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Short Review

Ionic liquids: Functionalization and absorption of SO_2

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Abstract

Room-temperature ionic liquids (ILs), which have excellent properties, such as high gas absorption abilities, extremely low volatility and tunable structures, are regarded as environmentally-friendly absorbents and widely used in SO_2 absorption and separation. As a result, a large number of ILs have been synthesized to capture SO_2 from flue gas or simulated gas, but a part of them just have physical interaction with SO_2 and can hardly absorb SO_2 when the content of SO_2 is very low. Hence, functional ILs, which can chemically absorb a large amount of SO_2 with low contents, have been designed and synthesized for SO_2 capture. Up to now, many kinds of functional ILs were investigated for SO_2 absorption from flue gas. In this review, the functional ILs are classified into guanidinium based ILs, hydroxyl ammonium based ILs, imidazolium/pyridinium based ILs, quaternary ammonium based ILs, phosphonium based ILs, and other kinds of ILs according to their cations. The capacities of SO_2 absorption in these ILs, the mechanism of the absorption, and the ways to enhance the absorption are briefly introduced. The prospect of functional ILs for their application in SO_2 removal is presented. The present problems and the further studies are also discussed.

Keywords: Ionic liquid; SO_2; Absorption; Functionalization

1. Introduction

Since the Industrial Revolution, coal and other fossil fuels are widely used everywhere in the world. Meanwhile, due to high contents of S-contained compounds in fossil fuels, million tons of SO_2 are emitted into air per year by burning for energy, causing serious air pollution. The most effective way to control the emission of SO_2 from flue gas by combustion of fossil fuels is flue-gas desulphurization (FGD). Up to now, many absorbents, such as limestone, magnesium oxide, ammonia water and seawater, are used to capture SO_2 and all of them can decrease the pollution of SO_2. However, SO_2 is also a useful resource in the chemical industry. Most of the processes and absorbents only pay attention to the control of air pollution caused by SO_2 and ignore the recycle of SO_2, because the absorbents are very difficult to regenerate and recover SO_2. The absorption processes are irreversible and can result in secondary pollution. Although organic amines can be used to reversibly absorb SO_2 from flue gas, the process suffers from solvent loss. Therefore, it is urgent to explore new absorbents for the reversible, efficient, and environmentally-friendly capture of SO_2.

Room-temperature ionic liquids (ILs) are regarded as environmentally benign solvents because of their unique physicochemical properties, such as extremely low vapor pressure, high thermal and chemical stability, designable structure and excellent solvent power for organic and inorganic compounds. Due to these properties, ILs have been drawn much attention on SO_2 capture, and have been used as absorbents to capture and recover SO_2 from flue gas, exhibiting excellent performance for SO_2 capture.

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As we know, the concentrations of SO_2 in flue gas are very low, like 2000 ppm. Hence, ILs must have high capacity and selectivity for low-concentration SO_2 in flue gas, and can be reused with high stability. Normal ILs [1–5], which do not have the chemical interaction between ILs and SO_2, cannot be used to capture SO_2 from flue gas, as the SO_2 capacity is extremely low when the concentration of SO_2 is very low in flue gas. As a result, a number of functional ILs, which can absorb low-concentration SO_2 in flue gas with high absorption capacity, are expired to design and synthesize to capture SO_2 from flue gas. In this paper, we reviewed the functional ILs used for the capture of low-concentration SO_2, the mechanism of the absorption, effect of absorption conditions and absorption intensification. Lastly, we also tried to look into the future of functional ILs for SO_2 capture.

2. Functional ILs for SO_2 capture and absorption mechanism

What are functional ILs for SO_2 capture? The difference between functional and normal ILs is that functional ILs have chemical interaction with SO_2 and can absorb low-concentration SO_2. It is reported that both chemical and physical absorptions exist for functional ILs [6]. Further study shows that two IL molecules can theoretically absorb one SO_2 molecule by chemical interaction [7], and the chemical absorption amount follows the chemical equilibrium. For normal ILs, only physical absorption exists, and the solubility of SO_2 in normal ILs follows Henry's Law. Fig. 1 illustrates the chemical and physical absorptions of SO_2 and the absorption mechanism by functional ILs, such as 1,1,3,3-tetramethylguanidinium lactate ([TMG]L) and monoethanolaminium lactate ([MEA]L).

However, the interaction between ILs and SO_2 can hardly be measured. Wu et al. reported a method to distinguish functional and normal ILs [8]. For some functional ILs, special atoms, groups or structures exist in cations as functional groups to meet the need of SO_2 capture. For example, 1-(2-diethyl-aminoethyl)-3-methylimidazolium hexafluorophosphate ([Et_2NEmim][PF_6]) and 1-(2-diethyl-aminoethyl)-1-methylpyrrolidinium hexafluorophosphate ([Et_2NEmpyr][PF_6]) are functional ILs for SO_2 capture, as they have tertiary amino in the cations [9]. But not all of the ILs have special atom, group or structure. To distinguish these ILs, several kinds of ILs with 1,1,3,3-tetramethylguanidinium ([TMG]) and monoethanolaminium ([MEA]) as cations were synthesized, and used to absorb SO_2 under a low content of 3 vol%, as shown in Table 1. It is found that the pK_a of the organic acids formed the anions of ILs plays a key role on the absorption of SO_2 and can be used to differentiate functional from normal ILs. If the pK_a of an acid is larger than that of sulfurous acid, the IL synthesized from the acid as an anion is a functional IL and can chemically absorb SO_2 with a large absorption capacity. If not, the IL is a normal IL and can only physically absorb SO_2.

Base on this theory, we try to choose functional ILs reported in the literatures and summarize the SO_2 absorption capacity and the mechanism of these ILs with different kinds of cations.

2.1. Guanidinium based functional ILs

Guanidinium based ILs are the first kind of functional ILs used for SO_2 capture. Han et al. synthesized [TMG]L [11] and used it to capture SO_2 from simulated flue gas [6]. This IL can be prepared by neutralization of 1,1,3,3-tetramethylguanidine with lactic acid under ambient condition, and can absorb SO_2 from a simulated flue gas effectively with a high absorption capacity. The result shows that the molar ratio of SO_2 to IL can reach 0.978 at 313 K and 8 vol% of SO_2 in a simulated gas. The temperature and the partial pressure of SO_2 can influence the absorption capacity of ILs. When the temperature increases to 333 K, the mole ratio of SO_2 to IL decreases to 0.775. When the partial pressure of SO_2 reaches 0.12 MPa, the mole ratio of SO_2 to IL increases to 1.7 at 313 K. The absorbed SO_2 can be reversibly desorbed by vacuum or heating treatment, and the IL can be reused. They also found that [TMG]L could hardly absorb CO_2, just 0.012 mol CO_2/mol IL.

Due to the excellent property and high capacity of SO_2, more and more TMG-based functional ILs were designed and synthesized. Zhang et al. [12] synthesized three kinds of TMG-based functional ILs, 1,1,3,3-tetramethylguanidinium phenate ([TMG][PhO]), 1,1,3,3-tetramethylguanidinium 2,2,2-trifluoroethanol salt ([TMG][Te]) and 1,1,3,3-tetramethylguanidinium imidazolium ([TMG][Im]). And they found that both the saturated molar

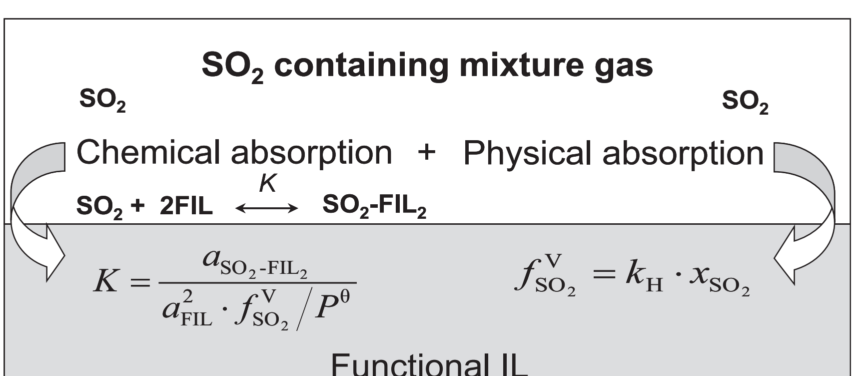

Fig. 1. The mechanism of SO_2 capture by functional ILs (Reprinted with permission from Ref. [7]. Copyright (2011) American Chemical Society.).

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