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Catalytic CO$_2$-MEA absorptions with the aid of CaCO$_3$, MgCO$_3$, and BaCO$_3$ in the batch and semi-batch processes

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ABSTRACT

Three solid chemicals, CaCO$_3$, MgCO$_3$, and BaCO$_3$, were tested to accelerate the CO$_2$ absorption with monoethanolamine (MEA) solvents to verify the effect of heterogeneous catalysis. The experiments were conducted in a batch process at $20 \pm 0.2\,°C$ and a semi-batch process under room temperature. For the batch process tests, CaCO$_3$, MgCO$_3$, and BaCO$_3$, accelerated the CO$_2$ absorption with MEA solutions at 1, 3, and 5 mol/L, respectively. The overall absorption periods were reduced by around 39.5%, 36.8%, and 36.8% in 3 M solution; and 31.9%, 19.1%, and 26.6% in 5 M solution. For the semi-batch process tests, CaCO$_3$ and MgCO$_3$ accelerated the CO$_2$ absorption with 5 M MEA solutions by 20% and 20%, from 57 s to 45 s to reach equilibrium at loading of 0.0 mol/mol, and 16% and 12% from 75 s to 63–66 s to reach equilibrium at loading of 0.20 mol/mol. These solid chemicals were good candidates of heterogeneous catalysts of CO$_2$–MEA absorption in an amine scrubbing process.

Introduction

The concentration of global CO$_2$ is predicted to rise by 750 ppmv by 2100 A.D. if no solution is carried out to solve the crisis (Wang et al., 2011). Among the three major approaches for carbon capture utilization and storage (CCUS), the post-combustion carbon capture (PCCC) has been deployed into industry in Boundary Dam from Saskpower Corp, Canada since 2014, and it is still under the stage of processing (Idem et al., 2015). The major challenges in academy and industry are: (1) to reduce energy costs/heat duty of CO$_2$ desorption to conduct CO$_2$ emissions at a commercial scale; (2) to accelerate the CO$_2$ absorption process to reduce the height of an absorber and the costs of process equipment and operations.

The first problem has been studied and investigated for decades. MEA is the most commonly used amine solvent in industry for CO$_2$ absorption as a benchmark. The CO$_2$-MEA (monoethanolamine) absorption process is technologically viable and commercially available, due to its fast reaction rates and relatively low costs (Rao et al., 2004). However, MEA has several disadvantages such as solvent degradation, corrosion, and especially high energy costs for amine regeneration (Davidson, 2007). Most researchers focus on the offset of MEA's disadvantages instead of the enhancement of its advantages (Liang et al., 2015). Liang et al., (2016) conducted a thorough study of the CO$_2$ desorption with MEA with the aid of solid acid catalysts γ-Al$_2$O$_3$ and H-ZSM-5, which verified the effects of Lewis acid and BrØnsted acid/proton donor. Shi et al (2014) and Liu et al (2017) conducted the CO$_2$ desorption with MEA-MDEA blended solvent with various solid acid catalysts: γ-Al$_2$O$_3$, H-ZSM-5, MCM-41, and SO$_4^{2-}$/ZrO$_2$ etc. Liu et al., (2017) evaluated the effects of acidity of

different catalysts on heat duty reduction. They (Liang et al., 2015) focus on CO_2 absorption within an amine scrubbing process in the field of (1) vapor liquid equilibrium (VLE) models (Shi et al., 2012), (2) reaction kinetics (Sema et al., 2012), (3) CO_2 solubility studies of amine (Rayer et al., 2012).

The second challenge is the research interest of this study. Although CO_2-MEA absorptions are spontaneous and instantaneous (Pires et al., 2011), researchers are still working hard on the studies of the acceleration of CO_2 absorption to reduce the height of an absorber of an industrial amine scrubbing process (Idem et al., 2013). Both the "energy efficient" and "timely" methods are beneficial for the current amine scrubbing process (Rochelle, 2009). The faster CO_2 absorption rates result in the lower equipment and operations costs of the absorption tower (Phan et al., 2014).

One solution to solve the second challenge is the adoption of catalysts. The idea of "catalysts for CO_2 absorption" has been proposed by Service (2010) with a unique and cheap method as a startup of the exploration of heterogeneous catalysts. That study designs a small metal-containing organic compounds, replacing the function of a certain enzyme named "superoxide dismutase" (Service, 2010). Based on the literature survey, the related works on "catalytic CO_2 absorption of MEA" are quite limited because CO_2-MEA absorption is instantaneous. Based on a recent review (Liang et al., 2015), numerous studies have been conducted on the kinetics of non-catalytic CO_2-amine interactions (Sema et al., 2012). It is discovered that some alkaline centered solid sorbents can enhance gas-solid CO_2 adsorption in a fixed-bed reactor (Lee et al., 2006, Guo et al., 2011, 2015, 2017). The results indicate that K_2CO_3, with the supports of MgO, Al_2O_3, or TiO_2 sorbent, shows good characteristics as heterogeneous catalysts in CO_2 adsorption and regeneration via a gas-solid interphase (Lee et al., 2006). Meanwhile, Phan et al. (2014) studied the catalysis of CO_2 absorption in aqueous solution. The organic oxoanions (OX^-) facilitate CO_2-H_2O interaction, with tertiary amine R_3N as base to tune the pH of aqueous solution (Phan et al., 2014). The inorganic oxoanions

(OX^-) (Lewis base) facilitate the reaction with the Lewis acid CO_2, potentially acting as a catalyst (Astarita et al., 1981; Danckwerts, 1981).

In fact, the heterogeneous alkaline catalyst (K_2CO_3) supported by AC, Al_2O_3, and TiO_2 enhances CO_2 adsorption (gas-solid phase) (Lee et al., 2006), and liquid anion (OX^-) enhances CO_2 absorption with H_2O (gas-liquid phase) (Phan et al., 2014). The combinations of "solid alkaline" + "CO_2 absorption" have been a special research interest. To examine the potential of "heterogeneous catalysts," Idem et al. (2013) proposed an idea of "heterogeneous alkaline catalysts for CO_2 absorption." The inorganic carbonate acts as potential solid alkaline/electro-donating/ Lewis base catalysts, and performs catalytic CO_2 absorption with amines (RNH_2) with the aid of solid chemicals via a semi-batch absorption process (Idem et al., 2013). That patent disclosure provides a method for employing a solid alkaline catalyst in the absorber to facilitate CO_2 absorption with the liquid amine (Idem et al., 2013). This thought has been verified by several sets of tests validating that $MgCO_3$ is helpful to CO_2-MEA interactions (Idem et al., 2013). Furthermore, the CO_2-DEA absorptions are effectively accelerated with the aid of $CaCO_3$ and $MgCO_3$ (Shi et al., 2017). Meanwhile, the term "alkaline catalyst" refers to proton acceptor catalysts, electron donor catalysts and the combination of both (Idem et al., 2013). The MgO, CaO, SrO, BaO, ZnO, ZrO_2, ThO_2, TiO_2, etc., and NaOH/Al_2O_3, Na/MgO, Na^+/Al_2O_3, K^+/Al_2O_3, Na^+/SiO_2, K^+/SiO_2 are categorized into "alkaline catalyst" and patented, for they are "Lewis base" or "electron donor/proton acceptor" (Idem et al., 2013).

This study was to expand the patent disclosure of "solid alkaline catalysts" and verify the effectiveness of three solid chemicals: $MgCO_3$, $CaCO_3$, and $BaCO_3$ as "heterogeneous catalysts." Only MEA solutions were tested as primary amine. Besides solid chemicals, other soluble chemicals, such as Li_2CO_3, Na_2CO_3, and K_2CO_3, were not selected. This study intended to: (1) Reinvestigate the classic "carbamate formation mechanism" and expand the idea of homogeneous "OH^-" catalysis into heterogeneous alkaline catalysis. (2) Verify the catalysis: to study CO_2-MEA

interactions in a batch process of stirred cell reactor at the concentration of 1–5 mol/L by plotting of CO_2 absorption profiles, with 0–25 g of $MgCO_3$, $CaCO_3$, and $BaCO_3$. (3) Adopt the catalyst: to perform CO_2-MEA absorption in a semi-batch process with structured packing in 5 M solution, with the aid of 0–8 g $CaCO_3$ and $MgCO_3$. Our findings indicated that $CaCO_3$ and $MgCO_3$ could be potential candidates packed into an absorber in the industrial amine scrubbing process.
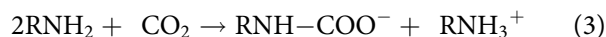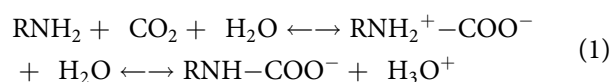
Theory

We re-investigated the theory of Zwitterion mechanism (Caplow, 1968) of CO_2-MEA interactions named "carbamate-formation." The role of hydroxide ion $[OH^-]$ in solution was discussed in detail, as a homogeneous basic catalyst. Then, we expanded the idea of aqueous $[OH^-]$ as homogeneous catalyst into solid base (MCO_3) for "heterogeneous catalysts." Based on the mechanism and role of $[OH^-]$, it was verified that solid alkaline chemicals were selected based on the re-investigation of "carbamate formation" mechanism (Idem et al., 2013). Finally, the absorption parameter was introduced (Narku-Tetteh et al., 2017) to estimate the catalysis clearly.

The Zwitterion mechanism of CO_2-MEA interactions

There are three common mechanisms of CO_2-amine interactions described by Vaidya and Kenig (2007; Idem et al., 2013). They are Zwitterion mechanism (Caplow, 1968), Termolecular mechanism (Crooks and Donnella, 1989), and base-catalyzed hydration mechanism (Donaldon and Nguyen, 1980). The based-catalyzed mechanism is more suitable for tertiary amine (R_3N) (Donaldon and Nguyen, 1980). The Zwitterion mechanism and Termolecular mechanism are suitable for primary and secondary amines, depending on whether the carbamate formation is via a "one step" or "two-step" process. The most suitable mechanism for CO_2-MEA is Zwitterion mechanism (Sema et al., 2012), and the Termolecular mechanism is better to describe the highly concentrated MEA at higher loadings

(Aboudheir et al., 2003). For the Zwitterion mechanism, Caplow (1968) investigated carbamate formation reactions with 15–20 types of primary/secondary amines (RNH_2/R_2NH), and he discovered the competition of "N-C bond formation step" and "zwitterion de-protonation step" for CO_2-amine interaction. If the de-protonation of Zwitterion to the base is very rapid, the "two-step" process can be regarded as a "one-step" process (Idem et al., 2013). Based on the Zwitterion mechanism (Caplow, 1968) for CO_2-MEA interactions, the reactions were briefly presented in [Equations (1)–(3)], and [Equation (3)] was the overall reaction:

$$RNH_2 + CO_2 + H_2O \longleftrightarrow RNH_2^+-COO^-$$
$$+ H_2O \longleftrightarrow RNH-COO^- + H_3O^+ \quad (1)$$

$$RNH_2 + H_3O^+ \rightarrow RNH_3^+ + H_2O \quad (2)$$

$$2RNH_2 + CO_2 \rightarrow RNH-COO^- + RNH_3^+ \quad (3)$$

Furthermore, the Zwitterion mechanism has been re-investigated in detail with molecular simulation methods (Xie et al., 2010). Xie et al. (2010) conducted simulated molecular structure, Energy Diagrams, Transition States and Activation Energy (Ea) of CO_2-MEA reactions via Zwitterion mechanism. The simulation works indicate the role of base in the facilitation of carbamate formation, where base can be OH^-, amine, or H_2O (Xie et al., 2010). Therefore, we extended to Lewis base such as alkaline earth metal carbonate MCO_3, and "M" could be Ca, Mg, and Ba in IIA group of the Periodic Table.

The $[OH^-]$ expanded to solid alkaline carbonate (MCO_3) as heterogeneous catalysts

CO_2 is acidic gas and Lewis acid, so that any Lewis base or proton donor/electron acceptor can facilitate CO_2 absorption in amine solvent or water. The CO_2-amine reactions can be enhanced with hydroxide $[OH^-]$ (Caplow, 1968), and CO_2-H_2O reaction can be boosted by oxoanions $[OX^-]$ (Phan et al., 2014) based on the "acid-base theory." Caplow (1968) indicates that the hydroxide ion $[OH^-]$ accelerates the carbamate formation as a proton acceptor. Hydroxide-catalyzed carbamate formation (aminolysis) reactions are described with two indistinguishable reaction pathways from kinetics study (Caplow, 1968).

Table 1. The elementary steps of catalytic CO_2 absorption.

Elementary steps	Reaction scheme	Description
E1	$RNH_2 + (*) \rightarrow RNH_{2(*)}$	Amine adsorption
E2	$RNH_{2(*)} + CO_2 \rightarrow RNH_2^+\text{-}COO^-_{(*)}$	Zwitterion formation
E3	$RNH_2^+\text{-}COO^-_{(*)} + RNH_2 \rightarrow RNH_2^+\text{-}COO^-_{(*)} + RNH_3^+$	Carbamate formation
E4	$RNH_2^+\text{-}COO^-_{(*)} \rightarrow RNH_2^+\text{-}COO^- + (*)$	Carbamate desorption

Firstly, hydroxide $[OH^-]$ functions as a general base which can facilitate proton loss in the transition state in Equation (1). Secondly, hydroxide facilitates the generation of an amine anion (R_2N^-) prior to the reaction with CO_2 (Caplow, 1968). The rate laws were written in Equations (4) and (5):

$$\text{rate} = k'(RNH_2)(OH^-)(CO_2) \text{ or } k''(R_2N^-)(CO_2) \tag{4}$$

(Caplow, 1968)

where k'' equals $k' K_w/K_a$, where K_w is the ion product of water and K_a is the amine dissociation constant, respectively.

$$r = k_{amine}(R_2NH)(CO_2) + k_{amine}'(R_2NH)(OH^-)(CO_2) \tag{5}$$

(Caplow, 1968)

From Equation (5), the first term is via an uncatalyzed pathway, and the second term is via a hydroxide-catalyzed pathway. (Caplow, 1968) Based on the experiments, the catalytic effect of $[OH^-]$ is stronger than the non-catalytic one, but the concentration of $[OH^-]$ is very small and constrained with chemical equilibrium. However, the homogeneous "proton acceptor or electron acceptor" in the CO_2-amine-H_2O systems is difficult to separate out of the amine solution in the desorber. The homogeneous catalysts (OH^-) are beneficial for CO_2 absorption but it may be detrimental to CO_2 desorption if dissolved in the amine solvents (Idem et al., 2013). The feasibility in CO_2 absorption column might jeopardize the process of desorber of CO_2 desorption. The advantages and disadvantages of liquid base catalysts require comprehensive considerations. On the other hand, the solid alkaline chemicals are abundant, easy to remove, and highly tunable with different types and masses. The solid alkaline chemicals could enhance the trace amount of $[OH^-]$ in the carbamate formation of CO_2-amine systems via a way of heterogeneous catalysis. The Lewis base can be adopted as catalysts to facilitate CO_2 absorption (Idem et al., 2013).

To exert the advantage and avoid the disadvantage of liquid base, we focused on "solid base chemicals/Lewis base" as "heterogeneous alkaline catalysts" rather than homogeneous catalysts. The heterogeneous catalysts could be employed in packing materials in the absorber (SI). Therefore, three "solid alkaline carbonate" (MCO_3, $M = Ca$, Mg, Ba) were selected as "Lewis base catalysts" to fit the requirement of both "Lewis base" and "heterogeneous catalysts." Since $MgCO_3$, $CaCO_3$, $SrCO_3$, and $BaCO_3$ are insoluble in water, they are good candidates as heterogeneous chemicals. In summary, we explored the potential of $CaCO_3$, $MgCO_3$, and $BaCO_3$.

The mechanism was proposed for heterogeneous catalysis that occurred on the solid surface in Supporting Information Figure S1 with four elementary steps listed in Table 1, as a beginning. The MEA molecules were pre-adsorbed onto the solid surface based on the elementary step (E1). The surface of solids contained a large number of active sites, which facilitated the amine adsorption. Then CO_2 molecules were approaching the solid surface, and reacted with MEA (RNH_2) with N-C bond formation to generate Zwitterion (E2). The activation energy (E_a) might be reduced by catalysts. The Zwitterion released proton to other MEA to generate carbamate ($RNH\text{-}COO^-$) and released heat (E3). The released heat facilitated diffusion and drove desorption of carbamate back to the aqueous phase (E4). The carbamate finally desorbed the surface and the reaction completed.

The absorption parameter for CO_2-Amine interactions

In order to evaluate the catalysis based on experiments, the concept of "absorption parameter" Equation (6) was introduced (Narku-Tetteh et al., 2017). This parameter is a useful selection criterion to discover the effects of CO_2 absorption among different single amines or amine blends

(Narku-Tetteh et al., 2017). However, MEA was the only amine for this study with equilibrium loadings of 0.50 mol/mol, the evaluation of absorptions was determined merely by initial absorption rates of carbamate formation in Equations (7) and (8) (Levenspiel, 1999), which was calculated by the linear section of absorption profile, the same as others (Narku-Tetteh et al., 2017).

$$\text{Absorption parameter} = \text{Initial absorption rate} \times \text{equilibrium loading} \qquad (6)$$

$$\text{Carbamate concentration}: C_C = C_{A0}(\alpha) \qquad (7)$$

$$\text{Initial absorption rate of carbamate formation} = -\frac{dC_c}{dt} = -C_{A0}\frac{d\alpha}{dt} \qquad (8)$$

Materials, experimental apparatus, and procedures

Materials

The solid chemicals were purchased from HuiShan Chemical Ltd., they were $CaCO_3$, $BaCO_3$, and $MgCO_3$. The pure CO_2 gas (99%) and CO_2/N_2 mixed gas (15% CO_2) were purchased from Tansool Chemical Ltd., and the chemicals MEA, HCl, and methyl orange were commercially available from Guoyao Chemical Ltd.

### Experimental apparatus and procedures

The experimental processes were built with a batch process (Shi et al., 2017) and a semi-batch process (Idem et al., 2013). The batch process was conducted in a stirred cell reactor with suspended chemicals, similar to other works (Shi et al., 2017). The absorption of CO_2 by suspension of solid chemicals was to verify the catalysis of solid chemicals as the initial step. The design of experimental apparatus in this study was based on "Mixed Flow Reactor," similar to other studies (Narku-Tettch et al., 2018). The semi-batch process (Idem et al., 2013) simulated the realistic CO_2 absorption column under room temperature with structured packing. The mixed gas of CO_2/N_2 was simulation of the flue gas of 13–15% CO_2, and 5 M MEA solvent was prepared as a benchmark for industrial application.

The CO_2–amine absorption in a batch apparatus

The batch process was built as a stirred cell reactor as Figure 1(A) with details provided (Shi et al., 2017). The internal diameter of the reactor is 8.4 cm, with a constant interfacial area of 55.4 cm^2 (Shi et al., 2017). Pure CO_2 was introduced into the reactor containing MEA solutions, and the reactor was placed into a cooling water bath to maintain the reaction temperature at 20 ± 0.2 °C. A probe of thermometer was placed into the solutions to detect the reaction temperature. The magnetic stir was stirring at the rate of 250 rpm (round per minute) to enhance the mass transfer. As it sieved, the size of the solid ball was close to 2 mm. The solids were wrapped into several balls with similar size, and then they were suspended onto the gas-liquid interface (Supporting Information). The intersection area of two solid balls were about 9.05–9.80 cm^2 (2.4–2.5 cm diameter each), with uncertainty of 0.1 cm (∼4%). The absorption was conducted with bubbles, for it reflected the realistic gas-liquid interactions in a column (Shi et al., 2017).

Experimental procedures and sampling

The experiments were completed as follows: 210 mL MEA solutions were prepared with concentrations of 1 mol/L, 3 mol/L, and 5 mol/L, respectively. The operation temperature was kept at 20 ± 0.2 °C. Even though the CO_2 absorption occurred at 40–60 °C (313–333K) in an industrial amine scrubbing process, 20 °C(293K) was selected as the standard condition (Sema et al., 2012), and the experimental results could be categorized as database and ready for the kinetic studies in future. Moreover, the operation temperature here was the same as that of another study of CO_2 absorption with DEA with the aid of $CaCO_3$ and $MgCO_3$ (Shi et al., 2017). Then CO_2 (99%) was introduced from a gas cylinder with the fixed flow rate at 1.00–1.50 L/min. The flow rate was switched from 1.00 L/min (1.0 and 3.0 M MEA) to 1.50 L/min (5.0 M MEA). Since 5.0 M MEA was condensed solution, the gas flow rate could not be too small. If the CO_2 flow rate was low enough, the rates of CO_2 absorption were difficult to distinguish for the cases with/without catalysts. Despite different CO_2 flow rates
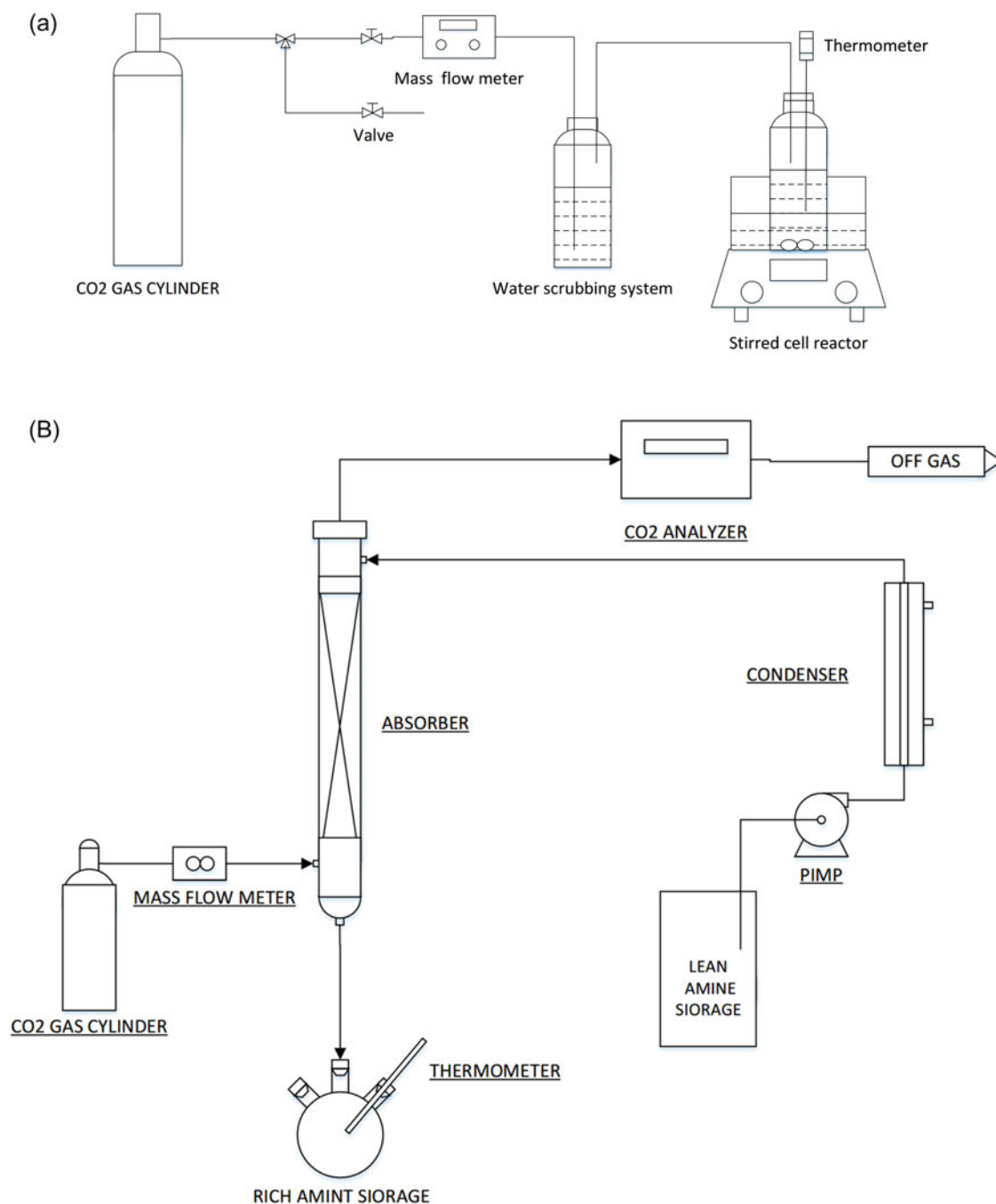
Figure 1. (A) Stirred cell reactor for catalytic CO_2 MEA interactions with a water scrubbing process beforehand. (B) The semi-batch process equipped with structured packing materials.

for the 3 M and 5 M solutions, the ratios of gas/liquid were 0.33 L/min.mol amine for 3.0 M MEA and 0.30 L/min. mol amine for 5.0 M MEA, close to each other.

During the CO_2 absorption process, a timer was used to record the time of different CO_2 loadings. In the middle of absorption, 1–2 mL solutions were pipetted and sampled into small bottles. The samples were collected every 0.5–1 min during 0–10 min and every 3–5 min after 10 min because of the decreased absorption rates. The timer was temporarily stopped during the sampling process, and then continued to record the absorption process.

The data acquisition and absorption profile

The overall uncertainty was close to 5–8% for the experiments. It was originated from three sections: 1) the flowmeter had a deviation of

1.00 ± 0.01 L/min, 2% AAD; 2) the CO_2 loading tests were conducted to these samples with a Chittick apparatus (Association of Official Analytical Chemists, AOAC), with an AAD of 2.5% (Horwitz, 1975). The experiments were conducted repeatedly at least twice for each set for consistency and accuracy. The CO_2 loadings (mol/mol) versus time (minute) were plotted from 0.0–0.50 mol CO_2/mol amine to demonstrate the overall absorption profiles (Narku-Tetteh et al., 2017). With different solid chemicals placed in the MEA solutions from 1–5 M, multiple curves were categorized for catalytic CO_2 absorption.

The CO_2–amine absorption in a semi-batch apparatus

The semi-batch process was built in Figure 1(B) to simulate an industrial CO_2 absorber of amine scrubbing process (Idem et al., 2013). Figure 1(B) was a process flow diagram (PFD) with pictures in Supporting Information. The column was made of glass with the length of 66 cm and outside diameter (o.d) of 3.3 cm and internal diameter (i.d.) of 2.8 cm; and it was packed with seven pieces of structured packing (6 cm in length with i.d. = 2.7 cm) made of stainless steel (Supporting Information). Different masses of $CaCO_3$ and $MgCO_3$ were pelletized with an average size of 2–3 mm and paved as a layer between two structured packing materials made of stainless steel (Supporting Information). Based on the experiments, the size of catalysts was neither too fine nor too big to inhibit the mass transfer of amine flow and gas flow rate. A gas cylinder and a centrifuge pump with liquid storage tank were prepared aside of the process. A CO_2 analyzer (0–20%) was installed at the exit gas to detect the CO_2% of the mixed gas after absorption. The mixed gas of N_2/CO_2 (15%) and the 5.0 M MEA solvent were introduced and confronted in the column via counter-current flow and started absorption.

The experimental procedures and data analysis

The mixed gas with flow rate of 1.2 L/min was firstly introduced into the semi-batch process and then waited for 5–10 min. Since most places were sealed with lubricant and glass cock for the process, there was only one gas exit connected to a CO_2 analyzer. The semi-batch system was full of mixed gas; and the analyzer exhibited the CO_2 concentration at a maximum value of 14.0–14.5%. The concentration at exit was 0.5–1.0% lower than the inlet gas, since the tubing and materials adsorbed trace amount of CO_2. Secondly, the 5 M MEA solutions were introduced after CO_2 concentration reached 13.5%. The liquid was introduced into the column from the top and flowed down to the storage bottle through structured packing material and catalysts. The liquid flow rate was fixed at 52.2 mL/min, measured with a graduated cylinder and timer.

The CO_2 absorption took place in the structured packing column; and CO_2% decreased sharply from 13.5% to 1.0% and then stayed still. The exact equilibrium concentration was determined by the ratio of gas/liquid flow rate, but the time to reach equilibrium was reduced by catalysts. Catalyst could not shift chemical equilibrium point (e.p), but it could cut the time to reach that point. The overall absorption took 50 to 80 s. The CO_2% versus t (s) was recorded for 5 M MEA solution under non-catalytic and catalytic ($MgCO_3$ and $CaCO_3$) conditions at two loadings of 0.0 and 0.20 mol/mol, representing fresh solvent and solvent under industrial operation conditions (Sakwattanapong et al., 2005).

Results and discussions

Brief summary of the catalysis for both sets of experiments

Figure 2 verified the effectiveness of solid chemicals as a beginning. According to results in batch process in Figures 3–5, the catalysis gradually increased with an increased mass of solids and increased CO_2 loadings. In short, $BaCO_3$ was less effective than $CaCO_3$ and $MgCO_3$ partly because of its bigger molecular weight. $CaCO_3$ was comparable and slightly better than $MgCO_3$. The catalytic effects of loadings (0.40–0.50 mol/mol) were stronger than that of loadings (0.20–0.40 mol/mol), and the period of CO_2 absorption was reduced by 20–30%. Even
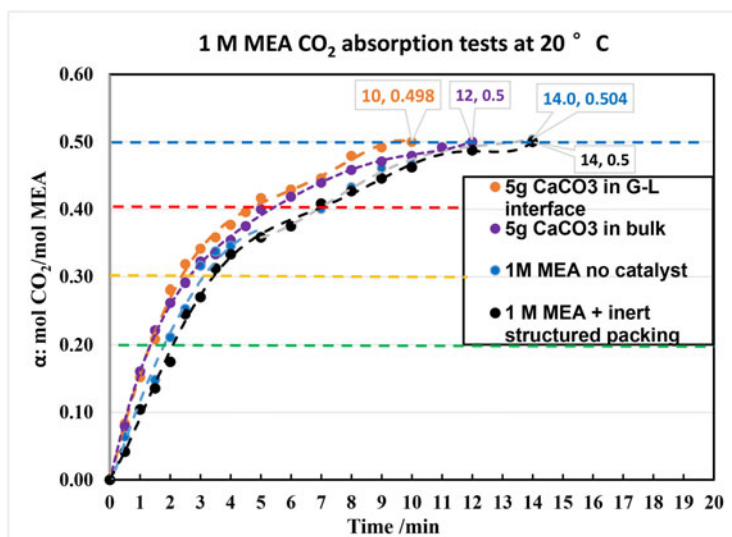
Figure 2. CO_2 absorption with 1 M MEA solutions with different cases, non-catalytic, inert packing material, and catalyst of 5 g of $CaCO_3$.

catalysts were mainly useful at 0.40–0.50 mol/mol, which covered 45–50% of absorption time and 25–33% of cyclic capacity of MEA at operation ranges (0.20–0.50 mol/mol). For the semi-batch process of Figure 6, fresh 5 M MEA solvent was quicker than 0.20 mol/mol for non-catalytic process, with 57 s versus 75 s. $CaCO_3$ could reduce the time to reach equilibrium by 12 s for fresh solvent and 0.20 mol/mol. $MgCO_3$ could reduce the time to reach equilibrium by 12 s for fresh solvent and 9 s for 0.20 mol/mol. The solid chemicals were promising catalysts, and $CaCO_3$ was preferred.

Catalytic CO_2 absorption profiles in the batch reactor with $CaCO_3$, $MgCO_3$, and $BaCO_3$

The verification of heterogeneous catalysis was firstly conducted in a batch process (Figure 2). The CO_2 was introduced with the flow rate of 1.0 L/min into 1 M MEA solvents. Four cases were tested: (A) no catalyst, (B) inert materials of structured packing (stainless steel), (C) solid chemicals placed in the liquid bulk, or (D) in gas-liquid interface. Based on Figure 2, it was clear that the non-catalytic Cases A and B were very close to each other, the overall process took 14 min. The catalytic Cases C and D took less time, and Case D (10 min) was slightly better than Case C (12 min), indicating that the solid catalyst worked better if placed in the gas-liquid

interface. Figure 2 also verified that the effect of heterogeneous catalysis was better than that of inert materials and non-catalysts.

After verification, the heterogeneous catalysis of 1, 3 M, and 5 M MEA solutions were tested with the aid of $MgCO_3$, $BaCO_3$, and $CaCO_3$. With the aid of solid chemicals, the time of absorption was reduced by different types and masses. The absorption profiles were plotted in Figures 3–5 with data in Supporting Information Table S1. Based on Figure 3(A–C), the non-catalytic CO_2 absorption process in 1 M MEA solutions took about 14 min to reach 0.50 mol/mol as a benchmark. With the aid of $CaCO_3$, it took 10 min with 5 g, 9 min with 10 g, 8 min with 15 g, and 7 min with 20 g $CaCO_3$ to reach 0.50 mol/mol (Figure 3(A)). For $MgCO_3$, it took 9 min with 5 g, 8.5 min with 10 g, 7 min with 15 g, and 8.0 min with 20 g (Figure 3(B)). The similar trend was demonstrated on $BaCO_3$. It took 12 min to reach 0.50 mol/mol CO_2 with 5 g, 11–12 min with 10 and 15 g, and 10 min with 15 and 20 g. At optimum, it took 8 min with 25 g $BaCO_3$ (Figure 3(C)). In short, the solid chemicals accelerated 1.0 M MEA solvents by 50% for 20 g $CaCO_3$, 50% for 15 g $MgCO_3$, and 42.9% for 25 g $BaCO_3$ at optimum (Supporting Information Table S1) with order $CaCO_3 \approx MgCO_3 > BaCO_3$.

Based on Figure 3(A–C), absorption profiles were divided into two sections. For the first part, the CO_2 loading increased sharply from 0.00 to
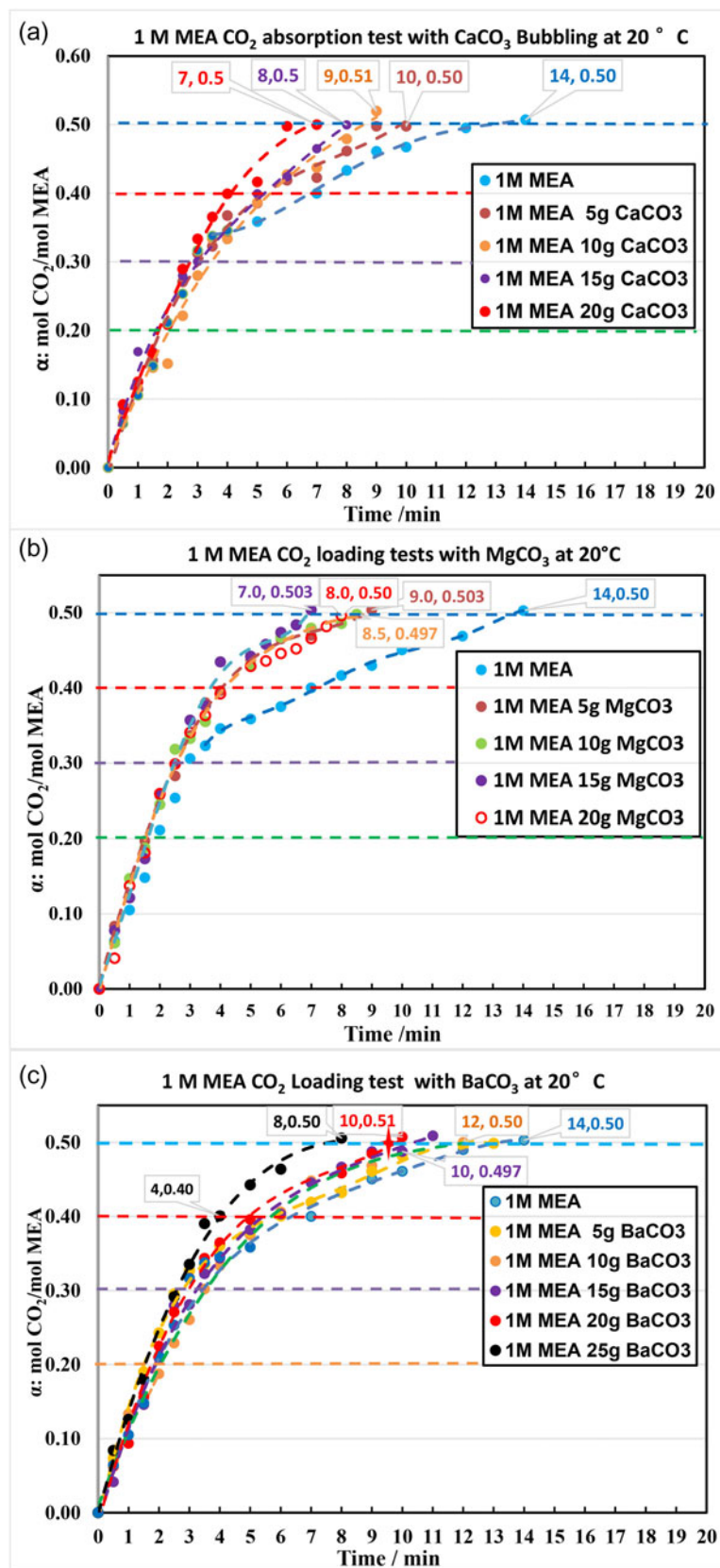
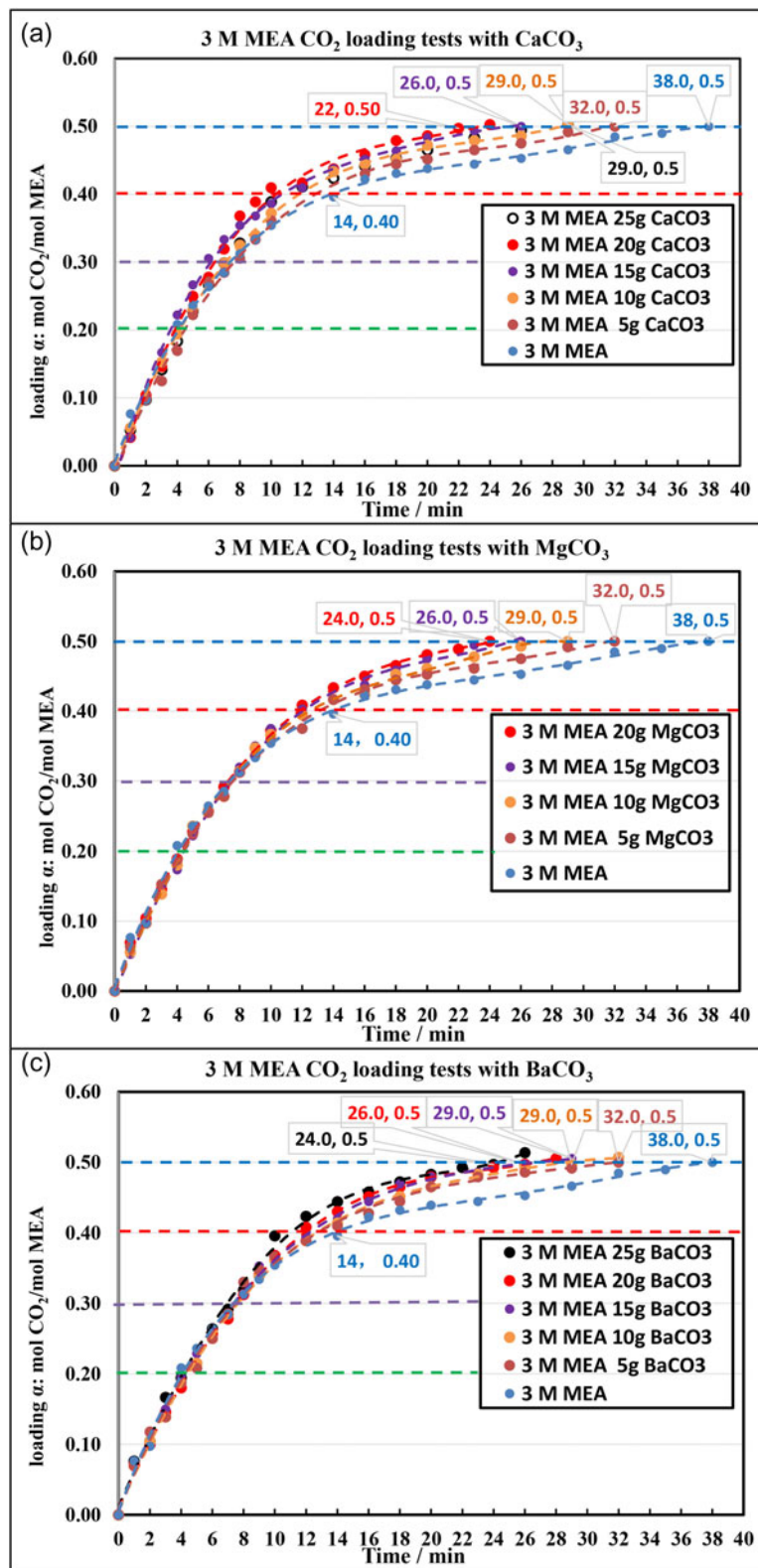**Figure 3.** CO_2 absorption with 1 M MEA solutions, with various types of catalysts: (A) $CaCO_3$; B $MgCO_3$; $BaCO_3$.

Figure 4. CO_2 absorption with 3 M MEA solutions, with three types of catalysts: (A) $CaCO_3$; (B) $MgCO_3$; (C) $BaCO_3$.

0.40 mol/mol where X_A of MEA reached 0.80. Moreover, from 0.0 to 0.2 mol/mol CO_2, these curves almost overlapped for catalytic and non-catalytic absorption, for CO_2-amine interactions were instantaneous (Levenspiel, 1999). The catalytic absorption was getting faster than the non-catalytic one at the loading of 0.20–0.40 mol/mol with much less free MEA molecules. For the
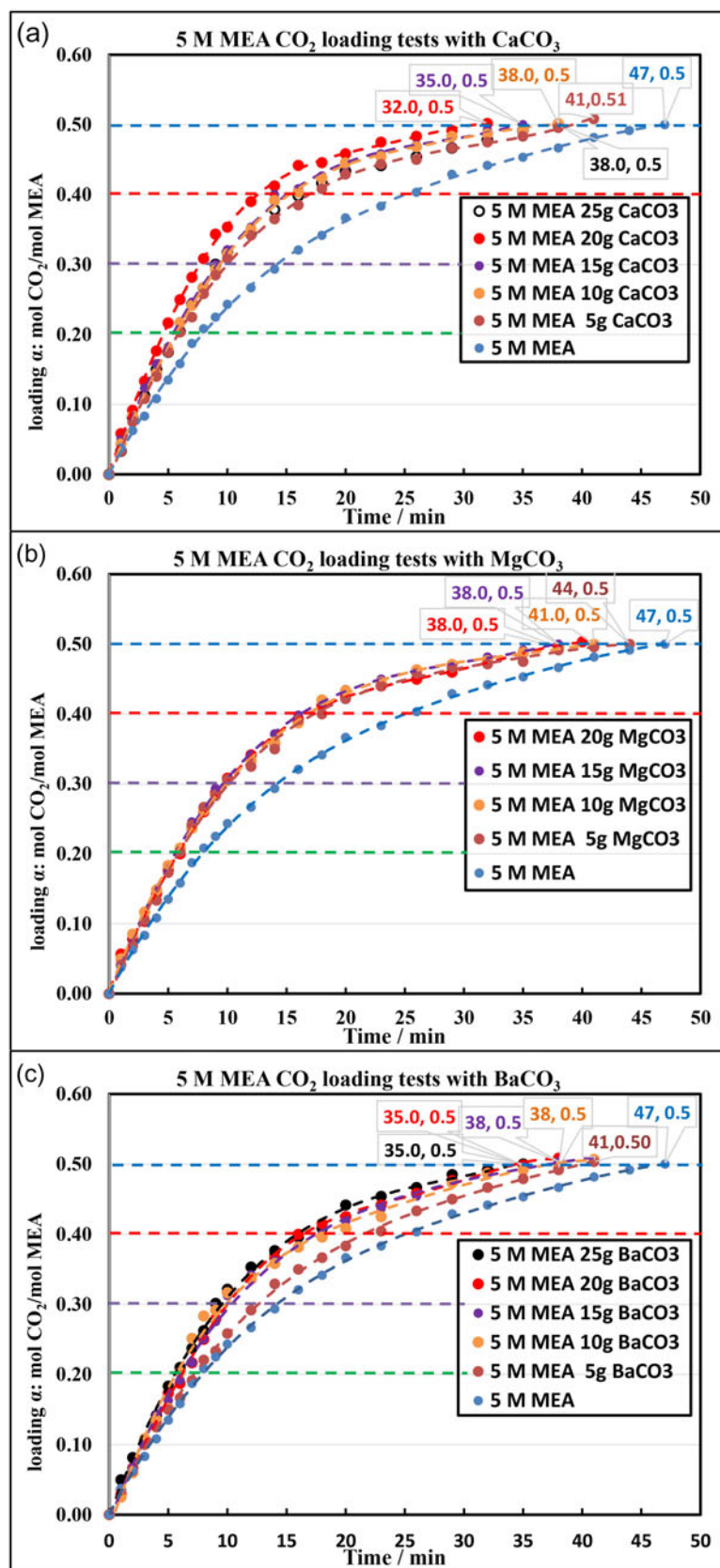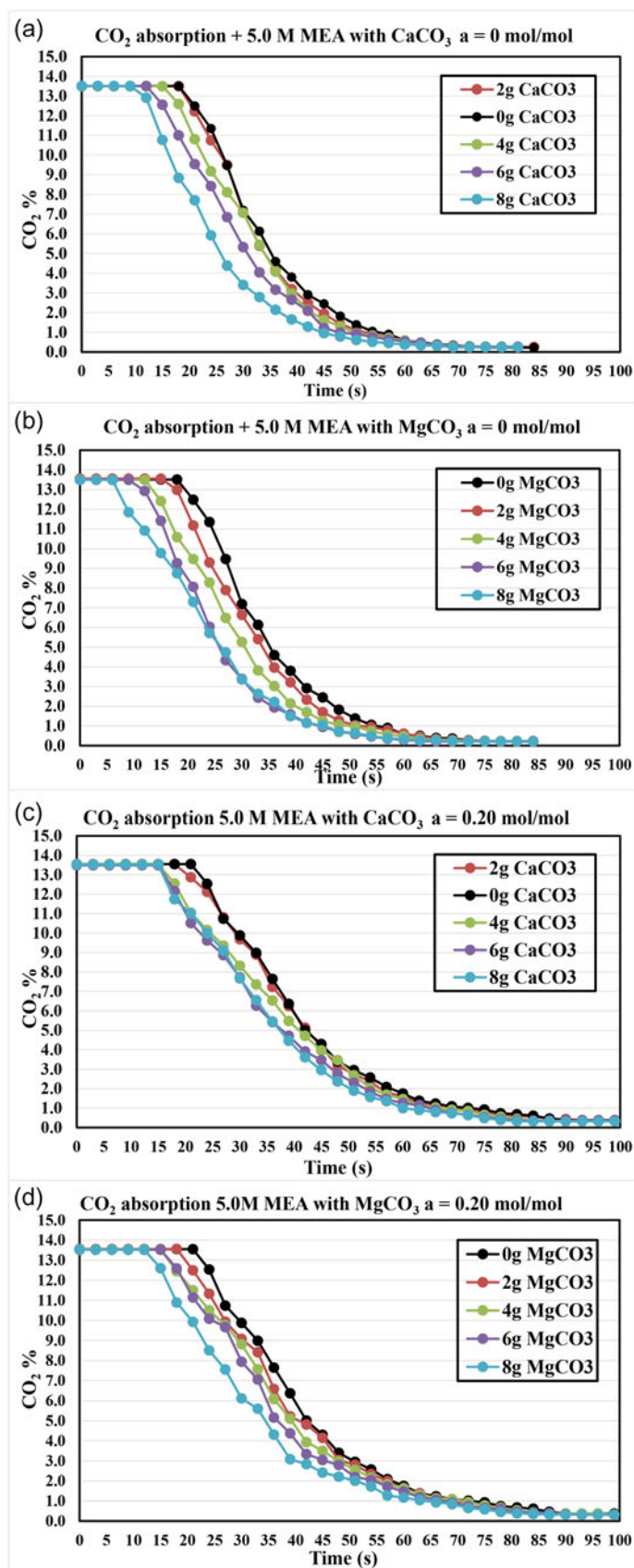
Figure 5. CO_2 absorption with 5 M MEA solutions, with three types of catalysts: (A) $CaCO_3$; (B). $BaCO_3$; (C) $BaCO_3$.

Figure 6. CO_2 absorption with 5 M MEA solutions in a semi batch process: (A) $CaCO_3$ for fresh solvent; (B) $MgCO_3$ for fresh solvent; (C) $CaCO_3$ for 0.20 mol/mol; (D) $MgCO_3$ for 0.20 mol/mol.

second part, the rich loading of 0.40–0.50 mol/mol was much slower than that of 0.0–0.40 mol/mol with 20% of the free MEA left, and bicarbonate (HCO_3^-) became the main product of CO_2 from ion speciation plot (Narisfar and Tafazzol, 2010).

For 3 M MEA solutions, the absorption profiles were plotted in Figure 4(A–C). Without catalysts, the absorption took 38 min for the whole process. The range of 0.0–0.40 mol/mol took 14 min, but the loading of 0.40–0.50 mol/mol took 24 min. Over 65% of the time was consumed in the rich loading for 3 M solutions. Based on Figure 4, 20 g $CaCO_3$ could reduce the overall time down to 22–23 min compared with 38 min of the non-catalytic process. 20 g $MgCO_3$ could reduce the overall time from 38 to 24 min. 25 g $BaCO_3$ could reduce the time from 38 to 24 min. In short, the catalytic effect was ordered as $CaCO_3 > MgCO_3 \approx BaCO_3$ according to Supporting Information Table S1.

The absorption profiles for 5 M solutions were plotted in Figure 5(A–C). Without catalysts, the absorption took 47 min. The range of 0.0–0.40 mol/mol took 26 min, and the range of 0.40–0.50 mol/mol took 21 min. Over 45% of the time was consumed at 0.40–0.50 mol/mol for 5 M solutions. The $CaCO_3$ (20g) reduced the overall time down to 30–31 min from 47 min. 20 g $MgCO_3$ could reduce the overall time from 47 to 38 min. 25 g $BaCO_3$ reduced the overall time from 47 to 35 min. The order of catalytic effect was $CaCO_3 > BaCO_3 > MgCO_3$.

In summary, the solid chemicals were more effective at the range of 0.40–0.50 mol/mol than 0.20–0.40 mol/mol for MEA concentrations of 1, 3, and 5 M. The loading of 0.40–0.50 mol/mol covered around 1/3 of cyclic capacity of MEA, because the period of 0.20–0.50 mol/mol was the operation conditions for industrial absorber (Sakwattanapong et al., 2005). The overall periods of CO_2-MEA were reduced by about 39.5%, 36.8%, and 36.8% for $CaCO_3$, $MgCO_3$, and $BaCO_3$, in 3 M solution; and about 31.9%, 19.1%, and 26.6% in 5 M solution (Supporting Information Table S1). Besides MEA, $CaCO_3$, and $MgCO_3$ accelerate CO_2-diethanol amine (DEA) absorption (Shi et al., 2017). The overall CO_2-DEA absorption periods were reduced to a maximum ratio of 22%, 28%, and 14% for $CaCO_3$ at 1, 3, 5M; and ratio of 11%, 28%, and 11% for $MgCO_3$ at 1, 3, 5 M (Shi et al., 2017). These results proved that these solid chemicals were catalytic effective in both primary and secondary amines. The acceleration effect on MEA is better than that on DEA, for MEA has bigger absorption rate constant k than DEA (Sema et al., 2012).

These results were compared with the effects of other solid catalysts on CO_2-amine absorption. They used a variety of solid absorption catalysts weighing 50 g with 4.0 mol/L BEA/AMP blended solvents to discover the order of catalysis. Their trend is summarized as K/MgO $\sim$ Ca(OH)$_2$ $\sim$ Cs$_2$O/α-Al$_2$O$_3$ > Cs$_2$O/Al$_2$O$_3$ $\sim$ BaCO$_3$ > blank > CaCO$_3$ for BEA/AMP blend. However, their poor performance of 50 g $CaCO_3$ for 4.0 M BEA/AMP solvents is due to a large degree of agglomeration, which affect the rate of absorption. For our case (without agglomeration) of 0–25 g solid catalysts, $BaCO_3$ was all effective for CO_2-MEA reaction at optimum of 25 g, and the $CaCO_3$ particle was all effective at 0–25 g at an optimized amount of 20 g. Because of different solvent system and different amount of catalysts used, it was hard to compare the results of different studies currently. A large number of fundamental studies need to be carried out to compare different heterogeneous catalysis on the same level.

Catalytic CO$_2$ absorption in a semi-batch process with CaCO$_3$ and MgCO$_3$

The results of a semi-batch process were conducted in Figure 6(A–D), with fixed gas flow rate of 1.2 L/min for 13.5% of CO_2 and liquid flow rate of 52.2 mL/min of 5.0 M MEA solvents. Similar process was built in the patent (Idem et al., 2013). However, the process was re-constructed with different sizes of column. The inert structured packing materials were installed to increase the area of gas-liquid interface, with solid catalysts installed between pieces (Supporting Information).

Figure 6(A–D) indicated that the results were divided into two parts: fresh 5 M MEA solution (0.0 mol/mol) under operation conditions
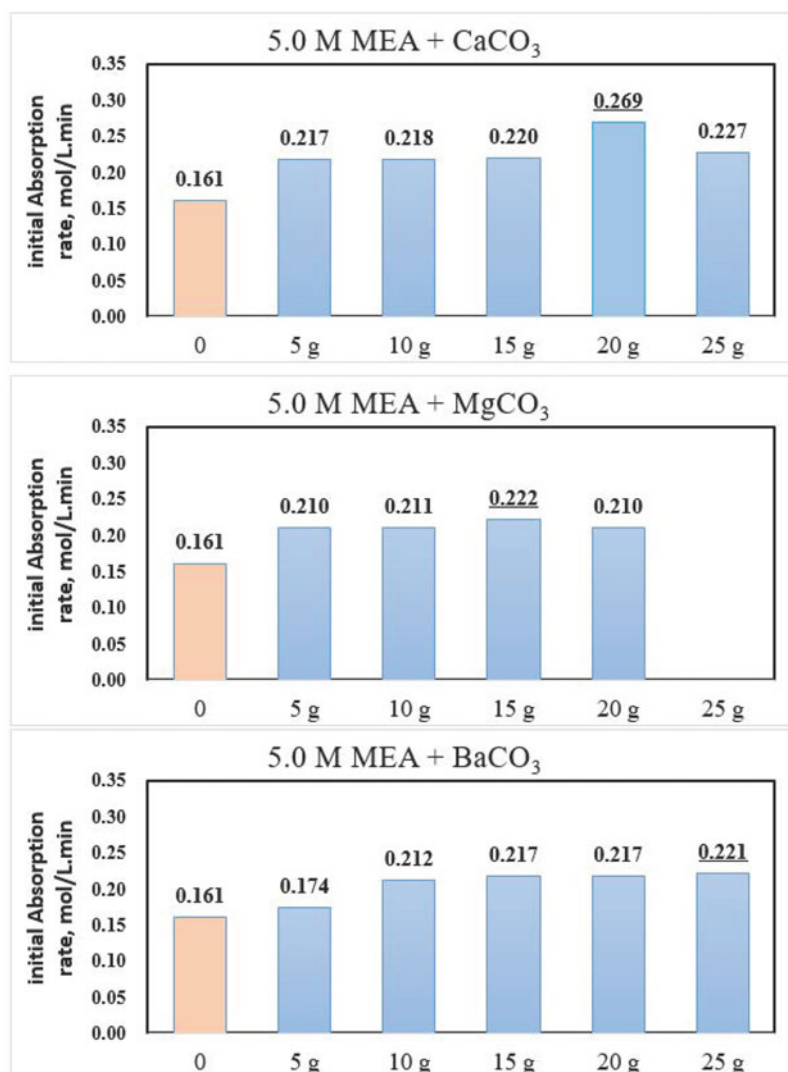
Figure 7. Initial absorption rate of 5 M MEA solutions, with different masses of: (A) $CaCO_3$; (B) $MgCO_3$; (C) $BaCO_3$.

(0.20 mol/mol). For the fresh solvent in Figure 6(A), the non-catalytic absorption took 57 s to convert CO_2% from 13.5% to 0.90% (<1%). With the existence of $CaCO_3$, it took 54 s (0.91%), 51 s (0.95%), 45 s (0.99%), and 45 s (0.95%) to reach CO_2% < 1% to complete the absorption process, with 2, 4, 6, and 8 g solid added. The maximum time reduction was by about 20%. According to Figure 6(B), it took 54 s (0.94%), 51 s (0.96%), 45 s (0.95%), and 45 s (1.03%) with $MgCO_3$ for the absorption process to achieve equilibrium CO_2%, with 2, 4, 6, and 8 g solid added. Both $CaCO_3$ and $MgCO_3$ had similar results for fresh solvent. For 0.20 mol/mol MEA solvent in Figure 6(C), the non-catalytic absorption took 75 s to convert CO_2% from 13.5% to 0.93% (<1%). With the existence of $CaCO_3$, it took 72 s (0.94%), 69 s (0.92%), 66 s (0.91%) and 63 s (0.90%) to

complete the process, with 2, 4, 6, and 8 g solid added. The maximum time reduction was 12 s (16% of 75s) for $CaCO_3$. Based on Figure 6(D), with $MgCO_3$, it took 72 (0.94%), 72 (0.94%), 69 (0.92%), and 66 s (0.93%) to complete the absorption process, with exact 2, 4, 6, and 8 g solid added. The maximum time reduction was 9 s (12% of 75 s) for $MgCO_3$. $CaCO_3$ was a little better than $MgCO_3$ for 0.20 mol/mol solvents. The results in Figure 6 were helpful for a pilot plant design. The solids in packing material could help to reduce the height of CO_2 absorption column.

The effect of catalysis based on initial absorption rates

The effect of the catalytic absorption was compared with the initial absorption rates based on

the absorption parameter (Narku-Tetteh et al., 2017) because only MEA was studied. The initial absorption rates of carbamate formation for 5 M MEA with non-catalytic and catalytic processes were important parameters in practice. The initial rates were calculated from the slopes of the absorption curves of Figure 5 via Equation (8), and then plotted in Figure 7.

Figure 7 demonstrated that the initial absorption rates of 5 M MEA under non-catalytic process was 0.161 mol/L min as a benchmark. This was different from other works (Narku-Tetteh et al., 2017), for they used 15% CO_2 mixed gas. The lower gas concentration results in lower absorption rates. For $CaCO_3$, the initial rates increased to 0.217–0.227 mol/L min and reached 0.269 mol/L min at an optimized mass of 20 g. For $MgCO_3$, the rates increased to 0.210 mol/L min and reached the maximum of 0.222 mol/L min at an optimized mass of 15 g. For $BaCO_3$, the initial rates increased to 0.210–0.218 mol/L min and reached the maximum of 0.221 mol/L min with 25 g $BaCO_3$. Based on heterogeneous catalysis (Levenspiel, 1999), the catalytic absorptions on the solid surface consisted of several elementary steps in Table 1. These results implied that the catalytic absorptions were associated with the enhanced mass transfer and reduced activation energy. The mechanism, kinetic models await further studies in detail with abundant experiments.

Conclusion

1. The idea was experimentally validated that the pelletized chemicals "$CaCO_3$, $MgCO_3$, and $BaCO_3$" were well-performed candidates for accelerating CO_2-MEA absorptions. These heterogeneous catalysts are alternative catalysts of liquid base [OH^-] for carbamate formation (Caplow, 1968) based on the idea of "Lewis base" or "Electron donor" (Idem et al., 2013). They were more effective if placed in the gas-liquid interface instead of bulk of liquid. The CO_2-MEA absorptions were a little slower without catalysts or with inert materials.

2. For the batch process, the catalytic effects were $MgCO_3 \approx CaCO_3 > BaCO_3$ in 1M MEA solutions, $CaCO_3 > MgCO_3 > BaCO_3$ in 3M MEA solutions and $CaCO_3 > BaCO_3 > MgCO_3$ in 5M MEA solutions with the aid of 5-20g of $MgCO_3$, $CaCO_3$, and 5-25g $BaCO_3$ at 20 °C. The optimized amounts of solid chemicals effectively reduced the absorption period at different ratios, from 20 to 40%.

3. The initial absorption rates of the 5M MEA solvents (30 wt. %) were calculated and plotted with various chemicals. These catalysts significantly enhanced both the initial absorption rates and the absorption rates at rich loadings. $CaCO_3$ achieved the optimized absorption rates at the weight of 20g.

4. $CaCO_3$ and $MgCO_3$ were placed between inert stainless-steel packing materials into a semi-batch process to demonstrate industrial implementations. Both chemicals reduced the absorption time by 12-20%, indicating shorter column and less operation costs. $CaCO_3$ was a little better than $MgCO_3$ in 5M MEA solution under the operation condition of 0.20 mol/mol.

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