Adsorption and Desorption of Carbon Dioxide on Sodium Oxide Impregnated Alumina

Mingheng Li,* Tong Li, Kenneth Kelley, and Cindy Pan

Department of Chemical and Materials Engineering, California State Polytechnic University, Pomona, California 91768, United States

ABSTRACT: Adsorption and desorption characteristics of carbon dioxide on sodium oxide impregnated alumina particles are investigated using a small-scale packed-bed reactor (PBR) at different feed concentrations (5–14%), different bed temperatures (25–300 °C), and in the presence or absence of steam. The adsorption capacities are calculated from the breakthrough curves measured in the PBR. The adsorption capacities at different temperatures suggest that a physisorption mechanism may dominate at low temperatures, while a chemisorption mechanism dominates at high temperatures. The presence of steam enhances CO$_2$ adsorption. Implications for adsorption-enhanced processes are discussed.

INTRODUCTION

Fossil fuel combustion supplies around 80% of energy and contributes to the majority of CO$_2$ emissions worldwide. With rapid economic growth and industrialization in developing countries, there has been an ever-increasing demand for energy, which poses tremendous challenges in reducing CO$_2$ emissions. This has motivated significant efforts in developing techniques for CO$_2$ capture in power plants, such as postcombustion capture, precombustion capture, and oxygen-fuel combustion.

Adsorptive CO$_2$ capture is well known for its ability to remove CO$_2$ from flue gas or other gas streams because of its high CO$_2$ uptake capacity. In order to enhance adsorption capacities, various adsorbents have been tested. Among these adsorbents, those that can adsorb CO$_2$ at elevated temperatures are desired because of the high partial pressure of CO$_2$ in flue gas. High temperatures, however, are often associated with either low CO$_2$ uptake capacities or a lack of availability of suitable materials.

An approach for adsorbing CO$_2$ at high temperatures is the enhancement of adsorption by reaction (AER). A typical example is steam reforming (SR), in which CO$_2$ and steam are converted to H$_2$ and CO via steam-reforming reactions. In the precombustion capture scheme, the fuel is oxidized to CO$_2$ and H$_2$ via steam-reforming/water-gas-shift (SR/WGS) reactions in the presence of steam. The fuel combustion products then enter the CO$_2$ capture unit before venting to the atmosphere. A list of common adsorbents that may be used for postcombustion CO$_2$ capture is available in the literature.

Although AER has been investigated by various groups, adsorption-enhanced reforming (AER) has emerged as a novel clean fuel processing technique that enables reforming, WGS, and H$_2$ purification in a single unit. Adsorption-enhanced WGS (AEWGS) has been investigated by various groups. The adsorbents used in such applications should have decent CO$_2$ capacities at elevated temperatures (500 °C or above for AER, and about 200–250 °C for low-temperature AEWGS). Since adsorption occurs simultaneously with the reaction, the CO$_2$ partial pressure seen by the adsorbent may be lower than what is suggested by the reaction stoichiometry. Reported adsorbents in AER applications are mainly alkali metal carbonates and oxides such as calcium oxide, hydrotalcite, lithium zirconate, and alumina. Interested readers are referred to a review paper and references therein for CO$_2$ adsorbents at elevated temperatures.

In the postcombustion capture scheme, the combustion product mixture leaves the stack as flue gas after heat recovery. A typical mole fraction of CO$_2$ in flue gas is 7.4–7.7% and 12.5–12.8% for gas and coal fired furnaces, respectively. Since the flue gas has a total pressure of about 1 atm, the partial pressure of CO$_2$ is fairly small. The flue gas may pass through emission control units (to remove particulates, SO$_x$, NO$_x$, etc.) and then enter the CO$_2$ capture unit before venting to the atmosphere. A list of common adsorbents that may be used for postcombustion CO$_2$ capture is available in the literature.

In oxygen-fuel combustion, the oxygen may be supplied by cryogenic air separation, where solid adsorbents are useful for removing CO$_2$ and other impurities before cryogenic distillation. If not removed sufficiently, these components may freeze and lead to blocking and plugging issues.

This work aims to investigate the characteristics of CO$_2$ adsorption and desorption on sodium oxide impregnated alumina under different operating conditions. The process variables include temperature (25–300 °C), CO$_2$ partial pressure (0.05–0.14 atm), and the presence (or lack thereof) of steam. This CO$_2$ sorbent has a relatively lower working temperature as compared to hydrotalcite and has potential applications in adsorption-enhanced WGS and methanol...
Industrial grade N$_2$ and CO$_2$ (purity >99%) from gas cylinders supplied by Praxair and Airgas are fed separately through rotameters followed by two Aalborg mass flow controllers (MFCs) to maintain the desired total flow rates and CO$_2$ concentration. Deionized water is supplied into the system using a GE peristaltic water pump. The experimental system is monitored and controlled using LabVIEW. Process data such as feed rates of N$_2$ and CO$_2$ and CO$_2$ outlet concentration are logged in real time. Before conducting any adsorption experiments, the Vaisala CO$_2$ concentration analyzer is calibrated by correlating the steady state analyzer readouts with known CO$_2$ concentrations (based on the set points in MFCs).

Figure 2 shows the mole fraction of CO$_2$ in the exhaust gas recorded by the analyzer in one run at room temperature (i.e., 25 °C), which included six adsorption and desorption cycles. From the real-time data recorded by LabVIEW, the following equation is used to calculate the capacity of the sorbate in the packed-bed reactor during the adsorption step:

$$N_{CO_2}^* = \int_0^\infty \left( \dot{F}_{N_2} \frac{y_0}{1 - y_0} - \dot{F}_{N_2} \frac{y(t)}{1 - y(t)} \right) dt$$

(1)

where \( \dot{F}_{N_2} \) is the molar flow rate of the carrier N$_2$ gas, \( y_0 \) is the inlet CO$_2$ mole fraction, and \( y(t) \) is the exit CO$_2$ mole fraction.

Similarly, the sorbate capacity during desorption is

$$N_{CO_2}^* = \int_0^\infty \dot{F}_{N_2} \frac{y(t)}{1 - y(t)} dt$$

(2)

The reported capacity in this work was calculated as the average of values determined by eqs 1 and 2. For each of the test conditions, the bed was saturated and flushed at least three times. The averaged capacity and standard deviation at each set of operating conditions were calculated and are presented in Figure 3.

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**Experimental Section**

Both in-house and commercially made sodium oxide impregnated alumina particles are used in the experiments. To prepare the sorbent particles in the lab, Na$_2$CO$_3$ is first dissolved in deionized water. Alumina particles from SASOL are then submerged in the solution. After soaking for 50 h, the particles are dried and heated before being loaded into the PBR. The commercial adsorbent is ActiSorb CL2 from Sud Chemie, which contains 85–95% alumina and 5–15% sodium oxide. Its Brunauer–Emmett–Teller (BET) N$_2$ surface area is 165 m$^2$/kg. The experimental setup is shown in Figure 1.
the appropriate graphs. Several factors that may contribute to the errors are the manual operation of the mode switch between adsorption and desorption as well as the measurement errors of the mass flow controllers and the CO₂ analyzer.

RESULTS AND DISCUSSION

Breakthrough Curves and Capacities at Dry Conditions. In-house made particles are used to measure the adsorption/desorption characteristics in the absence of steam. The flow rate to the reactor is 5 SLPM. Figure 4 shows that at the same temperature and CO₂ partial pressure, the adsorption capacity does not change much when the total flow rate varies between 2 and 5 SLPM. This is reasonable since the flow rate would affect the kinetics but not the equilibrium of CO₂ adsorption. However, a general trend indicates that higher total flow rates are associated with smaller variations in experimental data. One possible reason is that the residence time of the gases in the reactor is smaller when the flow rate is larger, thus reducing measurement error. Therefore, 5 SLPM is chosen for the total flow rate in all of the other experiments.

Representative curves of the CO₂ mole fraction measured at the outlet of the PBR during both adsorption and desorption in three separate runs using conditions $T = 250 \, ^\circ\text{C}$, $F_{\text{N}_2} + F_{\text{CO}_2} = 5 \, \text{SLPM}$, and $y_0 = 10\%$ for adsorption are shown in Figure 5.

The adsorption breakthrough and desorption elution curves in all cycles were plotted using the same initial time to examine the repeatability of the results. The transport phenomena as revealed by dynamic modeling of the convection-dispersion-adsorption process in PBRs\textsuperscript{26,27} are as follows. When the mixture is fed to the reactor, CO₂ is adsorbed on the surface of the adsorbate and no CO₂ is detected by the analyzer initially. As the loading of CO₂ on the adsorbent increases, the wave of CO₂ concentration in the gas propagates along the reactor. The breakthrough occurs when the wavefront reaches the outlet of the reactor. Subsequently, the CO₂ concentration detected by the analyzer gradually increases as the bed continues to approach saturation. When the bed reaches its full capacity, the process operates at a steady state in which the inlet concentration is equal to the outlet concentration. When the flow is reversed with pure N₂, CO₂ is gradually desorbed.
from the adsorbate. In each cycle, the difference between the calculated adsorption and desorption capacities is less than 5%, implying that the adsorption/desorption processes are reversible.\textsuperscript{19} For this particular case, the variation of adsorption or desorption capacity in different cycles is also less than 5%, suggesting the cycle is repeatable as well. The breakthrough capacity, calculated based on the time for the exhaust to reach 5% of its inlet concentration, is about two-thirds of the exhaust capacity.

As previously mentioned, the adsorption/desorption dynamics are investigated under different temperatures and CO\textsubscript{2} partial pressures. The results are summarized in Figure 6. It appears that the dependence of the capacity on the temperature is not monotonic. Instead, it has a valley at about 50 °C and a local peak at about 200 °C. In all cases within the scope of this study, initially the capacity is high, but as temperature increases, the capacity drops as if the system was following a physical adsorption mechanism. Somewhere between 50 and 200 °C, the system appears to transition from physical adsorption to chemisorption.

Thermogravimetric analysis (TGA) was used to investigate CO\textsubscript{2} adsorption on a different batch of homemade sodium oxide impregnated alumina particles in the temperature range of 150−250 °C. The capacity was calculated as the weight gain divided by the initial weight. The results are shown in Figure 7, which confirm the local peak of the adsorption capacity occurring around 200 °C.

The physisorption mechanism results in an inverse relationship between the temperature and capacity. As the internal energy of the adsorbate increases, the weak interactions between the adsorbent surface and the adsorbate are not strong enough for the two to remain bonded. Chemisorption follows a trend better represented by a quadratic function. Initially the increasing temperature helps supply the activation energy necessary for the adsorbate and adsorbent to undergo chemical bonding. These bonds are much stronger than the weak physisorption bonds, and they can withstand higher adsorbate kinetic energies. Eventually, when the temperature becomes too high for the adsorbent and adsorbate to remain bonded, the capacity begins to drop with increasing temper-
yield adsorbed carbonic acid, which undergoes deprotonation to yield adsorbed carbonate and protonated hydroxyl groups. The formation of carbonic acid may result from water being coadsorbed simultaneously with CO$_2$ or adsorbed before CO$_2$. This mechanism might explain the apparent enhancement of CO$_2$ adsorption on sodium oxide promoted alumina particles in the presence of H$_2$O.

**Implications to Adsorption-Enhanced Processes.** In industrial applications, low-temperature WGS occurs at 190–250 °C with copper/zinc oxide/alumina catalysts, while high-temperature WGS is performed at 350–450 °C with promoted iron oxide catalysts. The local peak in the CO$_2$ adsorption capacity versus temperature curve occurring around 200 °C is compatible with the working temperature of the low-temperature shift catalysts. As temperature goes beyond 250 °C, the CO$_2$ adsorption capacity on sodium oxide promoted alumina drops significantly. Therefore, it may not be ideal for use in high-temperature WGS.

This work shows that the adsorption capacity of sodium oxide promoted alumina at 200 °C is comparable to the one at room temperature. It might be a promising adsorbent to remove CO$_2$ from a hot waste stream without cooling to room temperature.

For adsorption-enhanced process applications, the breakthrough capacity is more meaningful than the saturation capacity calculated from eq 1 or 2. In other words, the switching from adsorption mode to desorption mode occurs much earlier before the bed is saturated with CO$_2$. Otherwise, the product stream may be contaminated with CO$_2$. Under experimental conditions in this work, the breakthrough capacity for sodium oxide promoted alumina particles is roughly two-thirds of the saturation capacity (see, e.g., Figures S and 8). The required adsorbent amount in the adsorption-enhanced processes is better estimated using the breakthrough capacity.

**CONCLUSIONS**

This work was devoted to studying the relationships between capacity and temperature, flow rate, and concentration of CO$_2$ in a packed-bed reactor. The variation of the flow rate did not affect the capacity much. At 25 °C, the physisorption mechanism was believed to be dominant, which was reflected in the relatively high adsorption capacity versus inlet CO$_2$ concentration relationship observed. Finally, the capacity versus temperature graph suggested that the adsorption mechanism of CO$_2$ on sodium oxide promoted alumina is initially physisorption at low temperature and chemisorption at high temperature. The capacity versus temperature curve appears to be the superposition of the individual physisorption and chemisorption curves. The local peak of adsorption capacity occurring around 200 °C is confirmed by TGA measurement. The presence of steam promotes CO$_2$ adsorption, probably attributed to the reaction of adsorbed H$_2$O with CO$_2$.

**AUTHOR INFORMATION**

Corresponding Author
*Tel.: +1-909-869-3668. Fax: +1-909-869-6920. E-mail: minghengli@cpp.edu.

ORCID
Mingheng Li: 0000-0002-6611-425X

Notes
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Figure 8. CO$_2$ outlet mole fraction in three (a) adsorption and (b) desorption cycles at $T = 250$ °C and $y_0 = 8\%$ in the presence or absence of steam. The dotted lines are thicker than the solid lines.


