

## Article

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**Modified heterogeneous catalyst aided regeneration of CO<sub>2</sub> capture amines: A promising perspective for a drastic reduction in energy consumption**

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## Abstract

In the CO<sub>2</sub> capture process, decreasing the energy consumption and increasing the desorption rate of loaded MEA-CO<sub>2</sub> during the regeneration process of monoethanol amine have been identified as major challenges that need to be addressed. To overcome these challenges, three modified heterogeneous mesoporous catalysts, CMK-3-SiO<sub>2</sub>, CMK-3-MCM-41, CMK-3-SBA-15, and SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> solid acid catalyst were initially synthesized and investigated to determine their catalytic effectiveness in the process of CO<sub>2</sub> and MEA solvent regeneration with CO<sub>2</sub> loading of 0.5±0.02 mol CO<sub>2</sub>/mol MEA at 97°C. According to the experimental results, the CMK-3 modified catalyst significantly decreases the energy requirement for CO<sub>2</sub> desorption. The catalytic performance of the synthesized catalysts was in the order of CMK-3-SiO<sub>2</sub> > CMK-3-MCM-41 > CMK-3-SBA-15 > SZ respectively. CMK-3-SiO<sub>2</sub> exhibited the best catalytic performance by enhancing desorption rate by 195%, and decreasing the energy requirement by 37.41% compared with the monoethanol amine as a blank run. Furthermore, the CMK-3-SiO<sub>2</sub> catalyst exhibited the best catalytic performance compared to the literature with an excellent stability and with no unfavorable effects on the MEA-CO<sub>2</sub> absorption activity for the regenerated amine solvent. This performance seems to be a result of the large mesoporous surface area (BET) and large number of Brønsted and Lewis acid sites. In addition, a reasonable reaction mechanism for the amine solvent regeneration with the CMK-3 heterogeneous catalyst is proposed.

**Keywords:** CO<sub>2</sub> capture process, Amine solvent regeneration, Energy penalty, Modified heterogeneous catalysts, desorption rate.

## Introduction

Mankind is facing urgent problems in global warming and ocean acidification<sup>1</sup>. The emission of carbon dioxide (CO<sub>2</sub>) to the atmosphere has become a considerable challenge in the past few decades<sup>2,3</sup>. In this context, CO<sub>2</sub> is known to be a primary greenhouse gas and a dominant contributor to global warming<sup>4</sup>. These concerns have spurred the development of capture processes designed specifically for CO<sub>2</sub> extraction from flue gases simply and economically<sup>5,6</sup>.

Currently, various promising technologies including post-combustion CO<sub>2</sub> capture and Oxy-fuel combustion are being developed and improved in order to mitigate the problem of immoderate CO<sub>2</sub> emission<sup>7,8</sup>. Post-combustion CO<sub>2</sub> capture technology is most widely used due to its capability to be retrofitted into existing power plants and its ability to handle large exhaust streams<sup>9</sup>. Generally, three principal techniques are applicable to post-combustion CO<sub>2</sub> capture, namely, chemical absorption, cryogenic distillation processes, and membrane separation technology<sup>10,11</sup>.

Chemical absorption technology using amine-based solvents has been identified as one of the most promising techniques, because of its significant advantages such as maturity and its great capacity to absorb large amounts of flue gas CO<sub>2</sub><sup>12,13</sup>. Although some progress has been made developing this technology, at least three major obstacles to its application still exist. These include enormous energy demands for the regeneration process of amine solvents, equipment corrosion, and degradation of the amine solvent<sup>14,3</sup>.

Recently, many studies have been undertaken to find ways to decrease the energy requirement for amine solvent regeneration, including solvent innovation, introduction of carbonic anhydrase, evolving higher performance desorption devices and other absorption/desorption inventions<sup>15,16</sup>.

Suggestions have been made to decrease the energy demands using vacuum stripping, solvent split-flow, and inter-cooling of the solvent, all in an effort to reduce the energy consumption<sup>17</sup>.

With regards to absorption/desorption innovation, a recent turning point focuses on using of novel solid sorbents to enhance the desorption rate (DR), thereby reducing the energy consumption of the regeneration process e.g. solid sorbent acids, nanoparticles, and metal oxides<sup>18</sup>. Additionally, the introduction of efficient solvents, including (i) single amines (diethylenetriamine (DETA) 1-(2-hydroxyethyl) pyrrolidine (1-(2-HE) PRLD) and 1-diethylamino-2-propanol (1DEA2P)); (ii) hybrid solvents, such as MEA-methanol and (iii) blends of amines have been discussed for CO<sub>2</sub> capture, also to decrease the energy requirement of amine solvent regeneration<sup>19</sup>. In subsequent studies, Wang et al. proposed that the addition of TiO<sub>2</sub> and other metal oxides could save up to more than 40% of desorption time for the regeneration of rich MEA solvent for loadings of 0.4 to 0.25mol CO<sub>2</sub>/mol amine, compared to that without catalyst<sup>20,21</sup>. Nevertheless, these catalysts still face two important issues which limit their application for the regeneration process of amine solvents, namely rapid loss of activity and small BET surface area<sup>22</sup>.

Given this scenario, a new technology was put forward by Bhatti et al. and Zhang et al. to decrease the required energy and improve the desorption rate by introduction of the Brønsted and Lewis acid and super solid acid catalysts SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>, metal oxide -ZrO<sub>2</sub> and ZnO<sup>23,24</sup>. In another work, Srisang et al. reported that SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> and HZSM-5-γ-Al<sub>2</sub>O<sub>3</sub> exhibit excellent catalytic properties towards CO<sub>2</sub> in comparison to the MEA blank due to the vital role that the Brønsted acid sites of the catalyst play<sup>25,26</sup>. Another novel approach was established by Liu et al. to use the solid acid catalysts to decrease the energy required by CO<sub>2</sub> desorption and amine solvent regeneration, revealing that these catalysts exhibit better system performance than MEA without catalysts<sup>27</sup>. Additionally, other new innovative techniques have been discussed that reduce energy

consumption such as using hybrid absorbents<sup>28</sup>, by the introduction of solid acid catalysts<sup>29</sup>, Zeolite catalyst, and metal ions (copper ions)<sup>30,31</sup>.

A thorough study of the literature shows that MEA was extensively used in the most recent studies as the standard solvent for capturing CO<sub>2</sub> because of its rapid CO<sub>2</sub> absorption, low charge, and suitable stability. These properties have rendered MEA as the benchmark solvent compared to other amines<sup>32,33</sup>. However, MEA itself has significant disadvantages, such as the vast amounts of energy needed for its regeneration which leads to high operating expense<sup>34</sup>.

Prior to the writing of this work, the above-mentioned methods of decreasing the regeneration energy consumption have not reached the desired and economical value for industrial application and this issue continues to be the dominant difficulty for extensive adoption of the CO<sub>2</sub> capture process, despite significant efforts to solve these challenges<sup>35,36</sup>. As a result, a great opportunity exists to develop a novel catalyst to further decrease the energy consumption for CO<sub>2</sub> desorption processes and this improvement can be accomplished through the combination of Brønsted acid sites of the SO<sub>4</sub><sup>2-</sup> and the basic sites of molecular sieve catalysts of SiO<sub>2</sub>.

The novelty of this work is in using a commercial method to synthesize and combine the Brønsted acid sites of the solid acid catalyst SO<sub>4</sub><sup>2-</sup> and the basic sites of molecular sieve catalysts of SBA-15, MCM-41, SiO<sub>2</sub> while avoiding the small surface area drawbacks of the SO<sub>4</sub><sup>2-</sup>. This is accomplished by modifying it with a carbon template to obtain the modified heterogeneous catalysts CMK-3 which are considered as a great opportunity to decrease the energy penalty for CO<sub>2</sub> desorption processes, furthermore reducing the energy cost of amine solvent regeneration.

In this study, modified heterogeneous catalysts CMK-3 have been synthesized and applied in order to utilize their favorable Brønsted acid sites (B), their tunable textural features, good stability

and high surface area. Nevertheless, no previous work has contributed to the application of CMK-3 carbon mesoporous catalysts for this purpose. Against this background, in this work, three mesoporous modified catalysts, namely: CMK-3-SiO<sub>2</sub>, CMK-3-MCM-41, and CMK-3-SBA-15 were prepared and introduced into rich-MEA to evaluate their performance towards CO<sub>2</sub> desorption and MEA solvent regeneration. Furthermore, a logical reaction mechanism of the MEA solvent with CMK-3 catalysts is proposed, and the effectiveness of the synthesized catalyst on the CO<sub>2</sub> absorption performance of lean 5M MEA is discussed.

## Experimental section

### Materials

Amine solvent purity more than 99.9%, SBA-15 mesoporous template, MCM-41, white powdered SiO<sub>2</sub>, and concentrated sulfuric acid H<sub>2</sub>SO<sub>4</sub> (98%) were purchased from Aladdin Industrial Corporation, Co. Ltd., China. These materials were used for the preparation of the CMK-3 modified catalysts (CMK-3-SBA-15, CMK-3-SiO<sub>2</sub>, and CMK-3-MCM-41).

### Catalysts preparation

An impregnation method with slight modification was used to synthesize CMK-3 as follows: Exactly 2.0g of one of the selected templates (SBA-15, SiO<sub>2</sub>, or MCM-41) was dissolved in double-distilled water and added to the pre-mixture which consisted of exactly 0.28g H<sub>2</sub>SO<sub>4</sub> with 2.5g of sucrose and 10g double-distilled water and stirred for 30 minutes at 300rpm to obtain a homogenized solution. The resulting premixture was then dried for 6h at 150°C. Another mixture consisting of 10.0g of H<sub>2</sub>O, 180mg sulfuric acid and 1.6g sucrose were added to the first mixture. To complete the carbonization and finalize the structure of the template, the silica mixture was

heated at 900°C for 6h under nitrogen. Then, to get this template free of carbon it was washed with 5% wt. of HF at 25°C and then dried at 110°C for 24h.

### Synthesis of SZ catalysts

The impregnation method was used to synthesize solid acid catalysts (SZ) with an insignificant modification. The desired mass quantity of zirconium nitrate was suspended in (DI) water under vigorous stirring at 25±2°C and 350rpm to acquire a completely mixed suspension. Then water was removed by drying at 120°C overnight and the dried sample was subjected to 350 °C for 2.5h. The obtained sample was immersed in a suitable amount of 0.5 mol/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution at a ratio of 10mL/g, with 2h of stirring at 25±°C to reach equilibrium. To acquire the SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> catalyst the obtained sample was subjected to 650°C under constant air for 4h.

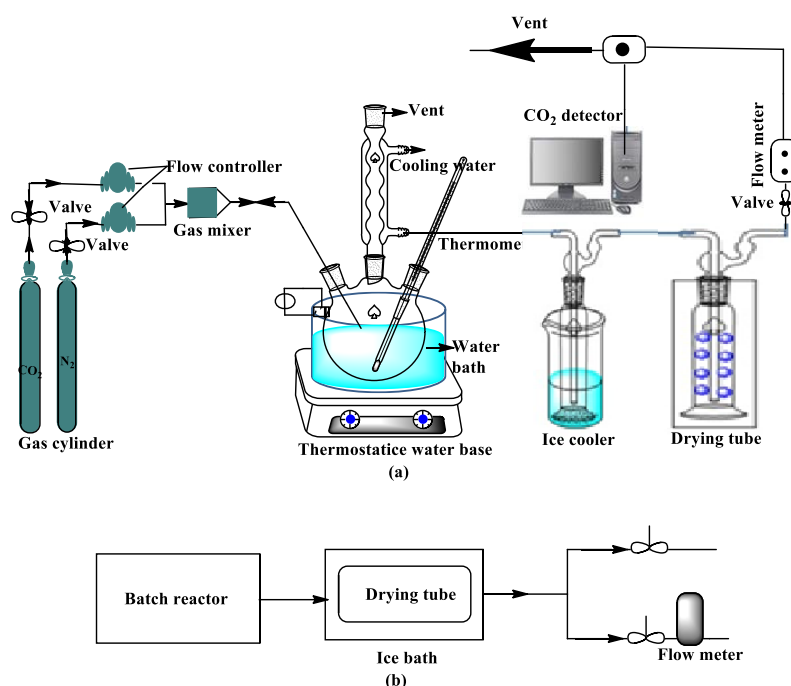
### Catalyst characterization

Pyridine adsorption-infrared spectroscopy (Py-IR) was performed to study the Lewis (L) and Brønsted (B) acid sites in the CMK-3 carbon mesoporous catalysts using a Nicolet iS10 IR spectrometer (100 scans, 4cm<sup>-1</sup> resolution, Thermo Scientific, America). The acidity strength properties of the catalysts can be detected by monitoring the pyridine thermal desorption. A Bruker Vector 22 spectrometer was used to acquire the ratios of Brønsted to Lewis acid sites (B/L) in the catalyst in the absorption mode with a resolution of 4cm<sup>-1</sup>.

A self-supporting wafer of each catalyst was prepared and loaded in the cell of the Py-IR. To remove the adsorbed air on the catalyst surface the wafer was preheated at 240°C for 60 minutes under oxygen flow, then the catalyst samples were cooled down to room temperature prior to detecting the background spectra. The quantitative analysis was then used to calculate the amount of Brønsted and Lewis acid sites and the total acid number of the sample. The Brønsted acid sites



(B) and Lewis acid sites (L) can be determined within the bands at around  $1560\text{cm}^{-1}$ ,  $1490\text{cm}^{-1}$ , and at  $1460\text{cm}^{-1}$  respectively. The pore structure and specific surface area of the synthesized catalysts were detected by TriStar II 3020 instrument (Micro metrics Instrument Corporation-Germany), with a  $\text{N}_2$  adsorption/desorption experiment that was operated at the temperature ( $-195^\circ\text{C}$ ) of liquid nitrogen. Individually samples were outgassed down to  $10^{-3}$  Torr after digestion at  $240^\circ\text{C}$  overnight.



**Fig. 1.** The experimental setup for a) CO<sub>2</sub> desorption experiment and b) CO<sub>2</sub> absorption under atmospheric pressure.

### CO<sub>2</sub> desorption experiment

Exactly 500mL of rich 5M MEA with  $0.5 \pm 0.02$  mol/mol of CO<sub>2</sub> was poured into a 1L three-necked round flask as presented in Fig.1.(a),(b). The initial concentration of MEA-CO<sub>2</sub> for all experiments was adjusted to be in the range of  $0.5 \pm 0.02$  mol/mol. CO<sub>2</sub> was bubbled gradually into the amine solution to get the CO<sub>2</sub>-rich loading. A blank test of MEA was performed before studying

the catalyst to examine the regeneration performance of the MEA solvent without catalyst and using the blank results as a baseline <sup>37</sup>.

In all experiments, 6.26g of particles 0.5-2mm in size of the synthesized catalyst were mixed with the 500mL MEA-CO<sub>2</sub> loaded solution to get a weight ratio of CMK-3 catalyst to the amine solvent of 1.0/80 (wt/wt) which was mixed with the MEA solution in the three-necked round flask. Then, a thermostatic hot oil bath was used to immerse the necked flask in and the batch reactor was linked to an oil circulator to heat and sustain the required temperature of the MEA solvent at 97°C for 180min. To monitor the temperature of the rich MEA solvent with and without catalyst and to ensure even temperature distribution, a thermometer and a magnetic stirrer bar were placed in the middle of the round flask with rotation speed of 300rpm. The amount of released CO<sub>2</sub> from rich MEA solvent was recorded to determine the starting point of the CO<sub>2</sub> stripping from MEA solvent. A gas flow meter controller was used at the beginning of each experiment to adjust the carbon dioxide (CO<sub>2</sub>) and nitrogen (N<sub>2</sub>) gas at the desired concentrations before they were passed into the bottom of the batch reactor. The infrared CO<sub>2</sub> detector was installed to detect the CO<sub>2</sub> exiting the top of the column after the desorption process. To ensure the accuracy of the obtained results for each experiment, MEA-CO<sub>2</sub> concentrations were measured in duplicate and the average of the acquired results was recorded as the final result.

### Absorption experiment

In order to evaluate the side effects of modified CMK-3 mesoporous catalyst on the performance of lean amine solvent (regenerated MEA), the CO<sub>2</sub> absorption performances of the fresh MEA solution and the recycled MEA solution after catalyst removal were compared. Approximately 100mL of 5M MEA was placed in the preheated water vessel at 40°C with CO<sub>2</sub> pressure controlled at 15.0 kPa. During the first 3h, 1mL samples were taken using an appropriate

pipette to study the absorption performance of the regenerated MEA by applying Chittick apparatus method as presented in Fig.S3. and Fig.S4<sup>37</sup>. More details about the Chittick apparatus method can be found in the Supporting Information.

### Evaluation of catalytic solvent regeneration performance

The CO<sub>2</sub> desorption heat duty (H, kJ/mol) was studied to evaluate the catalytic MEA solvent regeneration performance of MEA-CMK-3 catalytic systems, based on the expression Eq.1.

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

where H<sub>input</sub> (kJ/mol) is the heat duty in the first 3h of the (MEA-CMK-3) systems during CO<sub>2</sub> stripping and MEA regeneration process. The relative heat duty (RH) was determined according to Eq. 2. as the results of the ratio of the MEA-CMK-3 during first 180min (H<sub>i</sub>) divided by the blank (H<sub>b</sub>) for the same period.

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

The electrometer detector was used to detect the total heat input H<sub>i</sub> and recalculated to be in kJ/mol, while the regenerated amount of MEA solvent was recognized as the cyclic capacity of CO<sub>2</sub> (CC<sub>CO<sub>2</sub></sub>).

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

where CC<sub>CO<sub>2</sub></sub> (mol) is the desorbed amount of CO<sub>2</sub>, γ<sub>rich</sub> and γ<sub>lean</sub> refer to the initial amount of MEA-CO<sub>2</sub> (mol) and the final MEA-CO<sub>2</sub> loading. To estimate the catalytic activity, the regeneration performances were studied according to the following Eq.4.

$$RP = \frac{C_{CO_2} \times DR}{H_{CO_2}} \tag{4}$$

where the RP refers to the regeneration performance of MEA mol<sup>3</sup>/(kJ.min) and the DR is the desorbed rate of CO<sub>2</sub> (mol<sup>3</sup>/min).

Results and discussion

Characterization of CMK-3 catalyst

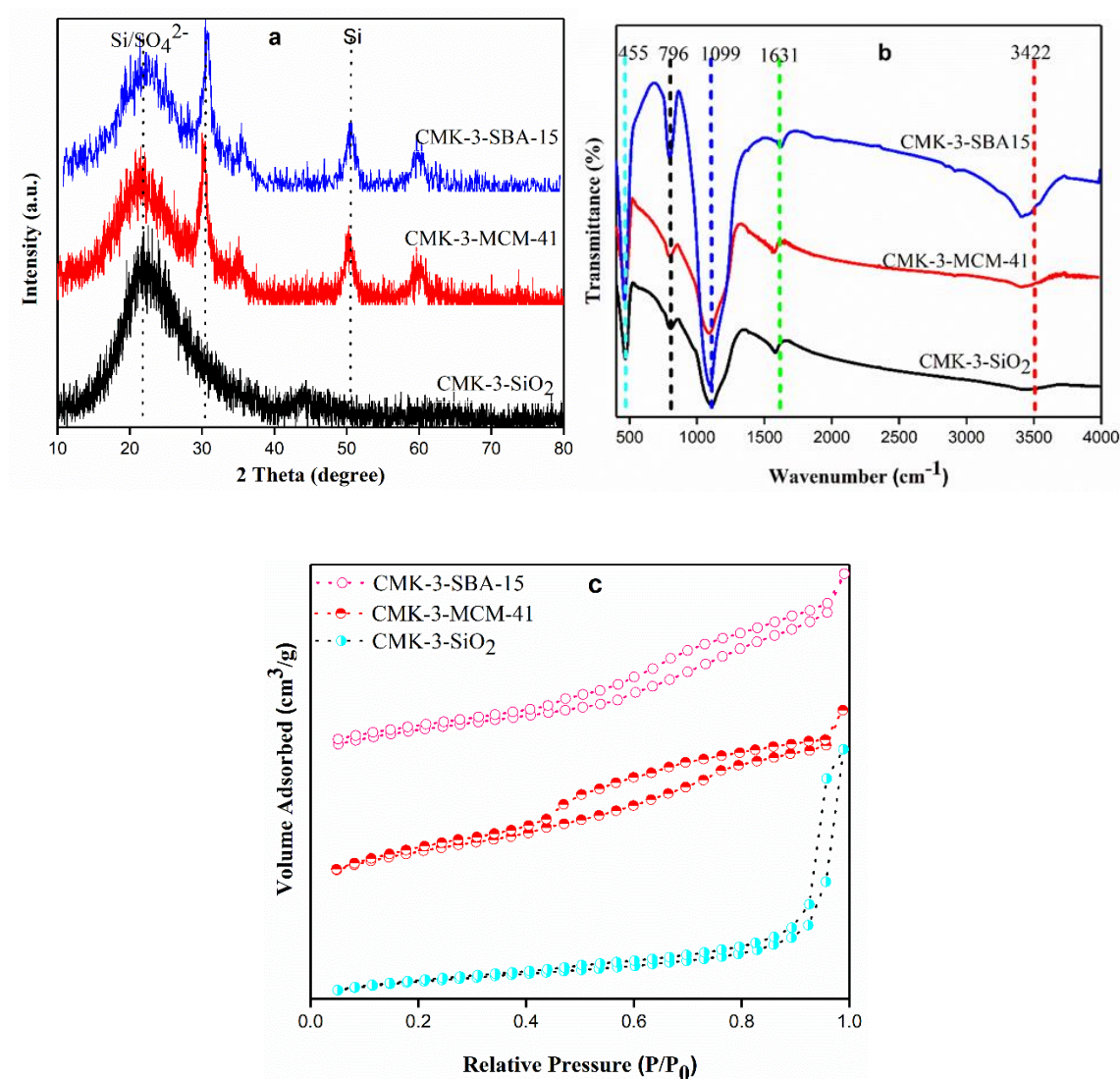
The XRD patterns of the CMK-3 catalysts are shown in Fig.2. (a). It is clear that the XRD peaks of CMK-3-MCM-41 and CMK-3-SBA-15 modified mesoporous catalysts show similarity while the secondary peaks in the case of CMK-3-SiO<sub>2</sub> have disappeared which proves the existence of an interaction between carbon and silicon mesopore in case of CMK-3-SiO<sub>2</sub>. In addition, the results indicate that some silica still exists as small particles distributed on the catalyst surface, which confirms that the interaction between MCM-41 and SBA-15 is incomplete from one side and the carbon surface on the other side in case of CMK-3-MCM-41 and SBA-15. The FT-IR spectrum of the CMK-3 catalysts is shown in Fig. 2 (b).

Table 1. Textural properties of CMK-3 catalysts.

Catalyst	BET (m <sup>2</sup> /g)			Pore Volume cm <sup>3</sup> /g	Average Pore diameter
	Microspore	Mesopore	Total		
SZ	13.01	52	65.1	0.08	18.23
CMK-3-SBA-15	19.91	98.93	118.84	0.177	3.66
CMK-3-MCM-41	28.2	207.39	235.59	0.211	3.64
CMK-3-SiO <sub>2</sub>	33.11	292.03	325.144	0.64	3.94

It is clear that the spectra of thiocarbonyl exhibits the identity for all of the CMK-3 catalysts. Their spectra showed a peak between 1050 and 1200cm<sup>-1</sup>, which is assigned to C=S groups.

The peaks at  $700\text{cm}^{-1}$  are linked to silicon function. This indicates that the main structure of CMK-3 catalyst was well-preserved after the mesopore was loaded. Moreover, there are no other bonds of impurities detected which complement and confirm the results obtained by XRD<sup>38</sup>.

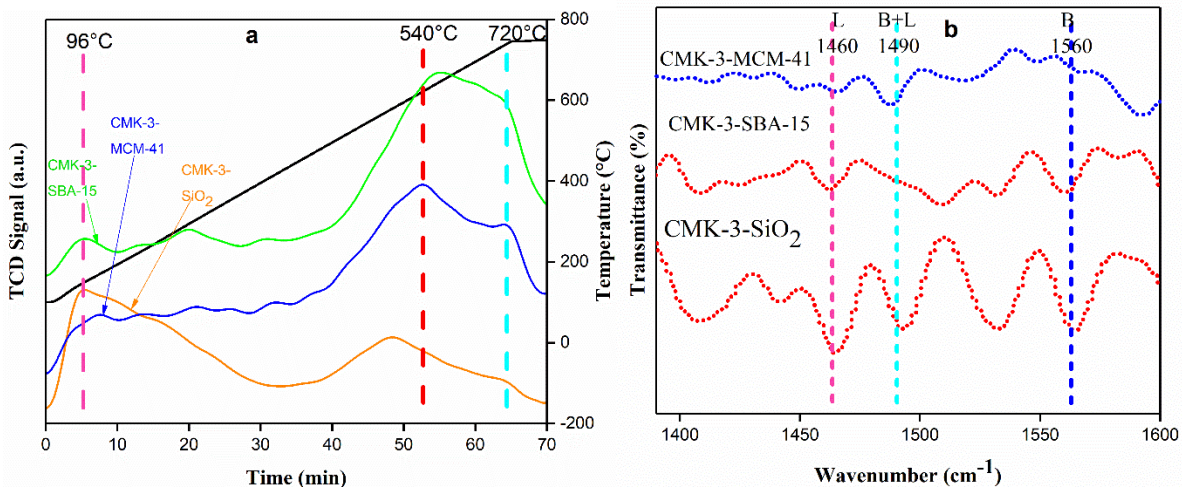


**Fig. 2.** (a) X-ray patterns, (b) FT-IR spectra, and (c) N<sub>2</sub> desorption isotherms of CMK-3 catalysts.

According to the obtained results of the modified CMK-3 carbon mesoporous catalyst, adding SiO<sub>2</sub> carrier clearly improved the BET and mesopore surface area (MSA) of the synthesized catalyst. The BET of the CMK-3 catalysts and the pore volume were increased according to the

following order: CMK-3-SiO<sub>2</sub> > CMK-3-MCM-41 > CMK-3-SBA-15 > SZ, and this result is illustrated in Fig. 2 (c) and Table 1.

NH<sub>3</sub>-TPD was applied to detect the acid site strength of the CMK-3 catalyst, and the obtained results are presented in Fig. 3 (a) and Table 2. The NH<sub>3</sub> desorption peaks proved that the acidic properties of the catalyst can be divided into: weak and strong acid sites at 50–250°C and over 500°C respectively. Desorption patterns display two main peaks at nearly 97°C and 540°C, which are assigned to the strong and weak acid sites. Table 2 lists the Lewis acid sites (L), Brønsted acid sites (B), and B/L acid sites of the four synthesized catalysts.



**Fig.3.** (a) NH<sub>3</sub>-TPD profiles, and (b) Py-IR spectrum of CMK-3 catalysts.

The obtained data confirm the acidity properties for the four synthesized catalysts and that the composition of CMK-3 with SiO<sub>2</sub> enhance the total acid sites as compared to CMK-3-SBA-15 and the super solid acid catalyst SZ. In addition, as shown in Table 2, the CMK-3-SiO<sub>2</sub> exhibits the highest Brønsted and Lewis acid sites, and the SZ possesses the lowest B and L acid sites. The Pyridine adsorption-infrared technique (Py-IR) was applied to determine the acid sites present on the synthesized catalyst surface. Strong bands are present at 1450cm<sup>-1</sup> and 1540 cm<sup>-1</sup> at 450°C for

1h, indicating that the surface of the CMK-3 catalyst has covalent bonds resulting from the S=O species<sup>39</sup>.

The obvious peaks recorded at  $1460\text{cm}^{-1}$ , indicated by L, are assigned to the existence of (L) species on all three catalysts. The peaks present at  $1490\text{cm}^{-1}$ , indicated by L+B, are attributed to the existence of a of Lewis and Brønsted acid sites species as shown in Fig.3 (b). The strong py-band at  $1460\text{cm}^{-1}$  is assigned to the (L) number of the synthesized catalyst because the py-chemisorption takes place on Lewis acid sites (L) in this area. Thus, it is rational to conclude that the strong acid sites value on CMK-3-SiO<sub>2</sub> catalyst is greater than that of CMK-3-MCM-41 and CMK-3-SBA-15 catalyst as listed in Table 2. The methods to calculate the Brønsted and Lewis acid sites (B, L) and (B/L) ratio can be found in the Supporting Information.

### The reliability of the experiment

To ensure the accuracy and reliability of the experiments, the desorbed amount of CO<sub>2</sub> in the liquid phase method and the CO<sub>2</sub> amounts in the gas phase method were measured and compared. According to the results obtained, absolute relative deviations (ARD) of the rich MEA were less than 3.50% as registered in Table 3. Therefore, we can conclude that the results in this experiment are reasonable and reliable.

### Catalytic performance

Figs.4 (a, b) present the curves of CO<sub>2</sub> desorption of 5M MEA with initial CO<sub>2</sub> loading of  $0.5\pm 0.02\text{mol/mol}$  with and without addition of the synthesized CMK-3 modified catalyst carbon mesoporous catalysts at  $97^{\circ}\text{C}$  as a function of time.

It can be seen that desorption performance of the synthesized catalysts with different sources of silica (SBA-15, MCM-41 or SiO<sub>2</sub>) during the first 180min of the experiment was enhanced compared to that of the blank run.

**Table 2.** Acidic properties of the CMK-3 catalysts.

Catalyst	Acidity (mmol/g)		Strength of the acidity (mmol/g)			
	Brønsted	Lewis	Brønsted / Lewis ratio	Strong acid	Weak acid	Total
SZ	0.23	0.091	2.53	0.452	0.691	1.503
CMK-3-SBA-15	0.33	0.128	2.54	0.812	0.932	1.384
CMK-3-MCM-41	0.22	0.067	3.33	0.987	0.987	1.974
CMK-3-SiO <sub>2</sub>	0.45	0.472	0.95	1.203	1.261	2.464

It is clear that in the first 90min there is a sharp decline in CO<sub>2</sub> desorbed and then a slight change was observed after that with both MEA with and without addition of catalyst. Therefore, the first 90 minutes was taken in consideration to study the catalyst performance and to investigate the spent energy during CO<sub>2</sub> stripping processes in this study.

Table 4 presents the results, (CC), Relative heat duty (RH) and (DR) for 5M MEA-CO<sub>2</sub> loading with and without catalysts. The best performance was recorded for CMK-3-SiO<sub>2</sub> compared to the MEA blank and other CMK-3 catalysts. The results exhibit that CMK-3-SiO<sub>2</sub> catalyst decreases the required heat duty by 37.41%, and enhances the cyclic capacity and desorption rate of CO<sub>2</sub> by 68% and 195% compared to that of the MEA without any catalyst, see Fig.6 (d). It is obvious that the RH of the synthesized catalyst was significantly decreased in the order of MEA-CMK-3-SiO<sub>2</sub> (62.59)> MEA-CMK-3-MCM-41 (69.70) > MEA-CMK-3-SBA-15 (78.50) > SZ (89.86) > No catalyst (100). MEA-CMK-3-SiO<sub>2</sub> exhibits the best catalytic performance while the SZ catalyst had the poorest catalytic performance. Generally, addition of CMK-3 and SZ catalysts into amine solution during the regeneration process significantly improved the desorption rate and the cyclic capacity and reduced the energy consumed in MEA regeneration.



**Table 3.** Mass Balance of the Gas and Liquid Phase Methods after 3h.

Catalyst	Gas phase (Mol/mol)	Liquid phase (Mol/mol)	AAD (%)
MEA-Blank	6.90 (0.30)	0.29	3.44
MEA- SZ	7.36 (0.33)	0.34	3.03
MEA- CMK-3-SBA-15	10.25 (0.46)	0.45	2.22
MEA- CMK-3-MCM-41	10.02 (0.45)	0.46	2.17
MEA- CMK-3-SiO <sub>2</sub>	10.69 (0.49)	0.49	0

The averat of (ARD) was calculated as 2.17

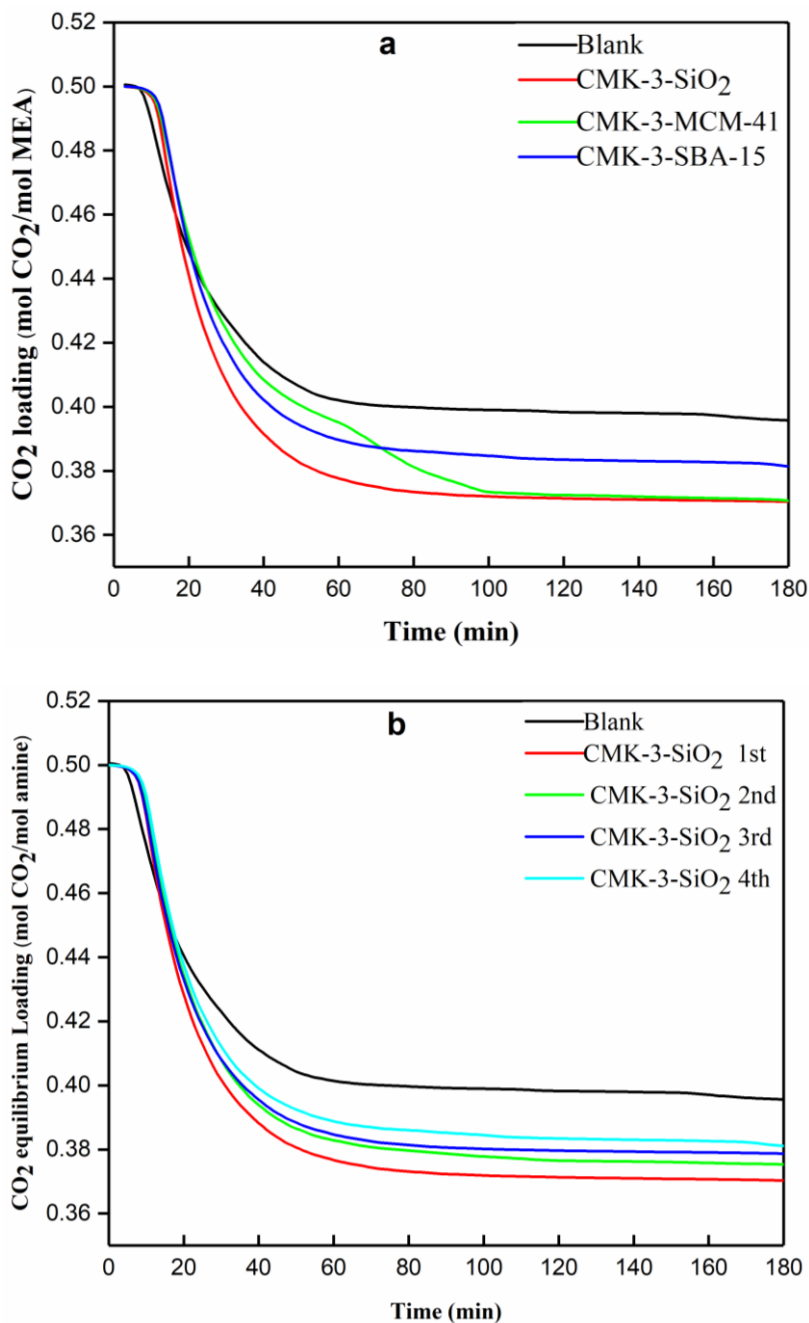
### Comparison of CMK-3 catalysts with the published catalysts

To the best of our knowledge, CMK-3-SiO<sub>2</sub> exhibited the best catalytic performance with lowest energy consumption by about 62.59% compared to the MEA blank as well as significantly improved the desorption rate than the catalysts in previous studies, such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, H-Y, MCM-41, SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>, SAPO-34 and HZSM-5 as listed in Table 5.

Hence, according to the acquired results the synthesized CMK-3-SiO<sub>2</sub> presents the superior catalytic performance as compared to the reported catalysts in this area at the same conditions during regeneration of the MEA solvent. It should be noted that the operational conditions were different for all the investigations, and the validation and comparison should be further studied.

**Table 4.** CO<sub>2</sub> desorption performance of MEA with and without catalyst at 97°C after 3h.

Catalyst	Relative heat duty (%)	Desorption Rate (*10 <sup>-3</sup> mol/min)	Cyclic Capacity (mol/mol)
MEA-Blank	100	1.62	0.29
MEA- SZ	89.86	1.88	0.28
MEA- CMK-3-SBA-15	78.50	2.50	0.31
MEA- CMK-3-MCM-41	69.70	2.55	0.34
MEA- CMK-3-SiO <sub>2</sub>	62.59	3.16	0.49

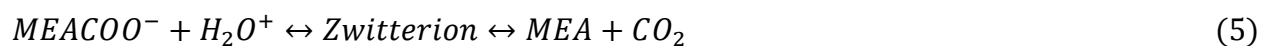


**Fig. 4.** CO<sub>2</sub> desorption profiles of MEA with a) fresh and b) recycled CMK-3 catalysts at 97°C.

**Catalytic mechanism**

The catalytic mechanism of CO<sub>2</sub> desorption in MEA solvent occurs via two main steps. According to the Zwitterion reaction mechanism for the CO<sub>2</sub> desorption process with a primary amine (e.g. MEA), the first step is breakdown of MEACOO<sup>-</sup> as shown in Eqs. 5 and 6, recognized

as proton transfer and carbamate formation. The second step is the deprotonation of  $\text{MEA}^{\text{H}^+}$  as shown in Eqs. 7,8.



Process of  $\text{MEA}^{\text{H}^+}$  deprotonation:



The main reasons for the enormous energy consumption of the monoethanol amine solvent regeneration process can be attributed to two factors. Firstly, the struggle of ( $\text{H}^+$ ) transmission from protonated amine to water owing to the higher basicity of primary amine MEA than  $\text{H}_2\text{O}$ . Secondly, the regeneration process of MEA solvent is a significant endothermic reaction and requires huge amounts of energy to force it to happen. Practically, addition of CMK-3 catalyst to the loaded MEA- $\text{CO}_2$  during the regeneration process can accelerate  $\text{MEA}^{\text{H}^+}$  deprotonation reactions and can decrease the energy of the deprotonation reaction making the  $\text{HCO}_3^-$  act as a catalyst and decreasing the activation energy of  $\text{H}^+$  liberation.

A proposed catalytic mechanism for MEA regeneration with CMK-3 catalyst is presented in Fig.5. The reaction is understood to take place through four steps:

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(I) A proton transfer to MEACOO<sup>-</sup>. (II) The semi-metal (e.g. Si) attacks the nucleophile part of oxygen molecule in the. MEACOO<sup>-</sup> and the chemisorption takes a position at oxygen molecules. (III) A transformation step for proton to the nearby nitrogen from the oxygen molecule which called an isomerization reaction. (IV) Immigration step for proton from sp<sup>2</sup> hybridization to sp<sup>3</sup> which results in broken conjugation nitrogen bond and then the carbon-nitrogen bond starts stretching.

Table 5. A summarized review of related studies for catalytic MEA-based solution regeneration during the CO<sub>2</sub> capture process.

	Amine system	Desorption temperature (°C)	Result	References
Supported catalyst Al <sub>2</sub> O <sub>3</sub> /HZSM-5	MEA	96	The CO <sub>2</sub> desorption rate was enhanced by 31.0% after addition weight ratios (2/1) of γ-Al <sub>2</sub> O <sub>3</sub> /H-ZSM-5 to the MEA sorbent	Zhang et al. <sup>23</sup>
ZrO <sub>2</sub> , ZnO	MEA	86	The CO <sub>2</sub> desorption rate for ZrO <sub>2</sub> was better than ZnO, and the amount of CO <sub>2</sub> desorbed improved by 31-32%.	Bhatti et al. <sup>24</sup>

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4				The heat duty to regenerate 5M MEA with	
5	HZSM-5, $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	MEA	95	catalyst was reduced by 30% improved	Srisang et al. <sup>25</sup>
6				absorption efficiency by 23.6%	
7					
8					
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11					
12				Addition of SAPO-34 to the 5M MEA could	
13	SAPO-34,			reduce the heat duty by 24.3% and enhanced	Zhang et al. <sup>29</sup>
14	SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub>	MEA	96	the CO <sub>2</sub> desorption rate by 28.2% compare	
15				to 17.1 and 14.1% only for SO <sub>4</sub> <sup>2-</sup> /TiO <sub>2</sub> .	
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21	bifunctional heterogeneous			The addition of SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> /SiO <sub>2</sub> 15% can	
22	catalysts SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub>	MEA	97	enhanced the desorption rate of CO <sub>2</sub> by	Zain et al. <sup>36</sup>
23	SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> /SiO <sub>2</sub>			35.1%.	
24					
25					
26					
27	CMK-3-SiO <sub>2</sub> ,			CMK-3-SiO <sub>2</sub> exhibited the best catalytic	
28	CMK-3-MCM-41,			performance by enhancing desorption	The present
29	CMK-3-SBA-15,	MEA	97	performance by 195% compare to MEA	work
30	and SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub>			without catalyst.	
31					
32					

This step requires large amounts of energy and hardly happens without catalyst, hence the addition of the CMK-3 catalyst to the reaction contributed significantly to accelerate the reaction by decreasing the energy required to break the carbon-nitrogen bond. As is known, the regeneration process of the primary amine (MEA) requires temperatures of 125°C to split the carbon-nitrogen bond, a temperature which results in corrosion of equipment and increases the total cost of the regeneration process for the rich amine.

In this study 97°C was designated as the temperature for MEA-CO<sub>2</sub> loading regeneration with the synthesized catalyst which resulted in significant improvement for the desorption experiment. As well, the consumption of energy and equipment corrosion was decreased significantly at this temperature, thus further decreasing the total operation cost.

**Table 6.** The textural properties comparison of CMK-3.

Catalyst	Total acid	B/L	B	BET	Basic acid site (mmol/g)	B*Basic acid site (mmol/g)	RP
Blank	0	0	0	0	0	0	0.46
HZSM-5	0.56	4.31	0.125	337.7	0.164	0.020	0.61
SZ	1.50	2.54	0.231	65.1	0.53	0.12	0.71
CMK-3-SBA-15	1.38	2.54	0.30	118.84	0.78	0.23	1.43
CMK-3-MCM-41	1.97	3.33	0.35	235.59	1.00	0.22	1.68
CMK-3-SiO <sub>2</sub>	2.46	0.95	0.45	325.14	1.13	0.51	1.97

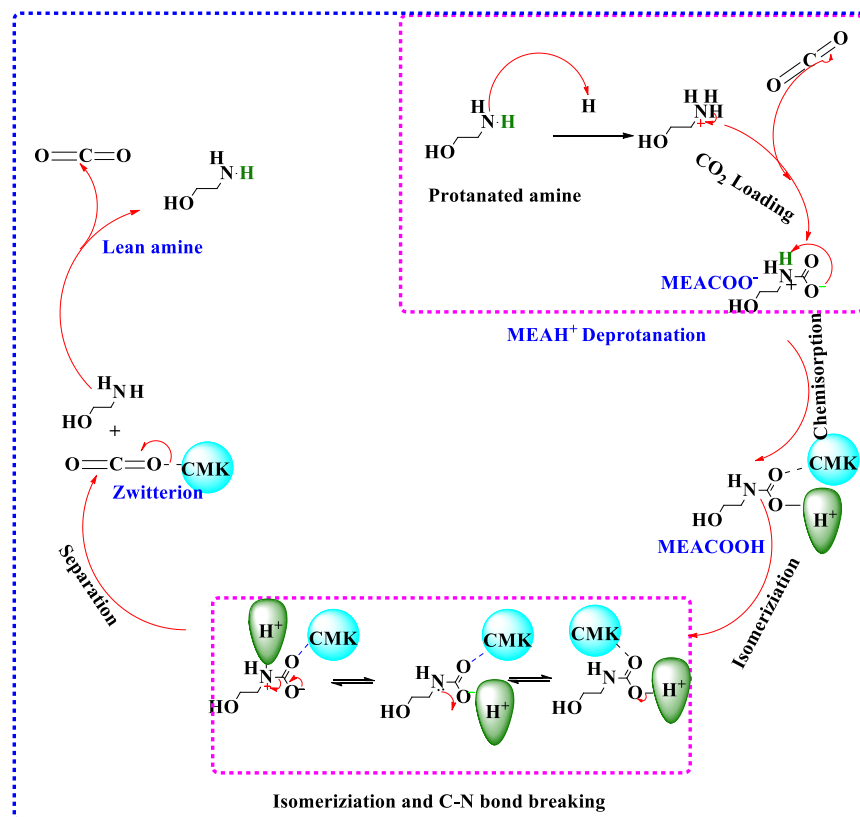
The unit of RP is (10<sup>-2</sup> mol<sup>3</sup>/KJ.min).

**CMK-3 catalytic CO<sub>2</sub> desorption performances**

During the CO<sub>2</sub> desorption process, there is a main stage which is called temperature ramp-up. In this stage the CO<sub>2</sub> loaded in the liquid phase (MEA solvent) apparently transfers to the gas phase. In this stage the catalytic solutions desorbed higher quantities of CO<sub>2</sub> during the experiments while MEA solvent without catalyst exhibited little change in the desorption rate at the same conditions as shown in Fig.S1. More details about the desorption rate changes can be found in Supporting Information.

Moreover, the (B), (SAS), and (TAS), Brønsted, Strong, and Total acid sites respectfully, which are assigned to the physical properties of the catalyst, were demonstrated in the reaction mechanism, have important impact on the catalytic performance of the catalyst toward CO<sub>2</sub>

desorption. Previous study by Bairq et al. mentioned the impacts of the B/L ratio on the regeneration of amine solvents<sup>36</sup>.

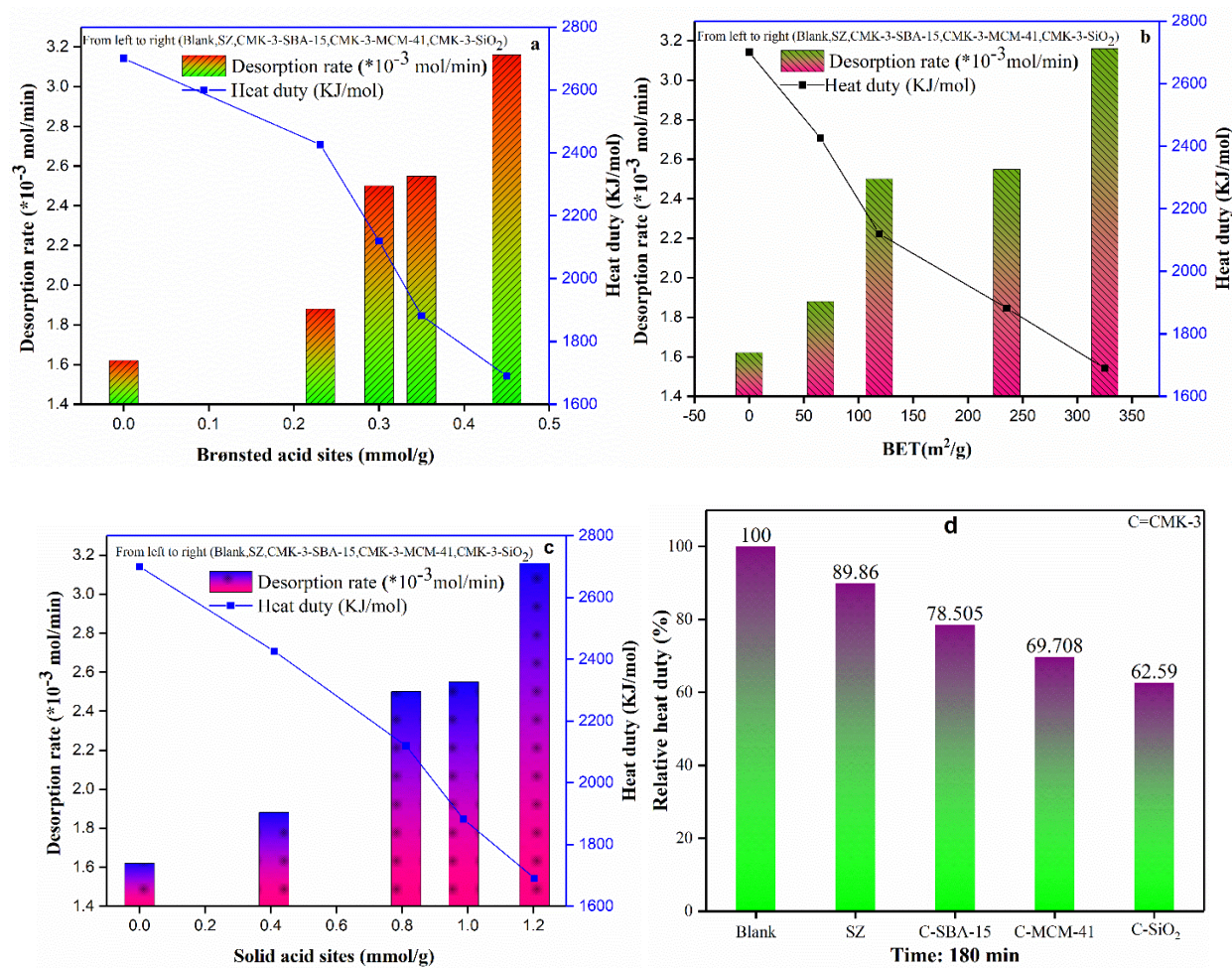


**Fig. 5.** Suggested mechanism of MEA regeneration with CMK-3 catalysts.

Table 6 lists the relation between the textural properties of the catalysts and their regeneration performance. From the obtained results, we can conclude that CMK-3-SiO<sub>2</sub> followed by CMK-3-MCM-41 have the biggest (BET), the strongest acid sites, and highest basic acid site feature, resulting in the best catalytic regeneration performance. The lowest strong acid sites, and basic acid site value were for SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> and CMK-3-SBA-15 respectively, thereby demonstrating that the basic acid sites and the other physical properties are important factors for promoting the CO<sub>2</sub> desorption and enhancing the regeneration process of loaded MEA-CO<sub>2</sub>. Figs.6(a, b and c) shows the relationship between the single catalytic advantages of the CMK-3 catalysts such as B, SAS and BET with the catalytic activities.

It is clear to see that the best catalytic performance can be achieved when the B and BET have high value and decreased when this value decreased, which confirms that these properties play a vital part in the catalytic performance of the synthesized catalyst during the regeneration process.

Based on these facts it can be concluded that the physiochemical properties such as BET, Brønsted and solid acid sites of the synthesized catalyst have a vital impact on the catalytic performance during stripping process of CO<sub>2</sub> and MEA solvent regeneration.

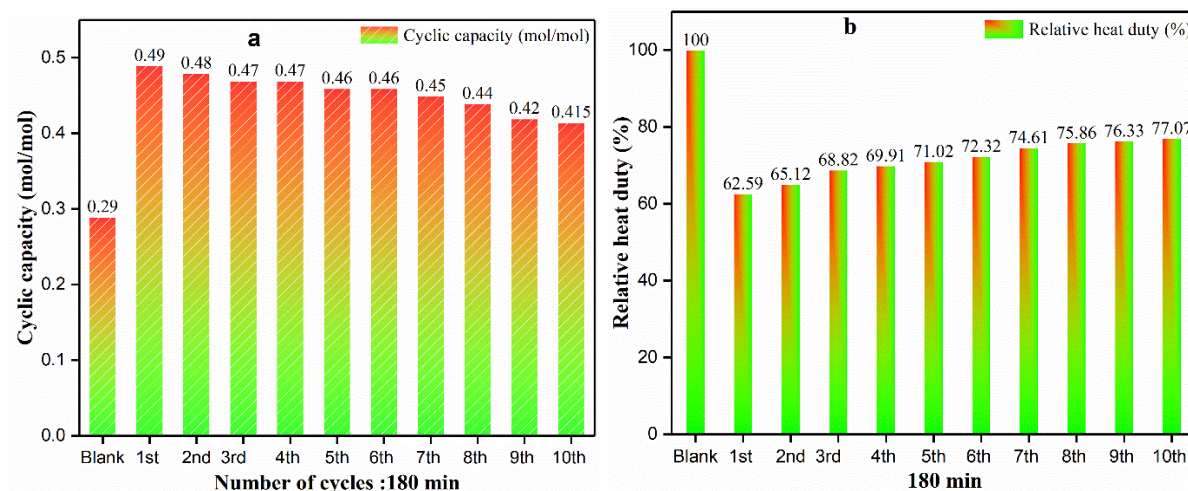


**Fig. 6.** Effects of single properties of CMK-3 catalysts (a) Brønsted acid sites, (b) BET surface area and (c) Solid acid sites, on the catalytic desorption performance, and (d) Relative heat duties of MEA regeneration with and without catalyst after 3h.



### Real stability of the cycled catalyst

In this work, the examination of the reusability of the catalyst for the MEA CO<sub>2</sub>-loaded solvent regeneration process was performed and the CMK-3-SiO<sub>2</sub> was chosen for ten cycle tests.



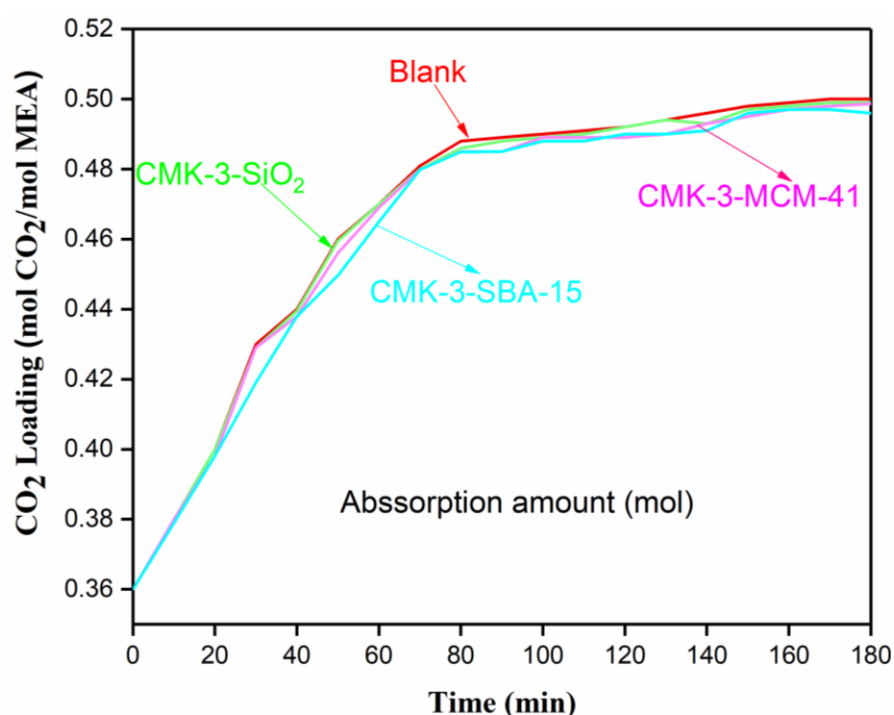
**Fig. 7.** Recyclability test (a) Cyclic capacity, and (b) Relative heat duty of spent CMK-3-SiO<sub>2</sub> catalyst after 10 cycles.

The changes in the energy consumption for the recycled catalysts after ten cycles was recognized as relative heat duty which increased from 62.59% to 77.07% and the cyclic capacity decreased from 0.49-0.42mol/mol as illustrated in Figs.7(a,b). Hence, we can say that approximately 85% of catalytic properties were still retained after ten cycles.

XRD and FT-IR patterns for the fresh and spent catalyst are presented in Figs.S2(a, b). Based on the obtained results there are no obvious changes in the physical and chemical properties of the cycled catalyst CMK-3-SiO<sub>2</sub> catalyst after using for ten cycles. This proves that the CMK-3-SiO<sub>2</sub> catalyst has excellent stability, and it can be recommended to be applied for CO<sub>2</sub> capture and amine solvent regeneration application.

### Impact of the catalysts on CO<sub>2</sub> absorption performance

Using a suitable amine-catalyst system in the regeneration process to decrease the energy required is becoming one of the favored techniques in post-combustion CO<sub>2</sub> capture technology. It is essential to evaluate the effect of the catalysts on the CO<sub>2</sub> absorption process to understand the side impacts of this modified catalyst on the used amine solution. To examine the impacts of catalyst usage on the performance of the regenerated MEA, two scenarios were created. Firstly, the CO<sub>2</sub> absorption for the fresh 5M MEA was studied. Secondly, the CO<sub>2</sub> absorption for the lean MEA with a CO<sub>2</sub> loading 0.36mol/mol was studied.



**Fig. 8.** CO<sub>2</sub> absorption curve of pure and regenerated MEA solvent.

Fresh amine solvent was used as a blank and compared with a lean MEA solvent after separation of CMK-3-SiO<sub>2</sub>. As presented in Fig. 8, the CO<sub>2</sub> loading vs. time was plotted for the first 3h and the CO<sub>2</sub> absorption curves for both fresh and lean MEA are essentially identical. This confirms that there are no side effects of using modified heterogeneous catalyst CMK-3 in absorption and reabsorption of CO<sub>2</sub> in the regenerated MEA solvent.

## CONCLUSION

In conclusion, a series of modified mesopore catalysts with silica sources were successfully synthesized and applied to study their catalytic performances on MEA solvent regeneration as well as their effects on the regenerated MEA-CO<sub>2</sub> absorption properties. The experimental results revealed that the synthesized CMK-3 catalysts were significantly effective to decrease the energy consumption and enhance the desorption rate of CO<sub>2</sub> compared to the 5M MEA without catalyst and improving the MEA solvent regeneration by lowering the relative energy penalty of the operation.

The results of this study demonstrate that the CMK-3-SiO<sub>2</sub> catalyst exhibited the best catalytic performance during the rich-MEA regeneration process by decreasing the relative heat duty by 37.41% by adding 6.25g of CMK-3-SiO<sub>2</sub> to the MEA. The desorption rate was enhanced by 195% compared with that for MEA as a baseline, a result of the complete interaction between the silicon oxide (SiO<sub>2</sub>) and carbon surface in the presence of SO<sub>4</sub><sup>2-</sup>. Moreover, the poorest catalytic activity was exhibited by SZ and CMK-3-SBA-15 due to the reduced BET, lower (B), and (L). It is also worth noting that all synthesized catalysts in this work had no side effects on the CO<sub>2</sub> absorption. Based on the above results of the synthesized CMK-3-SiO<sub>2</sub> catalyst such easy synthesis, high desorption rate, less heat duty required, and superior stability during the rich-MEA regeneration, it can be recommended for the industrial application to decrease the energy consumption for CO<sub>2</sub> capture and storage.

Future work can be carried out by further developing high-efficiency bifunctional catalysts with excellent properties and combining them with metal oxides to couple the advantages of metal oxides with the big surface area of the bifunctional CMK-3 catalysts. This work should include studying catalytic performance in a blended amine solvent such as MEA-AMP-MDEA or other mixed composition superior tertiary amines for CO<sub>2</sub> absorption-desorption processes. As well, the

study of the catalytic CO<sub>2</sub> desorption and amine solvent regeneration mechanism would assist in the design of more efficient and commercial catalysts for this purpose.

### Supporting Information

Additional details of the calculation method and physicochemical characterization of the catalysts, as well as more details about absorption/desorption experimentation, are given in the Supporting Information available on-line

### CONFLICTS OF INTEREST

There are no conflicts to declare.

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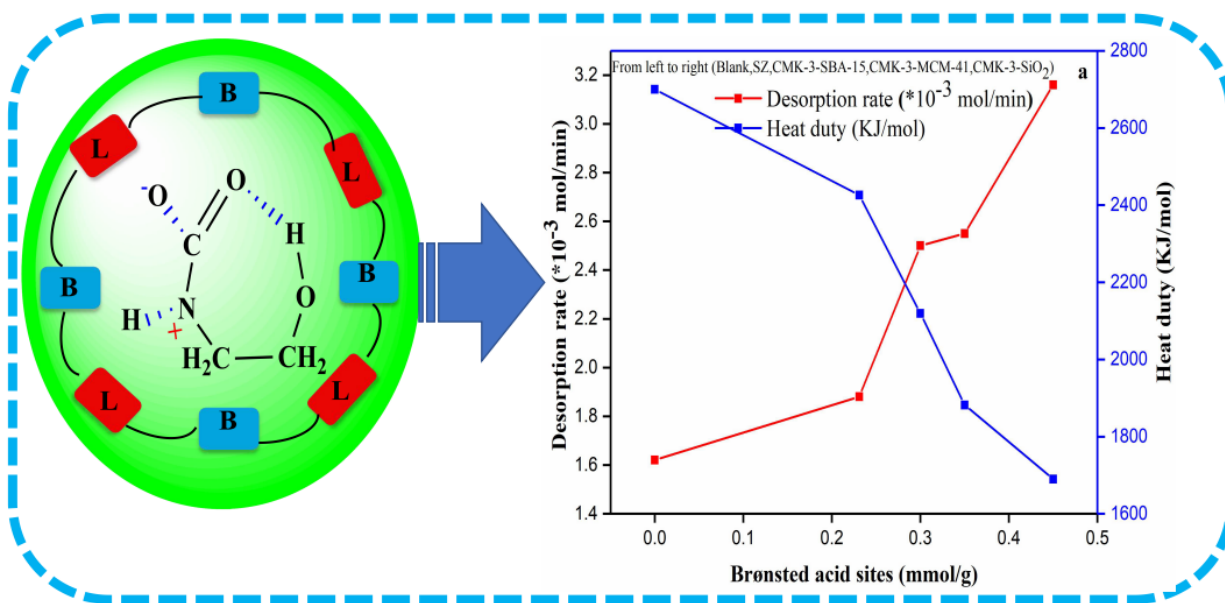
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<b>Nomenclature</b>	(FT-IR) Fourier transform infrared
Abbreviations	spectrometer
(CO <sub>2</sub> ) carbon dioxide	(ARD) Absolute relative deviations (%)
(MEA) Monoethanolamine	(NH <sub>3</sub> -TPD) Ammonia temperature-
(DR) Desorption rate (mol/min)	programmed desorption
(BET) Brunauer, Emmett, and Teller	(SAS) Solid acid sites (mmol/g)
(B) Brønsted acid sites (mmol/g)	Symbols
(L) Lewis acid sites (mmol/g)	(RH) Relative heat duty (%)
(SZ) Solid acid catalyst of ZrO <sub>2</sub> /SiO <sub>2</sub>	(CC) Cyclic capacity (mol)
(XRD) X-ray diffraction	(RP) Regeneration performance
(Py-IR) Pyridine-adsorption infrared	(mol <sup>3</sup> /(KJ.min)

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The addition of a heterogeneous catalyst to MEA-CO<sub>2</sub> loaded significantly enhanced the desorption rate of CO<sub>2</sub> and decreased energy consumption.

