Absorption of Sulfur Dioxide in Ionic Liquid Supported on Porous Silica Particles

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***Abstract*—1, 1, 3, 3-tetramethylguanidinium lactate (TMGL) has been studied for SO_2 removal. However, before using industrial scale application, several problems need to be solved, for example, the influence on SO_2 absorption at high temperature. This work investigates the SO_2 sorption of the 1, 1, 3, 3-tetramethylguanidinium lactate (TMGL) immobilized on porous silica particles under the conditions of low SO_2 concentration. The effects of SO_2 concentration and environment temperature were evaluated. The attained results clearly imply that both of them have significant influence on absorption performance. The SO_2 absorption capacity reduced as the SO_2 concentration decreased and the environment temperature increased.**

Keywords-supported ionic liquids; desulfurizer; sulfur dioxide; absorption capacity

I. Introduction

Sulfur dioxide is one of the important air pollutants, leading to a serious problem and has drawn much attention throughout the world. [1-6] Ionic liquids were found to be key absorbents, due to negligible volatility, high thermal and chemical stability, and tunable chemical properties, which have been widely used in gas separation. For instance, Han et al. [7] first synthesized a base-functionalized IL, 1, 1, 3, 3-tetramethylguanidinium lactate (TMGL), and reported that it can effectively absorb SO_2 from a simulated flue gas with high absorption capacity (0.978 mol SO_2/mol TMGL) and high selectivity. From then, various ionic liquids were explored for SO_2 capture.

Consider of the application of ionic liquids in industry, there are many problems need to be investigated.

(1)The high viscosity was the fatal weakness for SO_2 removal by TMGL. To overcome this problem, Li et al. [8, 9] synthesized poly (1, 1, 3, 3-tetramethylguanidine acrylate) (PTMGA) and crosslinked porous copolymer particles. Unfortunately, their internal pore structures would be collapsed or mostly lost after many cycles of SO_2 sorption. Subsequently, Li et al. [10] immobilized TMGL to porous silica (SiO_2) particles, which provided large gas-solid interface. They reported that it is an effective way to improve the absorption rate and capacity (1.9 mol SO_2/mol TMGL with pure SO_2) of TMGL. However, the absorption capacity (0.48 mol SO2/mol TMGL) decreased dramatically when the flow gas was mixture gas containing SO_2 of 2160ppm.

(2)The real flue gas is not only a simple combination of N_2 and SO_2. In addition, the concentration of SO_2 emitting from flue gas is not very high, always around 2000ppm. Severa et al. [11] has reported the SO_2 sorption by loading ionic liquid on activated carbon sorbents under simulated atmospheric conditions, and proved the importance of testing the performance of the ionic liquid absorption of SO_2 under simulated real world conditions.

(3)The temperature of flue gas is very high when it just emitted. A systematic research about the influence on the SO_2 absorption by TMGL at high temperature is not reported.

In this study, the SO_2 absorption performance by TMGL loaded porous silica (TMGL/SiO_2) at relatively low SO_2 concentration range (below 5000ppm) and temperature was be investigated.

II. Experimental Section

A. Materials

1,1,3,3-tetramethylguanidinium (TMG, ≥99.0%, Aladdin Co., LTD., China), L-lactic acid (86%, Sigma-aldrich (Wuxi) Life Science & Technology Co., LTD., China) and silica particles (SiO_2, particle diameter range is 150~280 μm, Sigma-aldrich Co., USA), nitrogen (N_2, ≥99.0%, Wenzhou Changsheng gas Co., LTD., China), and N_2/SO_2 mixture gas with 2.60% SO_2 (Changzhou Jinghua industrial gas Co., LTD., China)

B. Preparation and Characterization of TMGL/SiO_2

TMGL/SiO_2 with different immobilization ratio was prepared through the impregnation-vaporization process [10], and the TMGL/SiO_2 ratio x/1 was expressed as TMGL/SiO_2-x/1, equal to the TMGL/SiO_2 feed ratio x/1.

TMGL/SiO_2-x/1 and TMGL were characterized by Thermal Gravimetric Analyzer (TGA). The samples were heated to 600 ℃ in 10 ℃/min under nitrogen. A Micromeritics ASAP 2020 instrument was used to obtained properties of particles, including the pore size distribution, pore volume, and surface area.

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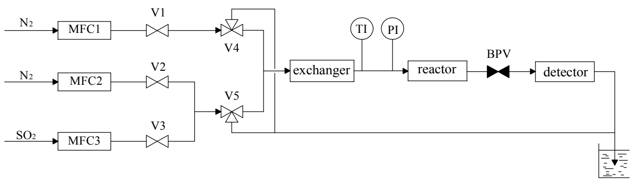

Figure 1. Experimental Setup.

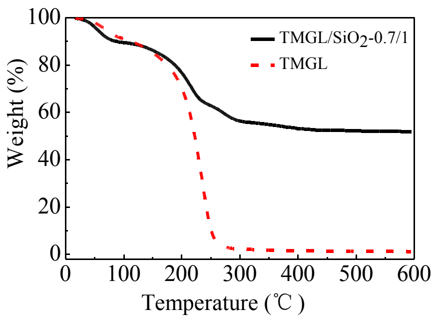

Figure 2. TGA curves of the TMGL/SiO_2-0.7/1 and TMGL.

C. *Absorption Experiment*

The prepared particles with different loadings (TMGL/SiO_2-x/1) were used in the sorption experiments. The simulated flue gas with different SO_2 concentration and total flow rate were controlled by changing N_2 and SO_2 mass flowmaters. The mixture gas flowed through the Modular Microreaction System (OI-MMRS 01.2009, Ehrfeld Mikrotechnik BTS GmbH, Germany), involving coax heat exchanger, pressure sensor module, and temperature sensor module and cartridge reactor. After sorption, the mixture gas flowed through the Bruker Alpha FT-IR Spectrometer (Bruker Optik Asia Pacific Limited, Germany) for the determination of SO_2 concentration. The experimental setup is shown in Figure 1.

Due to scarcely absorb N_2 on TMGL [12], in this work N_2 was used as carrier gas and the effect of N_2 on absorption performance was neglected. Step 1, valve 1 and 4 opened for the N_2 gas passed the experiment setup. Then, the sorbents with the same volume were filled in the reactor, while controlling the temperature by using circulating water bath connected to the heat exchanger. Step 2, valve 2, 3 and 5 were opened (with valve 1 and 4 closed), the mixture gas with a certain SO_2 concentration flowed into the system, while the change in the SO_2 concentration was measured and recorded by the flue gas analyzer.

III. Results and Discussion

A. *Characterization*

The prepared particles with different TMGL loadings and TMGL were investigated by TGA to get their weight ratio, shown in Figure 2.Compared with the TGA curve of the TMGL, the weight loss was about 36% between 130 ℃ and 350 ℃ as the TGA curve of the TMGL/SiO_2-0.7/1 sample shown, which can be considered as the decomposion of TMGL. Obviously, the change of the weight was correlated with the TMGL/SiO_2 feed ratio.

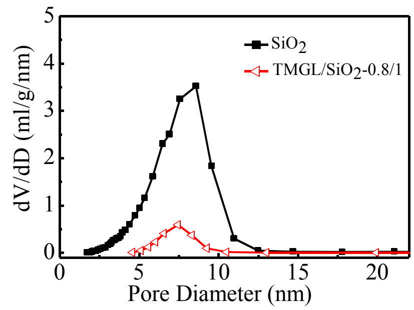

Figure 3. Pore size distribution of SiO_2, TMGL/SiO_2-0.8/1.

Figure 3 showed the particle size distribution of pours silica and TMGL/SiO_2-0.8/1. Obviously, the pore diameter of sorbents decreased after TMGL was immobilized on SiO_2,.

B. *Effect of SO_2 Concentration on Absorption Performance of TMGL/SiO_2*

Different SO_2 concentrations (0.1%, 0.2%, 0.3%, 0.4%, 0.5%) and total flow rate of 200 ml/min was controlled by N_2 mass flowmeter and SO_2 mass flowmeter. The temperature of the water bath was set to 45 ℃, TMGL/SiO_2-0.2/1 and TMGL/SiO_2-0.4/1 were used as sorbents, the effect of SO_2 concentration as shown in Figure 4.

As seen in the breakthrough curves, with the increase of SO_2 concentrations, the absorption rate showed an upward trend. It is more obvious for TMGL/SiO_2-0.4/1, with the SO_2 concentration increased from 0.1% to 0.5%, the breakthrough time reduced from 50 min to 15 min.

The degree of difficulty to reach phase equilibrium ($t_{0.9}$) was proposed by Chen et al. [13] to evaluate the absorption kinetics. In this work, $t_{0.9}$ and the SO_2 absorption capacity were calculated, shown in Table I. It is obvious that the SO_2 absorption capacity of TMGL/SiO_2-0.2/1 and TMGL/SiO_2-0.4/1 increased as the SO_2 concentration increased. In contrast, the value of $t_{0.9}$ gradually reduced with the increase of SO_2 concentration, which was more obvious for the higher TMGL/SiO_2 ratio. Under the same SO_2 concentration, the absorption capacity of TMGL/SiO_2-0.4/1 was always bigger than that of TMGL/SiO_2-0.2/1.

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Figure 4. Effect of SO_2 concentration on absorption performance of TMGL/SiO_2-0.2/1 (a), TMGL/SiO_2-0.4/1 (b).

TABLE I. THE RESULTS OF SO2 SORPTION UNDER THE DIFFERENT SO2 CONCENTRATION

Concentration (%)	**SO_2 Absorption Capacity (AC) and the degree of difficulty to reach phase equilibrium ($t_{0.9}$)**			
	TMGL/SiO_2-0.2/1		***TMGL/SiO_2-0.4/1***	
	AC (mol SO_2/ mol TMGL)	***$t_{0.9}$ (min)***	***AC (mol SO_2/ mol TMGL)***	***$t_{0.9}$ (min)***
0.1	***0.1170***	***12.6***	***0.2644***	***48.0***
0.2	***0.2173***	***11.0***	***0.3148***	***29.2***
0.3	***0.2292***	***7.8***	***0.3410***	***21.7***
0.4	***0.2542***	***6.2***	***0.3534***	***17.3***
0.5	***0.2749***	***5.7***	***0.3729***	***14.9***

C. Effect of Temperature on Absorption Performance of TMGL/SiO_2

The effect of environment temperature on SO_2 sorption was studied by setting up the circulating water bath temperature whilst maintaining the SO_2 concentration (0.4%) and the total flow rate (500 ml/min) constant, shown in Figure 5. For the different sorbent (TMGL/SiO_2-0.6/1, TMGL/SiO_2-0.8/1), the rate of SO_2 sorption increased as the temperature increased. The absorption performance indicates that chemical absorption involved in the process of SO_2 sorption.

However, as seen in Table II, with the environment temperature increased from 30 ℃ to 80 ℃, the SO_2 absorption capacity dropped by 30% at least. In addition, controlled the experimental conditions unchanged, the different between TMGL/SiO_2-0.6/1 and TMGL/SiO_2-0.8/1 are not obvious on the valve of absorption capacity. The absorption performance can be explained by the different pore characteristics with the TMGL/SiO_2 ratio changed.

IV. CONCLUSION

In this work, the SO_2 sorption performance on TMGL/SiO_2 under different conditions was investigated, including the SO_2 concentration and the environment temperature. Compared to the results reported in the literature for the capacity of TMGL/SiO_2 reached 1.9 mol SO_2 per mol TMGL with pure SO_2 gas, the absorption capacity significantly is smaller under the condition of the low SO_2 concentration. Results under different temperature suggest that the significant effect of temperature on the SO_2 absorption performance. Therefore, the SO_2 absorption by TMGL/SiO_2 under the high temperature should be avoided. It should be pointed out that further work need be carried. For example, the real flue gas is not only involve SO_2 with low concentration, but also other gases included, such as NO_x, CO, which may have influence on the SO_2 absorption behavior.

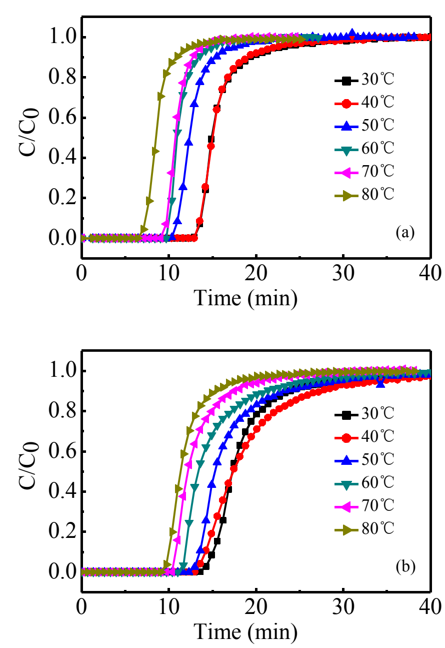

Figure 5. Effect of temperature on absorption performance of TMGL/SiO_2-0.6/1 (a) ,TMGL/SiO_2-0.8/1 (b).

TABLE II. THE RESULTS OF SO2 SORPTION IN DIFFERENT TEMPERATURE

Temperature (℃)	**SO_2 Absorption Capacity (AC) and the degree of difficulty to reach phase equilibrium ($t_{0.9}$)**			
	TMGL/SiO_2-0.6/1		***TMGL/SiO_2-0.8/1***	
	AC (mol SO_2/ mol TMGL)	***$t_{0.9}$ (min)***	***AC (mol SO_2/ mol TMGL)***	***$t_{0.9}$ (min)***
30	***0.4777***	***14.7***	***0.4229***	***18.2***
40	***0.4445***	***14.7***	***0.4848***	***21.4***
50	***0.3833***	***11.9***	***0.3809***	***18.5***
60	***0.3605***	***10.4***	***0.3541***	***16***
70	***0.3004***	***10.0***	***0.3129***	***13***
80	***0.2724***	***8.4***	***0.2803***	***11.5***

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