption reaches equilibrium. In addition, Fig. 2 indicates that the higher the absorption temperature, the lower the absorption capacity of NO in IL. For instance, the absorption capacity of NO by the IL decreases from 0.413 mol NO/mol IL to 0.200 mol NO/mol IL with increasing the absorption temperatures from 20 °C to 40 °C. The results

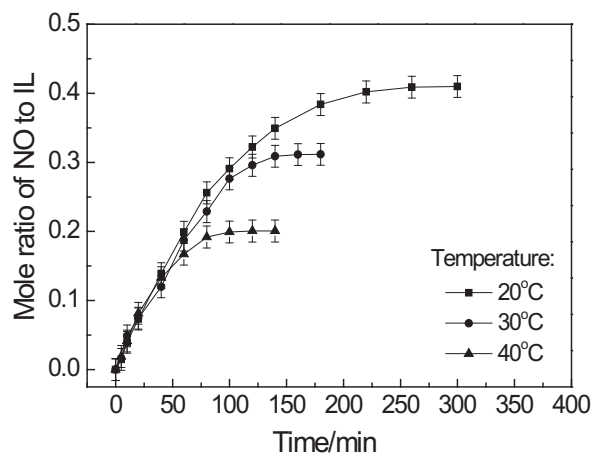


Fig. 2. Effect of temperature on NO absorption by IL [Bmim]₂FeCl₄ with a NO concentration of 0.4%.

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