Effective Capture of Carbon Dioxide Using Hydrated Sodium Carbonate Powders

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Abstract: The emission of CO2 has been considered a major cause of greenhouse effects and global warming. The current CO2 capture approaches have their own advantages and weaknesses. We found that free-flowing hydrated sodium carbonate (Na2CO3) powders with 30 wt % water can achieve a very high CO2 sorption capacity of 282 mg/g within 60 min and fast CO2 uptake (90% saturation uptake within 16 min). The results suggest that the alkaline solution resulting from the dissolution of partial Na2CO3 can freely attach onto the hydrated Na2CO3 particles, which provides an excellent gas–liquid interface for CO2 capture, leading to significantly enhanced CO2 sorption capacity and kinetics.

Keywords: hydrated sodium carbonate; CO2 capture; free-flowing powders

1. Introduction

Emission of CO2 is identified as the main contributor to global climate change. Reducing the levels of CO2 in the atmosphere has become a pressing issue worldwide, and capturing and sequestering CO2 as an option to decrease levels of CO2 has been widely explored [1–4].

A number of promising materials for CO2 capture were reported [5–10]. The best developed are probably aqueous amines [11,12], including monoethanolamine (MEA) [13,14] and diethanolamine (DEA) [15,16]. However, liquid amines have some serious disadvantages, including amine evaporation [17,18], corrosion to equipment [19], and high energy cost for regeneration [20,21]. A feasible way to reduce the corrosivity and the regeneration energy is to use supported amine adsorbents [22–26], but the raw materials are currently too expensive to be applied in large-scale industrial settings [27].

As an alternative to supported amine sorbents, alkali metal carbonates such as K2CO3 and Na2CO3 as solid sorbents have received wide attention with both high sorption capacity and low cost [28–32]. However, the main problem of using carbonates is their slow reaction kinetics [33–35]. Cooper and co-workers reported that dry K2CO3 solution (K2CO3 aqueous solution coated with hydrophobic silica powders) exhibited significantly increased CO2 uptakes [36], but the recyclability of this sorbent was poor. It has been generally accepted that K2CO3 is superior to Na2CO3 in terms of both CO2 uptake capacity and kinetics [37–39]. However, using Na2CO3 will be more competitive for
large-scale industrial applications because of its lower cost, especially if one can dramatically promote the rate of the key reaction:

\[ \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons 2\text{NaHCO}_3 \]  

(1)

One of the most common approaches to tackle this problem is to disperse Na₂CO₃ powders on solid supports [40,41], but such a strategy also reduces CO₂ sorption capacity because the inclusion of the supports greatly decreases the amount of active components per unit mass [42].

In this report, we demonstrate that support-free hydrated sodium carbonate powders (HSCPs) prepared by simply mixing a certain amount of water and Na₂CO₃ powders exhibit effective CO₂ capture. The alkaline solution resulting from the dissolution of partial Na₂CO₃ can freely attach into hydrated Na₂CO₃ particles, which provides an excellent gas–liquid interface for CO₂ capture, leading to significantly enhanced CO₂ sorption capacity and kinetics. The elimination of supports not only reduces the overall cost of raw materials, but also increases the CO₂ sorption capacity, both of which are critical for large-scale applications.

2. Experimental

2.1. Preparation of HSCPs

Na₂CO₃ (99.8%) was purchased from Tianjin Qilun Chemical Technology Co. Ltd., Tianjin, China. Na₂CO₃·H₂O (99%) was purchased from Aladdin Co. Ltd., Shanghai, China. MEA (99%) was purchased from Jiangsu Yonghua Chemical Technology Co. Ltd., Changshu, China. CO₂ (99.9%) was supplied by Zhuozheng Gas Co. Ltd., Guangzhou, China. All the chemicals were used as received without further purification. A series of HSCPs with different Na₂CO₃ contents were prepared by thoroughly mixing an appropriate amount of Na₂CO₃ and deionized water at room temperature.

2.2. Characterization

X-ray diffraction (XRD) patterns of the samples were recorded using a Bruker D8 diffractometer (Bruker, Karlsruhe, Germany) with Bragg–Brentano θ–2θ geometry (20 kV and 5 mA), using a graphite monochromator with Cu Ka radiation.

To measure the CO₂ capture capacity of the HSCP samples, 5.0 g HSCP was charged into a 50 mL container, which was exposed to CO₂ using a balloon containing a sufficient amount of CO₂ gas (ca. 5 L with a pressure of ca. 1.05 bar). The amount of CO₂ captured by each HSCP sample was measured using a balance. A muffle furnace (Luoyang BSK Electronic Materials Co. Ltd., Luoyang, China) was used to regenerate the sorbents at 250 °C for 1 h, which was mixed with water to reform HSCPs.

3. Results and Discussion

Figure 1a shows the CO₂ uptake kinetic curves using various HSCPs (labelled as HSCP-X, where X is the mass percentage of Na₂CO₃ in the mixture) as a sorbent at 30 °C. It was found that HSCP-10 to HSCP-60 had a very low CO₂ sorption capacity (<32 mg/g of HSCP). The CO₂ uptake capacity rapidly rose to 156 mg/g when the mass fraction of Na₂CO₃ was increased to 65 wt %, i.e., HSCP-65, but it still suffered from low sorption kinetics. Further increasing mass fraction of Na₂CO₃ led to another significant increase in term of both sorption capacity and kinetics. At the optimum concentration of 70 wt % (i.e., HSCP-70), the CO₂ uptake capacity reached 282 mg/g within 60 min, and the t₉₀ (the time to achieve 90% of this capacity) was only 16 min. This capacity is much higher than that of other Na₂CO₃-based CO₂ sorbents reported in the literature, which varies between 32 and 140 mg/g [43,44]. Although HSCP-75 achieved the highest capacity (286 mg/g), its CO₂ sorption rate was relatively slow and t₉₀ was about 45 min.
It was found that too high a concentration of Na$_2$CO$_3$ in HSCP would actually lower the CO$_2$ uptake capacity. When the concentration of Na$_2$CO$_3$ in HSCP reached 80 and 85 wt %, the CO$_2$ uptake capacity decreased to 124 and 46 mg/g, respectively. Theoretically, the CO$_2$ sorption capacity is directly related to the amount of Na$_2$CO$_3$ in HSCPs when the content of water is more than 14.5 wt % according to Equation (1). Thus, the conversion ratio of Na$_2$CO$_3$ is a good indicator of the CO$_2$ sorption behaviour. As shown in Figure 1b, with an increasing mass fraction of Na$_2$CO$_3$, the conversion ratio of Na$_2$CO$_3$ decreased initially, then dramatically increased to a maximum value close to 100% before declining again. After 60 min of reaction, HSCP-70 exhibited the highest conversion rate (97.1%), which suggested that most of Na$_2$CO$_3$ was consumed. The HSCPs with a low mass fraction of Na$_2$CO$_3$, such as HSCP-10, also showed a high conversion ratio, in which Na$_2$CO$_3$ dissolved in water to form a solution, due to its high degree of hydrolysis [45]. However, their corresponding CO$_2$ uptake capacity is low because of the limited amount of Na$_2$CO$_3$ presented (Figure 1a). The other two sets of data in Figure 1b represent the conversion ratios of Na$_2$CO$_3$ after five and 15 min of reaction. For HSCP-70, its conversion ratio increased rapidly from 5 to 15 min, but changed little from 15 to 60 min, which suggested that most of Na$_2$CO$_3$ was consumed within 15 min, thus showing a high reaction rate.

Figure 1. (a) CO$_2$ sorption kinetics of various HSCPs at 30 °C; (b) conversion ratio of Na$_2$CO$_3$ in various HSCPs and different reaction time.
Overall, the above results show that the concentration of Na$_2$CO$_3$ in HSCPs has a great influence on CO$_2$ capture, which can be explained by the fact that the morphology of HSCPs varies from aqueous solution and slurry, to powders with an increasing Na$_2$CO$_3$ concentration. At low Na$_2$CO$_3$ concentrations, the HSCPs exist as an aqueous solution or slurry as shown in Figure 1b (inset), which is not ideal for CO$_2$ capture because of the low gas–liquid contact surface area. However, HSCP-70 is a sample of free-flowing powders (Figure 2) with a much higher gas–liquid contact surface area. This is why it has a rapid reaction rate and a high CO$_2$ uptake capacity.

In order to better understand the mechanism of CO$_2$ sorption by HSCPs, the XRD patterns (Figure 3) of various Na$_2$CO$_3$-based compounds were collected, including the reaction products of HSCP-70 after 0, 5, 15, and 60 min of sorption reaction at 30 °C. The XRD pattern of HSCP-70 was very close to the standard pattern of Na$_2$CO$_3$·H$_2$O, which contains only 14.5 wt % water. This indicates that HSCP-70 contains extra water. As such, we also studied the CO$_2$ sorption by pure Na$_2$CO$_3$·H$_2$O, but it exhibited a low CO$_2$ sorption capacity and rate (Figure 4). This suggests that the extra water contained in the sorbent plays a significant role in CO$_2$ sorption. It indicates that the reaction proceeds most rapidly and effectively when Na$_2$CO$_3$, H$_2$O, and CO$_2$ are present simultaneously. Based on the above results, we propose that the extra water on the surface of HSCPs helps to form a basic alkaline aqueous environment. When CO$_2$ diffuses to the surface of HSCPs, it reacts with the basic aqueous media. Since the reaction is exothermic, the generated heat triggers the decomposition of sodium carbonate hydrates, meanwhile releasing water to drive the reaction to proceed continuously. In addition, along the reaction of HSCP-70 and CO$_2$, we also found that the characteristic peaks of Na$_2$CO$_3$ disappeared gradually, then intermediate structures, such as Na$_3$H(CO$_3$)$_2$·2H$_2$O (i.e., Na$_2$CO$_3$·NaHCO$_3$·2H$_2$O) and Na$_2$CO$_3$·3NaHCO$_3$, appeared after reacting for five and 15 min, respectively. Eventually, virtually pure NaHCO$_3$ formed after 60 min of reaction, which is expected.
Figure 3. XRD patterns of various Na$_2$CO$_3$ based compounds and the reaction products of HSCP-70 after 0, 5, 15, and 60 min of CO$_2$ sorption reaction at 30 °C.

The amine-based CO$_2$ capture system is a proven technology that is already commercialized. To prevent excessive corrosion, typically 30 wt % MEA aqueous solution is used [11]. As shown in Figure 4, a 30 wt % MEA aqueous solution showed similar CO$_2$ uptake kinetics initially, but its overall sorption capacity was relatively low (111 mg/g versus 282 mg/g for HSCP-70). We also studied the CO$_2$ sorption capacity of pure water as a control, whose CO$_2$ uptake capacity was ca. 0.7 mg/g (Figure 4).
Figure 4. CO$_2$ sorption kinetics of HSCP-70, pure water, 30 wt % MEA aqueous solution, and Na$_2$CO$_3$·H$_2$O at 30 °C.

We also studied the CO$_2$ uptake kinetics at different temperatures and the recyclability of HSCP-70. The suitable temperature range for CO$_2$ capture was determined to be 30–50 °C (Figure 5). A higher temperature will cause excessive evaporation of water in HSCP-70, and a lower temperature will cause the formation of Na$_2$CO$_3$·7H$_2$O (as shown in Figure 6), both of which lead to a lower CO$_2$ uptake of HSCP-70. HSCP-70 also exhibited excellent recyclability with little deterioration in CO$_2$ sorption capacity and reaction rate after recycling (Figure 7).

Figure 5. CO$_2$ sorption kinetics of HSCP-70 at different temperatures.
16 min). The elimination of support and the low cost of Na$_2$CO$_3$ make this technology more competitive for large-scale applications. In addition, based on the reaction principles, HSCPs should also have high potential in capturing other acid gases, including SOx, NOx, H$_2$S, and Cl$_2$.

In summary, we have demonstrated that support-free HSCPs can be used as effective sorbents for CO$_2$ capture with a high capacity (282 mg/g) and fast sorption rate (90% saturation uptake within 16 min). The elimination of support and the low cost of Na$_2$CO$_3$ make this technology more competitive for large-scale applications. In addition, based on the reaction principles, HSCPs should also have high potential in capturing other acid gases, including SOx, NOx, H$_2$S, and Cl$_2$.

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