SO₂ interference on separation performance of amine-containing facilitated transport membranes for CO₂ capture from flue gas

Dongzhu Wu^a, Chenhu Sun^b, Prabir K. Dutta^b, W.S. Winston Ho^{a,*}

^a William G. Lowrie Department of Chemical and Biomolecular Engineering and Department of Materials Science and Engineering, The Ohio State University, 151 West Woodruff Avenue, Columbus, OH 43210-1350, USA

^b Department of Chemistry and Biochemistry, The Ohio State University, 100 West 18th Avenue, Columbus, OH 43210-1340, USA

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ABSTRACT

Post-combustion carbon capture using membranes is a key approach to control CO₂ emissions from power plants using fossil fuels. The minor contaminants, such as SO₂ and O₂, may influence the long-term membrane performance. With the presence of SO₂ in the feed gas, SO₂ could preferably react with amine carriers and hinder the permeation of CO₂ in the amine-containing facilitated transport membranes. Possible amine degradation and competitive reactions would reduce membrane performance with real flue gas. With SO₂ concentrations of 0.7–5 ppm, two amine-containing facilitated transport membranes were tested at 57 and 102 °C, respectively. Unstable membrane performance was observed at 102 °C for the membrane containing Lupamin® as fixed-site carrier and potassium glycinate (K-Gly) as mobile carrier in the presence of SO₂. On the contrary, two membranes containing polyvinylamine (PVAm) as fixed-site carrier and amino acid salts as mobile carriers showed stable separation performance in the presence of 1–3 ppm SO₂ at 57 °C. Therefore, the operating temperature plays a significant role in the membrane stabilities in the presence of SO₂. In addition, the infrared (IR) spectra of the membrane components exposed to SO₂ with respect to exposure time were collected. It was found that the amines reacted with SO₂ to form sulfite products irreversibly at 102 °C. The spectral results were consistent with the observed membrane separation performance. The stable membrane performances of the facilitated transport membranes at 57 °C with SO₂ at ppm levels indicate the applicability of the developed amine-containing membranes for use in CO₂ capture from real flue gas.

1. Introduction

Carbon dioxide (CO₂) is believed to contribute the most to the current global warming [1–6]. Burning fossil fuel, such as coal, is one of the main sources for the anthropogenic CO₂ emission [1]. In order to manage the continuously increasing CO₂ level in the atmosphere, a variety of approaches are proposed by the U.S. Department of Energy (DOE) [7,8]. CO₂ capture and sequestration from the flue gas generated by coal-fired power plants is an important strategy for the control of CO₂ level in the atmosphere [7,8]. Low capture cost and energy consumption are the prerequisites for a successful technology [7,8]. Many technologies for post-combustion CO₂ capture exist; however, no clear winner has been identified [2]. Despite the operation confidence and system maturity, sorption-based techniques are not the optimal process for CO₂ capture because of the high energy penalty [1,9]. Therefore, membrane separation draws attention as it possesses advantages, such as energy efficiency, cost-effectiveness, operational simplicity, and environmental friendliness [1,10].

High permeance and selectivity are required in order to achieve the flue gas CO₂ capture (> 90% CO₂) and cost (\$40/t CO₂) targets set by DOE [5,7,11]. The solution-diffusion mechanism is a well-accepted gas transport principle through polymeric membranes, which has been applied for CO₂ separation membranes [12]. Studies, for this type of membrane, have focused on the polymer chain modifications and new material developments [13]. However, its low selectivity, especially when testing at 50–60 °C, hinders its actual applicability in the real gas separation system [13]. The facilitated transport membranes, on the other hand, could cross the Robeson upper bound due to the interaction between the reactive carriers in the membrane and the gas molecules, leading to an increase in both permeance and selectivity [14–16]. In CO₂/N₂ separation, carriers with amino functional groups were identified to be good candidates for the facilitated transport of CO₂ molecules [13]. In virtue of the developments in facilitated transport membranes, amine-containing polymer membranes are feasible for CO₂ capture from flue gas [17,18].

Treating real flue gas may be problematic since it contains not

* Corresponding author.

E-mail address: ho.192@osu.edu (W.S. Winston Ho).

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Nomenclature

P_{CO_2}	Permeability of CO_2 , Barrer ($10^{-10} \text{ cm}^3(\text{STP}) \text{ cm}/(\text{cm}^2 \text{ s cmHg})$)
P_{N_2}	Permeability of N_2 , Barrer
l	Membrane thickness, cm
J_{CO_2}	Steady state flux of CO_2 , $\text{cm}^3 (\text{STP})/\text{cm}^2/\text{s}$
Δp_{CO_2}	Partial pressure difference of CO_2 across the membrane, cmHg

Greek letters

α_{CO_2/N_2}	Selectivity of CO_2 vs. N_2
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simply just CO_2 and N_2 . The minor contaminants, such as SO_2 and O_2 , may be the major factors that can limit the long-term stability of a membrane process [19,20]. As a result, the effects of SO_2 and O_2 on the membrane performance can become the key criteria to evaluate the practicality of CO_2 capture for flue gas via the membrane process [20]. With the presence of SO_2 in the feed gas, SO_2 can preferably react with carriers and hinder the permeation of CO_2 in the facilitated transport membrane [21,22]. Possible amine degradation and competitive reactions raise the concerns on the amine-based facilitated transport membranes and sorbents for use in the real flue gas [9,23–25]. Therefore, the stability of the amine-containing polymer membranes upon exposure to SO_2 needs to be evaluated at different operating temperatures and SO_2 concentrations [26].

The stabilities of the conventional amine-containing sorbents have been examined extensively [23,24,27,28]. However, different observations and results were reported in the literature, depending on the nature of the materials and various operating temperatures. Jones et al. investigated the stability of supported amine adsorbents to SO_2 in flue gas CO_2 capture at 35°C [27]. Their study demonstrated the strong reaction between amines and SO_2 . Moreover, their cyclic experiments suggested that the adsorbent might reach an equilibrium after the initial significant deactivation caused by the amine degradation during the first cycle. The multicomponent adsorption to the amine adsorbent and the synergetic effect from a gas mixture were examined in a follow-up study by Jones et al. [28], where they demonstrated the stable operation of the supported amine adsorbent after exposing to 200 ppm SO_2 in the feed gas at 35°C . They concluded that the long-term operation could be feasible in real flue gas capture because of the actual SO_2 concentration being only 1–10 ppm after sulfur removal treatment. However, Hallenbeck and Kitchin reported the effect of SO_2 on the primary amine functionalized resin for the post-combustion CO_2 capture [23]. By exposing to 431 ppm SO_2 , they pointed out that the SO_2 was responsible for the significant reduction of the CO_2 capture capacity over 19 cycles, and the regeneration was nearly impossible. As a result, a flue gas desulfurization (FGD) process that could maintain a low level of SO_2 concentration was suggested before CO_2 capture in their proposed system.

On the contrary, consistent stable results were demonstrated for amine-containing facilitated transport membranes. Wang et al. studied the effect of SO_2 on the transport performance of a fixed-site carrier membrane with tertiary amino groups [21]. A noticeable CO_2 permeance reduction was observed based on their results. However, the membrane performance remained stable with 5000 ppm SO_2 at 22°C , indicating an opportunity of employing the membrane process in real flue gas CO_2 capture even without a SO_2 polishing step. In their facilitated transport model, it was reported that the SO_2 partial pressure was much lower on the membrane surface due to the severe concentration polarization at a mixed gas condition. Another study on a polyvinylamine (PVAm)-piperazine membrane also by Wang et al. demonstrated similar membrane stability results after exposing to 2%

SO_2 at the same temperature [17]. Moreover, promising membrane stability results were also obtained by Hägg et al. [29]. In their pilot-scale test of the fixed-site carrier polymeric membrane containing PVAm, they demonstrated stable performance after exposing to 70 ppm SO_2 at 45°C over a period of 6 months. In another study by Hägg et al., they investigated the stability of the PVAm membrane by introducing high content contaminants, such as 5% O_2 , 200 ppm SO_2 , and 2000 ppm NOx [19]. They reported that the membrane maintained an excellent performance upon exposure, indicating that the SO_2 was not highly absorbed on the fixed-site carrier membrane.

The above-mentioned studies reported the stable membrane performance in the presence of SO_2 over a wide concentration range. However, the operating temperatures were $\leq 45^\circ\text{C}$. The stability of the amine-containing polymeric membrane operated at higher temperatures has not been reported. The effects of SO_2 on the membrane performances of two membrane compositions were investigated in detail at two operating temperatures of 57 and 102°C , respectively. As the typical SO_2 concentration after the SO_2 polishing step was below 5 ppm [7,30,31], the SO_2 levels of 0.7, 1, 3, and 5 ppm were mainly employed in the present study. In order to identify the reaction products between reactive carriers in the membranes and SO_2 , and further understand the mechanism of the SO_2 effect on membrane performance, IR spectroscopy was employed for characterizing the treated membrane samples and the major membrane components. Since the major interest of this study was the SO_2 effect, absorption bands of the sulfur-related ions ($933, 961, 950, 1010 \text{ cm}^{-1}$) were identified to provide evidences of the interactions between SO_2 and amines [32]. The IR results explained the membrane performance reduction mechanism and the membrane stability dependence on operating temperatures. This work also showed that a lower testing temperature was preferable for the amine-containing facilitated transport membranes with SO_2 in the feed gas. Furthermore, this work elucidated the SO_2 interaction with the amine-containing carriers in facilitated transport membranes.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (PVA, Poval S-2217, 92% purity), containing a minor percentage of sulfonated groups, was donated by Kuraray America Inc. (Houston, TX, U.S.A.). A commercial aqueous solution, Lupamin® 9095 (MW 340,000), was given by BASF (Charlotte, NC, U.S.A.). Potassium hydroxide (KOH, pellets, > 85%), glutaraldehyde (50%, aqueous solution), glycine (98.5%), and piperazine (PZ) (99%) were purchased from Sigma-Aldrich. Polyvinylamine (PVAm, MW 1.2 million), was synthesized in the laboratory, which has been described in a published reference from our group [33]. All the chemicals were used without any further purification. Zeolite-Y (ZY) nano-particles, with an average pore size of $\sim 40 \text{ nm}$, were synthesized by the approach described in a previous paper from our group [34].

Biomax® polyethersulfone (PES) flat-sheet ultrafiltration (UF) membrane, with a molecular weight (MW) cut-off of 300 kDa, was purchased from EMD Millipore (Billerica, MA, U.S.A.) and used as the substrate for the membrane containing Lupamin® as fixed-site carrier and potassium glycinate (K-Gly) as mobile carrier (designated as M-1). The average pore size and porosity of the PES were 72.0 nm and 15.8%, respectively [35]. A lab-fabricated PES membrane on a polyester nonwoven fabric [36], with a similar surface morphology, was applied in the second membrane containing lab-synthesized PVAm as the fixed-site carrier and piperazine glycinate (PZ-Gly) as the mobile carrier (M-2) for reducing the composite membrane fabrication cost. The polyester nonwoven fabric (surface pore size of $13 \mu\text{m}$ and porosity of 76%) was provided by TriSep Corporation (Goleta, CA, U.S.A.). The detailed compositions of these two membranes are shown in Table 1 later in Section 2.2. It is worth noting that the PES substrates with comparable morphologies mainly provided the mechanical strength whereas the

Table 1
Summary of the compositions of the studied membranes.

Membrane no.	Membrane compositions
M-1	20 wt% XL-PVA, 5 wt% KOH, 40 wt% K-Gly, and 35 wt% Lupamin*
M-2	35 wt% lab-synthesized PVAm and 65 wt% PZ-Gly

selective layers gave the major separation performances of the composite membranes. Therefore, membrane stabilities were not affected by the substrate variation in our study in the presence of SO₂.

2.2. Membrane preparation

In the present work, two types of membranes were prepared. M-1 contained crosslinked PVA (XL-PVA), K-Gly, Lupamin* and KOH. First, PVA was dissolved in water with two successive steps: dissolved under room temperature overnight and then heated to 80 °C for two hours. KOH, as a catalyst, and glutaraldehyde, as a cross-linker, were added into the solution dropwise with a reaction time of 30 min and 2.5 h, respectively. The final XL-PVA solution composition was: 12 wt% XL-PVA, 3 wt% KOH, and 60 mol% crosslinking degree. Then, the resultant XL-PVA was applied in the subsequent coating solution preparation. Glycine and KOH were mixed stoichiometrically for obtaining K-Gly salt aqueous solution. Subsequently, the XL-PVA was blended with a proper amount of Lupamin* and K-Gly mixture. In order to achieve a very viscous coating solution, a small flow rate of N₂ was applied to purge away the water partially. Then, the coating solution was applied onto a flattened substrate containing a layer of ZY nano-particles with a controlled gap setting of 24.5 μm by using a GARDCO micrometer film applicator (Paul N. Gardner Company, Pompano Beach, FL, U.S.A.). ZY nano-particles were deposited via a vacuum assisted dip deposition approach reported elsewhere [35]. The membrane was dried in a convective oven at 112 °C for 90 min and then cooled down to room temperature before testing.

Regarding M-2, containing lab-synthesized PVAm and PZ-Gly, the membrane preparation procedures were described in a previous reference [33]. A thin ZY layer was again deposited on the lab-fabricated PES substrate with an average pore size of ~ 69 nm and surface porosity of ~ 17%. The membrane was coated by the same film applicator with a gap setting of ~ 4 μm on the ZY/lab-fabricated PES substrate.

The detailed membrane compositions are listed in Table 1. As shown, both membranes contained long chain PVAm (Lupamin* or lab-synthesized PVAm) and small molecule amino acid salts (K-Gly or PZ-Gly). As the SO₂ stability concern of the amine-containing polymer membranes falls into the reactivity of amine-containing components in the presence of SO₂, we compare the stability of these two membranes in this paper.

2.3. Membrane characterization

2.3.1. Gas transport property measurement

The gas transport performance was measured in a testing apparatus described elsewhere [37]. The membrane was loaded into a rectangular stainless steel cell with an effective area of 2.7 cm² and a counter-current flow configuration. A binary feed gas mixture of 20% CO₂ and 80% N₂, with a flow rate of 60 cc/min, and a sweep gas of argon (Ar), with a flow rate of 30 cc/min, were controlled by the mass flow controllers (Brooks instrument, Hatfield, PA, U.S.A.). SO₂ was introduced in the feed gas stream with a calculated flow rate for certain concentrations used in the tests. The feed and sweep side pressures were adjusted to be 1.5 psig and 1.2 psig, respectively. The transport experiments were carried out at 57 and 102 °C in a temperature controlled oven (Bemco Inc. Simi Valley, CA, U.S.A.). For the mem-

branes tested at 57 °C, both the water contents were set at the saturation water content of 17.2% at this temperature by humidifying the feed and sweep gases through 80 ml water in a 500 ml stainless steel humidifier (Swagelok, Westerville, OH, U.S.A.) filled with 60% (by volume) packing of glass [33]. Moreover, for the membrane tested at 102 °C, the water contents of 80% in the feed side and 57% in the sweep side were accurately controlled by two Varian Prostar 210 pumps (Varian Inc., Palo Alto, CA, U.S.A.), respectively.

The gas compositions of both retentate and permeate gas streams were analyzed by a gas chromatograph (GC) equipped with thermal conductivity detectors (TCDs) (Agilent Technologies, Palo Alto, CA, U.S.A.). A packed GC column (SUPELCO Carboxen* 1004, Sigma-Aldrich, St. Louis, MO, U.S.A.) was employed in this test. Both retentate and permeate gas streams passed through their respective water knockout vessels and were then dried in their respective drierite tubes before entering the GC. The separation performance is characterized by two parameters, which are permeance and selectivity. The first parameter, CO₂ permeance ($\frac{P_{CO_2}}{l}$), is defined as [12]:

$$\frac{P_{CO_2}}{l} = \frac{J_{CO_2}}{\Delta p_{CO_2}}$$

where P_{CO_2} is CO₂ the permeability, with a unit of Barrer (10⁻¹⁰ cm³(STP) cm/(cm² s cmHg)). The common unit for permeance is GPU (gas permeation unit, 1 GPU = 10⁻⁶ cm³(STP)/(s cm² cmHg)). The second parameter, CO₂/N₂ selectivity, is defined as:

$$\alpha_{CO_2/N_2} = \frac{P_{CO_2}}{P_{N_2}}$$

2.3.2. Scanning electron microscope (SEM) analysis

The membrane thicknesses and morphologies were characterized via an FEI Nova 400 NanoSEM (Hillsboro, OR, U.S.A.). All the images were analyzed by Clemex Vision Professional Edition (Longueuil, Quebec, Canada) software to obtain the membrane thicknesses.

2.3.3. Attenuated total reflection (ATR) analysis

As a widely used FTIR sampling tool, ATR generally allows qualitative or quantitative analysis of samples with little or no sample preparation, which greatly speeds up sample analysis. With ATR sampling, the IR beam is directed into a crystal of relatively higher refractive index. The IR beam reflects from the internal surface of the crystal and creates an evanescent wave, which projects orthogonally into the sample in intimate contact with the ATR crystal. Some of the energy of the evanescent wave is absorbed by the sample, and the reflected radiation (with reduced intensity) is returned to the detector. This ATR phenomenon is shown graphically in the representation of single reflection ATR in Fig. 1.

The obtained ATR spectra are similar to those collected by the transmission measurements. However, subtle differences exist because the ATR sampling depth of penetration depends on the wavelength of light, which makes IR absorption bands at the longer wavelength with higher absorbance than those of shorter wavelength. As a result, performing the ATR correction is a recommended procedure for qualitative analysis. Therefore, the unexposed and SO₂ exposed membrane samples were analyzed via ATR-Fourier transform infrared spectroscopy (FTIR, Waltham, MA, U.S.A.) by a Renishaw Raman IR microprobe equipped with a diamond crystal. Each spectrum was recorded as the average of 256 scans over the spectral range of 4000–800 cm⁻¹ with a resolution of 8 cm⁻¹. All spectra were processed by the ATR correction feature of the software package. This would scale the intensities by a factor that was inversely proportional to wavelength and its result would be more closely resembled to the transmission spectrum. For each characteristic peak, the relative peak height was obtained by drawing a baseline tangent to both shoulders of the band of interest and then measuring from the maximum height of

Fig. 1. Graphical illustration of a single reflection ATR.

the curve to the baseline. The relative peak area was integrated from the area between the curve and the linear baseline.

2.3.4. In-situ FTIR analysis

A Perkin-Elmer Spectrum 400 FTIR/FT-NIR spectrometer (Waltham, MA, U.S.A.) was used for the in-situ FTIR analysis with 256 scans taken with a resolution of 8 cm^{-1} . A custom gas cell incorporated in the spectrometer is shown in Fig. 2. The spectrum for potassium bromide (KBr) was used as a background. About 50 mg of the liquid sample was placed on the KBr window and pretreated in a flowing Ar at $150\text{ }^{\circ}\text{C}$ for at least 60 min. Instead of a low concentration of SO_2 ($\leq 5\text{ ppm}$) in membrane testing, 45 ppm SO_2 was applied in this IR study in order to obtain higher signal readouts. In addition, the amine degradation phenomenon could also be determined more pronouncedly by applying a high concentration of SO_2 in the IR study. The samples were first exposed to 45 ppm SO_2 at two corresponding membrane testing temperatures (57 and $102\text{ }^{\circ}\text{C}$). The chamber was insulated and coiled with a heating element, and the temperature was controlled by a thermocouple. In order to study the effect of CO_2 on SO_2 absorption and their competitive sorption, the sample was then exposed to a mixed gas stream (10% CO_2 and 45 ppm SO_2) at the corresponding two testing temperatures. All the aforementioned gas streams were balanced with N_2 . The gas flow rate was set to 100 cc/min and bubbled through a water saturator for all the experiments. The spectra were collected with respect to the exposure time. At last, all the samples were also tried to be regenerated by flowing N_2 for 17–18 h at $102\text{ }^{\circ}\text{C}$, and the spectra were collected.

3. Results and discussion

3.1. Membrane characterization by SEM

As mentioned in the previous section, two membranes containing different amine carriers were synthesized and studied. The cross-sections of the two membranes are shown in Fig. 3. Fig. 3a presents the cross-sectional image of M-1 containing Lupamin® and K-Gly. As shown, the top dense layer was the selective polymer layer containing amino groups for CO_2 transport, which provided the major separation performance. It shows a thickness of $\sim 500\text{ nm}$. The layer beneath it was the thin ZY layer that was deposited on the Millipore PES substrate. The published study from our group indicated that the ZY layer could possibly improve the separation performance because of this thin ZY layer had the inter-particle pore size smaller than the pore size of the PES substrate and reduced the penetration during coating [35]. The

bottom portion was the nanoporous PES substrate that provided the mechanical strength.

Fig. 3b exhibits the cross-section of M-2 containing an ultra-thin membrane of lab-synthesized PVAm and PZ-Gly on the ZY/lab-fabricated PES substrate. Similarly, the top dense layer was the amine-containing polymer cover layer that could selectively separate CO_2 from a gas mixture, which showed a thickness of $\sim 175\text{ nm}$. The layer beneath it was the thin ZY layer deposited via the same deposition approach [35]. The bottom layer was the PES substrate fabricated in our lab as mentioned in the previous section. Although different PES substrates were employed, this variation was not expected to be important as the PES substrates mainly provided the mechanical strength in the composite membranes.

The separation mechanism of the facilitated transport membranes is shown in Fig. 4. Both the fixed-site and mobile carriers can react with CO_2 molecules and transport them through the membrane from the feed to permeate side. PVAm (Lupamin® and lab-synthesized PVAm), serving as the fixed-site carrier, transports the CO_2 via a hopping mechanism [10,33,38]. Amino acid salts (K-Gly and PZ-Gly), serving as the mobile carriers, react with CO_2 at the feed side to form the reaction products and then diffuse to the permeate side based on the concentration gradient [10,33]. The CO_2 molecules are released from the abovementioned two types of the carriers on the permeate side and swept away by the sweep gas. On the other hand, N_2 can only diffuse through the membrane by the solution-diffusion mechanism. Thus, the facilitated transport membranes result in both high CO_2 permeance and CO_2/N_2 selectivity. When SO_2 existed in the feed gas stream, it could also react with amine due to its higher acidity than CO_2 . Therefore, the membrane separation performances might be affected to some extent. The SO_2 interference will be discussed in detail in the later sections.

3.2. M-1 membrane containing Lupamin® and K-Gly tested at $102\text{ }^{\circ}\text{C}$

3.2.1. Effect of SO_2 on membrane performance of M-1 at $102\text{ }^{\circ}\text{C}$

In a capture process, compressing the flue gas to increase the CO_2 driving force is necessary in some circumstances. The gas compression results in a temperature rise. For instance, the flue gas temperature can rise from its typical temperature of $57\text{ }^{\circ}\text{C}$ to about $102\text{ }^{\circ}\text{C}$ after compression to 1.5 atm. Hence, the effect of SO_2 on membrane performance of M-1 was investigated by introducing 5 ppm SO_2 at $102\text{ }^{\circ}\text{C}$. All membrane samples were tested with and without SO_2 . The recovery process was carried out by removing the SO_2 from the feed gas stream. The same process was applied for all the following experiments. As illustrated in Fig. 5, the membrane was initially stable at a CO_2 permeance of $\sim 1180\text{ GPU}$ and a CO_2/N_2 selectivity of above 350 for 15 h with 20% CO_2 and 80% N_2 on a dry basis (humidified to 80% water vapor during the transport measurement). After introducing

Fig. 2. Schematic diagram of the custom gas cell for in-situ FTIR measurement.

Fig. 3. SEM images of the cross-sections of the two composite membranes: (a) M-1 containing Lupamin® and K-Gly on ZY/Millipore PES substrate and (b) M-2 containing lab-synthesized PVAm and PZ-Gly on ZY/lab-fabricated PES substrate.

Fig. 4. Schematic representation of the transport mechanism of the facilitated transport membrane.

5 ppm SO_2 in the feed gas, the membrane performance dropped continuously over a testing course of 24 h. The final CO_2 permeance before stopping the SO_2 was ~ 1030 GPU, which showed a drop of 12.7% compared to the initial stable result. Subsequently, a stable CO_2 permeance of ~ 990 GPU and a CO_2/N_2 selectivity of above 350 were observed for over 10 h following the stop of the SO_2 exposure for about 10 h and before reintroducing SO_2 . This implied that the carrier degradation by SO_2 at 102°C could be irreversible. Moreover, this membrane was re-exposed to 5 ppm SO_2 after this recovery process. The CO_2 permeance again dropped continuously to ~ 867 GPU, indicating a performance drop of 12.4% using the result of ~ 990 GPU as the basis. The second exposure also confirmed the detrimental

effect on the amine carriers and the carrier degradation by SO_2 at 102°C . As shown in Fig. 5, the membrane was stable following the stop of SO_2 after its second exposure.

As depicted in this figure, the CO_2/N_2 selectivity values also showed a similar dropping trend as the CO_2 permeance results upon exposure to SO_2 . For instance, the overall trend of CO_2/N_2 selectivity also reduced upon exposure to SO_2 during the time range of 60–90 h in Fig. 5.

As hypothesized by Wang et al. [21], SO_2 competed with CO_2 to react with amine carriers, and it transported to the permeate side in their facilitated transport membrane. With a hypothesis of the reversible reaction between SO_2 and amines, the CO_2 permeance of the membrane would drop less upon the second SO_2 exposure because the reaction product existed inside the membrane. However, the similar drops observed from our two SO_2 exposures indicated the irreversibility of the reaction between SO_2 and the amine carriers in the membrane at the high operating temperature of 102°C .

3.2.2. Effect of SO_2 concentration on membrane performance of M-1 at 102°C

To investigate the effect of SO_2 concentration on the membrane performance of M-1, transport measurements were performed at various SO_2 concentrations. The membrane performances after introducing different concentrations of SO_2 are demonstrated in Fig. 6. Regardless of the gradual or rapid CO_2 permeance drops shown in Fig. 6, continuous performance drops were observed for all the tested membranes over a testing course of 42 h in the presence of SO_2 ranging from 0.7 to 5 ppm. A significant reduction was illustrated for the membrane tested with 5 ppm SO_2 , indicating the detrimental effect for amine-containing polymer membrane at 102°C . The reactivity of the amine carriers and SO_2 was high since a low concentration of ~ 0.7 ppm still degraded the active carriers at this temperature. As a result, we believe that the performance drop was mainly due to: (1) SO_2 degradation of the carriers in the membrane and (2) the competitive

Fig. 5. Membrane performance of M-1 by introducing 5 ppm SO_2 at 102°C and its performance recovery after removing SO_2 : two separate SO_2 exposures.

Fig. 6. Effect of SO₂ concentration on CO₂ permeance of M-1 at 102 °C (the dash line indicates the starting time of introducing SO₂ in the feed gas stream; the CO₂/N₂ selectivity values were above 350).

reaction between SO₂ and CO₂ [21]. SO₂ was more competitively reactive than CO₂ owing to its higher acidity, and it could react with active carriers in membrane immediately upon exposure. Due to the irreversible reaction at 102 °C, it degraded the carriers gradually. Therefore, continuous membrane performance drops were observed in our study. Moreover, there was a larger CO₂ permeance drop upon increasing the SO₂ concentration from 0.7 ppm to 5 ppm.

3.2.3. Effect of high temperature recovery on membrane performance of M-1 at 102 °C

In order to understand the irreversibility of the reaction between SO₂ and amine carriers, the membrane was treated at an elevated temperature for recovery after stopping the SO₂ exposure. Fig. 7 illustrates the CO₂ permeance drop after incorporating SO₂. As illustrated, the CO₂ permeance dropped from 1150 to 1000 GPU after introducing 0.7 ppm SO₂ over a testing course of 18 h. Similarly, the CO₂ permeance was not recovered by discontinuing the SO₂ incorporation in the feed gas, i.e., it remained about 1000 GPU. But, by elevating the testing temperature to 120 °C, the CO₂ permeance dropped significantly, from 990 to 410 GPU during the testing course of about 4 h, due to the low water retention at this high temperature [15]. Then, the testing temperature was returned to 102 °C. However, the CO₂ permeance only recovered back to ~990 GPU at 102 °C, indicating the irreversibility of the reaction between SO₂ and the amine carriers and the formation of stable reaction products.

3.2.4. IR study of Lupamin® and K-Gly in M-1 at 102 °C

Typically, CO₂ reacts with the primary amine groups to generate carbamate, protonated amine, and bicarbonate by the following reactions [10,39].

The main products of the SO₂ reaction are sulfite and bisulfite, which are considered as stable products that can deteriorate membrane permeation properties [21,24,26].

The sulfite species give rise to absorption bands in the 1000–850 cm⁻¹ region. Particularly, the sulfite ion shows two absorption bands at 1010 and 961 cm⁻¹, which are attributed to the asymmetric and symmetric S=O stretching [27,40]. The vibrational modes ν_1 and ν_3 for aqueous SO₃²⁻ at 933 and 966 cm⁻¹ were reported elsewhere [41]. In addition, sulfate (SO₄²⁻) gives an absorption band within the range of 1105 and 1140–1190 cm⁻¹, which was not observed in our spectral data [40]. Moreover, the protonated amine (-NH₃⁺) has been identified as giving rise to an absorption band around 1480 cm⁻¹, which can be assigned to the -NH₃ bending mode [42].

The 5 ppm SO₂ treated M-1 sample from the previous test in Section 3.2.1 was examined using an ATR-IR and compared to the fresh membrane without SO₂ exposure. The ATR spectra are shown in Fig. 8. The spectra of the two membrane samples illustrated an obvious peak difference in the characteristic bands of 961 and 1010 cm⁻¹, which can be assigned to the sulfite ion (SO₃²⁻). It can be inferred that the SO₂ reacted with membrane components and formed sulfite ions in the membrane. Due to its stable nature, the reaction products could not revert back to SO₂ and the free amine carriers on the permeate side. Thus, the membrane underwent a slow degradation process because of

Fig. 7. Effect of high temperature recovery on CO₂ permeance of M-1.

Fig. 8. ATR spectra of the SO_2 treated M-1 sample and the fresh M-1 membrane sample.

the gradually increasing amount of sulfite that titrated the amine carriers in the membrane, which was consistent with the transport performance data.

In order to study the M-1 instability further in the presence of SO_2 at 102°C , each membrane component listed in Table 1 containing amine functional groups was exposed to SO_2 and a CO_2/SO_2 mixture at 102°C by applying the in-situ FTIR method described in Section 2.3.4. The FTIR spectra were collected with respect to the exposure time. The above-mentioned ATR spectra of the fresh and SO_2 -treated membrane samples indicated that the exposure to SO_2 produced absorption peaks at ~ 961 and 1010 cm^{-1} , which can be assigned to the $\text{S}=\text{O}$ stretching vibrations of sulfite ions. However, as discussed in the following paragraphs, we only observed an obvious growth of the band at 961 cm^{-1} upon exposure of SO_2 to each of the different membrane components. Therefore, our focus was on the peak growth at 961 cm^{-1} .

The growth of peak intensity of $\text{S}=\text{O}$ stretching vibrations of sulfite ions at the 961 cm^{-1} region was normalized to the final peak intensity after SO_2 exposure. The growth of IR peak intensity as a function of time was plotted during the exposure of each of the amine carriers to

SO_2 and the mixture of SO_2 and CO_2 . The normalized IR peak intensities of the sulfite species versus time for the exposures of K-Gly to the mixture of 10% CO_2 and 45 ppm SO_2 and to 45 ppm SO_2 are shown in Fig. 9. Two inserts in Fig. 9 clearly indicate the interaction between K-Gly and SO_2 , where the sulfite species generated is present. From Fig. 9, the growth of sulfite peak at 961 cm^{-1} due to the reaction between K-Gly and SO_2 started from 40 min and reached steady state at 120 min. In the case of the mixed gas, the growth of sulfite peak started from 20 min and reached steady state at 80 min. The shorter times for the mixed gas suggested that CO_2 might promote the SO_2 interaction with the amine carrier. FTIR results from the study by Jones et al. also showed the strong reaction between SO_2 and amine carriers [27], which is consistent with our spectra.

Figs. 10 and 11 show the IR spectra of Lupamin® after exposing to SO_2 and the mixture of SO_2 and CO_2 , respectively, at 102°C . As shown, the sulfite band was detected at 961 cm^{-1} . However, Lupamin® solution contains 7 wt% of PVAm and 14 wt% sodium formate [43]. The characteristic bands at 1370 and 1580 cm^{-1} in Figs. 10 and 11 could be attributed to the formate species [44]. More importantly, it

Fig. 9. The growth of normalized IR peak intensity vs. time for K-Gly at 102°C : (a) Black square: at 961 cm^{-1} for 10% CO_2 and 45 ppm SO_2 ; (b) Red circle: at 961 cm^{-1} for 45 ppm SO_2 ; (c) Black diamond: recovery with N_2 for 17 h after 10% CO_2 and 45 ppm SO_2 exposure; (d) Red triangle: recovery with N_2 for 17 h after 45 ppm SO_2 exposure. Top inset: representative IR spectra before and under 10% CO_2 and 45 ppm SO_2 exposure, and after N_2 recovery; bottom inset: representative IR spectra before and under 45 ppm SO_2 exposure, and after N_2 recovery.

Fig. 10. FTIR spectra of Lupamin® in Ar (black curve), after exposure to 45 ppm SO₂ for 120 min at 102 °C (blue curve), and after recovery with N₂ purge (red curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Fig. 11. FTIR spectra of Lupamin® in Ar (black curve), after exposure to 10% CO₂ and 45 ppm SO₂ for 120 min at 102 °C (blue curve), and after recovery with N₂ purge (red curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

was reported that formate species could react with SO₂ to form sulfite or bisulfite [45]. Thus, for Lupamin®, the formation of sulfite species could be due to the interaction between the considerable amount of sodium formate and SO₂. The sulfite species formed in both Lupamin® and K-Gly carriers could not be removed after treating the exposed

amine carriers with N₂ for 17 h as shown in Figs. 9–11. These results indicated the irreversibility of the reactions between the membrane components and SO₂ at the high temperature of 102 °C. Therefore, the reactions between the amine carriers and SO₂ shown in the spectra explained the continuous permeance reduction of the membrane after exposing to SO₂ at the high temperature of 102 °C.

3.3. Membrane performances at 57 °C

The typical flue gas after FGD treatment is at a discharge temperature of 57 °C with 40–50 ppm SO₂ [30]. The SO₂ level can be further reduced to 1 ppm by a SO₂ polishing step using a caustic scrubber, i.e., 20 wt% sodium hydroxide (NaOH) [30]. A variety of polymeric membranes have been developed to decarbonize the flue gas at such a low SO₂ concentration [2,11,46]. However, the operating temperature of these membranes used was usually 20–30 °C, in which the capital and operating costs associated with cooling the flue gas could be substantial. Therefore, the membrane that can be operated at 57 °C can decrease the capture cost.

The separation performance of the M-1 membrane containing Lupamin® and K-Gly was investigated at 57 °C with SO₂ present in the feed gas. Moreover, because of the successful synthesis of the high MW PVAm, a selective layer with an excellent separation performance can be obtained by blending PVAm with PZ-Gly [33]. Therefore, M-2, containing lab-synthesized PVAm and PZ-Gly, was also chosen, and its stability was investigated at 57 °C. The SO₂ concentrations of 1 and 3 ppm were employed as they are the actual low levels of SO₂ after the real flue gas is treated by the SO₂ polishing step.

3.3.1. Effect of operating temperature on membrane performance of M-1

The M-1 performance stability in the presence of 1–3 ppm SO₂ at 57 °C is shown in Fig. 12. The CO₂ permeance was first stable at ~ 316 GPU at the feed gas of 20% CO₂ and 80% N₂ on a dry basis. It was lower than the CO₂ permeance of M-1 at 102 °C mainly due to the following reasons: (1) the water content of 17.2% at 57 °C was significantly lower than the water content of 80% at 102 °C; and (2) the reactivity and mobility of both fixed-site and mobile carriers were lower at the lower temperature [47]. As shown, the CO₂ permeance first reduced and stabilized at ~ 279 GPU after introducing 1 ppm SO₂. Then, the CO₂ permeance dropped from 279 GPU to 250 GPU and stabilized after increasing the SO₂ concentration from 1 ppm to 3 ppm. Nevertheless, no sign of performance recovery was observed after stopping SO₂ incorporation in the feed gas. Compared to the continuous performance drop of the membrane tested at 102 °C even upon exposure to a low concentration of 0.7 ppm SO₂, M-1 showed stable separation performance with 1–3 ppm SO₂, indicating the importance of operating

Fig. 12. M-1 separation performance stability by introducing 1–3 ppm SO₂ at 57 °C.

temperature for the membrane stability with SO₂.

Fig. 12 also indicates the CO₂ permeance drops after exposing to 1 and 3 ppm SO₂, which were 11.7% and 20.8%, respectively. The reductions in the CO₂ permeance suggested that SO₂ interfered with the CO₂ transport of the membrane upon exposure to SO₂. However, besides the CO₂ permeance drop, the stable CO₂ permeances with 1 and 3 ppm SO₂ indicated that the interaction between SO₂ and membrane at 57 °C was much weaker than that at 102 °C. This weak interaction between the amines and SO₂ will be further explored in the IR study later, and it can also be inferred that lowering the operating temperature could be a remedial approach to apply membranes for CO₂ separation with SO₂ in the feed gas stream.

3.3.2. IR study of Lupamin® and K-Gly in M-1 at 57 °C

In order to understand the mechanism of the stable separation performance of M-1 at 57 °C, the amine-containing components (Lupamin® and K-Gly) were again exposed to SO₂ and CO₂/SO₂ mixture, and their spectra with respect to exposure time were collected by employing the in-situ FTIR setup described in Section 2.3.4. Figs. 13 and 14 depict the IR spectra of exposing K-Gly to SO₂ and the CO₂/SO₂ mixture, respectively. Unlike the noticeable sulfite characteristic peak observed previously, only a weak peak at ~ 950 cm⁻¹ was identified, which was attributed to the symmetric stretching of absorbed SO₂. Although they could not be purged away completely by N₂, the relatively low peak intensity validated the weak interaction between K-Gly and SO₂.

Figs. 15 and 16 show the IR spectra of exposing Lupamin® to SO₂ and the CO₂/SO₂ mixture, respectively. As shown, an obvious sulfite peak at the wavenumber of ~ 961 cm⁻¹ could be observed in both figures, indicating the interaction between the sodium formate in Lupamin® and SO₂ at 57 °C.

As a result, the stable membrane performance shown in Fig. 12 can be explained by the above-mentioned IR results. Firstly, the performance drop at 57 °C was mainly due to the weakly bound SO₂ in K-Gly. As Lupamin® solution contains sodium formate, the observed strong characteristic peak at 961 cm⁻¹ in Figs. 15 and 16 was mainly due to the interaction between the formate ions and SO₂. It was inferred that the long-chain PVAm in Lupamin® was not affected by SO₂ at 57 °C, which will be justified in the following IR study on lab-synthesized PVAm (no sodium formate) in Section 3.3.4. Although the SO₂ could react with the formate in Lupamin® chemically at 57 °C, the weak reaction between the mobile carrier of K-Gly and SO₂ was the key factor that the membrane performance of M-1 stabilized with a reduced CO₂ permeance after introducing low concentrations of SO₂. Accordingly, it is concluded that the IR results were consistent with the stable transport performance of M-1 after exposing to SO₂.

3.3.3. Effect of SO₂ on membrane performance of M-2 at 57 °C

Although stable performance can be obtained for M-1 at 57 °C, its low CO₂ permeance limits its applicability for CO₂ capture as it can increase the capture cost significantly. It is desirable to have a high CO₂ permeance membrane in order to reduce the membrane area and hence the CO₂ capture cost for flue gas application. As mentioned previously, the membrane, M-2, containing lab-synthesized PVAm and PZ-Gly showed improved separation performance at 57 °C, which was reported recently by our group [47]. Hence, the SO₂ stability of M-2 was investigated, and the detailed IR study on this membrane composition revealed the SO₂ interference mechanism.

The M-2 performance stability in the presence of 1–3 ppm SO₂ is shown in Fig. 17. The CO₂ permeance was stable at ~ 800 GPU for more than 8 h with the feed gas of 20% CO₂ and 80% N₂ on a dry basis. After introducing 1 ppm SO₂, the CO₂ permeance dropped and stabilized at ~ 758 GPU. In a similar way to the stable performance demonstrated in Fig. 12, M-2 also showed a stable performance after exposing to a low concentration of SO₂ at 57 °C. Subsequently, the SO₂ concentration was further increased to 3 ppm for the investigation of M-2 performance

stability. As shown in Fig. 17, the membrane performance again dropped and stabilized after exposing to 3 ppm of SO₂, i.e., it was reduced from 758 GPU to 726 GPU. The CO₂ permeance drops with 1 and 3 ppm SO₂, compared to original performance, were 6.6% and 9.7%, respectively. Although the performance could not be recovered after stopping the SO₂, it is noteworthy that the separation performances of M-2 could remain stable regardless of the permeance drop with either 1 or 3 ppm SO₂. More importantly, in the comparison of the separation performances with and without SO₂ at 57 °C shown in Fig. 12, the M-2 membrane containing lab-synthesized PVAm and PZ-Gly showed a significant improvement on the CO₂ permeance, indicating the potential of this membrane for CO₂ capture from flue gas.

This membrane, with the same composition, was also fabricated into spiral-wound membrane modules for testing with real flue gas in the National Carbon Capture Center (NCCC) [48]. As the real flue gas contained not only SO₂ and O₂ but also other contaminants, e.g., NO_x, the stability of the membrane underwent a more stringent condition in this field test than the lab test. However, this membrane showed a stable separation performance, a CO₂ permeance of > 800 GPU and a CO₂/N₂ selectivity of > 150, over a testing course of more than 200 h in this field test [48]. That result coincided with our results shown in Fig. 17. These results have suggested that this membrane could be stable at 57 °C in the presence of low concentrations of SO₂. In addition, these results have also suggested the great potential of the amine-containing facilitated transport membrane for use in CO₂ capture from flue gas.

3.3.4. IR study of the lab-synthesized PVAm and PZ-Gly in M-2 at 57 °C

The ATR spectra of the SO₂ treated M-2 sample in Section 3.3.1 and fresh M-2 sample are shown in Fig. 18. In comparison to the above-mentioned spectral results of the 102 °C tested membrane sample in Fig. 8, this treated sample did not show an obvious difference with the fresh sample in the sulfite species wavenumber region (961 cm⁻¹). There was only a very weak rise at ~ 950 cm⁻¹ that could be found after a rigorous analysis on the spectra. Therefore, the interactions between the membrane components of M-2 and SO₂ were very weak at 57 °C.

In order to further investigate the stability of M-2 at 57 °C and understand the SO₂ interaction mechanism, a detailed FTIR study was conducted for the individual membrane components, PVAm and PZ-Gly listed in Table 1, with the same setup as described previously in Section 2.3.4. Likewise, these components were exposed to 45 ppm SO₂ in this IR study for a higher signal acquisition. Figs. 19 and 20 depict the IR spectra of exposing PZ-Gly to SO₂ and the mixture of SO₂ and CO₂ as a function of time, respectively. As shown in Fig. 19, after exposing to 45 ppm SO₂ at 57 °C for 2 h, no peak was generated at 961 cm⁻¹, but a

Fig. 13. FTIR spectra of K-Gly in Ar (black curve), after exposure to 45 ppm SO₂ for 120 min at 57 °C (blue curve), and after recovery with N₂ purge (red curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Fig. 14. FTIR spectra of K-Gly in Ar (black curve), after exposure to 10% CO₂ and 45 ppm SO₂ for 120 min at 57 °C (blue curve), and after recovery with N₂ purge (red curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Fig. 15. FTIR spectra of Lupamin® in Ar (black curve), after exposure to 45 ppm SO₂ for 120 min at 57 °C (blue curve), and after recovery with N₂ purge (red curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Fig. 16. FTIR spectra of Lupamin® in Ar (black curve), after exposure to 10% CO₂ and 45 ppm SO₂ at 57 °C for 120 min (blue curve), and after recovery with N₂ purge (red curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

weak peak was observed at 950 cm⁻¹, which was assigned to the symmetric stretching of absorbed SO₂. This result suggested that a weak SO₂ absorption in the mobile amine carriers occurred at 57 °C instead of the irreversible reaction at 102 °C. This 950 cm⁻¹ peak disappeared after the sample was purged by dry N₂ at 102 °C. However, the peak at 950 cm⁻¹ became stronger, illustrated in Fig. 20, after changing to the mixture of 10% CO₂ and 45 ppm SO₂. Similarly, it again disappeared

after the sample was purged by dry N₂ at 102 °C. After N₂ purge, interestingly, two new weak peaks generated at 966 cm⁻¹ and 933 cm⁻¹, which were assigned to sulfite. However, their low peak intensities suggested that only a small amount of sulfite species was generated. This result indicated that CO₂ could promote SO₂ reaction even at low temperature and the weakly absorbed SO₂ was the main product. In the consideration of the feed gas condition in the previous transport performance measurements, which used 20% CO₂ and 80% N₂ with 1 and 3 ppm SO₂ at 57 °C, the minor CO₂ permeance drops shown in Fig. 17 could be attributed to this weak interaction between PZ-Gly and SO₂.

Figs. 21 and 22 show the IR spectra of lab-synthesized PVAm by exposing to 45 ppm SO₂ and the mixture of 45 ppm SO₂ and 10% CO₂ at 57 °C, respectively. After carefully reviewing the sulfite characteristic peaks at the wavenumbers of 933, 950 and 961 cm⁻¹, no new peaks were generated and observed in the spectra shown in these two figures. The PVAm sample remained the same before and after exposing to SO₂ and the SO₂/CO₂ mixture. Therefore, neither chemical reaction nor physical absorption occurred by exposing PVAm to SO₂ and the mixture of SO₂ and CO₂ at 57 °C. In consideration of the obvious reaction between Lupamin® and SO₂ at 57 °C shown in Figs. 15 and 16, we could conclude that it was mainly due to the reaction between SO₂ and sodium formate in Lupamin®. In other words, PVAm, a long-chain fixed site carrier, could remain unchanged by exposing to SO₂ at this temperature. Therefore, it can be concluded that the M-2 can perform and be stable under low concentrations of SO₂ at 57 °C owing to the weak interaction between the amine carriers and SO₂ at the low testing temperature. The observed CO₂ permeance drops shown in Fig. 17 were due to the absorption of SO₂ by the mobile carrier, PZ-Gly. It can also be concluded that the generated minor amount of sulfite in the membrane was responsible for the CO₂ permeance reduction shown in this figure. These results are consistent with the reported literature results about the stabilities of the PVAm-containing facilitated transport membranes after exposing to SO₂ [17–19]. Our results have indicated that amine-containing membranes need to be operated at 57 °C or lower if SO₂ is present in the feed gas.

4. Conclusions

In order to investigate the interference of SO₂ on amine-containing facilitated transport membranes, two membranes were studied at 57 and 102 °C, respectively. The membrane stability studies were performed in detail to demonstrate the applicability of the membranes in CO₂ capture from flue gas. This work also highlights, in particular, the interference between SO₂ and amine-containing compounds. The effect of SO₂ concentration even at low levels on membrane performance was significant since considerably increased reductions of CO₂ permeance were observed by elevating the SO₂ concentration in the feed gas for both membranes. M-1 showed a permeance reduction and instability even at 0.7 ppm SO₂ at 102 °C. On the contrary, in spite of some CO₂ permeance reduction, both membranes exhibited a stable separation performance upon exposure to 1 and 3 ppm SO₂ at 57 °C.

IR spectroscopy was conducted to study the SO₂ interference mechanism on membrane performance. Compared to the pristine M-1 sample, sulfite species characteristic peaks were observed clearly in the SO₂-treated M-1 sample tested at 102 °C. However, no significant difference was identified between the IR spectra of the pristine M-2 sample and its SO₂-treated sample tested at 57 °C. Moreover, amine-containing compounds, long-chain PVAm and small molecules amino acid salts, in both membranes were exposed to 45 ppm SO₂ and the mixture of 10% CO₂ and 45 ppm SO₂ at 57 and 102 °C, respectively. On one hand, amine-containing compounds (Lupamin® and K-Gly) in M-1 showed a strong interaction with SO₂ at 102 °C, which was also irreversible as shown by the spectra. The Lupamin® reacted with SO₂ at 57 °C, due to its contaminant, sodium formate, as shown by IR spectra. On the other hand, a weak physisorption and a very small

Fig. 17. M-2 separation performance stability by introducing 1–3 ppm SO_2 at 57 °C.

Fig. 18. ATR spectra of the SO_2 treated M-2 membrane sample and the fresh M-2 membrane sample.

Fig. 19. FTIR spectra of PZ-Gly in Ar (black curve), after exposure to 45 ppm SO_2 for 120 min at 57 °C (blue curve), and after recovery with N_2 purge (red curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

amount of sulfite species were observed in the K-Gly of M-1 and the PZ-Gly of M-2 when exposed to SO_2 at 57 °C. Additionally, no interaction was detected between the lab-synthesized PVAm (without containing sodium formate) of M-2 and SO_2 at 57 °C. These spectra were in good agreement with the membrane performance results. More importantly, the stable and improved performance of M-2 indicates the applicability of applying this membrane in CO_2 capture in the real flue gas. It is suggested that, for amine-containing facilitated transport membranes, a

Fig. 20. FTIR spectra of PZ-Gly in Ar (black curve), after exposure to 10% CO_2 and 45 ppm SO_2 at 57 °C for 120 min (blue curve), and after recovery with N_2 purge (red curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

low operating temperature, e.g., 57 °C, is preferred if SO_2 is present in the feed. This study shows the potential of amine-containing facilitated transport membranes for flue gas CO_2 capture.

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Fig. 21. FTIR spectra of the lab-synthesized PVAm in Ar (black curve), after exposure to 45 ppm SO₂ at 57 °C for 120 min (blue curve), and for 300 min at 57 °C (blue dash curve) and after recovery with N₂ purge (red curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Fig. 22. FTIR spectra of the lab-synthesized PVAm in Ar (black curve), after exposure to 10% CO₂ and 45 ppm SO₂ at 57 °C for 120 min (blue curve), for 300 min at 57 °C (blue dash curve) and after recovery with N₂ purge (red curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

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