一种 SO₂ 固定及用于制备 BaSO₃ 或 BaSO₄ 的方法

张 飞 刘丽华 沙 峰 乔宪书 张建斌*

(内蒙古工业大学化工学院，呼和浩特 010051)

摘要： 在常温常压下，由乙二胺(EDA)和乙二醇及其衍生物(EGs)组成的混合体系可捕集 SO_2 并转化为一种 SO_2 储集材料(SO_2SM)。EDA+EGs 体系呈现了强的捕集性能(0.364~0.662 $g_{SO_2}\cdot g_{absorbent}^{-1}$)。FTIR，XPS 和 XRD 结果确证了 SO_2SM 为一种烷基亚硫酸盐。以 EG-SO_2SM 为原料制备具有多种形貌的 $BaSO_3$ 或 $BaSO_4$，在此过程中，EG-SO_2SM 不仅提供了原材料，而且可以释放 EDA 和 EG 用作表面活性剂，调控晶体的结晶化过程。

关键词： SO_2 捕集；SO_2 储集材料；烷基亚硫酸盐；$BaSO_4$

A SO₂ Fixation Method and Its Use in Preparation of BaSO₃ or BaSO₄

ZHANG Fei LIU Li-Hua SHA Feng QIAO Xian-Shu ZHANG Jian-Bin*

(College of Chemical Engineering, Inner Mongolia University of Technology, Huhhot 010051, China)

Abstract: An innovative SO_2 fixation into solid SO_2-storage materials (SO₂SMs) under mild condition was developed by employing the low-cost amine-glycol systems consisting of 1,2-ethanediamine (EDA) and ethylene glycol series (EGs). In particularly, the systems of EDA+EGs possessed a remarkable SO_2 capture capability from 0.364 to 0.662 $g_{SO_2}\cdot g_{absorbent}^{-1}$, which formed solid SO₂SMs after washing with alcohol and drying under vacuum. The resulting SO₂SMs were confirmed as alkyl sulfite by extensive characterization using FTIR, XPS and XRD techniques. Subsequently, the EG-based SO₂SM (EG-SO₂SM) was utilized to prepare $BaSO_3$ or $BaSO_4$ with different morphologies. The gradual release of EDA and EG from EG-SO₂SM not only yielded raw material but also generated EDA and EG that acted as efficient surfactants for the subsequent recrystallization process.

Keywords: SO_2 capture; SO_2-storage materials; alkyl sulfite; $BaSO_4$

0 Introduction

The emissions of SO_2 from the burning of fossil fuels cause severe environmental issues and adverse human health effects[1]; hence, it is of significance to reduce, capture and recycle SO_2. The current methods of SO_2 capture mainly include limestone scrubbing, ammonia scrubbing and organic solvents[2-4]. In par-

ticularly, the ammonia scrubbing could efficiently minimize secondary pollution problems and present a high SO_2 capture capability, but it also exhibits some significant inherent drawbacks, including volatility, corrosiveness and occasional decomposition[5-8]. Recently, Heldebrant et al. [9] developed a series of SO_2 binding organic liquids (SO₂BOLs) based on blends of amidine/alcohol or guanidine/alcohol, by which the
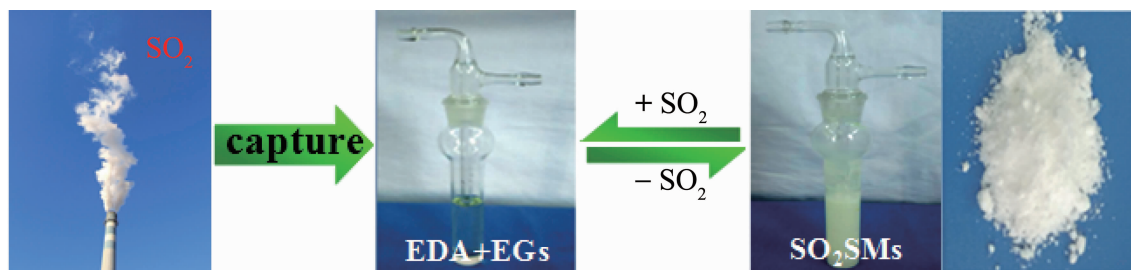
Fig.1　Formative process of the SO_2SMs by the equimolar of EDA and EGs to capture SO_2
in the ice-water bath under ambient pressure

loss of amines was effectively reduced. Although the method could effectively capture SO_2, the high cost might limit their industrial applications in large-scale SO_2 capture processes. Thus, developing a novel SO_2 capture and utilization technology with low-cost and excellent loading ability of SO_2 is highly desired.

In this work, to address high volatility and degradation problems of ammonia scrubbing, we developed an method to capture, store and transform SO_2 into a novel SO_2-storage materials (SO_2SMs) by using the system of 1,2-ethanediamine (EDA)/ethylene glycol derivatives (EGs) (Fig.1). In particular, the generated SO_2SMs could release SO_2 when exposed to high temperature according to the TGA result. Subsequently, the EG-based SO_2SM (EG-SO_2SM) was used to prepare $BaSO_3$ with a "leaf" morphology through the vapor diffusion method. Since this approach avoided the direct mixing of Ba^{2+} and SO_3^{2-}, it is easy to control the nucleation and growth of $BaSO_3$ crystals without the addition surfactant. Moreover, the aqueous EG-SO_2SM solution was also employed to prepare $BaSO_4$ with a block morphology by using H_2O_2 as the oxidant. Most importantly, the EG-SO_2SM not only yielded alkyl sulfite but also released EDA and EG that acted as efficient surfactants to guide the subsequent crystallization. As a result, the developed process offered an alternative approach to the comprehensive utilization of SO_2 and yielded well-controlled $BaSO_3$ and $BaSO_4$ with orderly crystal morphologies.

1 Experimental

1.1 Materials

The analytical grade EDA was purchased from Tianjin Reagent Company (China, Residue on ignition

$\leqslant 0.1\%$). The analytical grade EG, BDO, DEG, TEG and PEG 200 were purchased from Beijing Reagent Company (China, Content $\geqslant 99.0\%$). Compressed SO_2 (99.9%, V/V) was purchased from the Standard Thing Center (China). All reagents were obtained in the higher purity grade possibly and directly used as received without further purification.

1.2 SO_2 capture

In a typical experiment, SO_2 absorption experiment was carried out with approximately 15 g mixture of EDA and EG ($n_{EDA}/n_{EG}=1$) that was charged into a glass container with an inner diameter of 2 cm and a height of 15 cm under ambient pressure and room temperature. Subsequently, the pure SO_2 was bubbled into the solution at a rate of 60 mL·min^{-1}. The absorption amount of SO_2 in the absorbent was measured using an electronic balance with ±0.1 mg and was determined according to the increased mass every 5 min. The electrical conductivity and temperature of the systems were monitored every 1 min with a high sensitivity conductivity meter (DDSJ-308A).

1.3 Fixation of SO_2 into SO_2SMs

SO_2 was bubbled into the system EDA+EGs in the ice-water bath under ambient pressure for about 90 min. After the bubbling, the white solid was collected and washed with ethanol several times to dissolve the residual EDA and EGs, dried under vacuum at 60 ℃ for 10 h and then stored at room temperature. The SO_2SMs were characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR) and thermogravimetry analysis (TGA). XPS data were obtained with a KRATOS Axis ultra X-ray photoelectron spectrometer with a monochromatized Al $K\alpha$

X-ray ($h\nu$=1 486.6 eV) operated at 150 W. XRD patterns were collected on a powder X-ray diffractometer (Siemens D/max-RB) with Cu $K\alpha$ (λ=0.154 06 nm) radiation and scanning rate of $0.05° \cdot s^{-1}$ operated at working voltage of 40 kV and working current of 40 mA. FTIR spectra of SO$_2$SMs were taken as 1% dispersion in KBr powder using a Nexus 670 FTIR spectrometer with a resolution of 1 cm^{-1} in the range of 4 000~400 cm^{-1} and a base line correction was made for the spectra that were recorded in air at room temperature. TGA (Q50 V20.6 Build 31) was employed to measure the weight percentage of SO$_2$SMs. In the thermal stability experiment, the sample was heated up to 400 ℃ with a rate of 10 ℃·min^{-1} in an atmosphere nitrogen. Morphologies of the obtained BaSO$_3$ or BaSO$_4$ were examined via scanning electron microscopy (SEM, Quanta FEG 650) with an accelerating voltage of 20 kV.

1.4　Preparation of BaSO$_3$ and BaSO$_4$ with the EG-SO$_2$SM

In a typical experiment, BaSO$_3$ was prepared by hydrothermal synthesis method. Specifically, a certain concentration of SO$_2$SM was dissolved in 20 mL distilled water. At the same time, 10 mL of Ba(OH)$_2$ saturated limpid solution was added to a small jar that located in the reaction vessel (Fig.S1). The reaction temperature was controlled at 100 ℃ for 2.5 h in an oven; BaSO$_4$ was prepared by the dripping method. A 50 mL solution of BaCl$_2$ (2.5 mmol·L^{-1}) and H$_2$O$_2$ (0.15 mol·L^{-1}) were added into 50 mL EG-SO$_2$SM (0.1 g) aqueous solution in drop wise with an addition speed of 15 drop·min^{-1}. After the reaction, the resulting precipitates were separated from the mother liquids by filtration, washed with distilled water for several times and then dried at 120 ℃ for 5 h.

2　Results and discussion

2.1　SO$_2$ capture

A series of EDA+EGs were used to capture SO$_2$ and the results are shown in Table 1. In the capture processes, the compressed 99.9% SO$_2$ was continuously bubbled into 15 g of EDA+EGs solution for 90 min. The results indicated that the volatility of EDA was effectively reduced. This phenomenon can be explained by the formation of hydrogen bonding between -OH group and the -NH$_2$ group that results in the ionization of EDA[10]. In a typical experiment, the EDA+EG system was monitored by the changes in mass, temperature and electrical conductivity as shown in Fig.2. Fig.2a indicates that the capture capacity of SO$_2$ rapidly increased before 80 min and then slowly increased with the prolonged capture time. Simultaneously, the solution became sticky. Specifically, the capture reached about 90% saturation at the initial 80 min and there was no additional uptake from 80 to 110 min, which could be attributed to the reduction of mass transfer rate and the generation of alkyl sulfite. Fig.2b illustrates that SO$_2$ capture process was exothermal, in which the temperature rapidly increased to 116.3 ℃, then slowly decreased with prolonged time. As shown in Fig.2c, the conductivity of absorbent increased from 33 to 661 μS·cm^{-1} after SO$_2$ was bubbled, which suggested that the capture of SO$_2$ in absorbents was very quick. When the reaction was conducted for 30 min, the electrical conductivity increased to 146 800 μS·cm^{-1}, indicating

Table 1　Comparison of conductivity, capture capacity of SO$_2$, the removal efficiency of SO$_2$ of the EDA+EGs systems

EDA+EGs[a]	Conductivity of EDA+EGs (EGs)[b] / (μS·cm^{-1})	Capture capacity of SO$_2$ in EDA+EGs[c] / (g$_{SO_2}$·g$_{absorbent}^{-1}$)	Removal efficiency of SO$_2$ / %
EDA+EG	32.800(1.351)	0.662	66.2
EDA+BDO	10.620(0.057)	0.520	52.0
EDA+DEG	8.920(0.198)	0.513	36.4
EDA+TEG	5.550(0.130)	0.500	51.3
EDA+PEG200	3.340(1.635)	0.364	50.0

[a] n_{EDA}/n_{EG}=1; [b] at 25 ℃; [c] Uunder 101.325 kPa and 0 ℃.
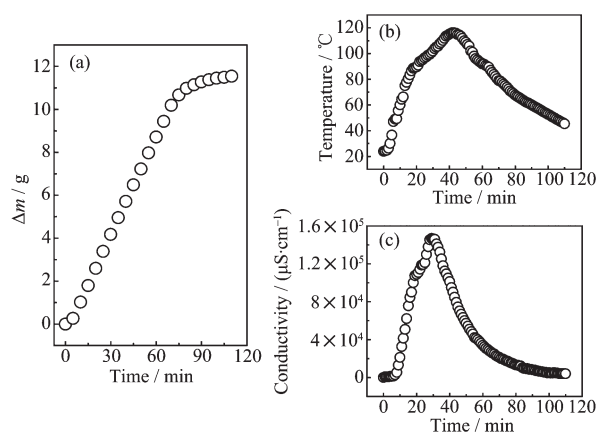
Fig.2　Changes of weight(a), temperature(b) and conductivity(c) for the EDA+EG system at 60 mL·min^{-1} SO$_2$ flow rate under 101.325 kPa and 25 ℃

Fig.3　Changes of weight for the EDA+EGs systems at 60 mL·min^{-1} SO$_2$ flow rate under 101.325 kPa and 0 ℃

the ionization degree of the system was very significant. Meanwhile, the temperature reached the maximum. With the proceeding of reaction, the solution became sticky and finally converted into white solid. At the end of the reaction, the conductivity value decreased to 4 020 μS·cm^{-1}, which clearly demonstrated that there was an apparent charge change between the low and high ionic strength solutions. With increasing system viscosity, the conductivity values of the solution decreased and the solid-state SO$_2$SM was formed at 90 min.

To control the reaction temperature, all the EDA+EGs systems were kept in an ice-water bath and the SO$_2$ capture process was monitored by measuring their mass change, as shown in Fig.3. It was evident that the capture capacity of SO$_2$ in these systems was in the order of EDA+EG>EDA+BDO>EDA+DEG>EDA+TEG>EDA+PEG 200. As can be seen from Fig. 3, the systems of EDA+EGs possessed various SO$_2$ capture capabilities ranging from 0.364 to 0.662 g$_{SO_2}$·g$_{absorbent}$$^{-1}$. Compared this result with the data in the literature, the maximum capture capability (0.662 g$_{SO_2}$·g$_{absorbent}$$^{-1}$) of the EDA+EG system was lower than results from Yang et al.[11] (1.09 g$_{SO_2}$·g$_{[EE_3AE]}$$^{-1}$), but higher than the results reported by Heldebrant et al.[9] (0.54 g$_{SO_2}$·g$_{DBUA}$$^{-1}$), Wu et al.[1] (0.31 g$_{SO_2}$·g$_{[TMG]L}$$^{-1}$), Lee et al.[12] (0.28 g$_{SO_2}$·g$_{[Bztmeda][MeSO_3]}$$^{-1}$), Yang et al.[13] (0.10 g$_{SO_2}$·g$_{FA}$$^{-1}$) and Huang et al(0.02 g$_{SO_2}$·g$_{[TMG][BF_4]}$$^{-1}$)[14].

2.2　Characterization of the SO$_2$SMs

Considering the EDA+EG system possessed a more remarkable SO$_2$ capture capacity than other systems, we next characterized the structure of EG-SO$_2$SM using XPS and FTIR techniques (Fig.4 and 5). Fig.4 shows the deconvolution of C1s, N1s, S2p and O1s XPS spectra of the EG-SO$_2$SM. The C1s spectra could be deconvoluted into three different peaks: C-C/C-H (284.8 eV), C-O (286.5 eV) and C-NH$_2$ (287.9 eV) [13,15]. Moreover, the N1s spectrum indicated the presence of C-N/N-H at 401.4 eV[15-16]. Taken together, the C1s and N1s spectra demonstrated that the EG-SO$_2$SM contained the moieties of C-H, C-O, C-N and N-H. To gain the chemical state of S atom in the interaction process of SO$_2$ with the EDA+EG system, the O1s and S2p spectra were deconvoluted according to the references[17-18]. The peak of O1s was observed at 531.3 eV, which was assigned to oxygen of C=O and C-O in EG and/or O=S and O-S (sulfonic groups, sulfate and sulfite) in SO$_2$[17,19]. The sulfur doublet for SO$_3$$^{2-}$ was found at 166.3 and 168.1 eV, which corresponded to the S2$p_{3/2}$ and S2$p_{1/2}$ transitions, respectively[18,20].

Subsequent, as shown in Fig.5, the FTIR spectrum of EG-SO$_2$SM shows that the peaks at 3 430, 2 170 and 1 574 cm^{-1} corresponded to N-H of -NH$_3$$^+$ in EG-SO$_2$SM[21-23], suggesting EG-SO$_2$SM was a primary amine salt. The peaks at 1 353, 1 144, 1 088, 989, 943 and 636 cm^{-1} were assigned to the structures of S=O and S-O[24-26], which were in good agreement with the characteristic peaks of S=O and S-O in standard
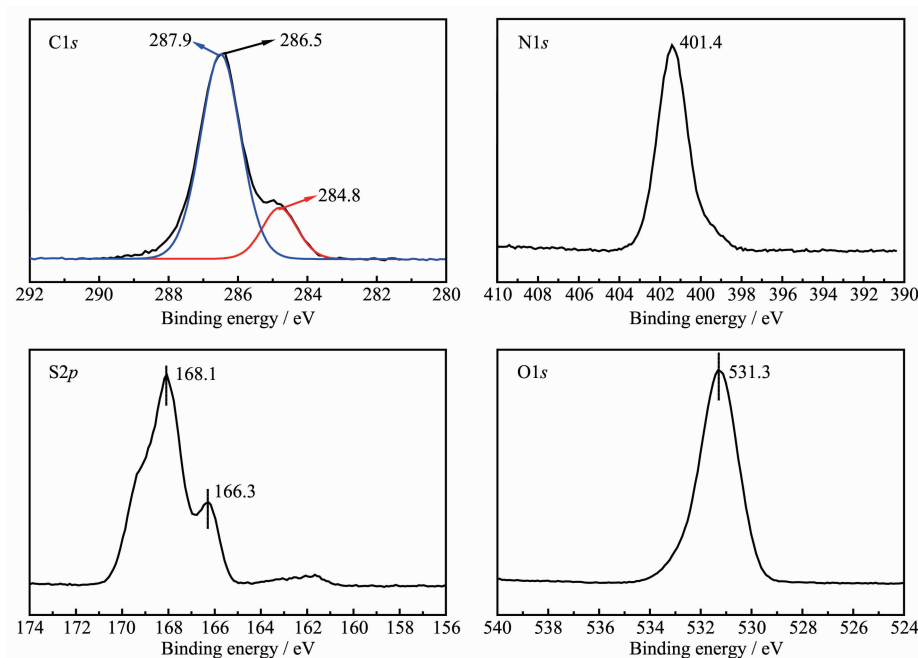
Fig.4　XPS spectra of the EG-SO₂SM

substance Na_2SO_3 and $BaSO_3$ (Fig.S2). It should be noted that the peak of 1 353 cm⁻¹ was not in agreement with standard substance (1 444 cm⁻¹). This phenomenon may be related to the EDA and EG from SO₂SM, which had an effect on the absorption peak. The results indicated the EG-SO₂SM contained the similar structure as -SO₃⁻, well consistent with the results of XPS. Heldebrant[9] puts forward the reaction mechanism of amidine/alcohol or guanidine/alcohol. The characteristic of this reaction is that the raw materials contain amino group and hydroxyl group. In our work, EDA and EG possess a similar structure

with Heldebrant reported raw materials. At the same time, based on the above experimental results and the study results of Heldebrant, the EG-SO₂SM was confirmed as an alkyl sulfite. Moreover, the results of XRD analysis (17.08°, 20.18°, 20.66°, 24.5°, 27° and 29.04°) revealed that the SO₂SMs possessed a high degree of crystallinity (Fig.S3). More characterization results of other SO₂SMs are shown in Fig.S3~5.

　　Besides, as shown in Fig.6, the TGA results shows that the weight loss of EG-SO₂SM is divided into two processes. The first weight loss of EG-SO₂SM is observed from 96 to 183 ℃ due to the decomposition of SO₂ and EDA. The second weight loss of EG-SO₂SM is observed from 183 to 319 ℃ due to the
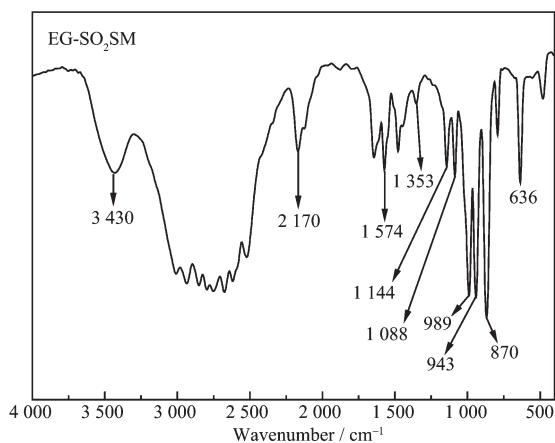
Fig.5　FTIR spectrum of EG-SO₂SM
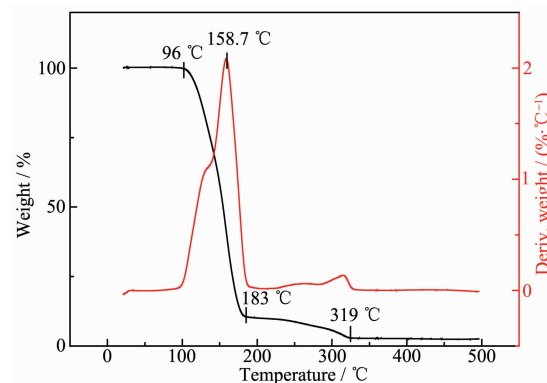
Fig.6　TGA of EG-SO₂SM

decomposition of EG. The results of TGA could provide evidence which the reaction mechanism of SO_2 and the systems of EDA +EG is similar to Heldebrant's study results; meanwhile, the results of TGA also indicate the SO_2SM could release SO_2 by heating.

2.3　Preparation of $BaSO_3$ and $BaSO_4$ with the EG-SO_2SM

On the basis of TGA result, SO_2 could be readily and gradually released from the EG-SO_2SM at elevated temperature. Therefore, the released SO_2 slowly reacted with Ba^{2+} ions to form leaf-like $BaSO_3$ at 100 ℃ for 2.5 h (Fig.7a). Furthermore, the aqueous EG-SO_2SM solution was employed to prepare block-like $BaSO_4$ by adding H_2O_2 as an oxidant (Fig.7b). Fig. 8 and 9 show that the XRD patterns and FTIR spectra results of $BaSO_3$ and $BaSO_4$ samples and their IR characteristic peaks are in good agreement with refer-

ences[24-27]. Notably, in these processes, the released EDA and EG from the EG-SO_2SM were acted as novel surfactants during the formation of crystals. The detailed processes for the formation of $BaSO_3$ and $BaSO_4$ and the mechanistic studies are under investigation and the result will be published in due course.
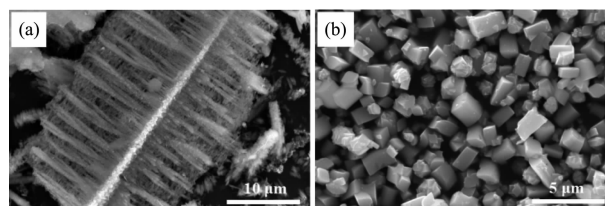
(a) Leaf-like $BaSO_3$ by the vapor diffusion method in hydrothermal reaction vessel at 100 ℃ for 2.5 h; (b) Block-like $BaSO_4$ by the solution of $BaCl_2$ and H_2O_2 being dropped to the aqueous EG-SO_2SM solution, where released EDA and EG from the EG-SO_2SM acted as novel surfactants

Fig.7　Representative applications of EG-SO_2SM
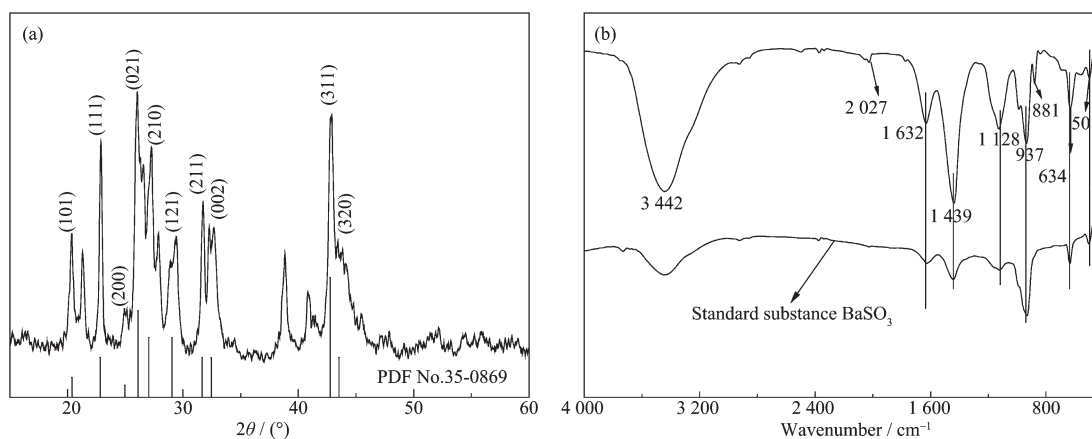

Fig.8　XRD pattern (a) and FTIR spectrum (b) of $BaSO_3$ sample
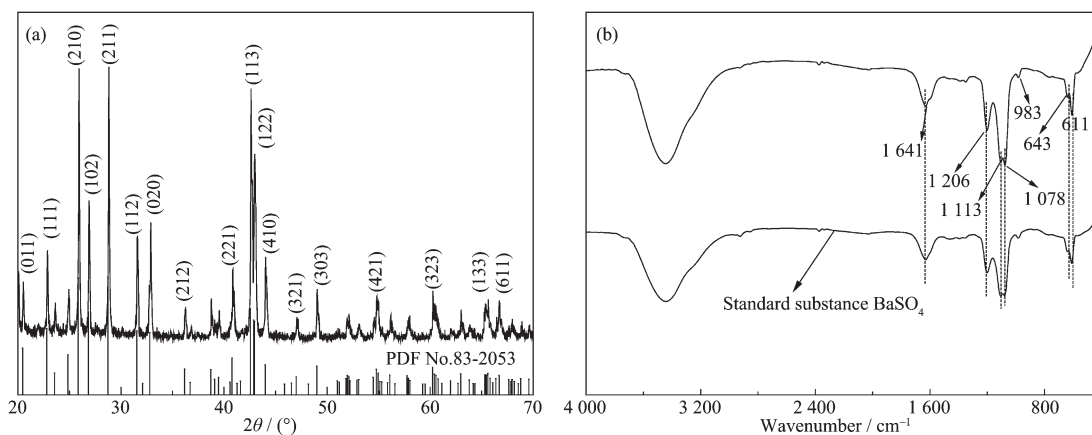

Fig.9　XRD pattern (a) and FTIR spectrum (b) of $BaSO_4$ sample

3　Conclusions

In summary, a novel SO_2 capture, storage and utilization method was successfully developed by utilizing EDA-EGs systems. In this process, SO_2 can react efficiently with the EDA-EGs systems under mild conditions to form the solid SO_2SMs, which could be used as the raw materials to prepare $BaSO_3$ or $BaSO_4$ with different morphologies. Moreover, the released EDA and EG from the EG-SO_2SM were acted as facilitative surfactants to guide the crystallization process of crystals.

Supporting information is available at http://www.wjhxxb.cn

References:

[1] Wu W, Han B, Gao H, et al. *Angew. Chem. Int. Ed.*, **2004**, **43**:2415-2417

[2] Renedo M J, Fernandez J. *Ind. Eng. Chem. Res.*, **2002**,**41**: 2412-2417

[3] Ortiz F J G, Vidal F, Ollero P, et al. *Ind. Eng. Chem. Res.*, **2006**,**45**:1466-1477

[4] Zheng Y J, Kiil S, Johnsson J E. *Chem. Eng. Sci.*, **2003**,**58**: 4695-4703

[5] Tailor R, Ahmadalinezhad A, Sayari A. *Chem. Eng. J.*, **2014**, **240**:462-468

[6] Tailor R, Abboud M, Sayari A. *Environ. Sci. Technol.*, **2014**, **48**:2025-2034

[7] Uyanga I J, Idem R O. *Ind. Eng. Chem. Res.*, **2007**,**46**:2558-2566

[8] Bollini P, Didas S A, Jones C W. *J. Mater. Chem.*, **2011**,**21**: 15100-15120

[9] Heldebrant D J, Koech P K, Yonker C R. *Energy Environ. Sci.*, **2010**,**3**:111-113

[10]Zhao T X, Guo B, Han L M, et al. *ChemPhysChem*, **2015**, **16**:2106-2109

[11]Yang D Z, Hou M Q, Ning H, et al. *Phys. Chem. Chem. Phys.*, **2013**,**15**:18123-18127

[12]Lee H J, Jung Y M, Lee K I, et al. *RSC Adv.*, **2013**,**3**:25944-25949

[13]Yang J, Hu D X. *RSC Adv.*, **2012**,**2**:11410-11418

[14]Huang J, Riisager A, Wasserscheid P, et al. *Chem. Commun.*, **2006**,**38**:4027-4029

[15]Desimoni E, Casella G I, Cataldi T R I, et al. *Surf. Interface Anal.*, **1992**,**18**:623-630

[16]Wang T J, Shemood P M A. *Chem. Mater.*, **1995**,**7**:1020-1030

[17]Kante P K, Bandosz T J. *Carbon*, **2010**,**48**:654-667

[18]Baltrusaitis J, Usher C R, Grassian V H. *Phys. Chem. Chem. Phys.*, **2007**,**9**:3011-3024

[19]Shen J G C, Kalantar T H, Herman R G, et al. *Chem. Mater.*, **2001**,**13**:4479-4485

[20]Smirnov M Y, Kalinkin A V, Pashis A V, et al. *J. Phys. Chem. B*, **2005**,**109**:11712-11719

[21]Heldebrant D J, Koech P K, Ang M T C, et al. *Green Chem.*, **2010**,**12**:713-721

[22]Wang H B, Jessop P G, Liu G J. *ACS Macro Lett.*, **2012**,**1**: 944-948

[23]Shang J P, Liu S M, Ma X Y, et al. *Green Chem.*, **2012**,**14**: 2899-2906

[24]Wang C M, Cui G K, Luo X Y, et al. *J. Am. Chem. Soc.*, **2011**,**133**:11916-11919

[25]Cui G K, Lin W J, Ding F, et al. *Green Chem.*, **2014**,**16**: 1211-1216

[26]Heldebrant D J, Koech P K, Yonker C R. *Energy Environ. Sci.*, **2010**,**3**:111-113

[27]Wang Q, Zhang D, Yang X L, et al. *Green Chem.*, **2013**,**15**: 2222-2229