



## Catalytic activity of facilely synthesized mesoporous HZSM-5 catalysts for optimizing the CO<sub>2</sub> desorption rate from CO<sub>2</sub>-rich amine solutions

Item Type	Article
Authors	Bhatti, Umair H.;Shah, Abdul K.;Hussain, Amjad;Khan, Hassnain Abbas;Park, Chan Young;Nam, Sung Chan;Baek, Il Hyun
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Manuscript Number: CEJ-D-19-12146R1

Title: Catalytic activity of facilely synthesized mesoporous HZSM-5 catalysts for optimizing the CO<sub>2</sub> desorption rate from CO<sub>2</sub>-rich amine solutions

Article Type: Research Paper

Keywords: CO<sub>2</sub> capture; CO<sub>2</sub> desorption rate; Desilication reassembly; Zeolite; Catalytic solvent regeneration

Corresponding Author: Dr. Il-Hyun Baek, PhD

Corresponding Author's Institution: Korea Institute of Energy Research

First Author: Umair H Bhatti, PhD

Order of Authors: Umair H Bhatti, PhD; Abdul K Shah, PhD; Amjad Hussain; Hassnain A Khan, PhD; Chan Young Park, PhD; Sung Chan Nam, PhD; Il-Hyun Baek, PhD

Abstract: Post-combustion CO<sub>2</sub> capture using aqueous alkanolamine solutions has a great potential to reduce anthropogenic CO<sub>2</sub> emissions but the large-scale deployment of this technique is hindered due to a highly energy-intensive solvent regeneration mainly because of poor CO<sub>2</sub> desorption kinetics. To overcome this limitation, we synthesized a series of mesoporous HZSM-5 catalysts through facile alkaline desilication and surfactant-induced re-assembly of dissolved species originating from the parent HZSM-5 crystals, and evaluated their performance to optimize the CO<sub>2</sub> desorption rate from benchmark 30 wt. % monoethanolamine (MEA) solution under mild temperature condition (40-82 °C). X-ray diffraction (XRD) patterns showed that the synthesized catalysts retained their crystallinity. Desilication by treatment in the alkaline medium led to a remarkable development of mesoporosity, with an increase in the Brunauer-Emmett-Teller (BET) surface area as well. The experimental results suggested that the synthesized catalysts significantly enhanced the CO<sub>2</sub> desorption rate at low temperatures (up to 350-580% at ≤ 82 °C), improved the total amount of desorbed CO<sub>2</sub> up to 60%, and minimized the heat duty by 24-37%. Detailed characterization revealed that the synergistic effect of higher mesoporosity and increased number of Lewis acid sites (LAS) and Brønsted acid sites (BAS) was crucial to improve the CO<sub>2</sub> desorption rate. Based on the characterization and experimental results, a plausible reaction mechanism for catalyst aided CO<sub>2</sub> desorption was also presented. This investigation highlights the role of catalysts in optimizing the CO<sub>2</sub> capture process and presents new understanding for the design of high-performance catalysts for this purpose.

Response to Reviewers: Reply to the comments from Reviewer 1

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Thank you very much for your time and effort for reviewing our manuscript. Your comments are all useful and we have carefully revised

through the manuscript accordingly. We believe the revision succeeded in clarifying the value of our work, and we hope you agree on it.

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Nonetheless, the authors understand that a simple economic impact of catalyst addition can be estimated from our study by simply considering (i) the cost of catalyst that was added to the solution and (ii) cost-saving in terms of energy-saving due to the catalytically optimized regeneration process. However, such a simple economic estimation shall not be valid and may mislead the readers. To conclude, the authors are of the opinion that a simple economic impact of catalyst addition can be estimated using the current experimental setup; however, such a simple analysis will not depict the real economic impact. The authors have accepted such limitations of this study on Page # 17 of the revised manuscript.

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Response: We thank the reviewer for this suggestion. A brief comparison of thermal amine scrubbing with high-temperature sorbent-based CO<sub>2</sub> capture has been added to the Introduction section.

Comment 4: The catalytic mechanism is better to be included in the highlights.

Response: Thank you very much for this comment. The catalytic mechanism has been added to the highlights for this research article.

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Reply to the comments from Reviewer 4  
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Thank you very much for your time and effort for reviewing our manuscript. Your comments are all useful and we have carefully revised through the manuscript accordingly. We believe the revision succeeded in clarifying the value of our work, and we hope you agree on it.

Comment 1: Many errors/typos can be found throughout the manuscript. Authors should revise it from this point of view. Some examples:

- a. Highlight number 3, please revise as "Mesoporosity and higher acid sites were determined to be the key properties to optimize CO<sub>2</sub> desorption". Authors should also consider the number of characters (see point 2);
- b. Page 25, line 44, please revise as "...αabs is the initial CO<sub>2</sub> loading..."

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Highlight # 3 has been rewritten and the character limit is considered for each highlight. In addition, the typo on Page 25 has also been corrected.

Comment 2: Highlights number 1 and 3 exceed the maximum allowed number of characters (maximum 85 characters, including spaces, per bullet point).

Response: We thank the reviewer for this comment. The authors have modified the highlights for this manuscript with consideration of character limitation.

Comment 3: All the acronyms (MSA, BSA; LAS, etc.) should be defined the first time they are used in the text.

Response: The reviewers makes an excellent suggestion. The acronyms have been defined the first time they were used in the manuscript.

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Reply to the comments from Reviewer 5  
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Comment 1: The pore size distribution curves should be provided to provide detailed information about the treat HZSM-5.

Response: Thank you for this valuable comment. The authors have added pore size distribution curves to the Figure 2 of the revised manuscript.

Comment 2: Relative characteristics of the used catalysts should be measured to confirm the conclusion that the prepared treated HZSM-5 owns good stability.

Response: The reviewer makes an excellent suggestion. The authors have recorded XRD patterns and Py-FTIR spectra of the spent catalysts because we found that the sum of acid sites (Lewis acid sites and Brønsted acid sites) was the most influencing catalytic property enhancing the CO<sub>2</sub> desorption rate. The obtained results are presented below and have been added to the Supporting Information for this article as well. It can be seen from the results that the spent catalysts retained their crystallinity and clear peaks for Lewis acid sites and Brønsted acid sites were also recorded in the Py-FTIR spectra, which indicates that the prepared catalysts are fully stable.

Comment 3: Some mistakes need to be corrected in this paper, and the author should check the whole manuscript carefully.

Response: Thank you for this valuable comment. The authors have got this paper proofread by a native English speaker, and are confident now that the grammatical mistakes and typos have been eliminated.

We are grateful to the reviewers for their valuable comments and suggestion that undoubtedly helped us improving the quality of the submitted manuscript. We sincerely hope that we have addressed all the concerns in a satisfactory manner.

Best regards,

Il Hyun Baek

Principal Researcher, Green Energy Process Laboratory,

Korea Institute of Energy Research, South Korea

Associate Professor,

University of Science and Technology, South Korea



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Nov 5, 2019

Professor Bingcai Pan, Associate Editor  
*Chemical Engineering Journal*  
School of the Environment,  
Nanjing University, Nanjing 210023, China

**Manuscript ID:** CEJ-D-19-12146

**Title:** Catalytic activity of facilely synthesized mesoporous HZSM-5 catalysts for optimizing the CO<sub>2</sub> desorption rate from CO<sub>2</sub>-rich amine solutions

Dear Prof. Pan,

We would like to express our warm gratitude to you and to the reviewers for reviewing the submitted manuscript. The suggestions/comments received from the editorial team and the reviewer have been adequately responded.

I would like to mention that we have added a co-author to the authors list due to his contribution in the preparation of revised manuscript.

I am uploading the revised manuscript along with the annotated manuscript, response to reviewer's comments, revised highlights, and revised Supporting Information for Publication.

In the annotated manuscript, the text highlighted with yellow, red, and green colors indicate the modified, deleted, and added parts, respectively.

Thank you for your kind consideration and I look forward to hearing from you soon.

Best regards,



Dr. Il Hyun Baek  
Principal Researcher, Green Energy Process Laboratory,  
Korea Institute of Energy Research, South Korea.  
Associate Professor  
University of Science and Technology, South Korea

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**Authors:** Umair H. Bhatti, Abdul K. Shah, Amjad Hussain, Hassnain A. Khan, Chan Young Park, Sung Chan Nam, and Il Hyun Baek

Dear Editor,

We would like to express our warm gratitude to you and to the reviewers for reviewing the submitted manuscript. The suggestions/comments from the editorial team and the reviewers are responded as follow.

### **Editorial Comments and Our Response**

**Comment 1:** Supporting Information for Publication should be formatted with a cover sheet listing authors, manuscript title, and the number of pages, figures, and tables.

**Response:** The Supporting Information for Publication has been formatted with a cover sheet as instructed.

## Reviewers' Comments and Our Response

### ----- **Reply to the comments from Reviewer 1** -----

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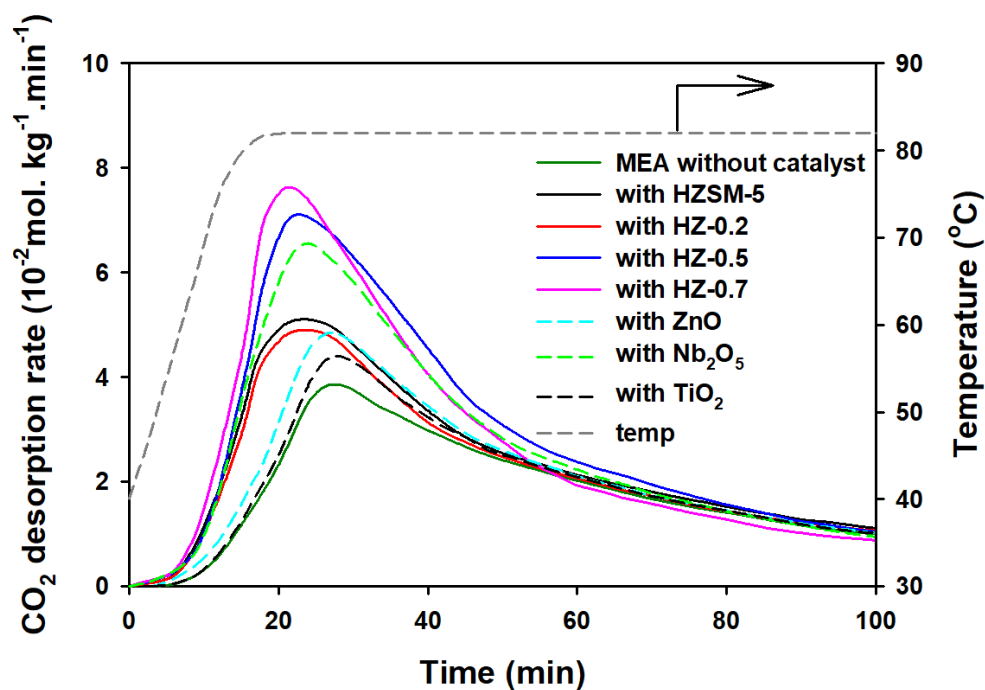
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**Figure 11:** Comparison of CO<sub>2</sub> desorption rates achieved from parent HZSM-5 and synthesized catalysts with previously reported catalysts

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## ----- **Reply to the comments from Reviewer 5** -----

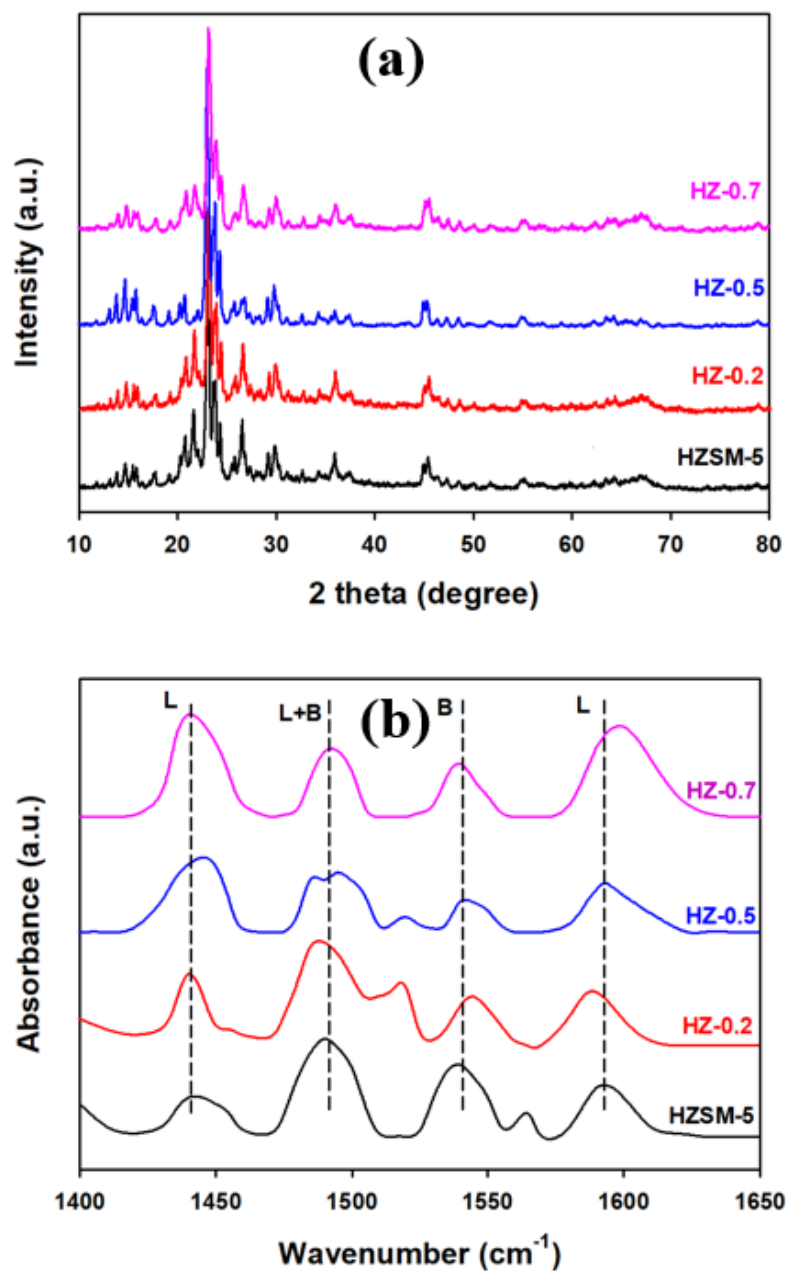
Thank you very much for your time and effort for reviewing our manuscript. Your comments are all useful and we have carefully revised through the manuscript accordingly. We believe the revision succeeded in clarifying the value of our work, and we hope you agree on it.

**Comment 1:** The pore size distribution curves should be provided to provide detailed information about the treat HZSM-5.

***Response:*** Thank you for this valuable comment. The authors have added pore size distribution curves to the Figure 2 of the revised manuscript.

**Comment 2:** Relative characteristics of the used catalysts should be measured to confirm the conclusion that the prepared treated HZSM-5 owns good stability.

***Response:*** The reviewer makes an excellent suggestion. The authors have recorded XRD patterns and Py-FTIR spectra of the spent catalysts because we found that the sum of acid sites (Lewis acid sites and Brønsted acid sites) was the most influencing catalytic property enhancing the CO<sub>2</sub> desorption rate. The obtained results are presented below and have been added to the Supporting Information for this article as well. It can be seen from the results that the spent catalysts retained their crystallinity and clear peaks for Lewis acid sites and Brønsted acid sites were also recorded in the Py-FTIR spectra, which indicates that the prepared catalysts are fully stable.



**Figure I2:** Characterization results of spent catalysts. (a) XRD patterns and (b) Py-FTIR spectra, L and B sites represent Lewis acid sites and Brønsted acid sites.

**Comment 3:** Some mistakes need to be corrected in this paper, and the author should check the whole manuscript carefully.

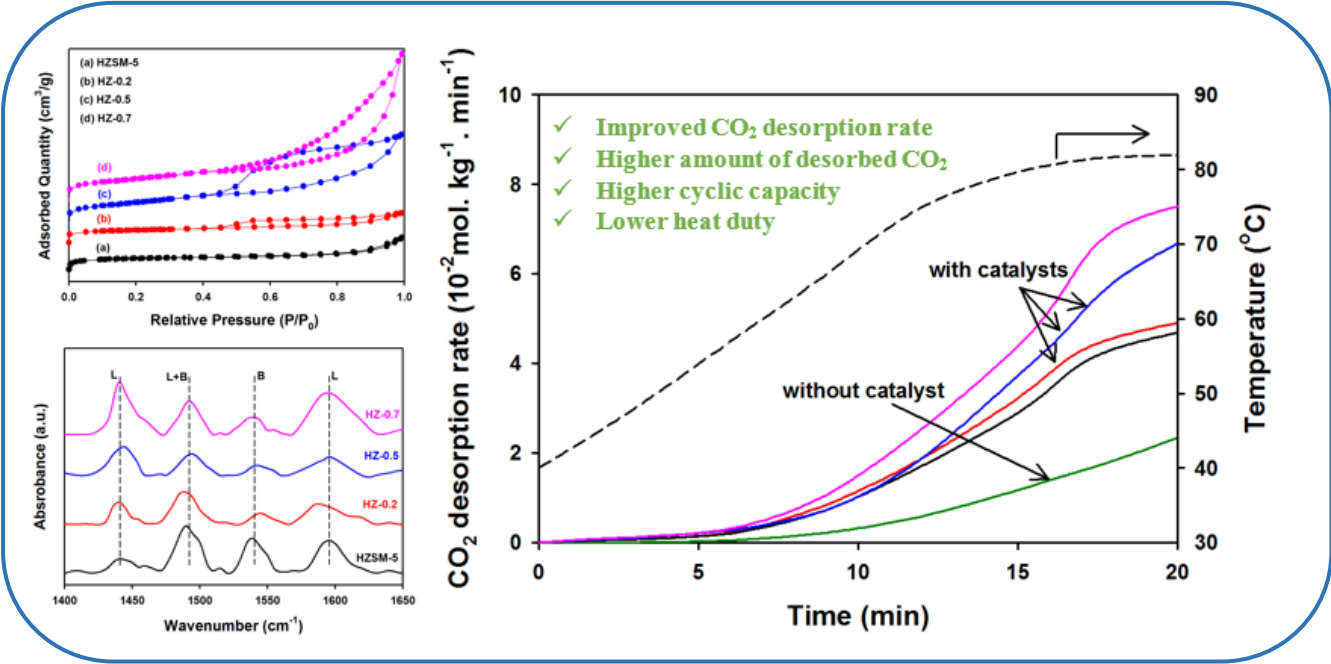
***Response:*** Thank you for this valuable comment. The authors have got this paper proofread by a native English speaker, and are confident now that the grammatical mistakes and typos have been eliminated.

We are grateful to the reviewers for their valuable comments and suggestion that undoubtedly helped us improving the quality of the submitted manuscript. We sincerely hope that we have addressed all the concerns in a satisfactory manner.

Best regards,

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Graphical Abstract/TOC



## HIGHLIGHTS

- Mesoporous HZSM-5 catalysts were prepared to optimize the CO<sub>2</sub> desorption rate.
- The synergistic effect of mesoporosity and acid sites was investigated.
- The synthesized catalyst enhanced the CO<sub>2</sub> desorption rate by 350–580%.
- Modified HZSM–5 catalysts reduced the regeneration energy requirement by 24–37%.
- The plausible reaction mechanism of catalyst facilitated regeneration was proposed.

# **Catalytic activity of facilely synthesized mesoporous HZSM-5 catalysts for optimizing the CO<sub>2</sub> desorption rate from CO<sub>2</sub>-rich amine solutions**

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## ABSTRACT

Post-combustion CO<sub>2</sub> capture using aqueous alkanolamine solutions has a great potential to reduce anthropogenic CO<sub>2</sub> emissions but the large-scale deployment of this technique is hindered due to a highly energy-intensive solvent regeneration mainly because of poor CO<sub>2</sub> desorption kinetics. To overcome this limitation, we synthesized a series of mesoporous HZSM-5 catalysts through facile alkaline desilication and surfactant-induced re-assembly of dissolved species originating from the parent HZSM-5 crystals, and evaluated their performance to optimize the CO<sub>2</sub> desorption rate from benchmark 30 wt. % monoethanolamine (MEA) solution under mild temperature condition (40–82 °C). X-ray diffraction (XRD) patterns showed that the synthesized catalysts retained their crystallinity. Desilication by treatment in the alkaline medium led to a remarkable development of mesoporosity, with an increase in the Brunauer–Emmett–Teller (BET) surface area as well. The experimental results suggested that the synthesized catalysts significantly enhanced the CO<sub>2</sub> desorption rate at low temperatures (up to 350–580% at  $\leq 82$  °C), improved the total amount of desorbed CO<sub>2</sub> up to 60%, and minimized the heat duty by 24–37%. Detailed characterization revealed that the synergistic effect of higher mesoporosity and increased number of Lewis acid sites (LAS) and Brønsted acid sites (BAS) was crucial to improve the CO<sub>2</sub> desorption rate. Based on the characterization and experimental results, a plausible reaction mechanism for catalyst aided CO<sub>2</sub> desorption was also presented. This investigation highlights the role of catalysts in optimizing the CO<sub>2</sub> capture process and presents new understanding for the design of high-performance catalysts for this purpose.

**KEYWORDS:** CO<sub>2</sub> capture; CO<sub>2</sub> desorption rate; Desilication re-assembly; Zeolite; Catalytic solvent regeneration

## HIGHLIGHTS

- Highly efficient mesopores HZSM-5 catalysts were synthesized by desilication re-assembly process.
- The synthesized catalyst enhanced the CO<sub>2</sub> desorption rate by 350–580%.
- Mesoporosity and higher acid sites were determined the key properties to optimize CO<sub>2</sub> desorption.
- Mesoporous HZSM–5 catalysts reduced regeneration heat requirement by 24–37%.
- The plausible reaction mechanism of catalyst facilitated regeneration was proposed.

## 1. Introduction

Rising levels of CO<sub>2</sub> in the atmosphere due to excessive use of fossil fuels have been widely recognized to be a primary contributor to global warming [1]. To keep global warming within 2 °C of pre-industrial levels, a significant amount of CO<sub>2</sub> must be captured prior to its release into the atmosphere [2]. Among various techniques developed for CO<sub>2</sub> capture, post-combustion CO<sub>2</sub> capture has gained significant attention because it can be easily retrofitted to an existing plant and has the operational flexibility during peak electricity demand [3]. The use of solid sorbents such as CaO, MgO, and Li<sub>4</sub>SiO<sub>4</sub> for capturing CO<sub>2</sub> is attractive due to process simplicity. However, poor sorption kinetics and requirement of high temperature for sorbent regeneration are the issues which still need to be addressed before deployment of this approach at commercial scale [4, 5].

To date, thermal amine scrubbing is arguably the most attractive CO<sub>2</sub> capture technique because it is reliable, technically mature, and capable of treating large gas volumes [6–8]. Nevertheless, certain drawbacks of this technology, including high capital cost, highly energy intensive stripper, facility corrosion, and solvent degradation have hindered the worldwide large-scale application of this approach [9–11]. The major energy penalty, accountable for around 70% of the total operating cost, originates from the solvent regeneration step, because a large amount of thermal energy is needed to regenerate the amine solvent at high temperatures around 120–140 °C [12–15].

Despite the considerable improvements made in process intensification to minimize the energy penalty, the inherent drawbacks of amine solvents are considered to be the primary reason for energy intensive operation [16, 17]. In this scenario, enormous efforts have been made to develop less energy intensive solvents. For instance, 2-(ethylamino)ethanol (EAE), 2-

(methylamino)ethanol (MAE), and N,N-dimethylethanolamine (DMEA) have been reported as alternative amine absorbents for energy-efficient CO<sub>2</sub> capture [18–20]. Non-aqueous amine solvents such as mixtures of amine and glycol ethers [21], and biphasic solvents including aqueous monoethanolamine (MEA)/1-propanol and triethylenetetramine (TETA) [22, 23] have also been reported as promising alternate to aqueous amine solutions. Hwang et al. developed and investigated the performance of a water-lean K<sub>2</sub>Sol solvent (a sterically diamine) using a bench-scale pilot plant unit and found that it required 35% lower regeneration energy than that of MEA [24, 25]. Bougie et al. introduced microwave irradiation as an effective alternative to thermal regeneration; and by combining the microwave irradiation concept with non-aqueous MEA solutions they demonstrated that a huge reduction in the solvent regeneration heat duty is possible [26, 27].

Another innovative approach to lower the regeneration energy penalty is the addition of a catalyst that can facilitate carbamate breakdown and subsequent CO<sub>2</sub> release at lower temperatures [28]. The addition of a catalyst was found to improve the CO<sub>2</sub> desorption at low temperatures and thus the temperature of solvent regeneration could be lowered [29–31]. Idem et al. investigated the solvent regeneration performance of MEA without and with two catalysts—HZSM-5 and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>—at 105 °C with initial CO<sub>2</sub> loading of 0.5 mol CO<sub>2</sub>/mol MEA [28, 32]. Their results suggested that both catalysts were effective in optimizing CO<sub>2</sub> desorption and minimizing the solvent regeneration heat duty. Liang et al. advanced this approach by developing various solid acid catalysts including SO<sub>4</sub><sup>-2</sup>/TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>/HZSM-5 and demonstrated that their addition to MEA solvent regeneration step could minimize the regeneration heat requirement by up to 34% [33–35]. In addition to evaluating the impact of catalyst addition on the energy penalty, they highlighted the key physiochemical properties such

as mesoporosity, concentration of acid sites, and Brønsted acid sites that influence the CO<sub>2</sub> desorption performance of a catalyst. Few other catalysts including metal ions and TiO(OH)<sub>2</sub> have also been reported to improve the CO<sub>2</sub> desorption rate at low temperature (<100 °C) [36, 37]. So far, this approach is in early stage and limited to a few catalysts; among which some are expensive and some are difficult to separate. Therefore, it is highly desired to develop more efficient, stable, and inexpensive catalysts that could significantly lower the temperature of the amine regeneration and substantially improve the CO<sub>2</sub> desorption to make this approach economically feasible.

HZSM-5, the most thoroughly studied catalyst for optimizing CO<sub>2</sub> desorption, is however a microporous sieve and has a narrow pore structure and limited mass transfer rate, which means that the access of CO<sub>2</sub> containing species to the active sites would be limited [38–40]. It is possible that if the key properties of HZSM-5 such as mesoporosity, acidity, and acid sites, could be improved, the catalytic performance would also improve accordingly.

Desilication in an alkaline medium is an effective method to improve the physiochemical properties of HZSM-5 including mesoporosity and surface acidity [41, 42]. With the aim of improving the key physiochemical properties of HZSM-5, we prepared a series of HZSM-5 catalysts using an alkaline desilication and surfactant induced re-assembly process under optimized process conditions. The prepared materials were thoroughly characterized using X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), Scanning electron microscope (SEM), ammonia temperature programmed desorption (NH<sub>3</sub>-TPD), and pyridine-adsorption infrared spectroscopy (Py-IR). The performance of the synthesized catalysts was then evaluated in CO<sub>2</sub> desorption experiments using CO<sub>2</sub>-rich MEA solution under a mild temperature range e.g. 40–82 °C. Furthermore, the impact of various physicochemical properties on the CO<sub>2</sub> desorption

performance was evaluated and used to draw the plausible reaction mechanism for the catalyst-aided solvent regeneration process. In addition, the stability of the synthesized catalysts was studied in five cyclic solvent regeneration experiments.

The originality and novelty of this work include (i) synthesis of a series of mesoporous HZSM-5 catalysts and their addition to the CO<sub>2</sub>-rich MEA solution to minimize the solvent regeneration heat duty (ii) evaluation of the catalytic performance in terms of cyclic capacity, CO<sub>2</sub> desorption rate, and regeneration heat duty (iii) investigation of the impact of various physicochemical properties of the catalysts on CO<sub>2</sub> desorption performance and (iv) analysis of the CO<sub>2</sub> desorption mechanism of mesoporous HZSM-5 catalyst facilitated amine solvent regeneration.

## **2. Experimental section**

### **2.1. Materials:**

Monoethanolamine (MEA, 99%, Acros), Cetyltrimethylammonium bromide (CTAB, >98%, Sigma-Aldrich), Sodium Hydroxide (NaOH, 97%, Sigma-Aldrich), and NH<sub>4</sub>-ZSM-5 (Zeolyst International, USA) were used as received. N<sub>2</sub> and CO<sub>2</sub> gases (99.999%) were purchased from Korea Nano Gas Co. Ltd.

### **2.2. Preparation of the catalysts:**

A series of hierarchical zeolite catalysts were prepared using the modified desilication re-assembly process [40]. This post-synthetic process had two main stages: desilication of the zeolite and ion-exchange with calcination after each stage. NH<sub>4</sub>-ZSM-5 was calcined at 550 °C for 5 h and used as the base material. Initially, a solution of organic surfactant CTAB (0.05 M, 20 mL/g zeolite) and different molar amounts of NaOH (0.2, 0.5, and 0.7 M, 20 mL/g zeolite) were prepared and poured into a round bottom reactor, mixed, and heated to 80 °C. Then,

immediately, a specific amount of HZSM-5 (20 mL/g) was poured into the reactor, and desilication of zeolite was carried out under continuous stirring (500 rpm) and reflux conditions for 12 h. Afterwards, the zeolite desilication reaction was stopped by ice quenching method and the solids were washed with DI water and dried at 120 °C for 8 h. The prepared samples were calcined for 5 h in static air at 550 °C at a heating rate of 5 °C/min to remove of the pore directing agent coating in order to create mesopores on the exterior surface of the zeolite. After that, the samples were further ion-exchanged with ammonium nitrate three times (0.5 M  $\text{NH}_4\text{NO}_3$ , 20mL/g, 60 °C, 2h) under reflux conditions, then washed with DI water, dried and calcined at 550 °C for 5h in order to get proton form of the hierarchical zeolites. The prepared samples were labeled HZ-0.2, HZ-0.5 and HZ-0.7, where the HZ coding represents the hierarchical zeolite and the 0.2, 0.5, and 0.7 coding indicates the respective concentrations of alkali (NaOH) used in the desilication of the zeolite.

### **2.3. CO<sub>2</sub> desorption experiments:**

CO<sub>2</sub> was absorbed in 30 wt. % MEA solution at typical absorber conditions (15 Vol. % CO<sub>2</sub>, 40 °C) using a continuous stirrer tank reactor (CSTR). The feed gas (85% N<sub>2</sub>, 15% CO<sub>2</sub>) was bubbled into the reactor (1 L/min) and the outlet gas was analyzed using a gas chromatograph (Agilent Technologies, 7890A). The absorption experiments were ended when the CO<sub>2</sub> concentration in the outlet gas was equal to the inlet concentration, i.e., 15 vol. %. The CO<sub>2</sub> loading values of the amine solutions were determined with a total organic carbon analyzer (TOC analyzer, Analytik Jena multi N/C 3100). For TOC analysis, the amine samples were diluted with DI water with a dilution ratio of 1:599 (amine: water) and exactly 500 µL of the prepared samples were injected to the analyzer, where the samples undergo catalytic combustion

and a Focus Radiation-Nondispersive Infrared Detector (FR-NDIR) detector detects the released CO<sub>2</sub>.

The solvent regeneration was studied using the experimental setup shown in Fig. 1. Briefly, a glass reactor of 250 mL capacity was used in this study. An oil circulator was attached to heat the amine solution and maintain desired temperature. A pressure gauge and a K-type thermocouple were used to record reactor inside pressure and the temperature of the amine solution. The solution was continuously stirred at 300 rpm using a magnetic bar while a condenser was mounted to condense and reflux water and amine vapors. The energy consumption of the CO<sub>2</sub> desorption experiments was determined using an electric energy meter (ADPOWER HP-100A). The electric energy for the heating oil circulator was provided through the electric energy meter and the electricity consumption was started to record once the temperature of the amine solution in the reactor reached 40 °C. Employed this way, the electric energy consumption for each experiment was recorded and then divided by the total amount of released CO<sub>2</sub> from respective experiments to obtain the heat duty value in kJ/mol CO<sub>2</sub> units. For each experiment, 100 g of CO<sub>2</sub>-rich MEA solution was added to the reactor and heated using the oil circulator. A pure stream of CO<sub>2</sub> gas was released when the amine solution was heated, which was mixed with N<sub>2</sub> gas (100 mL/min) before its analysis in the GC. In this way, the CO<sub>2</sub> in the outgassed stream was recorded as a function of time and temperature. In addition, liquid samples (~1 mL) were also taken every 20 minutes during the solvent regeneration experiments and the CO<sub>2</sub> loading values were determined using TOC analyzer. For catalytic experiments, 5 g of respective catalyst was added to 100 g amine solution at the start of the experiment at room temperature. Before each experiment, all pipelines and the reactor were purged with N<sub>2</sub> gas to remove any residual CO<sub>2</sub>. Each experiment had a temperature ramp-up stage in which the



temperature of the amine solution was continuously raised and the desired temperature point (i.e., 82 °C) was achieved, and an isothermal stage in which the temperature was kept constant at 82 °C for approximately 1.5 h. Using the ramp up stage, the effects of the catalysts on the CO<sub>2</sub> desorption rate can be recorded at lower temperatures (i.e., <82 °C).

#### **2.4. Characterization of the catalysts:**

The crystalline structure of the catalysts was analyzed by XRD (Rigaku D/max 2200PC diffractometer). The XRD patterns of the parent and desilicated zeolites are shown in Fig. 2a. All samples exhibited characteristic diffraction peaks of HZSM-5 (JCPDS: 44-0003) at  $2\theta$  of 14.8°, 23.1°, 23.9°, 24.4°, 30.1°, suggesting that the crystalline structure was well-maintained during alkaline treatment [43].

The nitrogen physisorption isotherms of the parent zeolite and modified zeolites are shown in Fig. 2b and the textural properties of the catalysts are summarized in Table 1. The parent zeolite had a type I isotherm, typical of microporous materials, with high nitrogen uptake at low pressures due to the interaction of the pore walls with the adsorbate and a plateau at high relative pressure [41]. The isotherms of all the alkaline treated materials were of type IV, typical for hierarchical materials. The alkaline treated materials showed higher nitrogen uptake at pressures higher than  $p/p_0=0.4$ , indicating the formation of new mesopores [44]. For the HZ-0.5 and HZ-0.7 catalysts, a sharp increase in nitrogen uptake was observed at  $p/p_0=0.4-1.0$ , indicating the abundance of mesopores.

The surface acidity of the parent and modified zeolites was determined by NH<sub>3</sub>-TPD. The obtained NH<sub>3</sub> desorption patterns are shown in Fig. 3a and the quantitative acidity values (mmol/g) are provided in Table 2. From Fig. 3a, two obvious peaks can be seen for all the

catalysts. The first peak appearing at low temperature around 130 °C indicates the weak acidic sites and the other at high temperature around 405 °C is ascribed to the strong acidic sites [44]. For all the desilicated samples, the NH<sub>3</sub> uptake at low temperature was higher than the parent HZSM-5 due to the extracted amount of Si leading to a lower Si/Al ratio and therefore a higher density of acid sites. However, a decrease in the strong acid sites was observed for all of the treated samples that is in accordance with the previous literature reports [40]. From the Table 2, it can be seen that the desilication re-assembly process enhanced the acidity of the catalysts. The overall trend in surface acidity was in the order of: HZSM-5 < HZ-0.2 < HZ-0.5 < HZ 0.7.

The pyridine adsorption IR technique was used to determine the nature of the acid sites. Pyridine molecules can attach to unsaturated metal sites (i.e., Lewis acid sites) resulting in the formation of LPy species. The LPy corresponding peaks appear at around 1440 and 1580 cm<sup>-1</sup>. At the same time, the pyridine molecules can react with proton donor sites on the surface OH groups (i.e., Brønsted acid sites) and show characteristic peaks at 1540 and 1630 cm<sup>-1</sup> [45–47]. The peak appearing at 1490 cm<sup>-1</sup> indicates the presence of Lewis acid sites (LAS) and Brønsted acid sites (BAS). The Py-IR spectra of the parent zeolite and synthesized catalysts are shown in Fig. 3b and the quantitative values for the acid sites are given in Table 2. For all the samples, distinctive peaks were recorded at around 1440, 1490, 1540, 1580, and 1630 cm<sup>-1</sup> indicating the presence of both types of acid sites i.e., Lewis acid sites (LAS) and Brønsted acid sites (BAS) on the catalysts.

### **3. Results and Discussion**

#### **3.1. CO<sub>2</sub> desorption performance**

The regeneration performance of CO<sub>2</sub>-rich MEA solution without and with all four catalysts is presented in Fig. 4. The CO<sub>2</sub> desorption from MEA without catalyst solution was limited at the start of the experiment at lower temperature (Fig. 4a and 4b). However, from 65 °C onwards, a

noticeable amount of CO<sub>2</sub> desorption was observed which kept on improving and reached the peak value of 3.85 (10<sup>-2</sup> mol. kg<sup>-1</sup>. min<sup>-1</sup>) at 82 °C and 27 min. All of the catalysts improved the CO<sub>2</sub> desorption rate and started to desorb noticeable amounts of CO<sub>2</sub> from 54 °C onwards. At lower temperatures the HZSM-5 noticeably improved the CO<sub>2</sub> desorption rate and achieved the peak CO<sub>2</sub> desorption rate value of 5.12 (10<sup>-2</sup> mol. kg<sup>-1</sup>. min<sup>-1</sup>) at 82 °C and 23 min. For the modified catalysts, the performance of HZ-0.2 was slightly poorer than that of the HZSM-5 but HZ-0.5 and HZ-0.7 substantially improved the CO<sub>2</sub> desorption rates. The inferior performance of the HZ-0.2 can be attributed to the presence of fewer acid sites and in particular limited Brønsted acid sites, which play a key part in the initial stage of the CO<sub>2</sub> desorption experiment. The HZ-0.5 and HZ-0.7 catalytic solutions desorbed greater amounts of CO<sub>2</sub> at lower temperatures and achieved peaks CO<sub>2</sub> desorption rates of 7.06 and 7.62 (10<sup>-2</sup> mol. kg<sup>-1</sup>. min<sup>-1</sup>) at 23 and 20 min, respectively. This is because these two catalysts were highly mesoporous and essentially possessed higher number of acid sites. This meant that more of the active sites were accessible and thus the chances of carbamate, carbonate, or bicarbonate colliding with the active sites was higher, resulting in faster CO<sub>2</sub> desorption. Consequently, the CO<sub>2</sub> was released at higher desorption rates from the HZ-0.5 and HZ-0.7 catalytic solutions.

The catalytic performance trend in term of CO<sub>2</sub> desorption rate was found to be HZ-0.7 > HZ-0.5 > HZSM-5 > HZ-0.2 > no catalyst. It should be noted that all of the catalysts improved the CO<sub>2</sub> desorption rate at lower temperatures and minimized the time of peak CO<sub>2</sub> desorption value. This is because in the non-catalytic solution, CO<sub>2</sub> desorption is entirely dependent on the provided thermal energy. When a certain amount of thermal energy is available to the solution, it carries out the endothermic CO<sub>2</sub> desorption reactions, and ultimately releases CO<sub>2</sub>. In contrast, in the catalytic solutions, the CO<sub>2</sub> is released via a combination of thermal energy and the

facilitation of the active acid sites. Below 64 °C, there was almost no CO<sub>2</sub> desorption from the non-catalytic system. The reason for this is because at those temperatures the available thermal energy was insufficient to break bonds and release CO<sub>2</sub>. However, as we can see for the catalytic solvents, the CO<sub>2</sub> is being desorbed at temperatures below 64 °C, which clearly indicates that the catalysts are facilitating CO<sub>2</sub> desorption by lowering the activation energy.

In addition to enhancing the CO<sub>2</sub> desorption rate, the catalytic solutions also released greater amounts of CO<sub>2</sub> that is highly advantageous in minimizing the amine solution regeneration heat duty. Since the heat duty of amine solvent regeneration is defined by the amount of CO<sub>2</sub> released per amount of energy provided during regeneration, the release of higher amount of CO<sub>2</sub> against unit energy supply will decrease the process heat duty. The improvements in the total amount of CO<sub>2</sub> desorbed during the regeneration experiments and the subsequent reduction in the solvent regeneration heat duty are shown in Fig. 5 and Table 3. It should be noted that the recorded heat duty was higher than the actual values. This is because the solvent regeneration experiments were conducted in a simplified batch reactor without insulators. The HZSM-5 solution desorbed around 31% greater amount of CO<sub>2</sub> and reduced the heat duty by around 29%. The synthesized catalysts increased the total amount of desorbed CO<sub>2</sub> by 24-60% and minimized the energy consumption by up to 37%. It should be noted that as the solvent regeneration experiments were performed using a semi-batch reactor and the heat duty was recorded using an electric energy meter, the obtained values for heat duty and energy saving due to catalyst addition cannot truly depict the practical stripping column.

### **3.2. Effect of various physicochemical properties:**

Previous studies on HZSM-5 aided solvent regeneration have shown that several physicochemical properties of the catalyst favor catalytic performance during solvent

regeneration [35]. In this study, as the HZSM-5 was post-treated with the aim of improving key physicochemical properties, it was necessary to analyze the effects of these properties on CO<sub>2</sub> desorption performance. Both the effects of a single property (total surface acidity) and combinations of various properties [MSA×total surface acidity, MSA×BAS, MSA× (LAS+BAS), and total acid sites (LAS+BAS)] were evaluated to understand the mechanism of catalyst facilitated solvent regeneration. The studied properties are listed in Table 4 and the obtained results are presented in Fig. 6.

Panels A and B of Fig. 6 show the influence of total surface acidity and a combination of mesoporous surface area (MSA) and total surface acidity (MSA×total surface acidity) on the overall amount of CO<sub>2</sub> desorbed during the solvent regeneration experiments. The results show that increase in total surface acidity and MSA×total surface acidity can improve CO<sub>2</sub> desorption performance. However, the trend was not linear. In fact, some catalysts with higher values of total surface acidity and MSA×total surface acidity desorbed less CO<sub>2</sub> than the ones having lower surface acidity and MSA×total surface acidity values. For example, the HZ-0.7 and HZ-0.2 catalysts had higher surface acidity and MSA×total acidity values than the HZ-0.5 and HZSM-5 catalysts, respectively. However, the amounts of CO<sub>2</sub> desorbed from the HZ-0.7 and HZ-0.2 catalytic solutions were lower than the amounts desorbed from the HZ-0.5 and HZSM-5 catalytic solutions, respectively. Fig. 6c shows how the combination of Mesoporous surface area and Brønsted acid sites (MSA×BAS) influenced the CO<sub>2</sub> desorption performance. The influence of MSA×BAS was valid for the HZ-0.5 and HZ-0.7 catalysts but invalid for the HZSM-5 and HZ-0.2 catalysts. This could be because the HZ-0.2 catalyst had far less Brønsted acid sites than HZSM-5 (0.099 mmol/g for HZ-0.2 while the HZSM-5 had 0.268 mmol/g). Nevertheless, the Mesopore area of the HZ-0.2 was higher than the Mesopore area of the HZSM-5 (163.3

m<sup>2</sup>/g for HZ-0.2 while 47.3 m<sup>2</sup>/g for HZSM-5). This shows that mesoporosity can improve the CO<sub>2</sub> desorption performance by providing better access to the active sites. However, the concentration of active sites is more important. Previous studies have also shown that a higher concentration of Brønsted acid sites is more effective, even when the Mesopore surface area is low [30, 48].

Panel d of Fig. 6 shows the influence of total acid sites (LAS+BAS) on the CO<sub>2</sub> desorption performance. A linear relation between the total acid sites (LAS+BAS) and the total amount of desorbed CO<sub>2</sub> was observed. It has been reported that the Brønsted acid sites are more effective at the initial stage of the experiments because at that point (i) the concentration of carbamate is higher and (ii) bicarbonate and carbonate are also present in the system at CO<sub>2</sub> loadings above 0.42 mol CO<sub>2</sub>/mol MEA [48, 49]. The Brønsted acid sites can provide protons to the carbamate, bicarbonate, and carbonate and thereby release significant amounts of CO<sub>2</sub> at an early stage of the experiment. However, as the experiments progress, the concentration of carbamate becomes low and the bicarbonates and carbonates are not present. At that stage, the presence of Lewis acid sites becomes more effective. Therefore, when we consider the total amount of CO<sub>2</sub> released from the entire experiment (ramp-up stage and isothermal stage), the sum of LAS and BAS become equally important and thus a linear dependence on the aggregate of LAS and BAS was observed.

### **3.3. Impact on solvent cyclic capacity**

CO<sub>2</sub> capture using amine-based solvents is a continuous absorption/regeneration cyclic process. The aqueous amine solution absorbs the CO<sub>2</sub> in the absorber column and then this CO<sub>2</sub>-rich solution is sent to the stripper column to release CO<sub>2</sub>. In the stripper, CO<sub>2</sub>-rich solution is thermally treated to release a certain amount of CO<sub>2</sub> and the CO<sub>2</sub>-lean solvent is then pumped

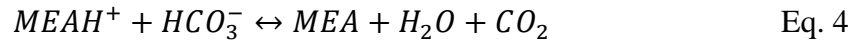
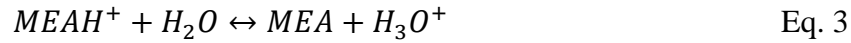
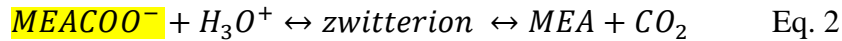
back to absorber column. A solvent that achieves a lower CO<sub>2</sub>-lean loading in the stripper will have more CO<sub>2</sub> intake capacity in the absorber. Furthermore, it has been determined that an energy-efficient solvent is the one that can release fair amounts of CO<sub>2</sub> in the stripper column at mild temperatures [50]. Because the catalytic regeneration of the amine solvent enhanced the CO<sub>2</sub> desorption rate and total amount of desorbed CO<sub>2</sub>, it was important to evaluate the impact of catalytic regeneration on the solvent's cyclic capacity as well. By definition, the cyclic capacity is the difference between the CO<sub>2</sub>-rich loading and CO<sub>2</sub>-lean loading. In this work, the cyclic capacity was defined as the difference between the initial CO<sub>2</sub> loading at the start of the experiments and the CO<sub>2</sub>-lean loadings at the end of the regeneration experiments, and was calculated using Eq. 1.

$$Q_{cyc} = \alpha_{abs} \left[ \frac{mol\ CO_2}{mol\ MEA} \right] - \alpha_{strp} \left[ \frac{mol\ CO_2}{mol\ MEA} \right] \quad \text{Eq. 1}$$

where  $Q_{cyc}$  is the solvent cyclic capacity (mol CO<sub>2</sub>/mol MEA),  $\alpha_{abs}$  and is the initial CO<sub>2</sub> loading, and  $\alpha_{strp}$  is the CO<sub>2</sub> loading at the end of the regeneration experiments. All four catalysts desorbed greater amounts of CO<sub>2</sub> than the non-catalytic solution and thus improved the solvent cyclic capacity accordingly (Fig. 7). The minimum improvement of around 31% was made by the HZ-0.2 catalyst while the HZ-0.5 catalyst achieved the maximum improvement of around 60%. A higher cyclic capacity is highly favorable for an efficient CO<sub>2</sub> capture process because a solvent with higher cyclic capacity will require a lower solvent circulation rate. The improvement in solvent cyclic capacity occurred because the catalytic solutions provided active sites and released CO<sub>2</sub> at a higher desorption rate at low temperatures. On the other hand, the CO<sub>2</sub> desorption from the non-catalytic solution entirely depended on the thermal energy provided and was limited under the studied temperature range.

### 3.4. Catalytic mechanism

The most widely accepted reaction mechanism for CO<sub>2</sub> absorption/desorption in a primary amine solution is via two step zwitterion formation [49]. The two main reaction pathways for regenerating amine solvent are carbamate breakdown and amine deprotonation. The difficulty with solvent regeneration arises from the fact that both carbamate breakdown and amine deprotonation are highly endothermic reactions (Eq. 2–4) [51]. For the carbamate breakdown, protons are required to form zwitterions and subsequently release CO<sub>2</sub> as shown in Eq. 2. The required protons can be provided by H<sub>3</sub>O<sup>+</sup> but again the formation of H<sub>3</sub>O<sup>+</sup> via proton transfer from MEAH<sup>+</sup> to H<sub>2</sub>O is energy demanding (Eq. 3) [38]. Consequently, the lack of H<sup>+</sup> in the system to take part in the carbamate breakdown reaction, and the endothermic nature of the reactions, makes it difficult to regenerate amine solution at lower temperatures.



The catalysts can provide protons (H<sup>+</sup>) or metal atoms (Al) that can attach to the N atom of the carbamate and subsequently change the configuration from sp<sup>2</sup> to sp<sup>3</sup>. As a result, the N–C bond will be stretched and the carbamate would split into MEA and CO<sub>2</sub> [28]. A plausible reaction mechanism for the HZSM–5 catalyst aided amine solvent regeneration is presented in Fig. 8.

At CO<sub>2</sub> loadings above 0.42 mol CO<sub>2</sub>/mol MEA (as in our case where the initial CO<sub>2</sub> loading was 0.51 mol CO<sub>2</sub>/mol MEA) bicarbonate and carbonate are also present in the system



[35, 49]. Both the bicarbonate and carbonate can receive protons and quickly release  $\text{CO}_2$  as shown in Eq. 5 and 6. At the start of the experiments, the catalytic efficiency was remarkable because the concentration of carbamate was high, and especially  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  were also present in the system. With a greater number of  $\text{CO}_2$  containing species present in system, the chance of acid sites colliding with carbamate, bicarbonate, and carbonate is higher, which leads to a substantial improvement in  $\text{CO}_2$  desorption at lower temperatures. In this way, from catalytic solutions,  $\text{CO}_2$  can be released at low temperatures and thus the solvent regeneration temperature can be reduced.

#### 4. Conclusions

In this study, hierarchical HZSM-5 zeolites were post-synthesized by alkaline desilication and surfactant induced reassembly process. The synthesized catalysts had higher BET surface area, mesoporosity, and surface acidity. The catalytic performance of the parent HZSM-5 and the synthesized catalysts were then tested for  $\text{CO}_2$  desorption using a  $\text{CO}_2$ -rich MEA solution in the temperature range of 40–82 °C. All catalysts optimized the MEA solvent regeneration performance by improving  $\text{CO}_2$  desorption rate, overall amount of desorbed  $\text{CO}_2$ , and solvent cyclic capacity. In addition, the heat duty of the amine regeneration was significantly decreased because the catalytic solutions desorbed greater amounts of  $\text{CO}_2$  under same operating conditions. Among the synthesized catalysts, HZ-0.2 had inferior performance than the parent HZSM-5 because the total concentration of acid sites on HZ-0.2 was lower than that of HZSM-5. Whereas, the HZ-0.5 and HZ-0.7 catalysts showed superior performance to HZSM-5 catalyst because of higher mesoporosity and optimized acid sites concentration. The effects of physicochemical properties of the catalysts on  $\text{CO}_2$  desorption were evaluated and it was found

that an increase in the total surface acidity and sum of Lewis acid sites and Brønsted acid sites improved CO<sub>2</sub> desorption from CO<sub>2</sub>-rich amine solution that consequently lowered the heat duty.

### **Supporting Information:**

Material characterization, SEM images of parent and synthesized catalysts, improvement in CO<sub>2</sub> desorption rate made by all four catalyst, and reusability of the catalysts

### **Acknowledgement:**

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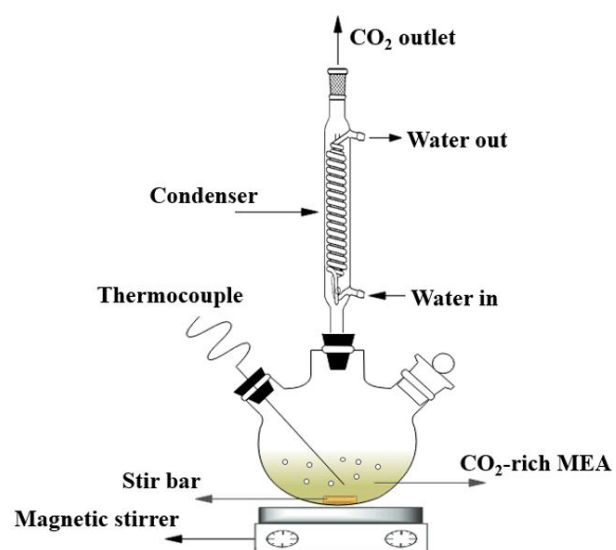
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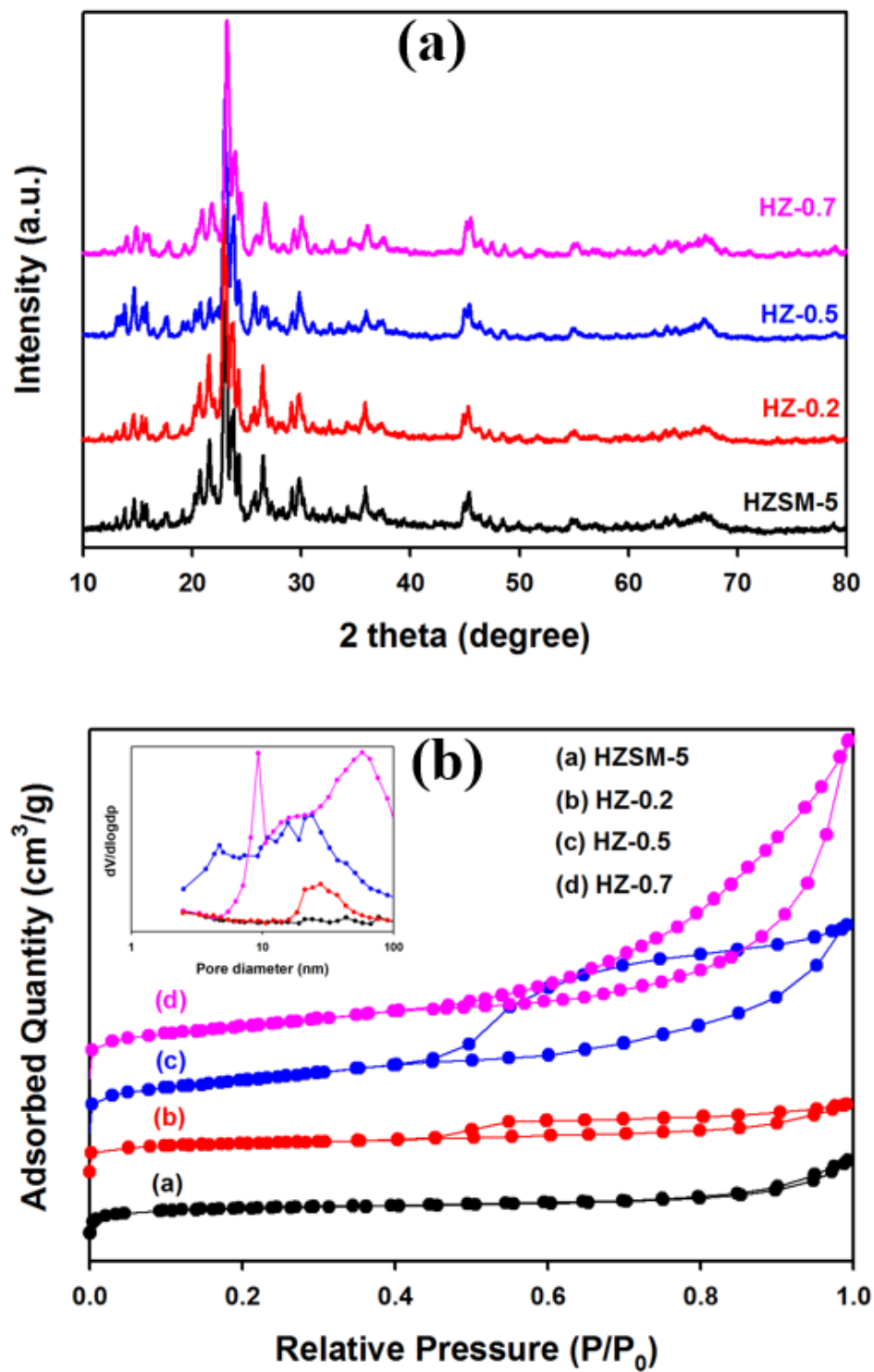
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## Manuscript figures

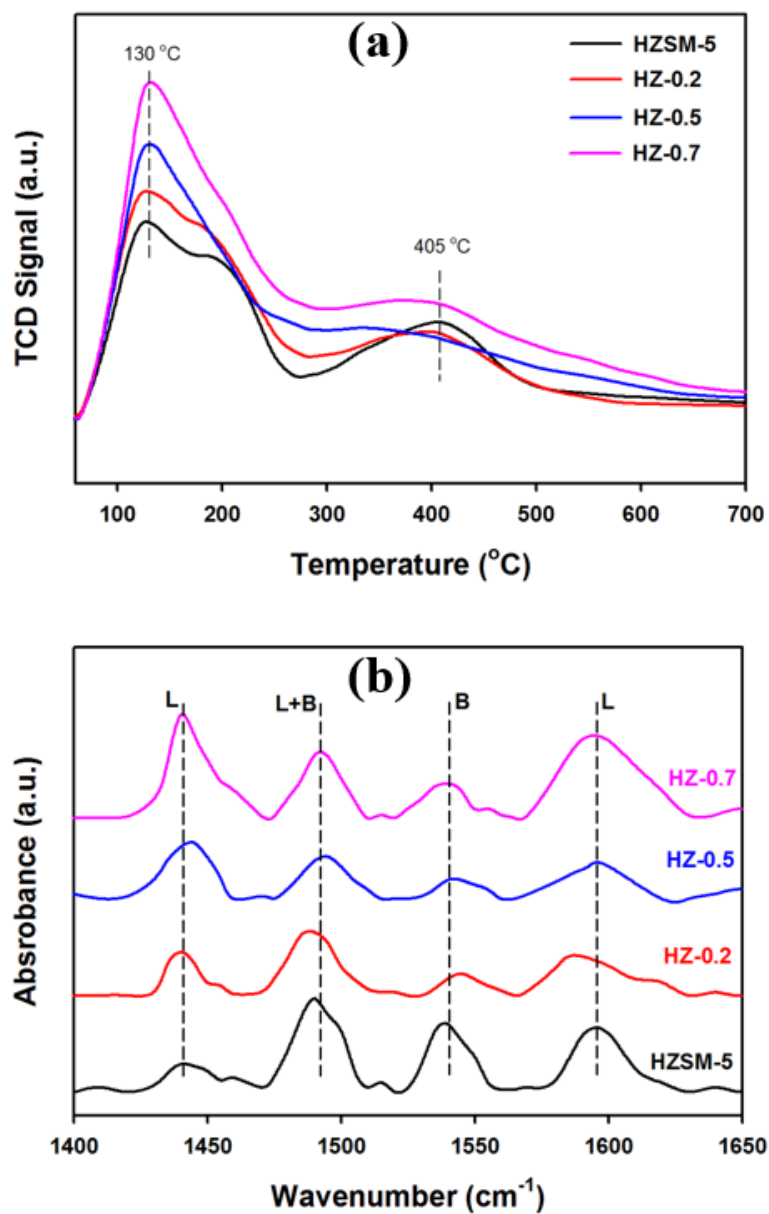


**Figure 1:** Schematic diagram of the experimental apparatus

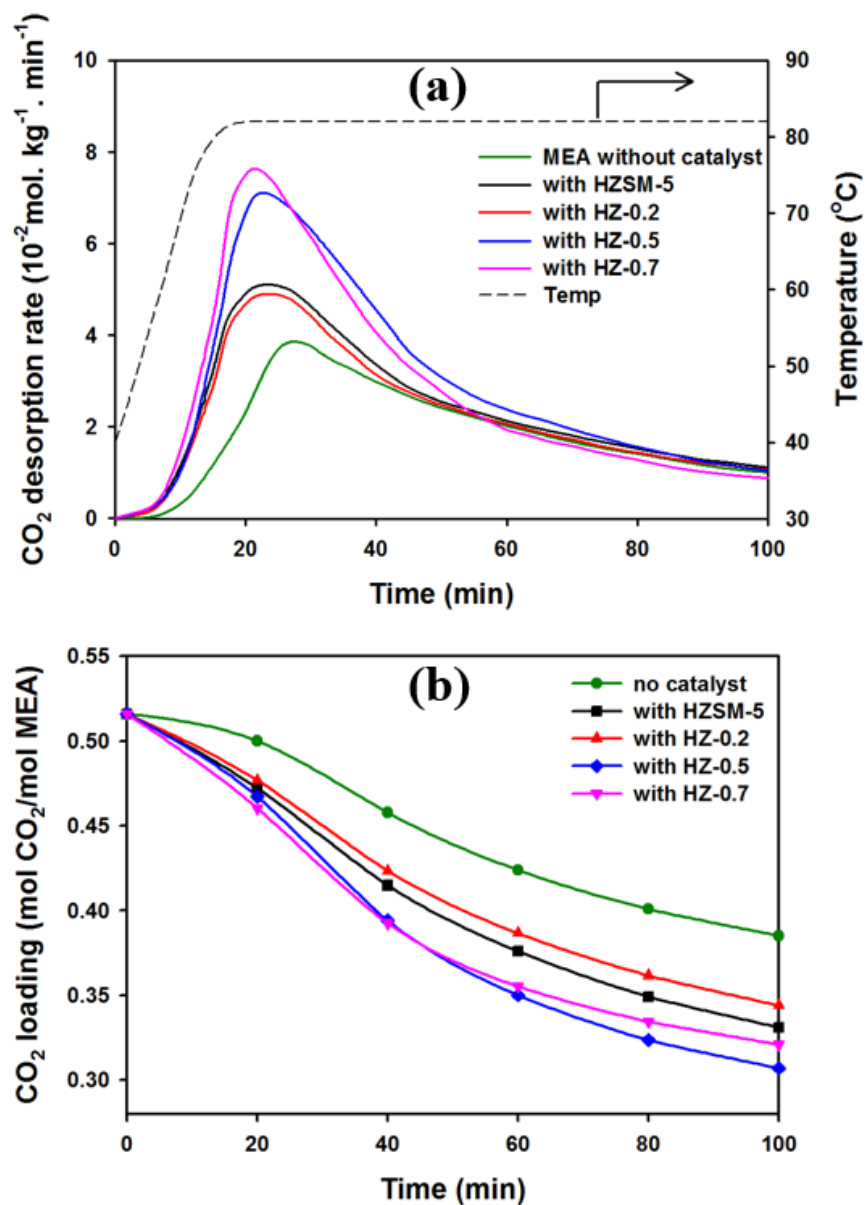




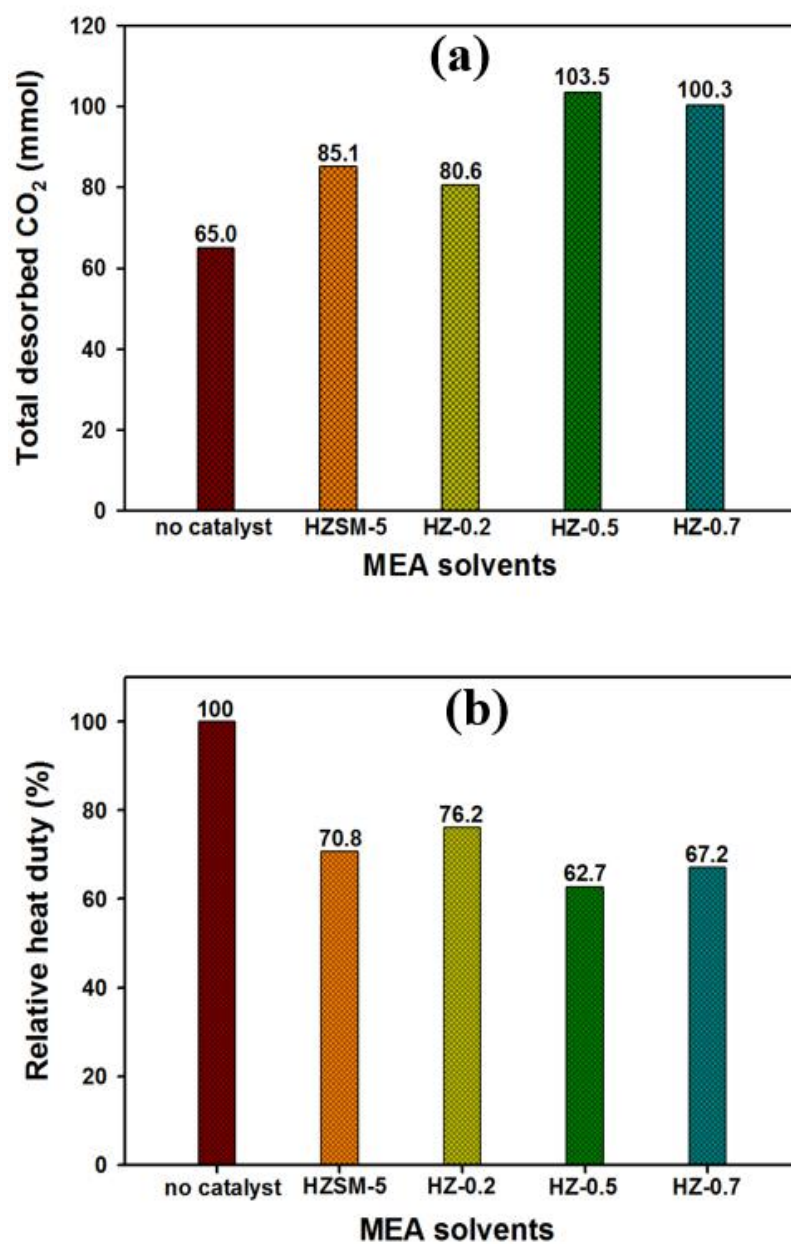
**Figure 2:** Characterization of the parent HZSM-5 and the prepared catalysts (a) XRD patterns (b) Nitrogen adsorption-desorption isotherms (inset: pore size distribution curves).



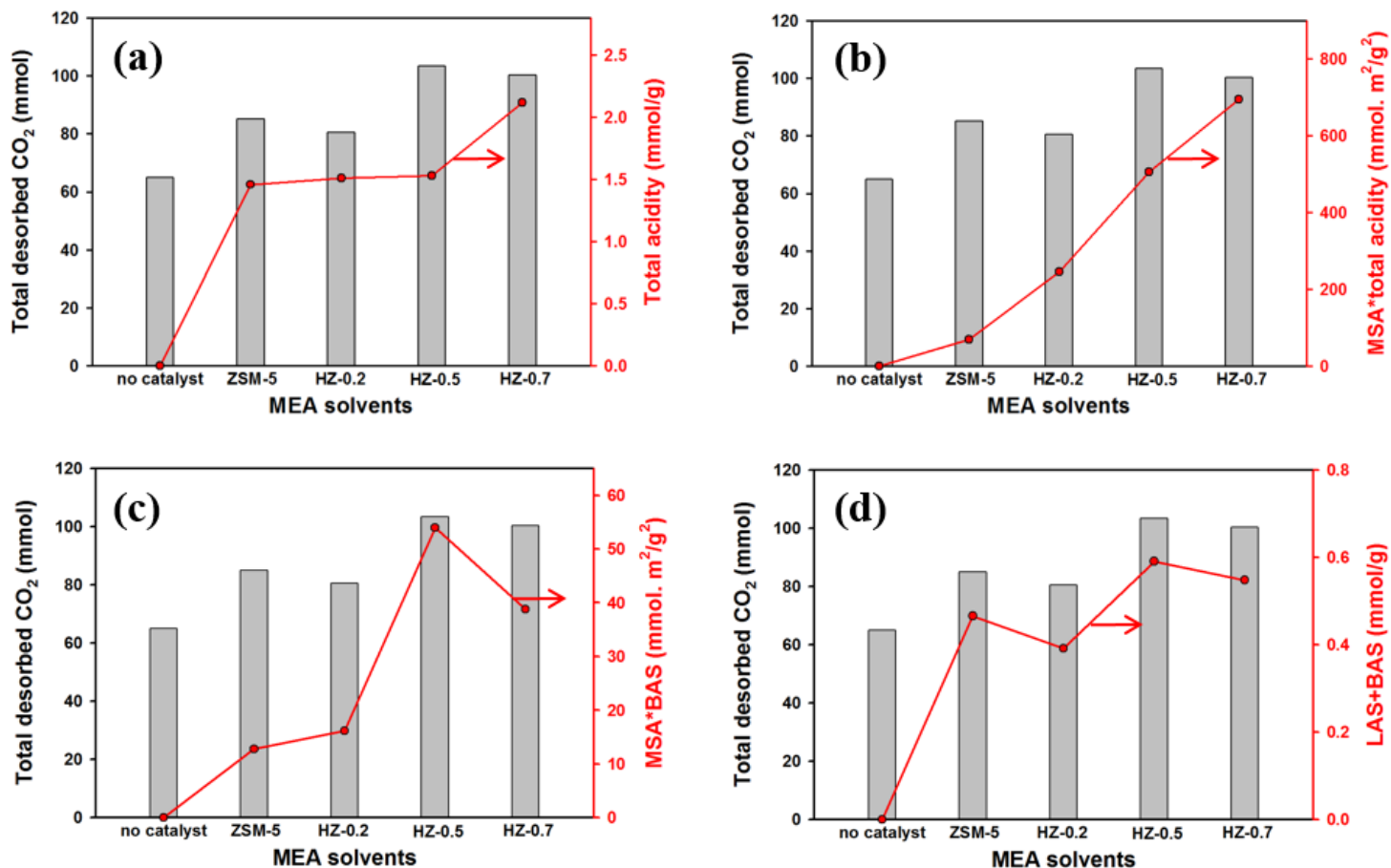
**Figure 3:** Characterization of the parent HZSM-5 and prepared catalysts (a)  $\text{NH}_3$ -TPD acidity profiles (b) Py-FTIR spectra, L and B sites represent Lewis acid sites and Brønsted acid sites.



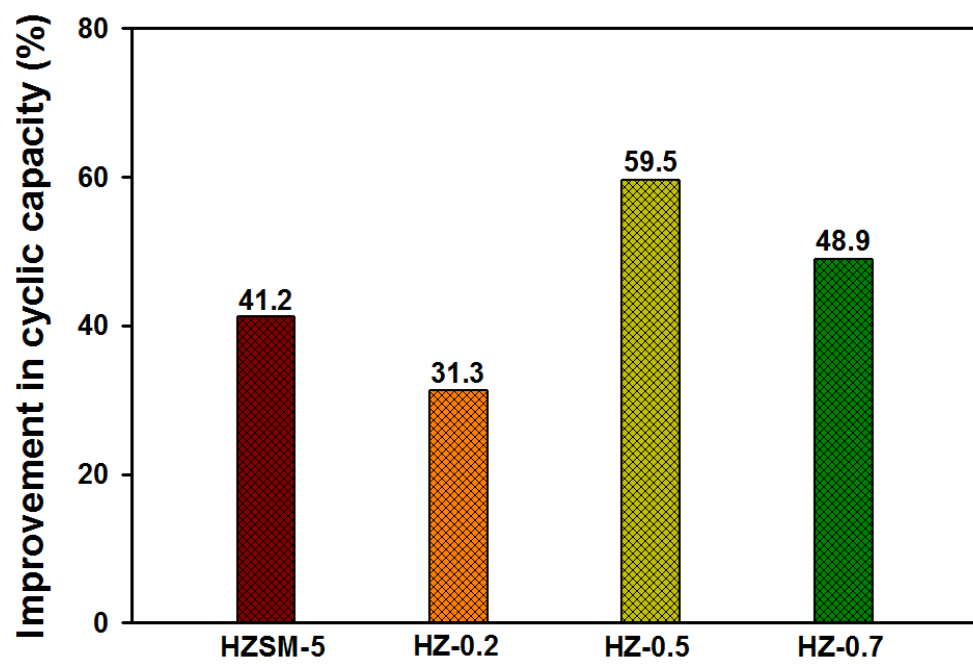
**Figure 4:** CO<sub>2</sub>-rich MEA solution regeneration performance without and with all catalysts (a) CO<sub>2</sub> desorption rate curves (b) CO<sub>2</sub> loadings of MEA solutions during the regeneration experiments without and with catalysts



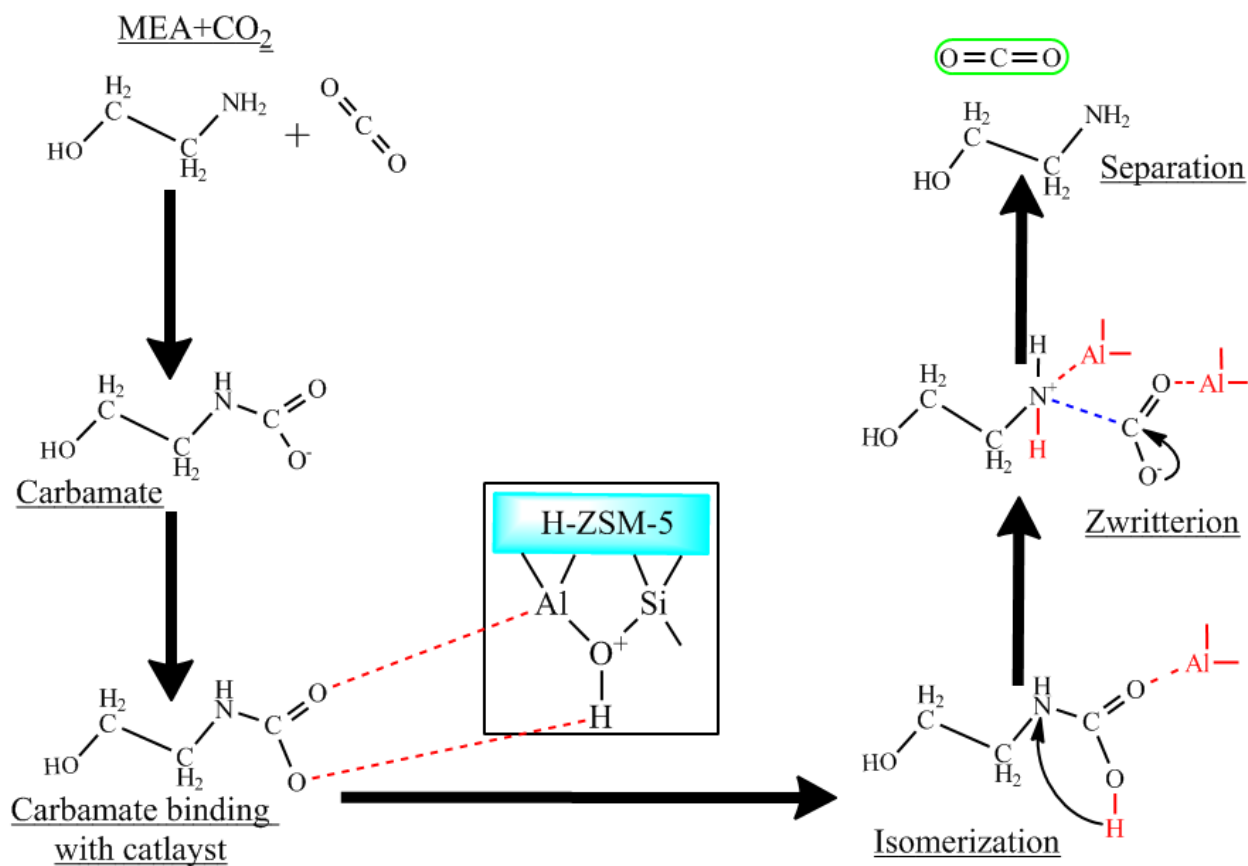
**Figure 5:** CO<sub>2</sub>-rich MEA solution regeneration performance without and with all catalysts (a) overall amount of CO<sub>2</sub> desorbed during the regeneration experiments (b) relative heat duty (%) of amine solvent regeneration



**Figure 6:** Influence of single and combined catalyst properties on the CO<sub>2</sub> desorption performance of CO<sub>2</sub>-rich MEA solutions (a) influence of total acidity determined by NH<sub>3</sub>-TPD (b) influence of MSA×total acidity (c) influence of MSA×BAS and (d) influence of total acid sites (LAS and BAS) determined by Py-IR



**Figure 7:** Improvements in solvent cyclic capacity made by all four catalysts



**Figure 8:** A plausible reaction mechanism for HZSM-5 catalyst facilitated carbamate breakdown during amine solvent regeneration process

## Manuscript tables

**Table 1:** Textural properties of the parent HZSM-5 and the synthesized catalysts determined by BET.

Catalyst	BET surface area (m <sup>2</sup> /g)			Pore volume (cm <sup>3</sup> /g)
	S <sub>BET</sub>	S <sub>Meso</sub>	S <sub>Micro</sub>	
HZSM-5	376.3	47.6	328.7	0.24
HZ-0.2	364.7	163.3	201.4	0.34
HZ-0.5	485.3	331.2	154.1	0.58
HZ-0.7	444.4	328.7	115.7	0.91

**Table 2:** Acidic properties of the parent HZSM-5 and synthesized catalysts. The strength of the acid sites was obtained by NH<sub>3</sub>-TPD technique whereas the type of the acid sites was determined using Py-FTIR.

Catalyst	Acidity by strength (mmol/g) <sup>a</sup>			Acidity by type (mmol/g) <sup>b</sup>			
	Weak	Strong	Total	LAS	BAS	B/L	Total acid sites
HZSM-5	0.80	0.66	1.46	0.198	0.268	1.35	0.466
HZ-0.2	0.89	0.63	1.51	0.293	0.099	0.34	0.392
HZ-0.5	1.1	0.44	1.53	0.428	0.163	0.38	0.591
HZ-0.7	1.53	0.59	2.12	0.430	0.118	0.36	0.548

<sup>a</sup> calculated by NH<sub>3</sub>-TPD

<sup>b</sup> calculated by Py-IR



**Table 3:** Amount of desorbed CO<sub>2</sub> from regeneration experiments for MEA solution without and with all four catalysts, and the heat duty of solvent regeneration. The solvent regeneration experiments were performed at 82 °C for 1.5 h.

Solvent	Amount of desorbed CO <sub>2</sub> (mmol)	Heat duty (kJ/mol CO <sub>2</sub> )	Relative Heat duty (%)
MEA only	65.0	3923.3	100
HZSM-5	85.1	2778.3	70.8
HZ-0.2	80.6	2988.2	76.2
HZ-0.5	103.5	2459.5	62.7
HZ-0.7	100.3	2635.9	67.2

**Table 4:** Various single properties of the catalysts and their combinations used to study their influence on the CO<sub>2</sub> desorption performance

Catalyst	Total acidity <sup>a</sup> (mmol/g)	Total acid sites <sup>b</sup> (mmol/g)	MSA×BAS (mmol.m <sup>2</sup> /g <sup>2</sup> )	MSA×Total acidity (mmol. m <sup>2</sup> /g <sup>2</sup> )
ZSM-5	1.46	0.466	12.76	69.496
HZ-0.2	1.51	0.392	16.17	246.13
HZ-0.5	1.53	0.591	53.98	506.4
HZ-0.7	2.12	0.548	38.78	695.36

<sup>a</sup> determined by NH<sub>3</sub>-TPD

<sup>b</sup> determined by Py-FTIR

## **Catalytic activity of facilely synthesized mesoporous HZSM–5 catalysts for optimizing the CO<sub>2</sub> desorption rate from CO<sub>2</sub>-rich amine solutions**

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## ABSTRACT

Post-combustion CO<sub>2</sub> capture using aqueous alkanolamine solutions has a great potential to reduce anthropogenic CO<sub>2</sub> emissions but the large-scale deployment of this technique is hindered due to a highly energy-intensive solvent regeneration mainly because of poor CO<sub>2</sub> desorption kinetics. To overcome this limitation, we synthesized a series of mesoporous HZSM-5 catalysts through facile alkaline desilication and surfactant-induced re-assembly of dissolved species originating from the parent HZSM-5 crystals, and evaluated their performance to optimize the CO<sub>2</sub> desorption rate from benchmark 30 wt. % monoethanolamine (MEA) solution under mild temperature condition (40–82 °C). X-ray diffraction (XRD) patterns showed that the synthesized catalysts retained their crystallinity. Desilication by treatment in the alkaline medium led to a remarkable development of mesoporosity, with an increase in the Brunauer–Emmett–Teller (BET) surface area as well. The experimental results suggested that the synthesized catalysts significantly enhanced the CO<sub>2</sub> desorption rate at low temperatures (up to 350–580% at  $\leq 82$  °C), improved the total amount of desorbed CO<sub>2</sub> up to 60%, and minimized the heat duty by 24–37%. Detailed characterization revealed that the synergistic effect of higher mesoporosity and increased number of Lewis acid sites (LAS) and Brønsted acid sites (BAS) was crucial to improve the CO<sub>2</sub> desorption rate. Based on the characterization and experimental results, a plausible reaction mechanism for catalyst aided CO<sub>2</sub> desorption was also presented. This investigation highlights the role of catalysts in optimizing the CO<sub>2</sub> capture process and presents new understanding for the design of high-performance catalysts for this purpose.

**KEYWORDS:** CO<sub>2</sub> capture; CO<sub>2</sub> desorption rate; Desilication re-assembly; Zeolite; Catalytic solvent regeneration

## 1. Introduction

Rising levels of CO<sub>2</sub> in the atmosphere due to excessive use of fossil fuels have been widely recognized to be a primary contributor to global warming [1]. To keep global warming within 2 °C of pre-industrial levels, a significant amount of CO<sub>2</sub> must be captured prior to its release into the atmosphere [2]. Among various techniques developed for CO<sub>2</sub> capture, post-combustion CO<sub>2</sub> capture has gained significant attention because it can be easily retrofitted to an existing plant and has the operational flexibility during peak electricity demand [3]. The use of solid sorbents such as CaO, MgO, and Li<sub>4</sub>SiO<sub>4</sub> for capturing CO<sub>2</sub> is attractive due to process simplicity. However, poor sorption kinetics and requirement of high temperature for sorbent regeneration are the issues which still need to be addressed before deployment of this approach at commercial scale [4, 5].

To date, thermal amine scrubbing is arguably the most attractive CO<sub>2</sub> capture technique because it is reliable, technically mature, and capable of treating large gas volumes [6–8]. Nevertheless, certain drawbacks of this technology, including high capital cost, highly energy intensive stripper, facility corrosion, and solvent degradation have hindered the worldwide large-scale application of this approach [9–11]. The major energy penalty, accountable for around 70% of the total operating cost, originates from the solvent regeneration step, because a large amount of thermal energy is needed to regenerate the amine solvent at high temperatures around 120–140 °C [12–15].

Despite the considerable improvements made in process intensification to minimize the energy penalty, the inherent drawbacks of amine solvents are considered to be the primary reason for energy intensive operation [16, 17]. In this scenario, enormous efforts have been made to develop less energy intensive solvents. For instance, 2-(ethylamino)ethanol (EAE), 2-

(methylamino)ethanol (MAE), and N,N-dimethylethanolamine (DMEA) have been reported as alternative amine absorbents for energy-efficient CO<sub>2</sub> capture [18–20]. Non-aqueous amine solvents such as mixtures of amine and glycol ethers [21], and biphasic solvents including aqueous monoethanolamine (MEA)/1-propanol and triethylenetetramine (TETA) [22, 23] have also been reported as promising alternate to aqueous amine solutions. Hwang et al. developed and investigated the performance of a water-lean K<sub>2</sub>Sol solvent (a sterically diamine) using a bench-scale pilot plant unit and found that it required 35% lower regeneration energy than that of MEA [24, 25]. Bougie et al. introduced microwave irradiation as an effective alternative to thermal regeneration; and by combining the microwave irradiation concept with non-aqueous MEA solutions they demonstrated that a huge reduction in the solvent regeneration heat duty is possible [26, 27].

Another innovative approach to lower the regeneration energy penalty is the addition of a catalyst that can facilitate carbamate breakdown and subsequent CO<sub>2</sub> release at lower temperatures [28]. The addition of a catalyst was found to improve the CO<sub>2</sub> desorption at low temperatures and thus the temperature of solvent regeneration could be lowered [29–31]. Idem et al. investigated the solvent regeneration performance of MEA without and with two catalysts—HZSM-5 and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>—at 105 °C with initial CO<sub>2</sub> loading of 0.5 mol CO<sub>2</sub>/mol MEA [28, 32]. Their results suggested that both catalysts were effective in optimizing CO<sub>2</sub> desorption and minimizing the solvent regeneration heat duty. Liang et al. advanced this approach by developing various solid acid catalysts including SO<sub>4</sub><sup>-2</sup>/TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>/HZSM-5 and demonstrated that their addition to MEA solvent regeneration step could minimize the regeneration heat requirement by up to 34% [33–35]. In addition to evaluating the impact of catalyst addition on the energy penalty, they highlighted the key physiochemical properties such

as mesoporosity, concentration of acid sites, and Brønsted acid sites that influence the CO<sub>2</sub> desorption performance of a catalyst. Few other catalysts including metal ions and TiO(OH)<sub>2</sub> have also been reported to improve the CO<sub>2</sub> desorption rate at low temperature (<100 °C) [36, 37]. So far, this approach is in early stage and limited to a few catalysts; among which some are expensive and some are difficult to separate. Therefore, it is highly desired to develop more efficient, stable, and inexpensive catalysts that could significantly lower the temperature of the amine regeneration and substantially improve the CO<sub>2</sub> desorption to make this approach economically feasible.

HZSM-5, the most thoroughly studied catalyst for optimizing CO<sub>2</sub> desorption, is however a microporous sieve and has a narrow pore structure and limited mass transfer rate, which means that the access of CO<sub>2</sub> containing species to the active sites would be limited [38–40]. It is possible that if the key properties of HZSM-5 such as mesoporosity, acidity, and acid sites, could be improved, the catalytic performance would also improve accordingly.

Desilication in an alkaline medium is an effective method to improve the physiochemical properties of HZSM-5 including mesoporosity and surface acidity [41, 42]. With the aim of improving the key physiochemical properties of HZSM-5, we prepared a series of HZSM-5 catalysts using an alkaline desilication and surfactant induced re-assembly process under optimized process conditions. The prepared materials were thoroughly characterized using X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), Scanning electron microscope (SEM), ammonia temperature programmed desorption (NH<sub>3</sub>-TPD), and pyridine-adsorption infrared spectroscopy (Py-IR). The performance of the synthesized catalysts was then evaluated in CO<sub>2</sub> desorption experiments using CO<sub>2</sub>-rich MEA solution under a mild temperature range e.g. 40–82 °C. Furthermore, the impact of various physicochemical properties on the CO<sub>2</sub> desorption

performance was evaluated and used to draw the plausible reaction mechanism for the catalyst-aided solvent regeneration process. In addition, the stability of the synthesized catalysts was studied in five cyclic solvent regeneration experiments.

The originality and novelty of this work include (i) synthesis of a series of mesoporous HZSM-5 catalysts and their addition to the CO<sub>2</sub>-rich MEA solution to minimize the solvent regeneration heat duty (ii) evaluation of the catalytic performance in terms of cyclic capacity, CO<sub>2</sub> desorption rate, and regeneration heat duty (iii) investigation of the impact of various physicochemical properties of the catalysts on CO<sub>2</sub> desorption performance and (iv) analysis of the CO<sub>2</sub> desorption mechanism of mesoporous HZSM-5 catalyst facilitated amine solvent regeneration.

## **2. Experimental section**

### **2.1. Materials:**

Monoethanolamine (MEA, 99%, Acros), Cetyltrimethylammonium bromide (CTAB, >98%, Sigma-Aldrich), Sodium Hydroxide (NaOH, 97%, Sigma-Aldrich), and NH<sub>4</sub>-ZSM-5 (Zeolyst International, USA) were used as received. N<sub>2</sub> and CO<sub>2</sub> gases (99.999%) were purchased from Korea Nano Gas Co. Ltd.

### **2.2. Preparation of the catalysts:**

A series of hierarchical zeolite catalysts were prepared using the modified desilication re-assembly process [40]. This post-synthetic process had two main stages: desilication of the zeolite and ion-exchange with calcination after each stage. NH<sub>4</sub>-ZSM-5 was calcined at 550 °C for 5 h and used as the base material. Initially, a solution of organic surfactant CTAB (0.05 M, 20 mL/g zeolite) and different molar amounts of NaOH (0.2, 0.5, and 0.7 M, 20 mL/g zeolite) were prepared and poured into a round bottom reactor, mixed, and heated to 80 °C. Then,

immediately, a specific amount of HZSM-5 (20 mL/g) was poured into the reactor, and desilication of zeolite was carried out under continuous stirring (500 rpm) and reflux conditions for 12 h. Afterwards, the zeolite desilication reaction was stopped by ice quenching method and the solids were washed with DI water and dried at 120 °C for 8 h. The prepared samples were calcined for 5 h in static air at 550 °C at a heating rate of 5 °C/min to remove of the pore directing agent coating in order to create mesopores on the exterior surface of the zeolite. After that, the samples were further ion-exchanged with ammonium nitrate three times (0.5 M  $\text{NH}_4\text{NO}_3$ , 20mL/g, 60 °C, 2h) under reflux conditions, then washed with DI water, dried and calcined at 550 °C for 5h in order to get proton form of the hierarchical zeolites. The prepared samples were labeled HZ-0.2, HZ-0.5 and HZ-0.7, where the HZ coding represents the hierarchical zeolite and the 0.2, 0.5, and 0.7 coding indicates the respective concentrations of alkali (NaOH) used in the desilication of the zeolite.

### **2.3. CO<sub>2</sub> desorption experiments:**

CO<sub>2</sub> was absorbed in 30 wt. % MEA solution at typical absorber conditions (15 Vol. % CO<sub>2</sub>, 40 °C) using a continuous stirrer tank reactor (CSTR). The feed gas (85% N<sub>2</sub>, 15% CO<sub>2</sub>) was bubbled into the reactor (1 L/min) and the outlet gas was analyzed using a gas chromatograph (Agilent Technologies, 7890A). The absorption experiments were ended when the CO<sub>2</sub> concentration in the outlet gas was equal to the inlet concentration, i.e., 15 vol. %. The CO<sub>2</sub> loading values of the amine solutions were determined with a total organic carbon analyzer (TOC analyzer, Analytik Jena multi N/C 3100). For TOC analysis, the amine samples were diluted with DI water with a dilution ratio of 1:599 (amine: water) and exactly 500 µL of the prepared samples were injected to the analyzer, where the samples undergo catalytic combustion



and a Focus Radiation-Nondispersive Infrared Detector (FR-NDIR) detector detects the released CO<sub>2</sub>.

The solvent regeneration was studied using the experimental setup shown in Fig. 1. Briefly, a glass reactor of 250 mL capacity was used in this study. An oil circulator was attached to heat the amine solution and maintain desired temperature. A pressure gauge and a K-type thermocouple were used to record reactor inside pressure and the temperature of the amine solution. The solution was continuously stirred at 300 rpm using a magnetic bar while a condenser was mounted to condense and reflux water and amine vapors. The energy consumption of the CO<sub>2</sub> desorption experiments was determined using an electric energy meter (ADPOWER HP-100A). The electric energy for the heating oil circulator was provided through the electric energy meter and the electricity consumption was started to record once the temperature of the amine solution in the reactor reached 40 °C. Employed this way, the electric energy consumption for each experiment was recorded and then divided by the total amount of released CO<sub>2</sub> from respective experiments to obtain the heat duty value in kJ/mol CO<sub>2</sub> units. For each experiment, 100 g of CO<sub>2</sub>-rich MEA solution was added to the reactor and heated using the oil circulator. A pure stream of CO<sub>2</sub> gas was released when the amine solution was heated, which was mixed with N<sub>2</sub> gas (100 mL/min) before its analysis in the GC. In this way, the CO<sub>2</sub> in the outgassed stream was recorded as a function of time and temperature. In addition, liquid samples (~1 mL) were also taken every 20 minutes during the solvent regeneration experiments and the CO<sub>2</sub> loading values were determined using TOC analyzer. For catalytic experiments, 5 g of respective catalyst was added to 100 g amine solution at the start of the experiment at room temperature. Before each experiment, all pipelines and the reactor were purged with N<sub>2</sub> gas to remove any residual CO<sub>2</sub>. Each experiment had a temperature ramp-up stage in which the

temperature of the amine solution was continuously raised and the desired temperature point (i.e., 82 °C) was achieved, and an isothermal stage in which the temperature was kept constant at 82 °C for approximately 1.5 h. Using the ramp up stage, the effects of the catalysts on the CO<sub>2</sub> desorption rate can be recorded at lower temperatures (i.e., <82 °C).

#### **2.4. Characterization of the catalysts:**

The crystalline structure of the catalysts was analyzed by XRD (Rigaku D/max 2200PC diffractometer). The XRD patterns of the parent and desilicated zeolites are shown in Fig. 2a. All samples exhibited characteristic diffraction peaks of HZSM-5 (JCPDS: 44-0003) at  $2\theta$  of 14.8°, 23.1°, 23.9°, 24.4°, 30.1°, suggesting that the crystalline structure was well-maintained during alkaline treatment [43].

The nitrogen physisorption isotherms of the parent zeolite and modified zeolites are shown in Fig. 2b and the textural properties of the catalysts are summarized in Table 1. The parent zeolite had a type I isotherm, typical of microporous materials, with high nitrogen uptake at low pressures due to the interaction of the pore walls with the adsorbate and a plateau at high relative pressure [41]. The isotherms of all the alkaline treated materials were of type IV, typical for hierarchical materials. The alkaline treated materials showed higher nitrogen uptake at pressures higher than  $p/p_0=0.4$ , indicating the formation of new mesopores [44]. For the HZ-0.5 and HZ-0.7 catalysts, a sharp increase in nitrogen uptake was observed at  $p/p_0=0.4-1.0$ , indicating the abundance of mesopores.

The surface acidity of the parent and modified zeolites was determined by NH<sub>3</sub>-TPD. The obtained NH<sub>3</sub> desorption patterns are shown in Fig. 3a and the quantitative acidity values (mmol/g) are provided in Table 2. From Fig. 3a, two obvious peaks can be seen for all the

catalysts. The first peak appearing at low temperature around 130 °C indicates the weak acidic sites and the other at high temperature around 405 °C is ascribed to the strong acidic sites [44]. For all the desilicated samples, the NH<sub>3</sub> uptake at low temperature was higher than the parent HZSM-5 due to the extracted amount of Si leading to a lower Si/Al ratio and therefore a higher density of acid sites. However, a decrease in the strong acid sites was observed for all of the treated samples that is in accordance with the previous literature reports [40]. From the Table 2, it can be seen that the desilication re-assembly process enhanced the acidity of the catalysts. The overall trend in surface acidity was in the order of: HZSM-5 < HZ-0.2 < HZ-0.5 < HZ 0.7.

The pyridine adsorption IR technique was used to determine the nature of the acid sites. Pyridine molecules can attach to unsaturated metal sites (i.e., Lewis acid sites) resulting in the formation of LPy species. The LPy corresponding peaks appear at around 1440 and 1580 cm<sup>-1</sup>. At the same time, the pyridine molecules can react with proton donor sites on the surface OH groups (i.e., Brønsted acid sites) and show characteristic peaks at 1540 and 1630 cm<sup>-1</sup> [45–47]. The peak appearing at 1490 cm<sup>-1</sup> indicates the presence of Lewis acid sites (LAS) and Brønsted acid sites (BAS). The Py-IR spectra of the parent zeolite and synthesized catalysts are shown in Fig. 3b and the quantitative values for the acid sites are given in Table 2. For all the samples, distinctive peaks were recorded at around 1440, 1490, 1540, 1580, and 1630 cm<sup>-1</sup> indicating the presence of both types of acid sites i.e., Lewis acid sites (LAS) and Brønsted acid sites (BAS) on the catalysts.

### **3. Results and Discussion**

#### **3.1. CO<sub>2</sub> desorption performance**

The regeneration performance of CO<sub>2</sub>-rich MEA solution without and with all four catalysts is presented in Fig. 4. The CO<sub>2</sub> desorption from MEA without catalyst solution was limited at the start of the experiment at lower temperature (Fig. 4a and 4b). However, from 65 °C onwards, a

noticeable amount of CO<sub>2</sub> desorption was observed which kept on improving and reached the peak value of 3.85 (10<sup>-2</sup> mol. kg<sup>-1</sup>. min<sup>-1</sup>) at 82 °C and 27 min. All of the catalysts improved the CO<sub>2</sub> desorption rate and started to desorb noticeable amounts of CO<sub>2</sub> from 54 °C onwards. At lower temperatures the HZSM-5 noticeably improved the CO<sub>2</sub> desorption rate and achieved the peak CO<sub>2</sub> desorption rate value of 5.12 (10<sup>-2</sup> mol. kg<sup>-1</sup>. min<sup>-1</sup>) at 82 °C and 23 min. For the modified catalysts, the performance of HZ-0.2 was slightly poorer than that of the HZSM-5 but HZ-0.5 and HZ-0.7 substantially improved the CO<sub>2</sub> desorption rates. The inferior performance of the HZ-0.2 can be attributed to the presence of fewer acid sites and in particular limited Brønsted acid sites, which play a key part in the initial stage of the CO<sub>2</sub> desorption experiment. The HZ-0.5 and HZ-0.7 catalytic solutions desorbed greater amounts of CO<sub>2</sub> at lower temperatures and achieved peaks CO<sub>2</sub> desorption rates of 7.06 and 7.62 (10<sup>-2</sup> mol. kg<sup>-1</sup>. min<sup>-1</sup>) at 23 and 20 min, respectively. This is because these two catalysts were highly mesoporous and essentially possessed higher number of acid sites. This meant that more of the active sites were accessible and thus the chances of carbamate, carbonate, or bicarbonate colliding with the active sites was higher, resulting in faster CO<sub>2</sub> desorption. Consequently, the CO<sub>2</sub> was released at higher desorption rates from the HZ-0.5 and HZ-0.7 catalytic solutions.

The catalytic performance trend in term of CO<sub>2</sub> desorption rate was found to be HZ-0.7 > HZ-0.5 > HZSM-5 > HZ-0.2 > no catalyst. It should be noted that all of the catalysts improved the CO<sub>2</sub> desorption rate at lower temperatures and minimized the time of peak CO<sub>2</sub> desorption value. This is because in the non-catalytic solution, CO<sub>2</sub> desorption is entirely dependent on the provided thermal energy. When a certain amount of thermal energy is available to the solution, it carries out the endothermic CO<sub>2</sub> desorption reactions, and ultimately releases CO<sub>2</sub>. In contrast, in the catalytic solutions, the CO<sub>2</sub> is released via a combination of thermal energy and the

facilitation of the active acid sites. Below 64 °C, there was almost no CO<sub>2</sub> desorption from the non-catalytic system. The reason for this is because at those temperatures the available thermal energy was insufficient to break bonds and release CO<sub>2</sub>. However, as we can see for the catalytic solvents, the CO<sub>2</sub> is being desorbed at temperatures below 64 °C, which clearly indicates that the catalysts are facilitating CO<sub>2</sub> desorption by lowering the activation energy.

In addition to enhancing the CO<sub>2</sub> desorption rate, the catalytic solutions also released greater amounts of CO<sub>2</sub> that is highly advantageous in minimizing the amine solution regeneration heat duty. Since the heat duty of amine solvent regeneration is defined by the amount of CO<sub>2</sub> released per amount of energy provided during regeneration, the release of higher amount of CO<sub>2</sub> against unit energy supply will decrease the process heat duty. The improvements in the total amount of CO<sub>2</sub> desorbed during the regeneration experiments and the subsequent reduction in the solvent regeneration heat duty are shown in Fig. 5 and Table 3. It should be noted that the recorded heat duty was higher than the actual values. This is because the solvent regeneration experiments were conducted in a simplified batch reactor without insulators. The HZSM-5 solution desorbed around 31% greater amount of CO<sub>2</sub> and reduced the heat duty by around 29%. The synthesized catalysts increased the total amount of desorbed CO<sub>2</sub> by 24-60% and minimized the energy consumption by up to 37%. It should be noted that as the solvent regeneration experiments were performed using a semi-batch reactor and the heat duty was recorded using an electric energy meter, the obtained values for heat duty and energy saving due to catalyst addition cannot truly depict the practical stripping column.

### **3.2. Effect of various physicochemical properties:**

Previous studies on HZSM-5 aided solvent regeneration have shown that several physicochemical properties of the catalyst favor catalytic performance during solvent

regeneration [35]. In this study, as the HZSM-5 was post-treated with the aim of improving key physicochemical properties, it was necessary to analyze the effects of these properties on CO<sub>2</sub> desorption performance. Both the effects of a single property (total surface acidity) and combinations of various properties [MSA×total surface acidity, MSA×BAS, MSA×(LAS+BAS), and total acid sites (LAS+BAS)] were evaluated to understand the mechanism of catalyst facilitated solvent regeneration. The studied properties are listed in Table 4 and the obtained results are presented in Fig. 6.

Panels A and B of Fig. 6 show the influence of total surface acidity and a combination of mesoporous surface area (MSA) and total surface acidity (MSA×total surface acidity) on the overall amount of CO<sub>2</sub> desorbed during the solvent regeneration experiments. The results show that increase in total surface acidity and MSA×total surface acidity can improve CO<sub>2</sub> desorption performance. However, the trend was not linear. In fact, some catalysts with higher values of total surface acidity and MSA×total surface acidity desorbed less CO<sub>2</sub> than the ones having lower surface acidity and MSA×total surface acidity values. For example, the HZ-0.7 and HZ-0.2 catalysts had higher surface acidity and MSA×total acidity values than the HZ-0.5 and HZSM-5 catalysts, respectively. However, the amounts of CO<sub>2</sub> desorbed from the HZ-0.7 and HZ-0.2 catalytic solutions were lower than the amounts desorbed from the HZ-0.5 and HZSM-5 catalytic solutions, respectively. Fig. 6c shows how the combination of Mesoporous surface area and Brønsted acid sites (MSA×BAS) influenced the CO<sub>2</sub> desorption performance. The influence of MSA×BAS was valid for the HZ-0.5 and HZ-0.7 catalysts but invalid for the HZSM-5 and HZ-0.2 catalysts. This could be because the HZ-0.2 catalyst had far less Brønsted acid sites than HZSM-5 (0.099 mmol/g for HZ-0.2 while the HZSM-5 had 0.268 mmol/g). Nevertheless, the Mesopore area of the HZ-0.2 was higher than the Mesopore area of the HZSM-5 (163.3

m<sup>2</sup>/g for HZ-0.2 while 47.3 m<sup>2</sup>/g for HZSM-5). This shows that mesoporosity can improve the CO<sub>2</sub> desorption performance by providing better access to the active sites. However, the concentration of active sites is more important. Previous studies have also shown that a higher concentration of Brønsted acid sites is more effective, even when the Mesopore surface area is low [30, 48].

Panel d of Fig. 6 shows the influence of total acid sites (LAS+BAS) on the CO<sub>2</sub> desorption performance. A linear relation between the total acid sites (LAS+BAS) and the total amount of desorbed CO<sub>2</sub> was observed. It has been reported that the Brønsted acid sites are more effective at the initial stage of the experiments because at that point (i) the concentration of carbamate is higher and (ii) bicarbonate and carbonate are also present in the system at CO<sub>2</sub> loadings above 0.42 mol CO<sub>2</sub>/mol MEA [48, 49]. The Brønsted acid sites can provide protons to the carbamate, bicarbonate, and carbonate and thereby release significant amounts of CO<sub>2</sub> at an early stage of the experiment. However, as the experiments progress, the concentration of carbamate becomes low and the bicarbonates and carbonates are not present. At that stage, the presence of Lewis acid sites becomes more effective. Therefore, when we consider the total amount of CO<sub>2</sub> released from the entire experiment (ramp-up stage and isothermal stage), the sum of LAS and BAS become equally important and thus a linear dependence on the aggregate of LAS and BAS was observed.

### **3.3. Impact on solvent cyclic capacity**

CO<sub>2</sub> capture using amine-based solvents is a continuous absorption/regeneration cyclic process. The aqueous amine solution absorbs the CO<sub>2</sub> in the absorber column and then this CO<sub>2</sub>-rich solution is sent to the stripper column to release CO<sub>2</sub>. In the stripper, CO<sub>2</sub>-rich solution is thermally treated to release a certain amount of CO<sub>2</sub> and the CO<sub>2</sub>-lean solvent is then pumped

back to absorber column. A solvent that achieves a lower CO<sub>2</sub>-lean loading in the stripper will have more CO<sub>2</sub> intake capacity in the absorber. Furthermore, it has been determined that an energy-efficient solvent is the one that can release fair amounts of CO<sub>2</sub> in the stripper column at mild temperatures [50]. Because the catalytic regeneration of the amine solvent enhanced the CO<sub>2</sub> desorption rate and total amount of desorbed CO<sub>2</sub>, it was important to evaluate the impact of catalytic regeneration on the solvent's cyclic capacity as well. By definition, the cyclic capacity is the difference between the CO<sub>2</sub>-rich loading and CO<sub>2</sub>-lean loading. In this work, the cyclic capacity was defined as the difference between the initial CO<sub>2</sub> loading at the start of the experiments and the CO<sub>2</sub>-lean loadings at the end of the regeneration experiments, and was calculated using Eq. 1.

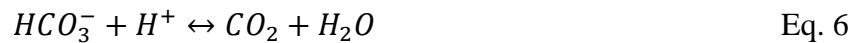
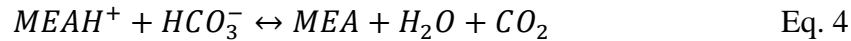
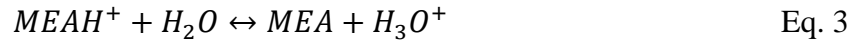
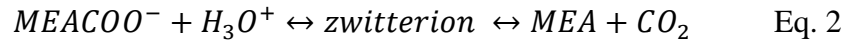
$$Q_{cyc} = \alpha_{abs} \left[ \frac{\text{mol CO}_2}{\text{mol MEA}} \right] - \alpha_{strp} \left[ \frac{\text{mol CO}_2}{\text{mol MEA}} \right] \quad \text{Eq. 1}$$

where  $Q_{cyc}$  is the solvent cyclic capacity (mol CO<sub>2</sub>/mol MEA),  $\alpha_{abs}$  is the initial CO<sub>2</sub> loading, and  $\alpha_{strp}$  is the CO<sub>2</sub> loading at the end of the regeneration experiments. All four catalysts desorbed greater amounts of CO<sub>2</sub> than the non-catalytic solution and thus improved the solvent cyclic capacity accordingly (Fig. 7). The minimum improvement of around 31% was made by the HZ-0.2 catalyst while the HZ-0.5 catalyst achieved the maximum improvement of around 60%. A higher cyclic capacity is highly favorable for an efficient CO<sub>2</sub> capture process because a solvent with higher cyclic capacity will require a lower solvent circulation rate. The improvement in solvent cyclic capacity occurred because the catalytic solutions provided active sites and released CO<sub>2</sub> at a higher desorption rate at low temperatures. On the other hand, the CO<sub>2</sub> desorption from the non-catalytic solution entirely depended on the thermal energy provided and was limited under the studied temperature range.



### 3.4. Catalytic mechanism

The most widely accepted reaction mechanism for CO<sub>2</sub> absorption/desorption in a primary amine solution is via two step zwitterion formation [49]. The two main reaction pathways for regenerating amine solvent are carbamate breakdown and amine deprotonation. The difficulty with solvent regeneration arises from the fact that both carbamate breakdown and amine deprotonation are highly endothermic reactions (Eq. 2–4) [51]. For the carbamate breakdown, protons are required to form zwitterions and subsequently release CO<sub>2</sub> as shown in Eq. 2. The required protons can be provided by H<sub>3</sub>O<sup>+</sup> but again the formation of H<sub>3</sub>O<sup>+</sup> via proton transfer from MEAH<sup>+</sup> to H<sub>2</sub>O is energy demanding (Eq. 3) [38]. Consequently, the lack of H<sup>+</sup> in the system to take part in the carbamate breakdown reaction, and the endothermic nature of the reactions, makes it difficult to regenerate amine solution at lower temperatures.



The catalysts can provide protons (H<sup>+</sup>) or metal atoms (Al) that can attach to the N atom of the carbamate and subsequently change the configuration from sp<sup>2</sup> to sp<sup>3</sup>. As a result, the N–C bond will be stretched and the carbamate would split into MEA and CO<sub>2</sub> [28]. A plausible reaction mechanism for the HZSM–5 catalyst aided amine solvent regeneration is presented in Fig. 8.

At CO<sub>2</sub> loadings above 0.42 mol CO<sub>2</sub>/mol MEA (as in our case where the initial CO<sub>2</sub> loading was 0.51 mol CO<sub>2</sub>/mol MEA) bicarbonate and carbonate are also present in the system

[35, 49]. Both the bicarbonate and carbonate can receive protons and quickly release  $\text{CO}_2$  as shown in Eq. 5 and 6. At the start of the experiments, the catalytic efficiency was remarkable because the concentration of carbamate was high, and especially  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  were also present in the system. With a greater number of  $\text{CO}_2$  containing species present in system, the chance of acid sites colliding with carbamate, bicarbonate, and carbonate is higher, which leads to a substantial improvement in  $\text{CO}_2$  desorption at lower temperatures. In this way, from catalytic solutions,  $\text{CO}_2$  can be released at low temperatures and thus the solvent regeneration temperature can be reduced.

#### 4. Conclusions

In this study, hierarchical HZSM-5 zeolites were post-synthesized by alkaline desilication and surfactant induced reassembly process. The synthesized catalysts had higher BET surface area, mesoporosity, and surface acidity. The catalytic performance of the parent HZSM-5 and the synthesized catalysts were then tested for  $\text{CO}_2$  desorption using a  $\text{CO}_2$ -rich MEA solution in the temperature range of 40–82 °C. All catalysts optimized the MEA solvent regeneration performance by improving  $\text{CO}_2$  desorption rate, overall amount of desorbed  $\text{CO}_2$ , and solvent cyclic capacity. In addition, the heat duty of the amine regeneration was significantly decreased because the catalytic solutions desorbed greater amounts of  $\text{CO}_2$  under same operating conditions. Among the synthesized catalysts, HZ-0.2 had inferior performance than the parent HZSM-5 because the total concentration of acid sites on HZ-0.2 was lower than that of HZSM-5. Whereas, the HZ-0.5 and HZ-0.7 catalysts showed superior performance to HZSM-5 catalyst because of higher mesoporosity and optimized acid sites concentration. The effects of physicochemical properties of the catalysts on  $\text{CO}_2$  desorption were evaluated and it was found

that an increase in the total surface acidity and sum of Lewis acid sites and Brønsted acid sites improved CO<sub>2</sub> desorption from CO<sub>2</sub>-rich amine solution that consequently lowered the heat duty.

### **Supporting Information:**

Material characterization, SEM images of parent and synthesized catalysts, improvement in CO<sub>2</sub> desorption rate made by all four catalyst, and reusability of the catalysts

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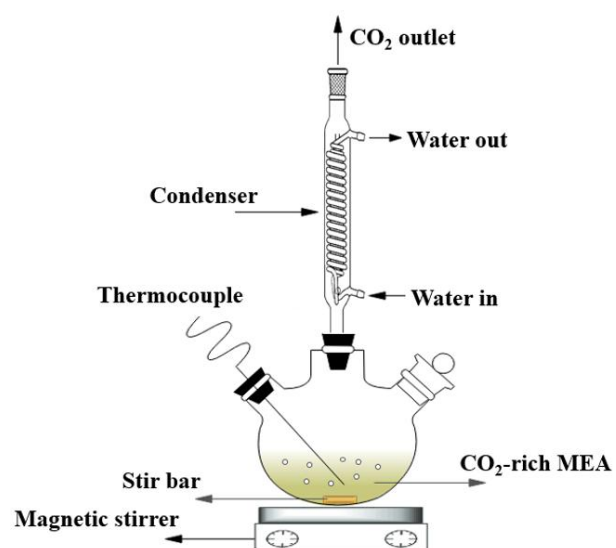
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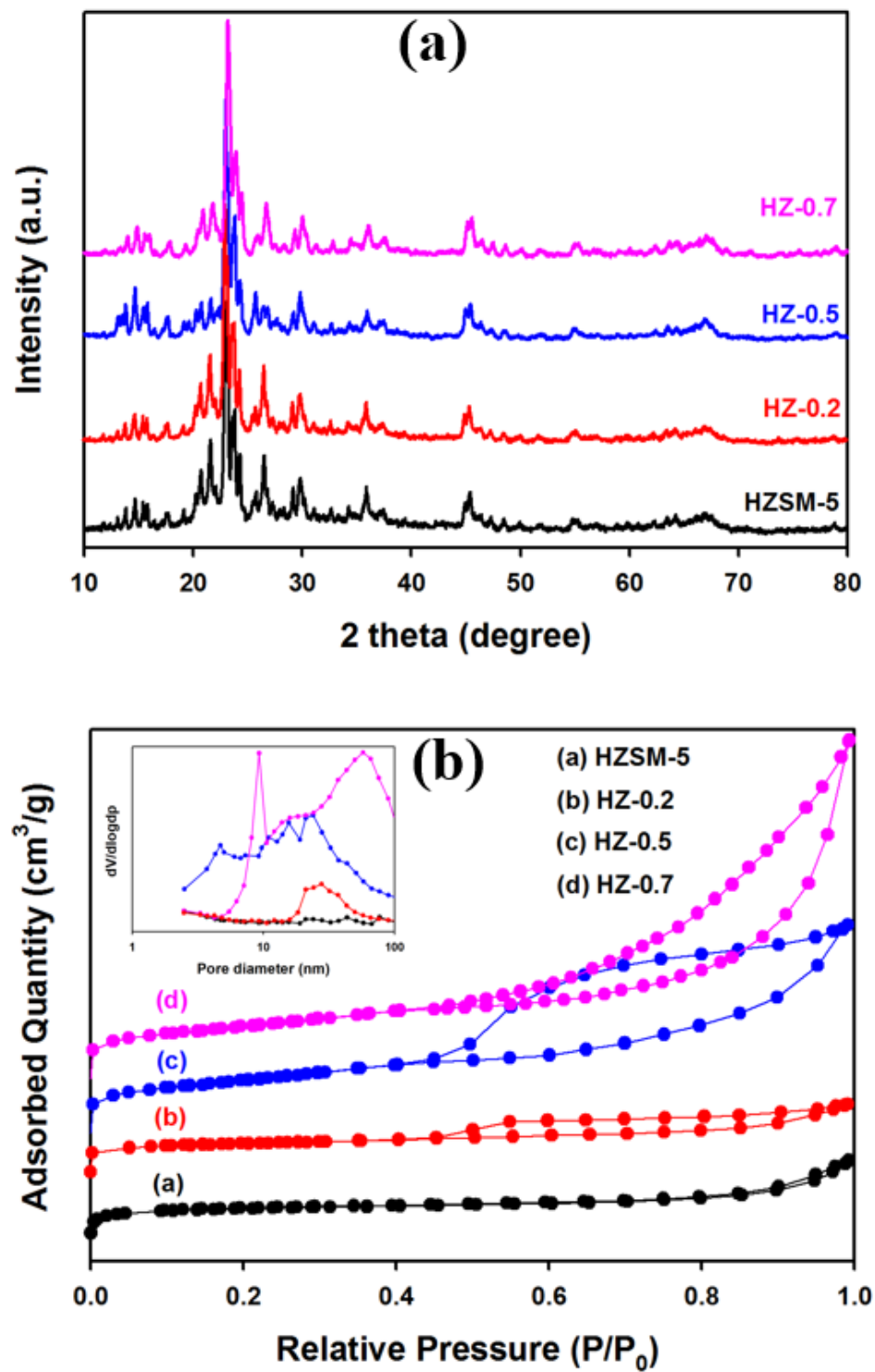
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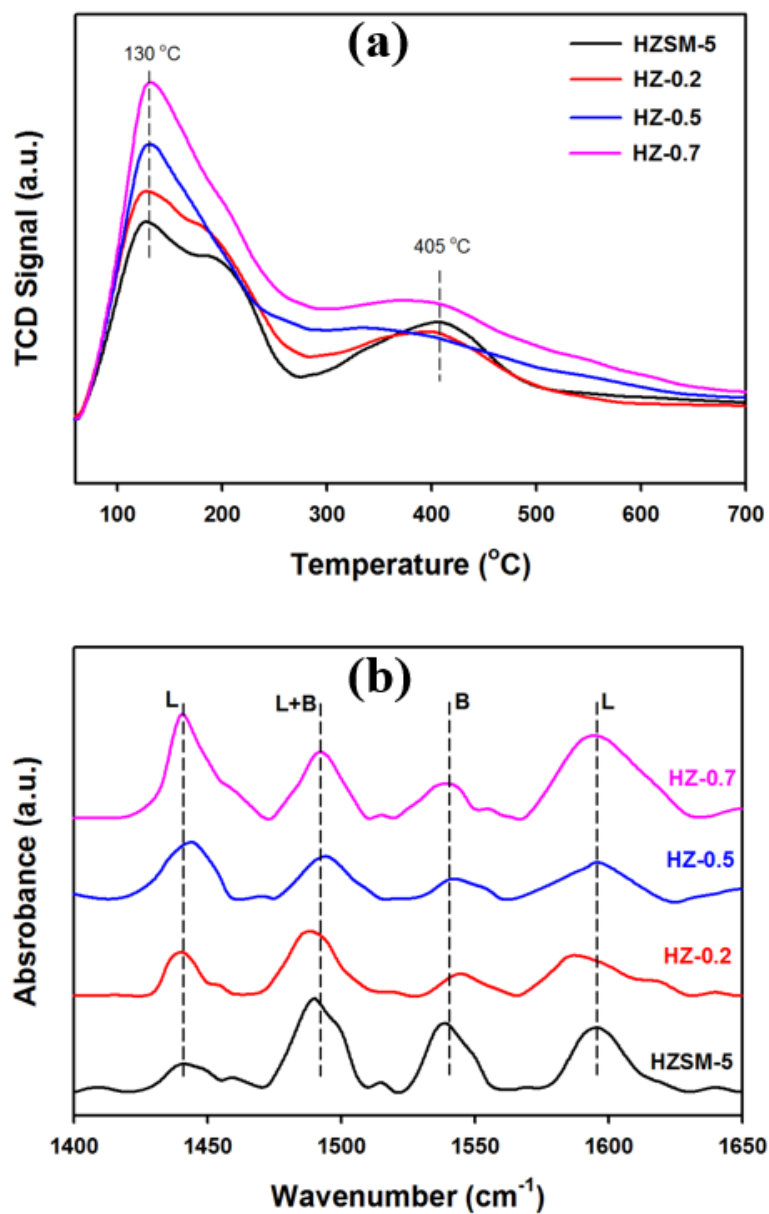
## Manuscript figures



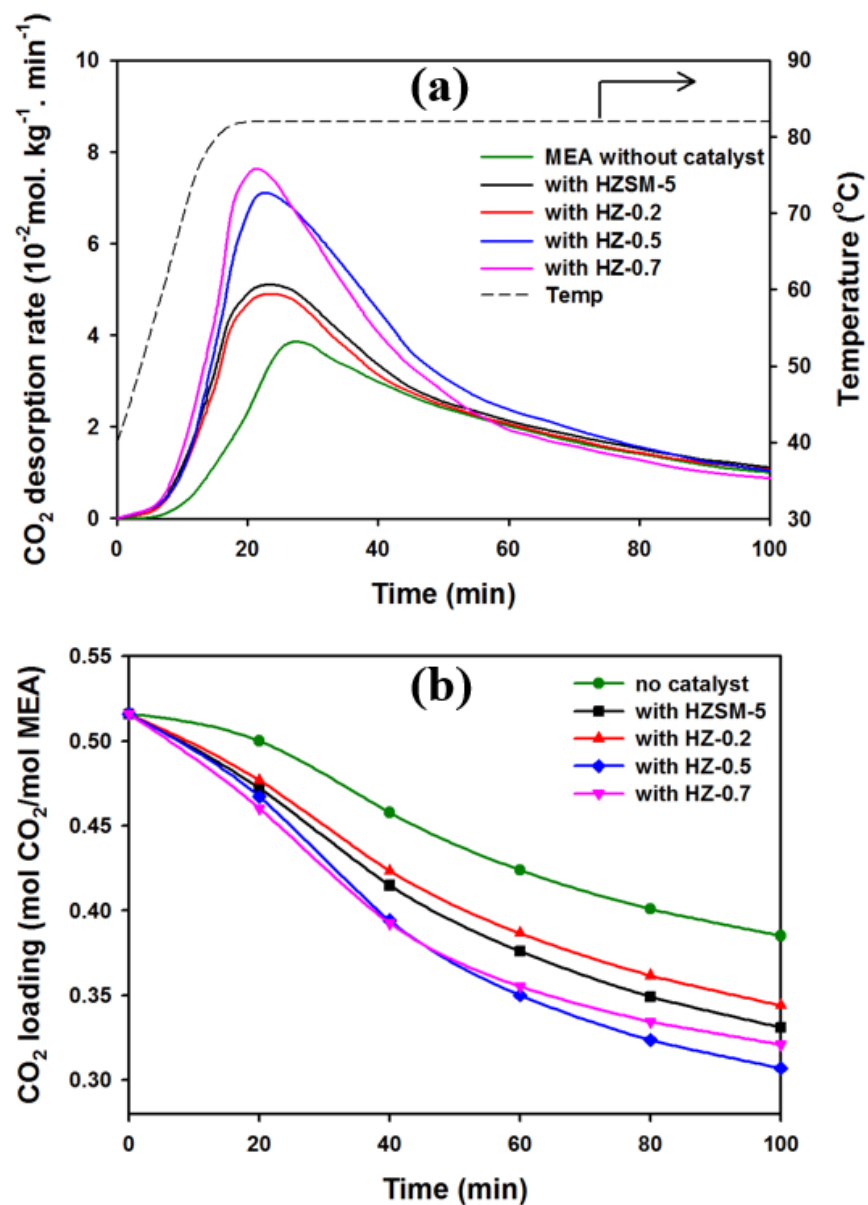
**Figure 1:** Schematic diagram of the experimental apparatus



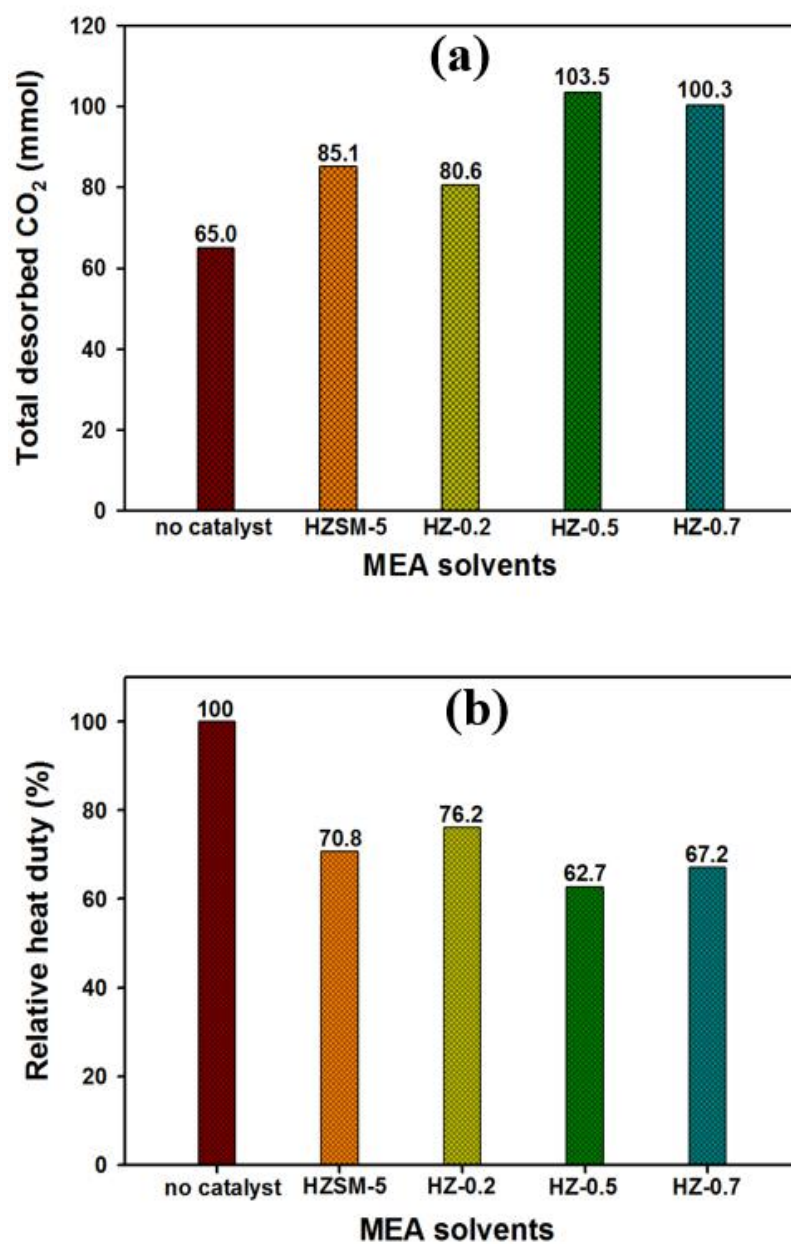
**Figure 2:** Characterization of the parent HZSM-5 and the prepared catalysts (a) XRD patterns (b) Nitrogen adsorption-desorption isotherms (inset: pore size distribution curves).



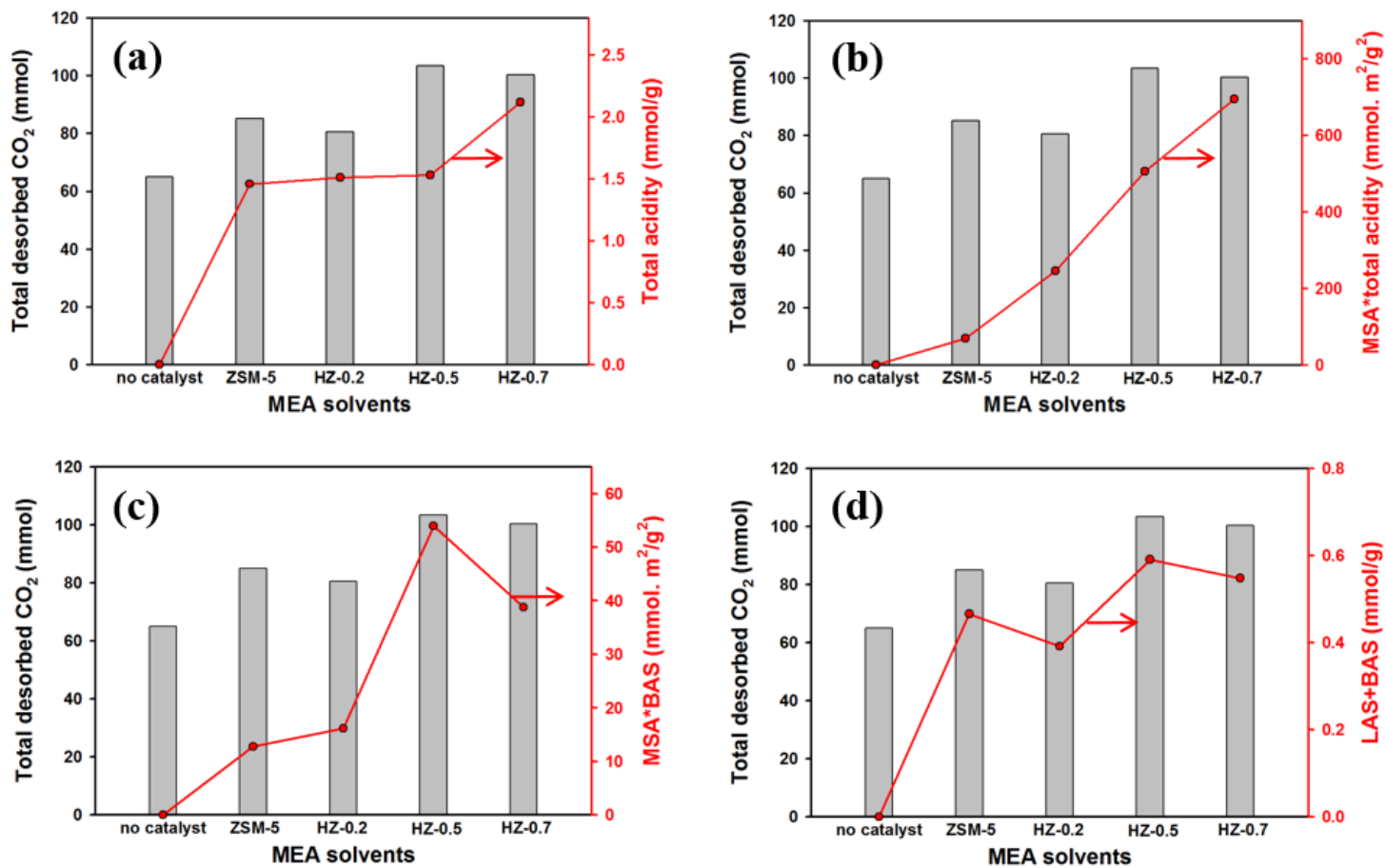
**Figure 3:** Characterization of the parent HZSM-5 and prepared catalysts (a)  $\text{NH}_3$ -TPD acidity profiles (b) Py-FTIR spectra, L and B sites represent Lewis acid sites and Brønsted acid sites.



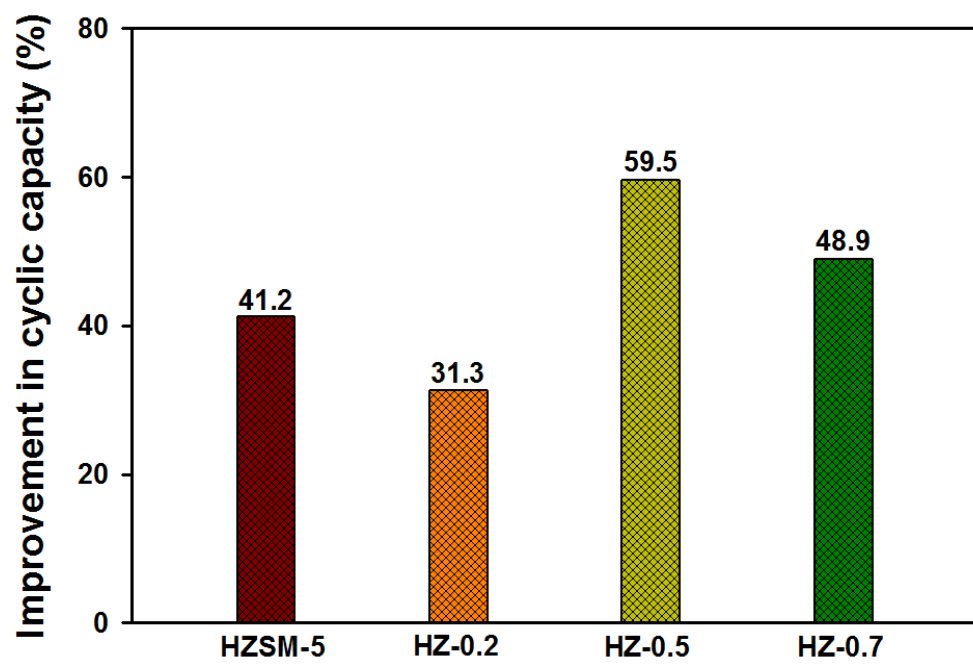
**Figure 4:** CO<sub>2</sub>-rich MEA solution regeneration performance without and with all catalysts (a) CO<sub>2</sub> desorption rate curves (b) CO<sub>2</sub> loadings of MEA solutions during the regeneration experiments without and with catalysts



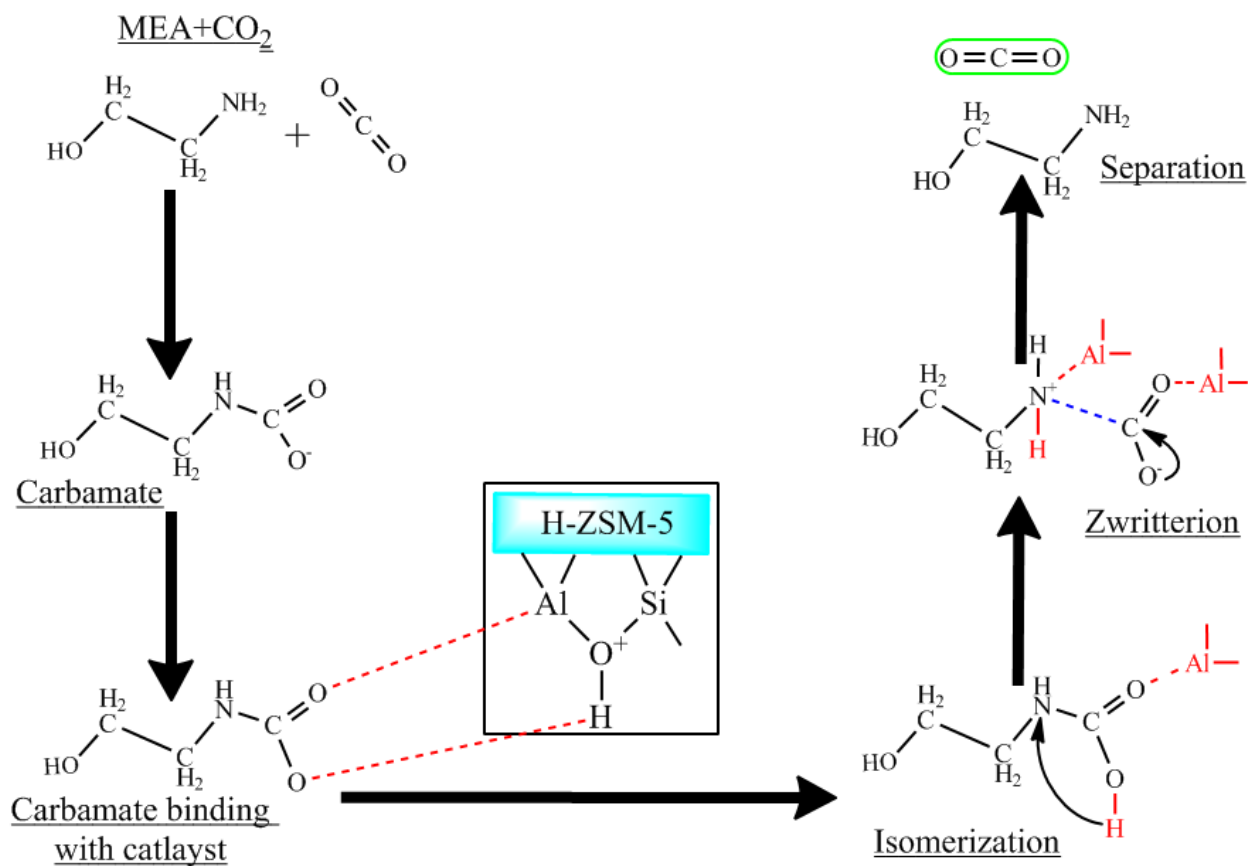
**Figure 5:** CO<sub>2</sub>-rich MEA solution regeneration performance without and with all catalysts (a) overall amount of CO<sub>2</sub> desorbed during the regeneration experiments (b) relative heat duty (%) of amine solvent regeneration



**Figure 6:** Influence of single and combined catalyst properties on the CO<sub>2</sub> desorption performance of CO<sub>2</sub>-rich MEA solutions (a) influence of total acidity determined by NH<sub>3</sub>-TPD (b) influence of MSA×total acidity (c) influence of MSA×BAS and (d) influence of total acid sites (LAS and BAS) determined by Py-IR



**Figure 7:** Improvements in solvent cyclic capacity made by all four catalysts



**Figure 8:** A plausible reaction mechanism for HZSM-5 catalyst facilitated carbamate breakdown during amine solvent regeneration process



## Manuscript tables

**Table 1:** Textural properties of the parent HZSM-5 and the synthesized catalysts determined by BET.

Catalyst	BET surface area (m <sup>2</sup> /g)			Pore volume (cm <sup>3</sup> /g)
	S <sub>BET</sub>	S <sub>Meso</sub>	S <sub>Micro</sub>	
HZSM-5	376.3	47.6	328.7	0.24
HZ-0.2	364.7	163.3	201.4	0.34
HZ-0.5	485.3	331.2	154.1	0.58
HZ-0.7	444.4	328.7	115.7	0.91

**Table 2:** Acidic properties of the parent HZSM-5 and synthesized catalysts. The strength of the acid sites was obtained by NH<sub>3</sub>-TPD technique whereas the type of the acid sites was determined using Py-FTIR.

Catalyst	Acidity by strength (mmol/g) <sup>a</sup>			Acidity by type (mmol/g) <sup>b</sup>			
	Weak	Strong	Total	LAS	BAS	B/L	Total acid sites
HZSM-5	0.80	0.66	1.46	0.198	0.268	1.35	0.466
HZ-0.2	0.89	0.63	1.51	0.293	0.099	0.34	0.392
HZ-0.5	1.1	0.44	1.53	0.428	0.163	0.38	0.591
HZ-0.7	1.53	0.59	2.12	0.430	0.118	0.36	0.548

<sup>a</sup> calculated by NH<sub>3</sub>-TPD

<sup>b</sup> calculated by Py-IR

**Table 3:** Amount of desorbed CO<sub>2</sub> from regeneration experiments for MEA solution without and with all four catalysts, and the heat duty of solvent regeneration. The solvent regeneration experiments were performed at 82 °C for 1.5 h.

Solvent	Amount of desorbed CO <sub>2</sub> (mmol)	Heat duty (kJ/mol CO <sub>2</sub> )	Relative Heat duty (%)
MEA only	65.0	3923.3	100
HZSM-5	85.1	2778.3	70.8
HZ-0.2	80.6	2988.2	76.2
HZ-0.5	103.5	2459.5	62.7
HZ-0.7	100.3	2635.9	67.2

**Table 4:** Various single properties of the catalysts and their combinations used to study their influence on the CO<sub>2</sub> desorption performance

Catalyst	Total acidity <sup>a</sup> (mmol/g)	Total acid sites <sup>b</sup> (mmol/g)	MSA×BAS (mmol.m <sup>2</sup> /g <sup>2</sup> )	MSA×Total acidity (mmol. m <sup>2</sup> /g <sup>2</sup> )
ZSM-5	1.46	0.466	12.76	69.496
HZ-0.2	1.51	0.392	16.17	246.13
HZ-0.5	1.53	0.591	53.98	506.4
HZ-0.7	2.12	0.548	38.78	695.36

<sup>a</sup> determined by NH<sub>3</sub>-TPD

<sup>b</sup> determined by Py-FTIR

**Declaration of interests**

- The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: