

IMPACT OF KIT-6 CATALYST ON REDUCING THE ENERGY CONSUMPTION OF MEA-CO₂ LOADED REGENERATION PROCESS

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ABSTRACT

The intensive energy penalty for amine solvent regeneration in the absorption/desorption process considered one of the major obstacles of this technology. Therefore, a series of a super solid acid catalyst (SO₄²⁻/SnO₂, SO₄²⁻/ZrO₂, and mesoporous silica Kit-6) were synthesized and studied separately to investigate their effectiveness on monoethanolamine (MEA) solvent regeneration at 97°C. It has been observed that all the catalysts promote the CO₂ desorption performance, the Kit-6 exhibit the best catalytic performance which can enhance the desorption rate by 43.90% and reduce the energy consumption by 34.6% compare to monoethanolamine (MEA) without catalysts, whereas other solid acid catalysts, SO₄²⁻/SnO₂ and SO₄²⁻/ZrO₂ exhibited a significant change in amine regeneration performance at the same conditions. The rich-MEA regeneration performance order was MEA-Kit-6 > MEA-SO₄²⁻/SnO₂ > MEA-SO₄²⁻/ZrO₂ > MEA without a catalyst. Based on the obtained results, the application of this work will open a new path in CO₂ stripping process to reduce the regeneration energy requirements and enhancing the desorption rate, which would decrease the operating costs of rich amine solvent regeneration.

Keywords: MEA solvent regeneration, Post-combustion CO₂ capture, Solid acid catalysts, CO₂ desorption, Brønsted acid sites.

NONMENCLATURE

- (MEA) Monoethanolamine*
- (CCPC) CO₂-capture post-combustion*
- (FT-IR) Fourier transform-infrared spectrometer*
- (BET) Brunauer, Emmett, and Teller*
- (XRD) X-Ray diffraction*
- (Py-IR) Pyridine adsorption-infrared spectroscopy*
- (NH₃-TPD) Ammonia-temperature programmed desorption*
- (BET) Brunauer, emmett, and teller*
- Symbols*
- (γ) CO₂ loading (mol CO₂/mol amine)*
- CCCO₂ Cyclic capacity (mol)*
- (H) Regeneration heat duty (kJ/mol)*
- (RH) Relative heat duty (%)*
- (RP) Regeneration performance (mol³/(kJ min))*
- (DR) Desorption rate (mol/min)*
- (H⁺) Hydrogen ion*

1. INTRODUCTION

The continuously increasing emissions of carbon dioxide (CO₂) and increasing air CO₂ concentration produced by the soaring energy demand and the urgent need to mitigate abundant greenhouse gas (GHG) emissions in order to slacken global warming has led to the development of capture processes equipped specifically towards the removal of CO₂ simply and cost-effectively because of its huge abundance.[1, 2].

These concerns have led to the development of capture processes designed specifically towards the removal of CO₂ from flue gases simply and cost-effectively [3-5].

To date, there are three promising technologies for CO₂ capture and decreasing the heat duty required including process options for CO₂ capture: pre-combustion process, post-combustion and oxy-fuel. Among the improved technologies used in CCUS, Post Combustion considered to be the most recently established and extensively used regarding its proficiency to be retrofitted into an existent power plant and capacity of handling a vast amount of exhaust stream. [9]. The CO₂ enhanced oil recovery (EOR) method deemed to be an effective technique for reducing CO₂ emissions regarding the storage of carbon dioxide (CO₂), CO₂-capture post-combustion (CCPC) technology, which targets to absorb CO₂ produced from flue gases of the power plants by an amine-scrubbing procedure. The main drawbacks of this technology are the huge heat duty of CO₂ desorption. Recently, it is been known that the solvent regeneration process estimates to be around 70% of the whole energy cost of the CO₂-capture process. [10].

Recently, using amine-based solvents as a chemical absorption technology using has become one of the most popular techniques because of its maturity and excessive capacity to absorb great amounts of flue gas [11, 12]. Although the advantages of using this technology at least there are three major hindrances still limiting the applying of this, including huge energy demands for amine solvent regeneration especially for primary amine which was comprises as 80% of the total cost of the CO₂ capture, amine solvent degradation and the corrosion of the equipment which considered as one of the biggest barriers for applying this technology [13-15].

In recent years, many efforts have been devoted to decrease the energy requirement for amine solvent regeneration by introduction of carbonic anhydrase, developing higher performance desorption devices and other absorption/desorption inventions[16-18].

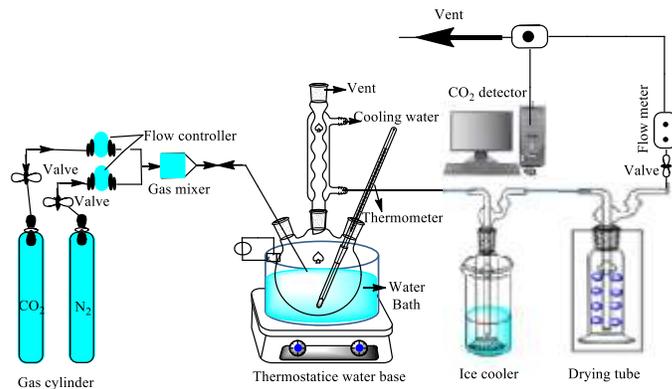


Fig. 1. The experimental setup for CO₂ absorption/desorption experiment under atmospheric pressure.

Related study by Khalipour et al Suggested a new inventions to reduce the energy demands of CO₂ desorption by using developed Heat Exchanger Network, and other suggested another new methods include solvent split-flow, vacuum stripper, solvent inter-cooling and multi-pressure of the capture method, all in an effort to decrease the energy penalty [19-21]. The introduction of solid sorbents, nanoparticles, and metal oxides in CO₂ absorption/ desorption process have become a turning point to improve the desorption rate, thereby decreasing the regeneration heat required in the amine solutions [22, 23].

In this study, Kit-6 mesoporous catalysts ,SO₄²⁻/SnO₂ and SO₄²⁻/ZrO₂ have been extensively synthesized and applied in order to utilize their favorable Basic Acid Sites (BAS) associated with the linked hydroxyl groups in the parts of -Kit-OH, resulting in high surface area, and strong BAS.

2. METHODS

2.1 Synthesis of the catalysts

Solid acid catalysts SO₄²⁻/SnO₂ and SO₄²⁻/ZrO₂ were synthesized based on impregnation method with a slightly modified [24]. The desired amount of zirconium nitrate was dissolved in water under vigorous stirring at room temperature to get a fully mixed suspension. After stirring for 20 minutes at 350rpm, water was evaporated at 110oC for 24h followed by pre-calcination at 300oC for 3h. The resulting material was immersed in an appropriate amount of 0.5mol/L (NH₄)₂SO₄ solution at a ratio of 15mL/g and the mixture left for 1h with constant stirring at room temperature to reach equilibrium. The obtained sample was incinerated at 650oC under constant air for 3h, and the obtained catalyst containing SiO₂ was designated

SZ/SiO₂. The SO₄²⁻/SnO₂ catalyst synthesis method was almost the same as that of supported solid acid catalysts SO₄²⁻/ZrO₂ but Sn²⁺ instead of ZrO₂. Zirconium nitrate was subjected to 300°C for 3 hours, and then the obtained material was immersed in 0.5 mol L⁻¹ (NH₄)₂SO₄ solution. After drying at 110°C, it was also incinerated at 600-650°C for 3h.

2.2 Catalysts Characterization

2.2.1 X-ray diffraction analyses

X-ray diffraction XRD-6100 (Shimadzu, Japan) was performed to characterize the synthesized catalysts. The XRD was operated at a D8-Advance with Bruker X-ray-Powder diffract meter emitting Cu K α radiation (40 kV, 40 mA) in the range of 2 $^{\circ}$ and 80 $^{\circ}$ and Cu K γ radiation (40 kV, 40 mA) in the range from 10 $^{\circ}$ -80 $^{\circ}$. Diffraction data were exposed with an exact scanning speed of 0.5 $^{\circ}$ of 8 $^{\circ}$ /min and 2 θ angle of 0.02 $^{\circ}$ at 25 $^{\circ}$ C.

2.2.2 N₂ adsorption-desorption experiment

To detect the specific surface area and the pore structure of the synthesized catalysts a N₂ adsorption /desorption experiment at the temperature of liquid nitrogen (-196 $^{\circ}$ C) was applied by using a TriStar II 3020 instrument (Micrometrics Instrument Corporation Germany). To clean the catalyst surface, each sample was degassed in advance at 230 $^{\circ}$ C for 12h and finally outgassed down to 10⁻³ Torr.

2.3 CO₂ absorption experiment of the lean amine

In order to evaluate the side effects of the synthesised catalysts on the performance of regenerated MEA solvent, the CO₂ absorption performances of the fresh MEA solution and the recycled MEA solution after catalyst removal were studied and compared by using the equipment shown in Fig. 1. Approximately 100mL of 5M MEA solution was immersed in the water bath at 40 $^{\circ}$ C with CO₂ partial pressure of 15.0kPa. To analyze the CO₂ loading changes, 1mL liquid samples were taken for analyzing at 0, 1, 5, 10, 20, 40, 60, 90, 120, and 180min by an appropriate pipet and analyzed according to the titration technique of the Chittick apparatus method.

2.4 Study catalytic performance

The CO₂ desorption heat duty (H, kJ/mol) was used to evaluate the catalytic MEA solvent regeneration

performance of MEA-Kit-6 catalytic systems, based on the expression Eq.1. The CO₂ desorption heat duties (H) and H_{loss}, was essentially from the initial point of heating the oil bath from 55 to 97 $^{\circ}$ C and maintaining it at 97 $^{\circ}$ C during the period of heating, which can be detected and deducted.

$$H_{CO_2} = \frac{H_{input} \cdot time}{CO_2 \cdot mol \cdot time} = \frac{Electric(KJ)}{CO_2(mol)} \quad (1)$$

Where H_{input} (kJ/mol) is the heat duty in the first 3h of the (MEA-Kit-6) systems during CO₂ stripping and MEA regeneration process. The relative re-boiler heat duties (RH) were calculated with Eq. 2. as the ratio of the MEA-catalyst systems heat duty in the first 180 min (H_i) divided by the blank heat duty (H_b) (H, kJ/mol) for the CO₂ desorption.

$$RH\% = \frac{H_i}{H_b} \times 100 \quad (2)$$

The total heat input H_i was detected by electrometer detector, while the amount of regenerated MEA was recognized as the cyclic capacity of CO₂ (CC_{CO₂}).

$$CC_{CO_2} = (\gamma_{rich} - \gamma_{lean}) \times C_{MEA} \times V_{MEA} (molCO_2) \quad (3)$$

where CC_{CO₂} (mol) refers to the amount of CO₂ desorbed, γ_{rich} and γ_{lean} are the amount of initial CO₂ (mol) loading of the MEA solvent and the CO₂ loading of the regenerated MEA solution, and C (mol/L) and V (L) are the concentration and volume of MEA solvent respectively. To estimate the catalyst activity in this study, regeneration performance (RP, mol³/(kJ.min)) was calculated as following in Eq.4.

3. RESULTS

CO₂ desorption curves of 5M MEA solution with initial CO₂ loading of 0.5 \pm 0.01mol/mol as a function of time at the desorption temperature of 97 $^{\circ}$ C with or without 6.25g of the synthesized catalysts are shown in Fig.2. It can be seen that desorption performance of the synthesized catalysts with different kind of catalysts (SO₄²⁻/SnO₂, SO₄²⁻/ZrO₂, and mesoporous silica Kit-6) during the first 180min of the experiment was enhanced compared to that of the blank run. It is clear that there is a sharp decline in CO₂ loading in the

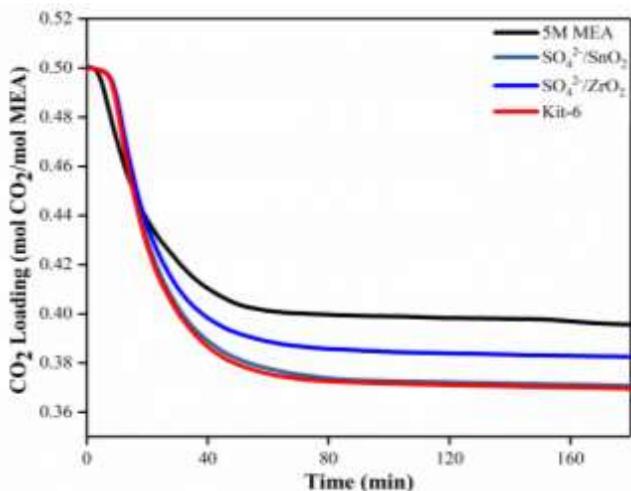


Fig. 2. CO₂ desorption profiles of MEA with and without catalysts at 97°C.

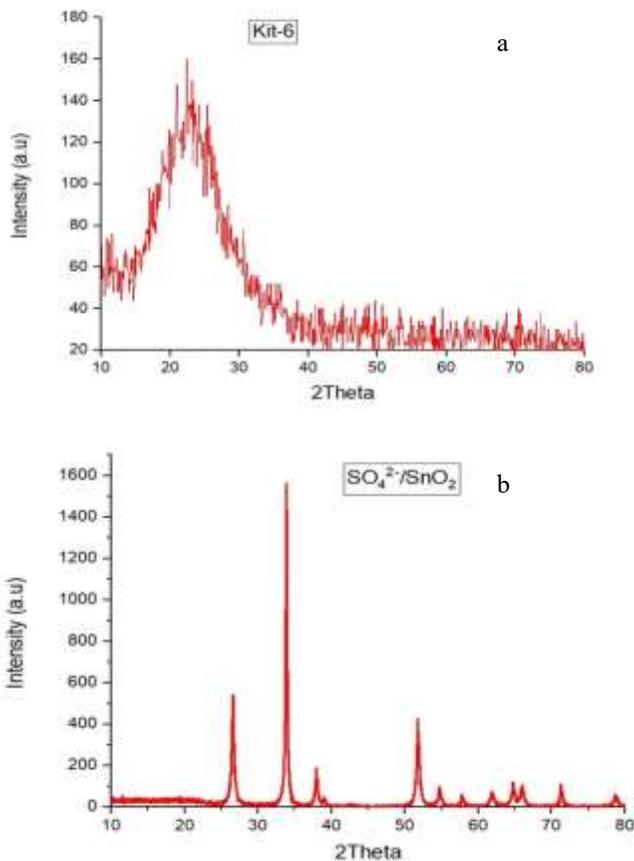


Fig. 3. (a) and (b) X-ray patterns Kit-6 and SO₄²⁻/SnO₂ catalysts.

first 90min and then the change was only slight after that of with and without catalyst. Therefore, the study of the catalysts performance on CO₂ desorption, MEA regeneration and the consumed energy during CO₂

stripping processes was based on the first 90min. From the obtained results, the highest value of CO₂ desorption performance was recorded for Kit-6 by comparing to the other catalysts. The results exhibit that Kit-6 catalyst decreases the required heat duty by 34.6%, and enhances the cyclic capacity and desorption rate of CO₂ by 43.9% compared to that of the MEA blank as a baseline.

The XRD patterns of the Kit-6 and SO₄²⁻/SnO₂ catalysts were presented in Fig.3.(a,b). It can be observed that the Kit-6 showed broad peak which assigned to the Si₂+ XRD peaks of SO₄²⁻/SnO₂ catalysts showed mine sharp peak assigned to SO₄²⁻ while the secondary peaks in the assigned to the Sn₂+ ione which proved this results indicate that complete interaction between SO₄²⁻ and SnO₂ to form the solid acid catalyst using the impregnation method.

4. CONCLUSION

The experimental results showed that the synthesized catalysts were significantly effective to reduce the energy consumption and enhancing desorption rate of CO₂ compare to the 5M MEA without catalyst and improving the MEA solvent regeneration by lowering the relative energy penalty of CO₂ stripping process. The results of this work also demonstrated that the Kit-6 catalyst exhibited the best catalytic performance in terms of desorption rate, heat duty, and reusability during the rich-MEA regeneration process which reduced the relative heat duty by 34.6% by adding 6.25g of Kit-6 to the MEA and enhancing the desorption rate by 43.90% compared with that for MEA as a baseline.

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