

Catalytic performance and mechanism of meso-microporous material Beta-SBA-15 supported FeZr catalysts for CO₂ desorption in CO₂ loaded aqueous amine solution

Yufei Huang[†], Xiaowen Zhang, Hongxia Gao*, Paitoon Tontiwachwuthikul, Zhiwu Liang*

Joint International Center for CO₂ Capture and Storage(ICCS), Provincial Hunan Key Laboratory for Cost-effective Utilization of Fossil Fuel Aimed at Reducing CO₂ Emissions, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, PR China
Email: hxgao@hnu.edu.cn, zwliang@hnu.edu.cn (Dr. Z Liang)

ABSTRACT

The highly energy requirement of rich amine solvent regeneration process is the biggest obstacle for the industrial application of amine-based CO₂ capture technology. In this work, to reduce the heat duty of solvent regeneration, the novel composite materials zeolite Beta /SBA-15 (BS) with different zeolite Beta (β) content were synthesized by the hydrothermal method with β as the silicon source and were utilized to prepare Zr@BS and Fe-Zr@BS catalysts for amine regeneration. Experiments for CO₂ stripping were performed using amines (monoethanolamine (MEA), Diethanolamine (DEA) and 2-(Diethylamino) ethanol (DEEA)) with an initial CO₂ loading of 0.5 mol CO₂/mol amine at 370.15 K. Additionally, various techniques including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), N₂ adsorption-desorption experiment, ammonia and CO₂ temperature programmed desorption (NH₃/CO₂-TPD), and pyridine-adsorption infrared spectroscopy (Py-IR) were adopted to characterize and estimate the prepared catalysts. Also, the catalytic CO₂ desorption performances of seven different catalysts (β , SBA-15, three BS catalysts, Zr@BS and Fe-Zr@BS) were investigated in terms of the cyclic capacity, desorption rate and energy consumption. The experimental results showed that the catalytic performance of BS better than the individual catalysts, and that Fe-Zr@BS can enhance the desorption factor by 212% and reduce the energy consumption by 33% compared to the blank run. Furthermore, the Fe-Zr@BS catalysts have no influence on the amine absorption performance in terms of the absorption rate and have the advantages of good stability and easy regeneration. Based on the results of characterization and experiments, the possible catalytic mechanism for bifunctional Fe-Zr@BS catalysts catalyzed

amine regeneration for CO₂ stripping were proposed and the reusability of the catalysts were also investigated.

Keywords: CO₂ capture, BS, MEA, desorption, heat duty, Bronsted acid and base sites.

NONMENCLATURE

Abbreviations

BS	Beta /SBA-15 β
β	Zeolite Beta
MEA	Monoethanolamine
DEA	Diethanolamine
DEEA	2-(Diethylamino)ethanol
XRD	X-ray diffraction
FT-IR	Fourier transform infrared Spectroscopy
SEM	Scanning electron microscopy
NH ₃ /CO ₂ -TPD	Ammonia and CO ₂ temperature Programmed desorption
Py-IR	pyridine-adsorption infrared Spectroscopy
HD	Heat duty
DF	Desorption factor

1. INTRODUCTION

It is generally accepted that the continuing increase of fossil fuel consumption around the world has resulted in the increasing CO₂ concentration in the atmosphere, has a significant influence on the world's average temperature, and should be blamed for the widely evidenced global warming and climate change. CO₂ capture, utilization and storage technology (CCUS) is considered to be an effective and potentially economical technology, but it is yet to be extensively applied in electric power plants and industry to mitigate the CO₂

emissions from fossil fuel combustion. Monoethanolamine (MEA), a primary amine, has been demonstrated to have the capability for separating CO₂ from flue gas due to its high absorption capacity, high mass-transfer performance and low price properties. However, the application of aqueous MEA solution is limited by the high heat duty for solvent regeneration, solution degradation and corrosion of equipment, which are serious challenges to its large-scale industrial application. Consequently, increased attention is being paid to minimize the heat duty during MEA solvent regeneration for CO₂ capture[1].

Investigations to reduce the heat requirement in amine regeneration include Bhatti et al.[2], who investigated the introduction of various transition metal oxide catalysts into MEA solutions. The experimental results showed that these catalysts can provide acidic sites, resulting in more collisions between free protons with carbamates thus reducing the sensible heat by 25%-48% in the amine regeneration process. However, Lai et al. [3] reported that MoO₃ and V₂O₅ cannot serve as classic catalysts because they react with amine and would dissolve in the rich amine solution.

In addition, it has been reported that solid acid catalysts applied in CO₂ desorption decrease the heat duty as well as increase the CO₂ desorption rate. Idem et al.[4] demonstrated that HZSM-5 (predominantly a Brønsted acid catalyst) and γ-Al₂O₃ (predominantly a Lewis acid catalyst) can reduce the amine regeneration heat duty by 30%-40% by providing acid sites to change the reaction path of amine solvent regeneration. Zhang et al.[5] reported that SAPO-34 could also reduce the relative heat duty by 17.1%, compared to the baseline solvent MEA. However, the single molecular sieve has fewer acid sites and the pores were easily blocked, resulting in a serious degradation of the performance of the catalysts due to the increasing difficulty in mass transfer. Many researchers then improved the catalytic performance of molecular sieves by introducing metal oxides, which possess high acid (and basic) sites and have excellent hydrothermal stability. Zhang et al.[6, 7] recently reported the SO₄²⁻/ZrO₂/γ-Al₂O₃ and Al₂O₃/HZSM-5 could also reduce the relative heat duty by 36.9% and 34.2% respectively, compared to the baseline solvent MEA.

It is well known that SBA-15 has large pores, large surface area and good thermal stability compared with other mesoporous materials, factors which facilitate the introduction of metals into the framework. However, the pure SBA-15 molecular sieve has little acid sites, and this

is detrimental to the amine regeneration process. In order to overcome this problem, the introduction of β molecular sieve into SBA-15 support might enhance the catalytic performance of SBA-15 by increasing the number of catalytically acid sites and improving the rate of mass-transfer.

In this research, the novel composite materials zeolite Beta /SBA-15 (BS) with different zeolite Beta (β) content were synthesized by the hydrothermal method with β as the silicon source and were utilized to prepare Zr@BS and Fe-Zr@BS catalysts for amine regeneration. Seven different catalysts were compared for their amine desorption performance in terms of reaction rate, heat duty, cyclic capacity and CO₂ absorption rate. Additionally, the structure, surface area, and characteristics of the catalysts were elucidated by various characterization approaches, i.e. XRD, FT-IR, SEM, N₂ adsorption-desorption, NH₃/CO₂-TPD, and Py-IR. Based on the characterization data of the catalysts and the CO₂ desorption experiments, possible catalytic mechanisms for Fe-Zr@BS catalyzed amine regeneration for CO₂ stripping were proposed. Furthermore, the reusability of the bifunctional catalysts was also investigated.

2. EXPERIMENTAL SECTION

2.1 Chemicals

MEA (purity of 99%) and NH₃·H₂O (purity of 28-30%) were obtained from Shanghai Aladdin Industrial Corporation, China. Tetraethyl orthosilicate (98%) and EO₂₀PO₇₀EO₂₀ (Pluronic P123) were got from Shanghai Aladdin Biochemical Technology Co. Ltd., China. β molecular sieves were purchased from Tianjin NanKai University Catalyst Co. Ltd., China. Zirconium oxychloride hydrate (ZrOCl₂·8H₂O, purity of 98%) and DEEA (99%) were provided by Shanghai Macklin Biochemical Co. Ltd., China. DEA (98.6%-102.0%), Hydrochloric acid (HCl, 36-38%) and Ferric nitrate nonahydrate (Fe(NO₃)₃·9H₂O, 98.5%) were acquired from Sinopharm Chemical Reagent Co. Ltd, China. CO₂ (purity of 99.9%) and N₂ (purity of 99.99%) were obtained from Changsha Jingxiang Gas Co. Ltd., China. Methyl orange (0.10%wt) indicator was acquired from Tianjin Kermel Chemical Reagent Co. Ltd., China. All materials were used without further purification.

2.2 Experimental apparatus and procedure

A schematic diagram of the experimental apparatus for solvent regeneration and CO₂ stripping is shown in Figure 1. The CO₂ desorption device consists of a 1L

round-bottom flask equipped with one thermometer, an oil bath, a condenser, a mass flow meters, a power meter, an infrared CO₂ analyzer and a gas cylinder.

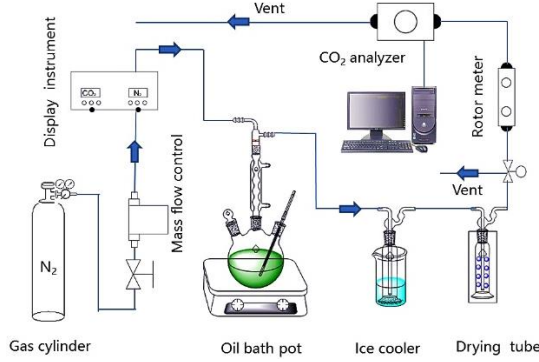


Figure 1. Schematic diagram of experimental device for amine solution regeneration process.

2.3 Theory

The instantaneous CO₂ desorption rate (r , mol/(s*L)) can be calculated by the CO₂ concentration of the outlet gas monitored with the CO₂ analyzer, as presented in Equations 1.

$$r = \frac{1}{V} (n_{CO_2}^{in} - \frac{X_{CO_2}^{out}}{1 - X_{CO_2}^{out}} \cdot n_{N_2}) \quad (1)$$

where $n_{CO_2}^{in}$ (mol/s) and n_{N_2} (mol/s) are flow rate of CO₂ and N₂ of the feed gas, respectively, $X_{CO_2}^{out}$ is the mole fraction of CO₂ in the outlet gas, and V (L) is the volume of the desorbed amine solution.

The amount of CO₂ desorbed from the loaded amine solution is defined as the cyclic capacity (Q_C , in mol), which can be calculated by Equation 3.

$$\alpha_{lean} = \alpha_{rich} - \frac{r \cdot \Delta X_{CO_2} \cdot 60}{C} \quad (2)$$

$$Q_C = (\alpha_{rich} - \alpha_{lean}) \cdot C \cdot V \quad (3)$$

where, α_{rich} (mol CO₂/mol amine) is the initial loading of amine solution, α_{lean} (mol CO₂/mol amine) represents the loading of the regenerated amine solution, ΔX_{CO_2} is the change in the mole fraction of CO₂ in the outlet gas in one minute, and C (mol/L) is the concentration of the desorbed amine solution.

The CO₂ desorption rate (\bar{r} , mol/min) of amine solution can be defined as the amount of CO₂ produced from amine solution over a specific period time as illustrated in Equation 4.

$$\bar{r} = \frac{Q_C}{t} \quad (4)$$

Here, t is the reaction time and represents 60 minutes in this work.

In the process of amine regeneration, the heat duty (HD, kJ/mol) can be defined as the overall amount energy consumed for each mole of CO₂ desorbed from the amine solution as shown in the Equation 5, and the

relative heat duty (RH, %) used in this work is presented in the equation 6.

$$HD = \frac{E/t}{Q_C/t} \quad (5)$$

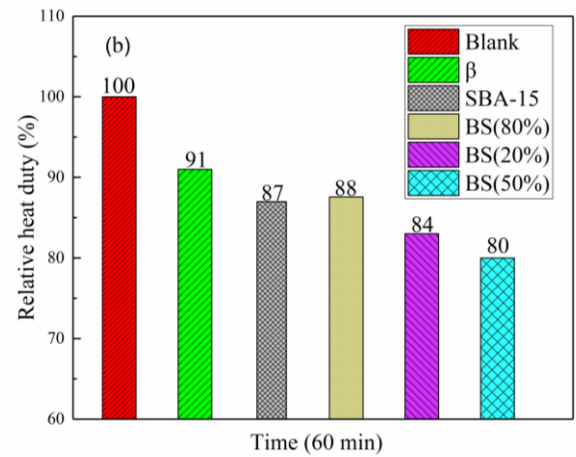
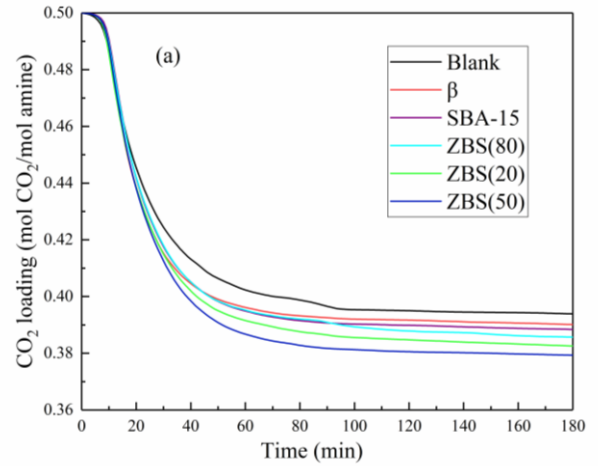
$$RH = \frac{HD}{HD_{baseline}} \times 100 \quad (6)$$

where, E/t is the amount of energy consumed by the oil bath to heat the amine solution over a fixed time. Q_C/t is the total amount of CO₂ desorbed in the same amount of time. The relative energy requirement for 5 M MEA solution regeneration without catalysts was taken as the baseline and regarded as 100%.

In addition, a desorption factor (DF, mol³/(kJ·min)) was introduced to evaluate the overall performance of the catalyst, and the calculation of DF is shown in Equation 7.

$$DF = \frac{\bar{r} \cdot Q_C}{HD} \quad (7)$$

2.4 Results



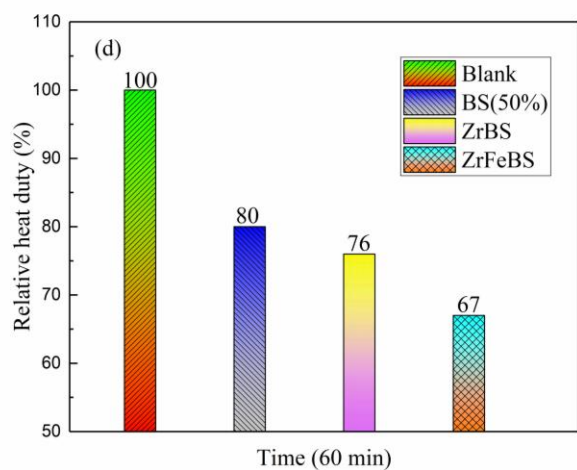
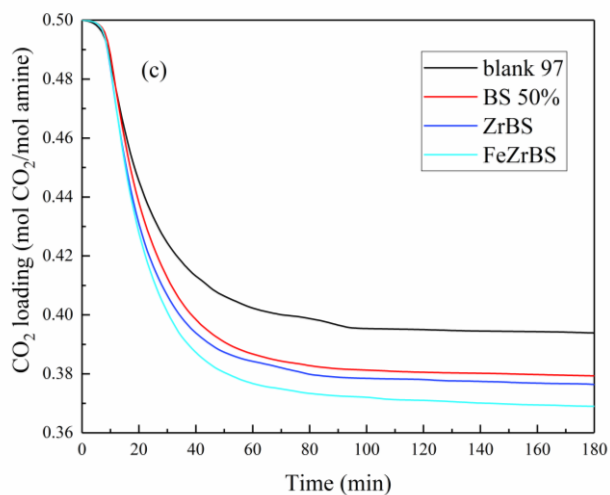


Figure 2. CO₂ desorption performance in MEA solution with different catalysts at 370.15K

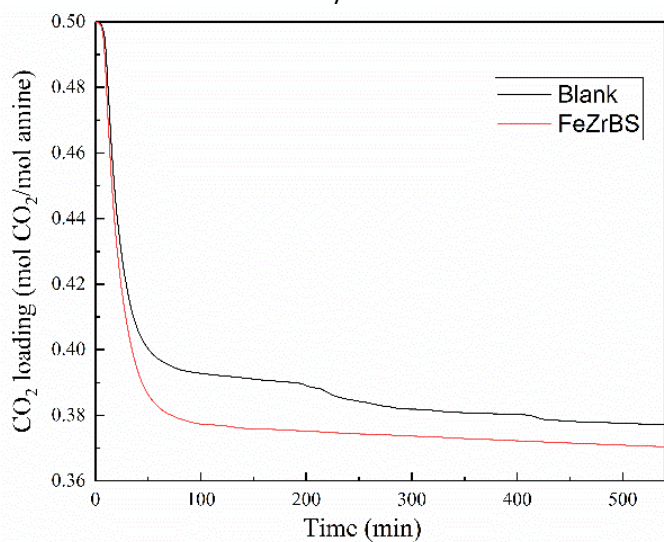


Figure 3. Experimental regeneration curves in the liquid phase for loading change.

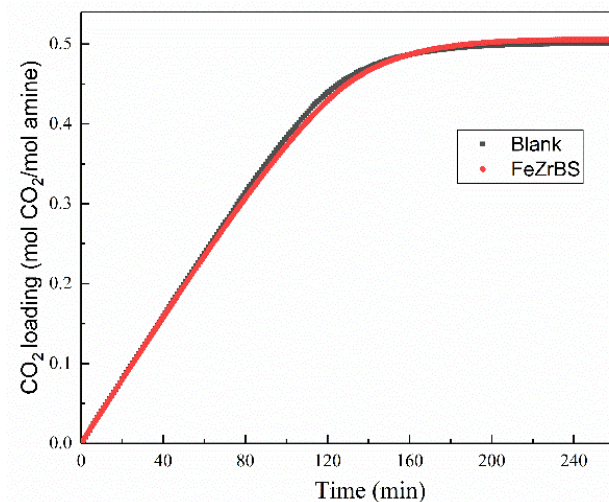


Figure 4. Effect of catalyst on absorption properties of amine solution.

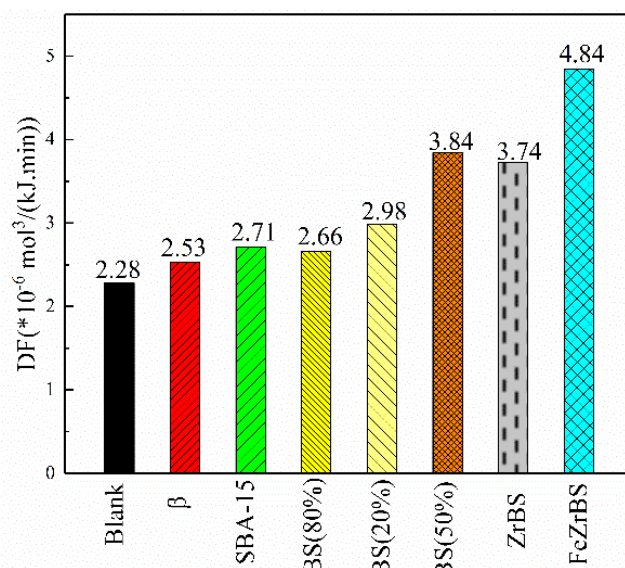


Figure 5. The desorption factor of MEA solution with or without catalysts.

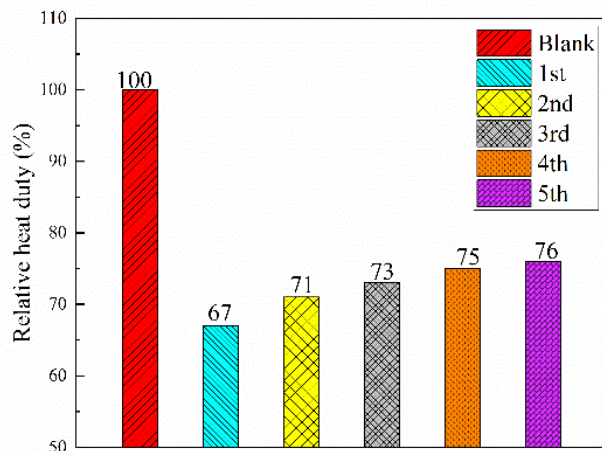


Figure 6. Recyclability test of the Fe-Zr@BS for relative heat duty

2.5 Conclusions

In this work, the solvent regeneration performance of five different catalysts was investigated in terms of heat duty and CO₂ desorption rate. The catalytic activities of these catalysts decreased in the order as: Fe-Zr@BS > Zr@BS > BS (50%) > BS (20%) > BS (80%) > SBA-15 > β > blank run. The experimental results showed that that Fe-Zr@BS can enhance the desorption factor by 212% and reduce the energy consumption by 33% compared with the blank experiment. In addition, a possible catalytic amine solvent regeneration mechanism was suggested over the catalyst Fe-Zr@BS. Furthermore, Fe-Zr@BS catalyst has good stability and has no adverse influence on the CO₂ absorption performance of amine solution. Findings from this work demonstrated that Fe-Zr@BS has the advantages of higher catalytic performance, easy separation and good stability, indications that it has great potential for application in industrial CO₂ capture process.

REFERENCE

- [1] Ling H, Gao H, Liang Z. Comprehensive solubility of N₂O and mass transfer studies on an effective reactive N,N-dimethylethanolamine (DMEA) solvent for post-combustion CO₂ capture. *Chemical Engineering Journal*. 2019;355:369-79.
- [2] Bhatti UH, Shah AK, Kim JN, You JK, Choi SH, Lim DH, et al. Effects of Transition Metal Oxide Catalysts on MEA Solvent Regeneration for the Post-Combustion Carbon Capture Process. *ACS Sustainable Chemistry & Engineering*. 2017;5:5862-8.
- [3] Lai Q, Toan S, Assiri MA, Cheng H, Russell AG, Adidharma H, et al. Catalyst-TiO(OH)₂ could drastically reduce the energy consumption of CO₂ capture. *Nat Commun*. 2018;9:2672.
- [4] Shi H, Naami A, Idem R, Tontiwachwuthikul P. Catalytic and non catalytic solvent regeneration during absorption-based CO₂ capture with single and blended reactive amine solvents. *International Journal of Greenhouse Gas Control*. 2014;26:39-50.
- [5] Zhang X, Zhang X, Liu H, Li W, Xiao M, Gao H, et al. Reduction of energy requirement of CO₂ desorption from a rich CO₂-loaded MEA solution by using solid acid catalysts. *Applied Energy*. 2017;202:673-84.
- [6] Zhang X, Hong J, Liu H, Luo X, Olson W, Tontiwachwuthikul P, et al. SO₄²⁻/ZrO₂ supported on γ -Al₂O₃ as a catalyst for CO₂ desorption from CO₂-loaded monoethanolamine solutions. *AIChE Journal*. 2018;64:3988-4001.
- [7] Zhang X, Liu H, Liang Z, Idem R, Tontiwachwuthikul P, Jaber Al-Marri M, et al. Reducing energy consumption of CO₂ desorption in CO₂-loaded aqueous amine solution using Al₂O₃/HZSM-5 bifunctional catalysts. *Applied Energy*. 2018;229:562-76.