Improved CO$_2$ Sorption Performance of Calcium Oxide (CaO) Sorbent with Nickel Oxide Additive

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Abstract. Currently, carbon capture and storage (CCS) technology appeared to be the most viable method to reduce carbon dioxide (CO$_2$) emission from its existing sources. This paper reports the improved performance of calcium oxide (CaO)-based sorbents with the addition of nickel oxide (NiO) as an additive (denoted as CaO:NiO) in CO$_2$ sorption process (CaO carbonation reaction). Pure CaO was used as benchmarked sorbent in this study. The samples were synthesized using the sol-gel method and CaO:NiO were evaluated for their performance in CaO carbonation at different sorption temperatures, from its CO$_2$ sorption capacity, CO$_2$ sorption rate, and kinetic performance. CaO:NiO has demonstrated an excellent CO$_2$ sorption capacity of 0.79 mmol CO$_2$/mmol CaO, meanwhile pure CaO exhibited lower CO$_2$ sorption capacity of 0.61 mmol CO$_2$/mmol CaO at 600 °C. During the chemical reaction controlled stage, the CO$_2$ sorption rate of CaO:NiO was 0.78 mmol CO$_2$/mmol CaO.min at 600 °C compared to pure CaO with sorption rate of 0.18 mmol CO$_2$/mmol CaO.min. This study indicates that the addition of nickel oxide has successfully improved the CO$_2$ sorption rate and capacity of CaO for CaO:NiO. Based on the kinetic study, it has been observed that the diffusion controlled stage has a greater resistance towards the CO$_2$ sorption process (carbonation reaction) compared to rapid chemical reaction controlled stage. Experimental carbonation data for CaO:NiO fitted very well to the shrinking core model (SCM) with high correlation coefficient ($R^2 > 0.936$). The specific rate constants of rapid chemical reaction and diffusion-limited stages are directly proportional to the carbonation temperature. The activation energy required for CaO:NiO sorbent during the chemical reaction control stage was 31.81 kJ/mol.

1. Introduction

The concentration of carbon dioxide (CO$_2$) has been increasing predominantly worldwide due to the combustion of fossil fuels, which consequently causes many environmental problems such as global warming. This has led the researchers to focus on developing efficient approach to reduce CO$_2$ emissions. Currently, carbon capture and storage (CCS) technology appeared to be a direct alternative to efficiently separate CO$_2$ from industrial processes at this stage [1]. The most commonly used methods to capture CO$_2$ are absorption using amine solvent and adsorption on solid sorbents [1]. A wide range of potential solid sorbents have been explored recently, in which considerable attentions were given to calcium oxide (CaO) [2,3] as the application of amine-based solvent in industry faces many constraints [1].
CaO is widely available (raw material) [1], can be reused for multi-cycles reaction [3] and has great CO₂ sorption capacity (0.786 g-CO₂/g-adsorbent) [4]. However, CaO-based sorbents suffer from rapid decrease in capture efficiency due to sintering effect in the multicycle carbonation-calcination reactions [5]. There are still gaps for improvements in terms CO₂ uptake capacity in long term CaO carbonation which remain as the main challenge for researchers. Currently, many studies focused on the techniques to promote the stability of calcium oxide based sorbents in long term carbonation reaction. Among them, the addition of dopants or additives to CaO sorbents have received much attention as it able to reduce the tendency of sorbents to sintering [1]. Guo et al. [6] prepared a Zr-Mn stabilized calcium-based sorbent with great durability and adsorption capacity (0.60 g CO₂/g sorbent) after 65 cycles. Guo et al. [7] reported a CaO-based sorbent doped with Zr-Ce additive achieving excellent CO₂ uptake (0.65 g CO₂/g sorbent) in multi-cycle reactions. It has been proved that the addition of Zr-Ce additive promotes oxygen vacancy formation. Moreover, Yoon et al. [8] reported Zr-modified CaO sorbents with CO₂ sorption uptake of 70.5 wt% after 10 cycles. To date, metal oxides with Tammann temperatures (temperature at which sintering start) higher than the carbonation/calcination temperature were selected as dopants/additives for CO₂ capture application [1,9,10]. In this paper, nickel oxide (NiO) was adopted to explore the impact of additive on the carbonation process because it have been widely employed in the field of catalysis [11] and possess high Tammann temperature (≈ 840 °C).

The objectives of this research are: (1) to study the extent of reaction in terms of CO₂ sorption rate and capacity over a long period of carbonation at different temperature. This part of the study is crucial in understanding the role of NiO in the carbonation reaction by identifying the changes in their catalytic behaviors and comparing with the pure calcium oxide (CaO). (2) to investigate the reliability of shrinking core model in describing the carbonation kinetic of CaO-based sorbents in terms of activation energy. It is important to examine the reaction kinetic in order to understand the underlying mechanism of heterogeneous gas-solid reaction.

2. Experimental

2.1. Preparation of sorbents via sol-gel method

The CaO:NiO sorbent was prepared using sol-gel method via citrate route [11]. Calcium nitrate tetrahydrate (Ca(NO₃)₂.4H₂O, Merck >99%) and nickel (II) nitrate hexahydrate (Ni(NO₃)₂.6H₂O, Merck >99%) were used as precursors, while citric acid monohydrate (C₆H₅O₇.H₂O, Merck >99.5%) was used as catalyzing agent of the synthesis process. Predetermined amounts of metal nitrate precursors (molar ratio of Ca/Ni = 1:1) and citric acid monohydrate (molar ratio of total metal precursors/citric acid = 1:3) were mixed with distilled water (molar ratio of total metal precursors/water = 1:45). The mixture was vigorously stirred at 90 °C to form a wet gel. Then, the gel was dried at 100 °C for 3 hours. At last, the product was calcined in the furnace for 4 hours at 700 °C under air flow. The chunks that produced from calcination was then ground and sieved into fine powders. Pure CaO, which is used as the reference, was prepared using the same method using calcium nitrate tetrahydrate as a precursor.

2.2. Characterizations of sorbents

Shimadzu XRD-6000 diffractometer was used to perform the X-ray diffraction (XRD) analysis. The samples were scanned at 2θ within 20.00° - 80.00° at a scanning speed of 2.00°/min. The surface morphology and topography of the sorbents were examined by the scanning electron microscope (SEM) manufactured by Hitachi S-3400N. The energy dispersive X-Ray (EDX) equipped with SEM was adopted to analyze elemental composition and distribution of the sample.
2.3. CO\textsubscript{2} sorption activity study using thermogravimetric analyzer

A thermogravimetric analyzer (Perkin Elmer STA 6000) was utilized to analyze the carbonation behaviour of the samples. First, the sorbents undergo pre-treatment at 700 °C under N\textsubscript{2} gas flow for 10 minutes prior to the carbonation study in order to remove impurities. Then, the temperature was reduced at 20 °C/min to desired carbonation temperature (400 °C, 500 °C and 600 °C). Carbonation was then carried out under constant CO\textsubscript{2} flow in isothermal condition at desired sorption temperature for 60 minutes. The performance of sorbents was evaluated in terms of CO\textsubscript{2} sorption capacity (mmol CO\textsubscript{2}/mmol CaO) and CO\textsubscript{2} sorption rate (mmol CO\textsubscript{2}/mmol CaO.min\textsuperscript{-1}) based on the weight change recorded by the system.

2.4. Kinetic study via Shrinking Core Model (SCM)

The shrinking core model (SCM) was selected to obtain the reaction rate constants of the carbonation reaction. According to SCM, the carbonation reaction involves two phases: (1) the chemical reaction period and (2) diffusion limited period [2]. The different rate-controlling stages were described according to the Equation 1 [5]:

\[ t = \frac{1}{k_c} \left[ 1 - (1 - X_{\text{CaO}})^{\frac{1}{3}} \right] + \frac{1}{k_d} \left[ 1 - 3(1 - X_{\text{CaO}})^{\frac{2}{3}} + 2(1 - X_{\text{CaO}}) \right] \]  

where

- \( X = \text{CaO conversion} \)
- \( k_c = \text{chemical reaction rate constant (1/min)} \)
- \( k_d = \text{diffusion rate constant (1/min)} \)

3. Results and Discussions

3.1. Characterizations of calcium oxide based sorbents

The XRD patterns for calcium-based sorbents were shown in figure 1. All the CaO–based sorbents exhibited sharp and well-crystallized phase. It can be observed that calcium oxide (CaO) and nickel oxide (NiO) are the primary compounds for sorbent (CaO:NiO) synthesized from the Ca(NO\textsubscript{3})\textsubscript{2}.4H\textsubscript{2}O and Ni(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O precursors. The main characteristics peaks of CaO were observed at 2θ = 32.2°, 37.3°, 53.8°, 64.1° and 67.4° (JCPDS File No. 00-037-1497), which correspond to (1 1 1), (2 0 0), (2 0 2), (3 1 1) and (2 2 2) planes respectively [12]. NiO peaks were detected at 2θ = 37.3°, 43.3°, 62.9°, 75.4° and 79.4° (JCPDS File No. 00-047-1049). While the pure CaO consists of calcium oxide and calcium carbonate (figure 1). The reaction between CaO powder with CO\textsubscript{2} during the cooling or storage step after calcination resulted in the formation of CaCO\textsubscript{3} [7]. It is evident that the precursors used during the synthesis method had fully decomposed which led to the formation of metal oxide through the calcination process.

Based on the elemental composition analysis (EDX) on calcium oxide-based sorbents as shown in table 1, the CaO:NiO particles composed of calcium (31.0 wt.%), nickel (41.0 wt.%) and oxygen (28.0 wt.%). The CaO sample exhibits calcium as the major component. Both samples contained CaO which is the basic oxide formed through calcination. The EDX mapping further confirmed the homogenous distribution of Ca and Ni elements in the sorbent as shown in figure 2. Sol-gel synthesis route enables the formation of uniform dispersion of NiO on the surface of CaO. Therefore, the finely-dispersed NiO able to separate the CaO particles from aggregation, which could effectively reduce the sintering effect at high temperature [13].
Figure 1. XRD patterns of CaO and CaO:NiO samples prepared using the sol-gel method.

Table 1. EDX elemental composition of CaO-Based sorbents.

| Elemental Composition | Sample        | Wt. % |
|-----------------------|---------------|-------|
|                       | CaO           | Ca    | O    |
| Ni                    | -             | 41.0  |      |
| Ca                    | 55.0          | 31.0  |      |
| O                     | 45.0          | 28.0  |      |

Figure 2. Cross section of SEM micrograph attached with EDX mapping of Ca and Ni elements in the fresh CaO:NiO sorbent.

The surface morphologies of the CaO and CaO:NiO samples were shown in figure 3. The SEM micrographs of calcined CaO demonstrated fine particles with irregular in shape. In contrast, at approximately equal magnifications of 15,000×, the shape of CaO:NiO particles were almost spherical and this sorbent possesses more accessible pores (or void space). It is apparent that the CaO:NiO sorbent exhibits smaller particles (< 3 µm) compared to the pure CaO sample, evidenced by the scanning electron microscopy images in figure 3.

Figure 3. SEM micrographs of: (a) fresh CaO sorbent and (b) fresh CaO:NiO sorbent.
3.2. Evaluation on carbonation behavior of calcium oxide based sorbents

Figure 4 illustrates the CO₂ uptake profiles of CaO-based sorbents at different carbonation temperatures. According to figure 4(a), the addition of NiO able to increase the CO₂ uptake of calcium oxide based sorbents. CaO exhibited CO₂ uptake of 0.61 mmol CO₂/mmol CaO while CaO:NiO showed much higher sorption capacity of 0.79 mmol CO₂/mmol CaO at 600 °C, which is about 30% higher as compared to CaO (figure 4(a) and 4(b)). During the fast chemical reaction stage, the CO₂ uptake rate showed significant improvement with NiO as additives (figure 4(c)). With increasing the sorption temperature, the reaction rate of CaO:NiO was highly accelerated. Meanwhile, CaO was mildly influenced by the carbonation temperature with the highest sorption rate of 0.18 mmol CO₂/mmol CaO.min at elevated carbonation temperature. At higher temperature, particles will have more energy which accelerates the kinetic motion and resulted in more collision to occur [14]. In addition, the CaO:NiO sorbent composed of smaller particle sizes, which increases the available surface area for the collision process to take place. Thus, the addition of NiO to CaO sorbent significantly influenced the physical characteristics of the sorbent which increased the rate of CaO carbonation.

![Figure 4](image)

**Figure 4.** Carbonation activity of calcium oxide based sorbents at sorption temperatures of 400 °C, 500 °C and 600 °C: (a) CO₂ uptake capacity of CaO:NiO, (b) CO₂ uptake capacity of CaO and (c) CO₂ uptake rate of CaO:NiO and CaO for rapid chemical reaction controlled stage.

Shrinking core model (SCM) is employed to analyze the CO₂ capture behavior which proceeds under two controlling reactions regimes, namely chemical reaction and product layer diffusion controlled stages. The CO₂ sorption kinetics shown in figure 4(a) and 4(b) clearly indicates that the carbonation reaction rapidly takes place at elevated temperature by chemical reaction. The first stage is completely controlled by the rapid heterogeneous surface reaction which proceeds up to the first 2 minutes. During this stage of carbonation, the reaction between CO₂ and CaO lead to the development of CaCO₃ layer [5]. Subsequently, this stage is followed by a sudden change to a slower diffusion-controlled stage that lasted until 60 minutes. Hence, the reaction rate decreased due to diffusion limitation of CO₂ gas molecules through the impervious product layer to reach the unreacted CaO [5]. In this situation, smaller particle size able to provide shorter distance for CO₂ diffusion through the formed CaCO₃ layer [8].
Clearly, the CO$_2$ sorption on CaO:NiO sorbent takes place at a prompt rate compared to CaO regardless of the carbonation temperature. This phenomenon can be clarified by the difference in particle sizes [8], as evidenced in figure 3. According to the obtained results, CaO:NiO proved to be a favorable sorbent with CO$_2$ sorption capacity of 0.79 mmol CO$_2$/mmol CaO, followed by CaO with uptake capacity of 0.61 mmol CO$_2$/mmol CaO. The optimum temperature for rapid carbonation reaction to take place is 600 °C, and owing to the high CO$_2$ sorption rate of CaO:NiO at the optimum temperature, less amount of fresh sorbent could be consumed to capture a large amount of CO$_2$ from the industrial processes which significantly reduce the equipment cost and energy consumption [15]. Moreover, the sol-gel synthesis method able to produce a sample with uniform dispersion of metals and smaller particles, which resulted in improved CO$_2$ sorption uptake [8].

3.3. Kinetic study on the CaO carbonation reaction using SCM

Graphs were plotted based on equation 1 and the values of reaction rate constant, $k$ were calculated from the slopes. The results were summarized in table 2. The Arrhenius plots (figure 5) were drawn to determine the activation energy required at different rate-controlling regimes. In the chemical reaction controlled regime, the calculated activation energies for CaO and CaO:NiO were nearly the same value. While greater activation energy is required in the diffusion-controlled regime as there is a high resistance caused by the formed product layer. On the contrary, the addition of NiO to CaO sorbents tends to lower down the activation energy required to initiate the carbonation reaction in the diffusion-controlled phase. Besides, the specific rate constants of chemical reaction stage have higher values compared to other stages regardless of the carbonation temperatures. Based on the kinetic study, the SCM equation used in this paper fairly predicts the carbonation kinetics of calcium oxide based sorbents in capturing CO$_2$ and the validity is proven based on high R$^2$ value of (0.936-0.999) as shown in table 2.

Table 2. Kinetic parameters of sorbents carbonated at different temperatures.

| Sample       | Rate-Controlling Stage | Activation Energy, E$_a$ (kJ/mol) | Carbonation Temperature (°C) | a$k$ (1/min) | b$R^2$ | a$k$ (1/min) | b$R^2$ | a$k$ (1/min) | b$R^2$ |
|--------------|------------------------|-----------------------------------|-----------------------------|--------------|--------|--------------|--------|--------------|--------|
| CaO          | Chemical               |                                   | 400                         | 1.9×10$^{-2}$ | 0.993  | 6.4×10$^{-2}$ | 0.992  | 6.6×10$^{-2}$ | 0.992  | 31.06       |
|              | Transition             |                                   | 500                         | 1.0×10$^{-4}$ | 0.999  | 2.6×10$^{-3}$ | 0.999  | 6.2×10$^{-3}$ | 0.983  | 102.79      |
|              | Diffusion              |                                   | 600                         | 8.0×10$^{-5}$ | 0.999  | 1.7×10$^{-3}$ | 0.998  | 1.8×10$^{-3}$ | 0.985  | 78.79       |
| CaO:NiO      | Chemical               |                                   | 400                         | 7.9×10$^{-2}$ | 0.995  | 1.9×10$^{-1}$ | 0.966  | 2.9×10$^{-1}$ | 0.970  | 31.81       |
|              | Transition             |                                   | 500                         | 7.0×10$^{-4}$ | 0.990  | 9.5×10$^{-3}$ | 0.989  | 1.4×10$^{-2}$ | 0.936  | 75.45       |
|              | Diffusion              |                                   | 600                         | 6.0×10$^{-4}$ | 0.999  | 2.4×10$^{-3}$ | 0.946  | 2.7×10$^{-3}$ | 0.951  | 37.87       |

$^a$Reaction rate constant obtained from shrinking core model (SCM) graph
$^b$R$^2$ of the regression line drawn based on shrinking core model (SCM) graph

![Figure 5](image-url). Reaction rate constant values fitted to Arrhenius equation for: (a) CaO:NiO and (b) CaO.
4. Conclusions

In this research, sol-gel method was used to synthesize CaO sorbent with the addition of NiO additive. According to SEM analysis, the prepared CaO:NiO sorbent had smaller particles with homogenous distribution of Ca and Ni elements, as seen from EDX mapping. As a consequence, the CaO:NiO exhibit good CO₂ uptake capacity of 0.79 mmol CO₂/mmol CaO at elevated carbonation temperature (600 °C). Based on the kinetic study, the addition of NiO to CaO sorbent has found to be favoured in the CO₂ sorption process by lowering the activation energy required to initiate the reaction in both rate controlling regimes. This in turn means that when the activation energy is relatively low, the collisions between the particles with sufficient energy occurs at rapid phase, resulting in enhanced carbonation rate and minimizes the energy supply required for the real industrial application in CO₂ capture. Finally, this study has contributed to better understanding on the carbonation kinetic of CaO-based sorbents.

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