Evaluating CO\textsubscript{2} desorption performance in CO\textsubscript{2}-loaded MEA solution with bifunctional catalysts

Xiaowen Zhang, Helei Liu *, Paitoon Tontiwachwuthikul and Zhiwu Liang *

Joint International Center for CO\textsubscript{2} Capture and Storage (iCCS), Provincial Hunan Key Laboratory for Cost-effective Utilization of Fossil Fuel Aimed at Reducing CO\textsubscript{2} Emissions, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, PR China

* Author for correspondence:
Email: lhl0925@hotmail.com (Dr. H Liu) & zwliang@hnu.edu.cn (Dr. Z Liang)

Abstract

Organic amines based CO\textsubscript{2} capture has been regarded as the most mature technology for capturing CO\textsubscript{2} in industrial field. 30\% monoethanolamine (5 M MEA) solvent is considered as a benchmark solvent for the evaluation of amine solvent in CO\textsubscript{2} capture process. However, this process suffers from the mainly drawback in terms of high energy consumption for rich solvent regeneration. Recently, Idem et al. [1] pointed out that the introduction of solid acid catalyst into amine solution regeneration process greatly decreased the heat duty. Different single solid acid catalysts have been reported for this purpose [2], and molecular sieve catalyst HZSM-5 and amphoteric oxide Al\textsubscript{2}O\textsubscript{3} presented better catalytic performance. Liang et al. [3] reported that HZSM-5 shows a superior catalytic CO\textsubscript{2} desorption performance to Al\textsubscript{2}O\textsubscript{3} in MEA solutions at the high CO\textsubscript{2} loading, due to its remarkable Br\textsubscript{nsted} acid sites (BAS). On the other hand, Al\textsubscript{2}O\textsubscript{3} presents a better catalytic CO\textsubscript{2} desorption performance than HZSM-5 when the CO\textsubscript{2} loading is low, which could be attributed to the present of prominent Lewis active sites. Both of BAS and basic site could enhance the regeneration process in different way, respectively. Therefore, it is very interesting to investigate the desorption performance of the rich MEA with the bifunctional catalysts which simultaneously possess the BAS and basic sites. To the best of our knowledge, no study has been reported in literature on the application of the bifunctional catalysts for this purpose.

In this work, four bifunctional catalysts Al\textsubscript{2}O\textsubscript{3}/HZSM-5 (Al-ZSM) with different Al\textsubscript{2}O\textsubscript{3} and HZSM-5 weight ratios (0.5, 1, 2 and 3) were prepared by using the combined precipitation ultrasound method and employed to improve the desorption performance of the rich 5 M MEA solvent regeneration process. The comparison of the single catalysts Al\textsubscript{2}O\textsubscript{3} and HZSM-5 with Al-ZSM is completely shown in this work. Textural properties and acid/basic properties of these catalysts were detected with XRD, FT-IR, N\textsubscript{2} absorption-desorption, Py-IR and NH\textsubscript{3}/CO\textsubscript{2}-TPD techniques. In addition, the reusability of the bifunctional catalyst was studied.

As displayed on Figure 1, 1 L of 5 M MEA solution with an initial CO\textsubscript{2} loading of 0.5 mol CO\textsubscript{2}/mol amine was regenerated in a 2 L four-necked flask with oil bath. Exactly 12.5 g of the desired catalyst were put into the amine solution. The regeneration temperature was ranged from 60-96 °C, and maintained at 96 °C for 9 h. The change of CO\textsubscript{2} loadings were measured at 0.25, 0.5, 0.75, 1, 1.5, 2, 4, 6, and 9 h by using a Chittick apparatus.
The heat duty (H, kJ/mol) was monitored using the electricity meter and calculated using the following expression (1).

\[ H = \frac{\text{Heat input/time}}{\text{Amount CO}_2/time} = \frac{\text{Electricity(kj)}}{\text{CC(mol)}} \]  

(1)

The relative heat duty (RH, %) is defined shown in equation (2).

\[ RH = \frac{H_i}{H_{baseline}} \times 100\% \]  

(2)

where \(H_i\) and \(H_{baseline}\) are the heat duty (kJ/mol) of the different catalysts-MEA systems and catalyst-free -MEA system in the first 2 h of the CO\(_2\) desorption process, respectively.

The characterization results indicated that the textural properties, BAS and basic sites of Al-ZSM were improved after the introduction of Al\(_2\)O\(_3\). The catalytic activity of six catalysts (Al-ZSM1/2, Al-ZSM1/1, Al-ZSM2/1, Al-ZSM3/1, Al\(_2\)O\(_3\) and HZSM-5) in MEA solvent regeneration process for the whole 9 h duration performed at 96 °C are displayed in Figure 2. The CO\(_2\) loading reduced quickly in the first 2 h, hence, the calculation of heat duty was conducted on the first 2 h of the regeneration process. Apparently, all the catalysts facilitated the CO\(_2\) desorption process as compared with catalyst-free test. Among the four bifunctional catalysts, Al-ZSM2/1 presented the best catalytic performance and Al-ZAM 1/1 showed the lowest catalytic activity. On the other hand, the Al-ZAM 1/1 presented better catalytic performance than the single catalysts Al\(_2\)O\(_3\) and HZSM-5.

Figure 2 (C) showed the RH of MEA with different catalysts. The RH (%) decreased in the order of: blank test (100) > HZSM-5 (80.9) > Al\(_2\)O\(_3\) (79.1) > Al-ZSM1/1 (76.7) > Al-ZSM1/2 (75.3) > Al-ZSM3/1 (70.8) > Al-ZSM2/1 (65.8). With the introduction of catalysts, the RH of MEA decreased from 19.1% to 34.2% over the catalyst-free test. Therefore, the use of bifunctional catalyst in rich MEA solvent regeneration process hugely decreased the regeneration energy requirement. The Al-ZSM2/1 presented the best catalytic performance. The recyclability experimental results show that Al-ZSM possess an excellent stability. These results demonstrated that Al-ZSM catalysts are the promising industrial catalysts for the rich amine solvent regeneration process.
Figure 2. CO₂ desorption performance in MEA solution at 96 °C.

References