Desulfurization of Gases

Desulfurization of Flue Gas: SO_2 Absorption by an Ionic Liquid**

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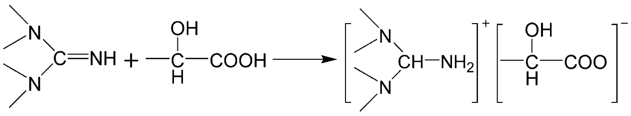
Air pollution has been drawing increasing attention throughout the world. SO_2, mainly emitted from fossil-fuel combustion, is one of major air pollutants. Up to now, flue-gas desulfurization (FGD) is one of the most effective techniques to control emissions of SO_2 from the combustion of fossil fuels, such as coal and petrol. A variety of processes for SO_2 control, such as wet FGD, dry FGD, and semidry FGD processes, have been commercially widely adopted.[1] However, these methods require a large amount of water and further treatment of the resultant wastewater is also needed, or they produce by-products such as calcium sulfate. Recently, dry and catalytic methods for SO_2 removal have attracted much interest due to their economic benefits,[2] and copper on alumina (CuO/Al_2O_3) catalyst sorbent is usually used. However, this method has some disadvantages, for example, the dust in the flue stream can deposit onto the sorbent and cause plugging, which affects the desulfurization efficiency, and in a fixed-bed operation, a large volume of pellets can cause high flow resistance.[3]

One of the most attractive approaches for the separation of a target compound from a mixture of gases in a gas stream is selective absorption into a liquid.[4] The interaction between the gases and the liquid determines the absorption efficiency. The ideal interaction should be neither too strong nor too weak, thus absorption and desorption can occur. The liquid or the solution should also endure the temperature of the gas stream. At the same time, the liquid should have very low vapour pressure. Generally, amines are used to chemically trap the acidic gas, such as CO_2 or SO_2, by way of forming amine carbonate or sulphate. However, this is not so useful in large-scale SO_2 capture, as the solution can evaporate into the gas stream.

Room-temperature ionic liquids (ILs, low-temperature molten salts) have many unusual properties,[5] such as extremely low vapor pressure, high thermal stability and chemical stability, excellent solvent power for organic and inorganic compounds. Therefore, they can be used as environmentally benign solvents for a number of chemical processes, such as separations[4a,6] and reactions.[7] It was reported that ILs can dissolve many gases, such as CO_2, ethylene, and ethane, especially at high pressure.[8] Recently, the absorption of CO_2 by using 1-*n*-propylamine-3-butylimidazolium tetrafluoroborate was studied by Bates et al.,[4a] and the results indicated that the IL can adsorb CO_2 from gases effectively.

Herein, we present the results of our study on the absorption of SO_2 by using our newly synthesized IL, which contained a basic functional group, an amine (guanidinum). The IL (**3**) was synthesized by direct neutralization of 1,1,3,3-tetramethylguanidine (TMG) (**1**) and lactic acid (**2**) (see Scheme 1).[9] To synthesize the IL, ethanol (100 mL) and TMG (2.30 g, 20.0 mmol) were loaded into a 250 mL flask in a water bath of 25 °C. A solution of lactic acid (20.0 mmol) in ethanol (35 mL) was then added into the stirring reaction mixture, and the reaction was allowed to proceed for 2 h. The solvent was then removed by evaporation under reduced pressure. The resulting crude oily residue was dissolved in ethanol (100 mL), treated with active carbon, filtered, the solvent was removed by evaporation under vacuum, and a colorless product was obtained with a yield of 92.6 %. The melting point of the IL was lower than −50 °C, which was determined by differential scanning calorimetry (DSC, Perkin-Elmer DSC-7).



1 **2** **3**

Scheme 1. Synthesis of TMG lactate IL from TMG and lactic acid.

The simulated flue gases were a mixture of N_2 (99.95 %) and SO_2 (99.95 %) with a SO_2 content of 8 % by volume. The experiment was carried out at ambient pressure and at 40.0 °C. The gas stream was bubbled through about 3.5 g of IL loaded into a glass tube with an inner diameter of 12 mm, and the flow rate was about 50 mL min^{-1}. The glass tube was partly immersed in a glycerol bath, the temperature of which was controlled. The weight of the IL solution was determined at regular intervals.

Figure 1 shows the molar ratio of absorbed SO_2 to original IL as a function of absorption time. At the beginning of the

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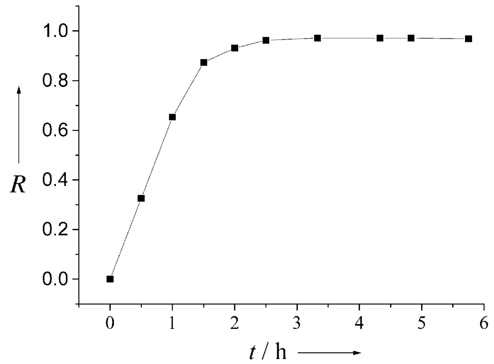


Figure 1. SO_2:IL molar ratio (R) as a function of time. Conditions: 40 °C, 1.0 bar.

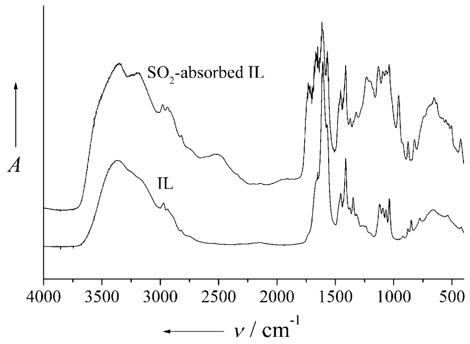


Figure 2. FTIR spectra of the IL and SO_2-absorbed IL.

experiment, the amount of SO_2 in the IL increases linearly with time, and an equilibrium was reached in about 3 hrs (i.e., the rate of absorption and desorption were the same). At this equilibrium the molar ratio of SO_2 to IL was 0.978:1 (0.305 g $SO_2 g^{-1}$ IL). The absorbed SO_2 was removed under vacuum at 40 °C, and the IL could be recovered and reused several times with a high capacity for SO_2 absorption.

The effect of temperature on the capture of SO_2 by the IL was also studied at ambient pressure. The molar ratio of SO_2 to IL at 40.0, 60.0, 94.0 °C were 0.978, 0.775, and 0.512, respectively. As expected, the absorption amount decreased with increasing temperature, which is not favorable for the absorption of SO_2 from hot flue gas. The results also demonstrate that the SO_2 gas absorbed at lower temperature can be desorbed partially at higher temperatures.

When the IL was exposed to pure SO_2 gas at 40.0 °C and 1.2 bar, the molar ratio of SO_2 and the IL reached 1.7. However, when the SO_2-saturated IL was exposed at atmospheric pressure to dried air, it released SO_2 and its weight decreased continuously until the molar ratio was 1:1. The elemental analysis of SO_2-absorbed IL showed that the ratio of N atoms to S atoms was 3:0.96, that is, the molar ratio of SO_2 to IL was very close to 1:1. The above results suggest that the IL can absorb SO_2 by both physical and chemical absorptions. At lower pressure, however, the gas is mainly absorbed chemically and the molar ratio of SO_2 to the IL is 1:1. The basic N–H group on the organic molecules can have a considerable effect on some reactions (such as ring-closing olefin metathesis, RCOM).[10] So it is useful that the N–H group can be reversibly protected by acidic CO_2 to form carbamic acid and deprotected by reducing the pressure.[10]

To obtain some information about the chemical interaction between SO_2 and the IL used in this work, we characterized the gas-free and gas-treated IL by FTIR and NMR. The FTIR spectra of the SO_2-absorbed IL and SO_2-free IL were determined (Figure 2). The IR spectrum of the SO_2-absorbed IL clearly shows: O–H (3000–3500 cm^{-1}), C–H in –CH_3 (2966 cm^{-1}), CH_3–N (2820 cm^{-1}), N–H (1620 cm^{-1}), S=O (1230 cm^{-1}), C=O in COO- (1722 cm^{-1}), intermolecular O···H in the cation (1666 cm^{-1}), C–N (around 1069 cm^{-1}), S–O (957 cm^{-1}). Compared with the FTIR spectrum of the IL, the spectrum of the SO_2-treated IL manifests new absorption bands at 1230 cm^{-1} and 957 cm^{-1}, which can be assigned to sulphate S=O and S–O stretches, respectively. The ^{1}H NMR spectra of the SO_2-treated IL and untreated IL are presented in Figure 3. The assignment of the resonances of the IL is shown in detail elsewhere.[9] Clearly, two new resonances are observed at $\delta = 5.86$ and 7.84 ppm, which are consistent with the formation of S–O–H and S=O···H.

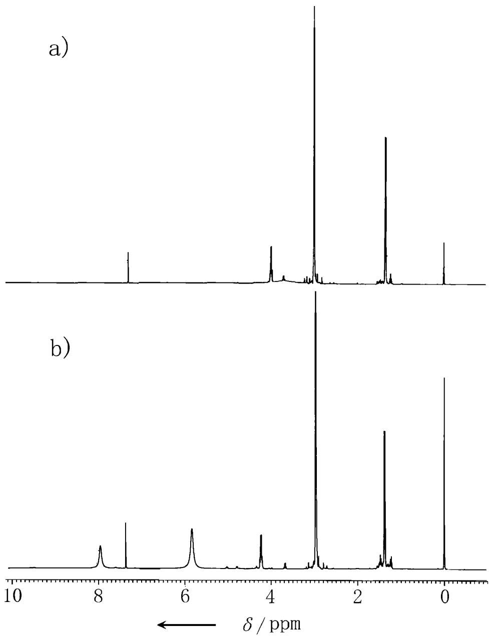
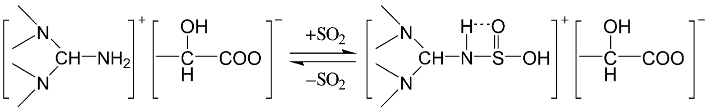


Figure 3. ^{1}H NMR spectra (400 MHz) of the IL (a) and SO_2-absorbed IL (b) in $CDCl_3$.

On the basis of the above results, we propose a reaction of the IL **3** with SO_2, which is shown in Scheme 2. SO_2 reacts with the NH_2 group on the cation, while the O atom on S=O probably forms intramolecular hydrogen bond with the H atom of the amine, as shown in Scheme 2.



Scheme 2. Proposed reaction between the IL and SO_2.

The two commonly used ILs, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), were also tested to see whether they absorb SO_2. At 40.0 °C and 1.0 bar, the absorption capacities were 0.14 wt% and 0.10 wt%, respectively. These results illustrate that the basic functional group is very important for the absorption of the gas.

Furthermore, we also studied the absorption of CO_2 with **3**. The absorption capacity of **3** with CO_2 was very low (0.25wt%), which indicates that the IL is selective towards SO_2.

In conclusion, the IL **3** can absorb SO_2 from a simulated flue gas effectively with a high absorption capacity. The absorbed SO_2 can be reversibly desorbed by vacuum or heating, and the IL can be reused. This method has potential applications such as the removal of SO_2 pollutants, and the separation of gas mixtures that contain SO_2.

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