

Catalyst-aided Regeneration of Amine Solvents for Efficient CO₂ Capture Process

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Abstract

Thermal amine scrubbing is the most advanced CO₂ capture technique but its largescale application is hindered due to the large heat requirement during solvent regeneration step. The addition of a solid metal oxide catalysts can optimize the CO₂ desorption rate and thus minimize the energy consumption. Herein, we evaluate the solvent regeneration performance of Monoethanolamine (MEA) and Diethanolamine (DEA) solvents without and with two metal oxide catalysts (TiO₂ and V₂O₅) within a temperature range of 40–86 °C. The solvent regeneration performance was evaluated in terms of CO₂ desorption rate and overall amount of CO₂ desorbed during the experiments. Both catalysts improved the solvent regeneration performance by desorbing greater amounts of CO₂ with higher CO₂ desorption rates at low temperature. Improvements of 86% and 50% in the CO₂ desorption rate were made by the catalysts for MEA and DEA solvents, respectively. The total amount of the desorbed CO₂ also improved by 17% and 13% from MEA and DEA solvents, respectively. The metal oxide catalyst-aided regeneration of amine solutions can be a new approach to minimize the heat requirement during solvent regeneration and thus can remove a primary shortfall of this technology.

Key words : CO₂ capture; amine solvent; metal oxide catalyst; solvent regeneration; catalyst

1. Introduction

Carbon capture and storage has been widely considered a short-to-midterm strategy to control the anthropogenic CO₂ emissions [1]. Post-combustion CO₂ using aqueous alkanolamine solutions is the most advanced and commercially available technique [2]. However, despite the in-depth understanding and large-scale availability of this technology, the worldwide deployment of this approach is hindered due to inherent drawbacks such as huge energy penalty, solvent degradation, and corrosiveness. In particular, the thermal energy required to perform the solvent regeneration accounts for 70-80% of the total process cost [3].

Significant attention has been paid to minimize the energy penalty of CO₂ capture process. Various new solvents have been formulated that require less thermal energy for regeneration. Biphasic solvents and ionic liquids has been proposed as alternative absorbents for energy-efficient CO₂ capture [4]. Furthermore, advanced process configurations have been proposed to optimize the process energy consumption. However, the issue of high energy penalty has not been solved yet [5].

Recently, some literature reports have shown that the addition of a solid catalyst to the amine solvent regeneration step can enhance the CO₂ desorption and thus minimize the regeneration energy [6]. The catalyst can provide acid sites (Lewis acid sites and Brønsted acid sites) that attack the carbamate to release CO₂ at low temperatures hence consuming less thermal energy [7].

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In this study, we investigate the solvent regeneration performance of a primary amine solvent i.e. Monoethanolamine (MEA) and a secondary amine solvent i.e. Diethanolamine (DEA) without and with two solid metal oxide catalysts named V₂O₅ and TiO₂. The CO₂ was absorbed in both solutions at typical absorber conditions and then the solvent regeneration performance was studied at 40–86 °C. The regeneration performances were evaluated in terms of total amount of desorbed CO₂ and CO₂ desorption rate. Finally, we have found that the addition of both catalysts can improve the solvent regeneration performance and thus can be an effective approach to reduce the energy penalty of CO₂ capture process.

2. Experimental Section

2–1. Materials:

MEA and DEA with purity of ~99% were purchased from Sigma-Aldrich. TiO₂ and V₂O₅ were purchased from Sigma-Aldrich in fine powder form with purity of 98 and 99%, respectively. CO₂ and N₂ gases (purity of 99.999%) were purchased from Korea Nano Gas Co. Ltd.

2–2. Experimental procedure

The solvent regeneration experiments were performed in a flat-bottomed glass reactor of 250 mL capacity shown in Fig. 1. An oil circulator was connected to the reactor to heat and maintain the desired temperature of the amine solvent. A thermocouple was used to measure the temperature of the amine solution. A condenser was used to condense and recycle the amine solvent. In addition, a magnetic stirrer was used to stir the solution continuously at 200 rpm.

The amine solutions of desired concentration (i.e. 30 wt. %) were prepared by mixing with DI water. Then, the amine solutions were saturated with CO₂ using a continuous stirred tank reactor (CSTR) at typical absorber conditions (313K, 1 atm, 15 vol. % CO₂). The CO₂ saturation was realized when the concentration of the CO₂ in the outlet gas reached to 15 vol. %. The CO₂ loadings of the amine solvents were determined using a total organic carbon analyzer (TOC, Analytik Jena multi N/C 3100). To study the solvent regeneration performance, 100 mL of the CO₂-loaded amine solvents was used in each experiment. In the catalytic experiments, 5 g of re-

spective catalyst was added to the solution at the start of the experiment and 3 minutes of equilibration time was provided at room temperature. As the solution was heated, the CO₂ gas started to desorb from the reactor that was mixed with predetermined flow of N₂ gas prior to its analysis in a gas chromatograph. The N₂ gas was used as a reference gas.

2–3. Characterization

The acidic properties of the catalysts were determined using Pyridine-FTIR technique and the obtained spectra are presented in Fig. 2. Pyridine molecules react with the unsaturated metal atoms (i.e. Lewis acid sites) and show the characteristic peak at 1440 cm⁻¹ and 1585 cm⁻¹. Pyridine molecules can also react with H⁺ donor sites (i.e. Brønsted acid sites) and the characteristic peak appears at 1540 cm⁻¹ [8]. The peak which appears at around 1490 cm⁻¹ indicates the combination of Lewis and Brønsted acid sites. It can be seen from the figure that sharp and strong peaks appeared at 1440 cm⁻¹ and 1585 cm⁻¹ for both catalysts indicating that both catalysts possess Lewis acid sites. On the other hand, the characteristic peak of Brønsted acid sites at 1540 cm⁻¹ only appeared for V₂O₅ catalyst which shows that

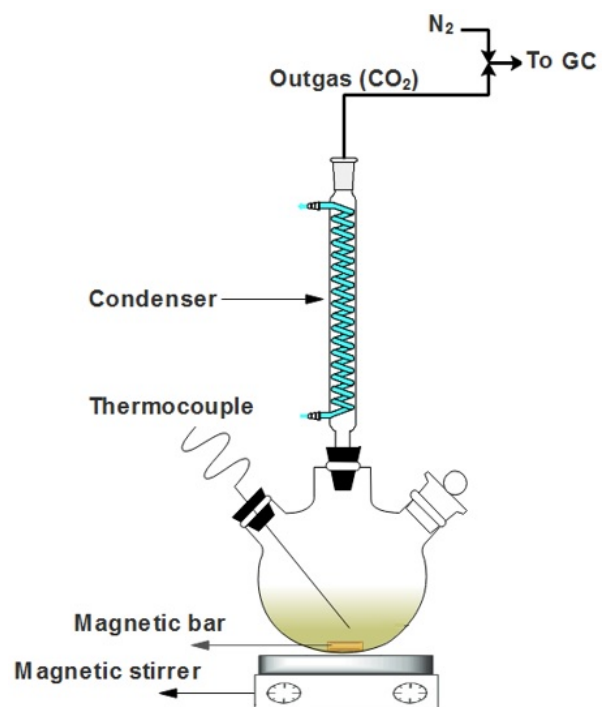


Fig. 1: Schematic diagram of the experimental apparatus

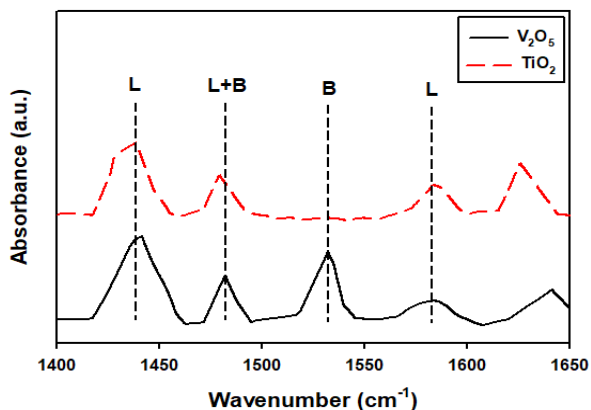


Fig. 2: Pyridine-FTIR spectra of TiO_2 and V_2O_5 catalysts. 'L' and 'B' denote to Lewis acid sites and Brønsted acid sites

only the V_2O_5 catalyst contains Brønsted acid sites.

3. Results and discussion:

The CO_2 desorption curves of MEA and DEA solutions without and with both catalysts are presented in Fig. 3. It can be seen from the figure that both catalysts improved the CO_2 desorption rate and desorbed greater amounts of CO_2 in comparison with the non-catalytic solutions. The performance of V_2O_5 catalyst was superior than TiO_2 as it desorbed greater amounts of CO_2 and, most importantly, lowered the temperature of peak CO_2 desorption point. This is because Brønsted acid sites present on V_2O_5 are very effective in breaking the carbamate by providing free protons (H^+). Our previous work has

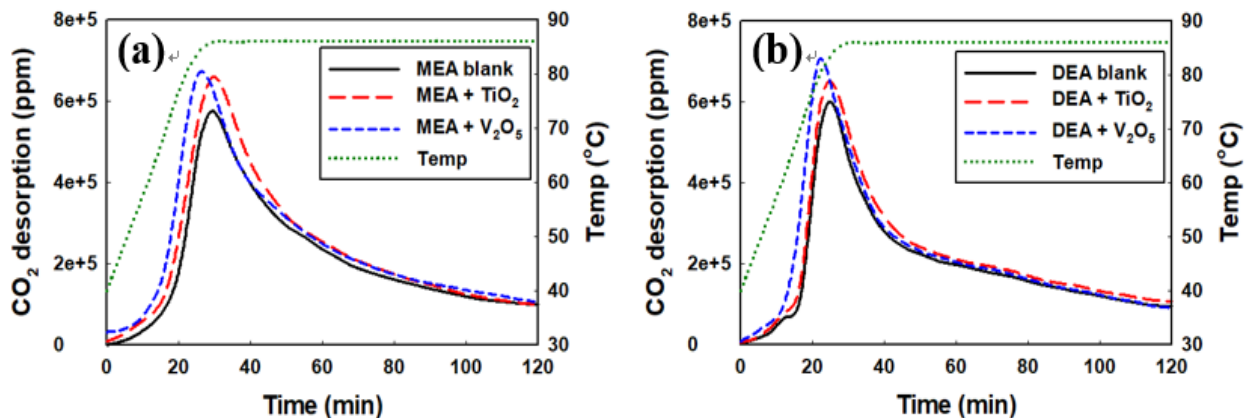


Fig. 3: CO_2 desorption curves of amine solvents without and with 5 wt. % catalysts as a function of time and temperature. (a) CO_2 desorption curve of MEA without and with catalyst (b) CO_2 desorption curve of DEA without and with catalyst.

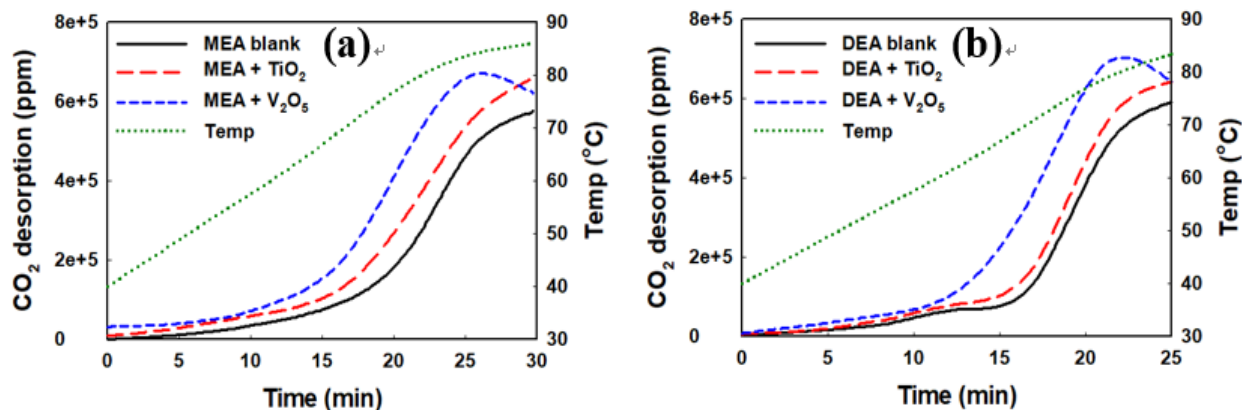


Fig. 4: CO_2 desorption curves for MEA and DEA solutions without and with TiO_2 and V_2O_5 catalysts during the temperature ramp-up stage.

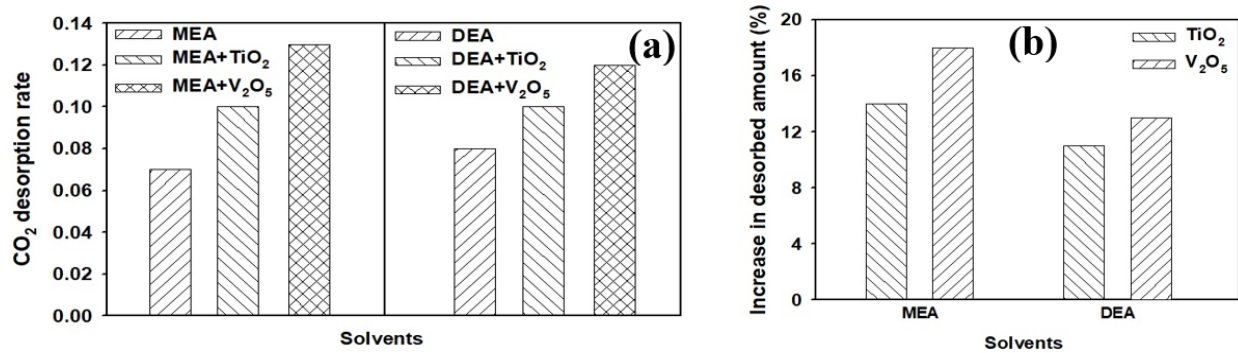


Fig. 5: (a) CO₂ desorption rates for MEA and DEA solvents without and with TiO₂ and V₂O₅ catalysts (b) Improvement in CO₂ desorbed amounts for the MEA and DEA solutions with TiO₂ and V₂O₅ catalysts in comparison with the non-catalytic MEA and DEA solutions.

showed that the Brønsted acid sites are more favorable in the CO₂-rich loading (at the start of the regeneration experiments). On the other hand, in case of TiO₂ catalyst, only Lewis acid sites were present, which are more beneficial in the lean loading region [9].

Overall, an increment of 13% and 17% in the total amount of desorbed CO₂ was recorded from TiO₂ and V₂O₅ catalysed MEA solutions. In the same manner, up to 13% greater amounts of CO₂ were released from TiO₂ and V₂O₅ catalysed DEA solutions.

3-1. CO₂ desorption at low temperatures

In addition to desorbing greater amounts of CO₂, the catalytic solutions also tended to optimize the CO₂ desorption rate during the temperature ramp-up stage at low temperatures. The CO₂ desorption curves for MEA and DEA solutions without and with both catalysts during the temperature ramp-up stage are shown in Fig. 4. It can be seen that from ~60 °C onwards, a noticeable improvement in the CO₂ desorption is observed from the catalytic solutions. This is because the acid sites present on the metal oxide catalysts assist the carbamate breakdown at low temperature and subsequently release CO₂. The Brønsted acid sites can protonate the carbamate whereas the Lewis acid sites can accept the lone pair of electrons from the “N” atom of the carbamate. In this way, the configuration of N atom changes from sp² to sp³ and the N-C is stretched due to catalytic activity and eventually breaks down with less thermal energy.

3-2. Rate of CO₂ desorption:

The rate of CO₂ desorption is defined as the CO₂ transfer rate from the liquid phase (amine solvent) to gas phase. Given that an equal amount of thermal energy is provided to all solutions, the catalytic solutions tended to desorb CO₂ with a higher desorption rate which results in a lower solvent regeneration heat duty. The CO₂ desorption rate was calculated using Eq. 1.

$$r = \frac{(\alpha_{rich} - \alpha_{lean})}{t} \quad \text{Eq. 1}$$

Where r is the rate of CO₂ desorption, α_{rich} and α_{lean} are the CO₂ loadings of the amine solutions at the start and end of the experiments respectively, and t is the duration of the experiment. The CO₂ desorption rate of amine solvents without and with catalysts are shown in Fig. 5. The TiO₂ catalyst improved the CO₂ desorption rate by 43% and 25% for MEA and DEA solutions, respectively. For V₂O₅ experiments, an improvement of 86% and 50% in the CO₂ desorption rate was recorded for MEA and DEA solutions, respectively.

4. Conclusions

The regeneration performance of MEA and DEA solvents was investigated without and with two metal oxide catalysts- TiO₂ and V₂O₅- within a temperature range of 40–86 °C. It has been found that both catalysts are capable of improving the solvent regeneration performance by desorbing greater amounts of CO₂ with higher CO₂ desorption rates. Overall,

improvements of up to 17% and 86% in the total amount of desorbed CO₂ and CO₂ desorption rate were observed from catalytic solutions. In comparison with the conventional solvent regeneration technique, the new approach of catalyst-aided regeneration shows the promise to minimize the solvent regeneration heat duty. A continuous stripper column should be used to evaluate the catalyst performance and impact of different parameters on catalytic activity.

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