High-Temperature Sorbents for CO_2 Made of Alkali Metals Doped on CaO Supports

Ettireddy P. Reddy and Panagiotis G. Smirniotis*

Chemical and Materials Engineering Department, University of Cincinnati, Cincinnati, Ohio 45221-0012

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A number of basic sorbents based on CaO were synthesized, characterized, and tested for the sorption of CO_2 and selected gas mixtures simulating flue gas. Our studies resulted in highly promising sorbents based on Cs/CaO, which demonstrated zero affinity for N_2 and O_2 and very low affinity for water. Moreover, we observed high CO_2 sorption capacities and rapid sorption/desorption characteristics in a wide temperature range reaching temperatures as high as 700 °C. The "key" feature of this family of sorbents is their basic nature, which allows for the selective chemisorption of CO_2. These unique characteristics of this family of sorbents offer high promise for the development of advanced industrial sorbents for the effective CO_2 removal. The performance of the alkali metals as dopants on CaO follows the order $Li < Na < K < Rb < Cs$, which reveals a strong relationship between the sorption characteristics and the increase of the electropositivity or equivalently atomic radii of the alkali metals. From XPS investigations, including the surface atomic ratios of Cs 3d/C 1s, and Ca 2p/C 1s, it is observed that the adsorption of CO_2 is preferably taking place on Cs_2O rather than CaO. The XPS analysis further show that the surface atomic ratio between Cs $3d_{5/2}$ and Ca 2p core levels appreciably increase for the sorbents prepared with ∼20 wt % loading of Cs on CaO. For higher Cs loadings, the performance did not improve further due to the formation of paracrystalline Cs_2O on the CaO support surface. CsOH- and Cs_2CO_3-doped CaO sorbents provided significantly higher adsorption of CO_2 than CsCl mainly due to the formation of a highly dispersed Cs_2O on the CaO support.

1. Introduction

The availability of clean, affordable energy is essential for the prosperity of any developed country. At the same time, atmospheric concentrations of carbon dioxide are expected to increase unless energy systems reduce the carbon load to the atmosphere. The rapid increase of the Earth's population over the past few decades combined with the improvement of the quality of life are directly related to the dramatic increase of man-made CO_2 concentrations, since both of the above reasons are linearly related to the production and consumption of energy primarily obtained from fossil fuels (nuclear energy consists of a small percentage of the energy used). While for the CO_2 produced from nonenergy related activities (CO_2 released by oceans, CO_2 produced from agricultural and animal activities, CO_2 remaining untransformed due to deforestation, CO_2 related to volcanic activities, etc.), humans have no means of controlling directly or collecting the CO_2 emitted, all the activities utilizing fossil fuels can in principle lead to accumulation of the CO_2 produced during the process. This, gives us the opportunity to collect the CO_2 emitted in almost all cases of utilizing fossil fuels containing carbon (perhaps with the exception of automobiles and aircraft) and potentially transform it to something which does not cause problems to the atmosphere or store it deep into the sea and/or abandoned gas and oil wells.

The first step in carbon sequestration is the CO_2 separation and removal from flue gas, or any tailpipe leaving, which commonly contains relatively large concentrations of water, oxygen, nitrogen, and lower concentrations of nitrogen and sulfur oxides and other gases such as carbon monoxide, etc. Depending on the potential application, the CO_2 separation may have to be performed at a very wide range of temperatures without excluding relatively high temperatures (i.e., 700 °C).

High aluminum content zeolites have been extensively used for separation of gases including carbon dioxide from gas mixtures. The relation between the properties of various zeolites and their CO_2 adsorption behaviors in PSA (pressure swing adsorption) was presented in an early study by Inui et al.[1,2] It was concluded that chabazite and 13X zeolite were the most proper choice for this process while the next best candidates were erionite and 4A zeolite. The highest adsorption of CO_2 on MS-13X was 89.6 mL/g at an adsorption pressure equal to 10.8 kg/cm^2.[2] From the temperature-programmed desorption (TPD) profiles presented in that work one could observe that CO_2 was practically desorbed at temperatures not higher than 260−300 °C, thus limiting the process for separation at relatively high temperatures. It should be also noted that some zeolites exhibited a low and high-temperature desorption peak in the above temperature range. The patent of Ojo et al.[3] has recently received considerable attention for removal of carbon dioxide from gas mixtures at low temperatures (ranging from 5 to 50 °C). This separation is based on Al-rich X faujasite (or formaly LSX, which stands for low silicon X faujasite), which was exchanged with various monovalent, divalent or trivalent ions selected from groups IA, IIA, and IIIA of the periodic table. However, the sorbents described in that invention can only be used to purify mixtures of gases which are less polar than CO_2, a characteristic which limits its use for cases where the gas stream contains other compounds such as SO_2 and H_2O. Moreover, those sorbents demonstrated relatively low concentrations of CO_2 at low temperatures. Other sorbents based on Li lead to sorbents which are unable to operate at high temperatures because of sublimation of lithium. Suzuki et al.[4] have utilized hydrophobic zeolites for the removal of CO_2 at ambient

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* Correspondence author. Telephone: (513) 556 1474. Fax: (513) 556 3473. E-mail: Panagiotis.Smirniotis@uc.edu.

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temperature in order to avoid the problem of coadsorbing water with relative success.

In this study, we developed sorbents with high capacity and selectivity for CO_2. These sorbents operate in a wide temperature range and are particularly effective at high temperatures (as high as 700 °C). This family of sorbents is based on alkali metals, and more specifically Cs supported on alkaline-earth-metal oxides.

2. Experimental Section

2.1. Sorbents Preparation. Various loadings of alkali-metal-doped calcium oxide sorbents were synthesized by the wet impregnation method using Aldrich (99.9%) CaO as the source of calcium oxide. The precursors used for loading of alkali metals were lithium chloride (Fisher) for lithium; sodium chloride (Fisher), sodium hydroxide (Fisher), and sodium carbonate (Fisher) for sodium; potassium chloride (Fisher) and potassium hydroxide (Fisher) for potassium; rubidium chloride (Aldrich) and rubidium hydroxide (Aldrich) for rubidium; and cesium chloride (Aldrich), cesium hydroxide (Aldrich), and cesium carbonate (Fisher) for cesium. All sorbents were prepared by mixing the appropriate amount of the alkali-metal precursor and calcium oxide such that the weight concentration of alkali metal is 10 and 20 wt % (based on alkali metal and CaO only). The appropriate amounts of alkali-metal precursor in distilled water and calcium oxide were mixed vigorously under heating. The distilled water added for the formation of the slurry in the proportion of 1 g of CaO to 80 cm^3 of aqueous solution of the alkali-metal precursor. The slurry was heated and stirred until the water was evaporated. The powder was ground to fine powder and dried in an oven at 125 °C overnight and subsequently calcined in helium atmosphere at 750 °C for 5 h. After the calcination step, the sorbents were stored in a glovebox under inert atmosphere in order to eliminate completely the chance for adsorption of impurities.

2.2. Sorption Experiments. The adsorption/desorption experiments on the above prepared sorbents along with pure calcium oxide were carried out with a Perkin-Elmer PYRIS-1 thermogravimetric analyzer apparatus. The TGA balance can measure accurately up to 1 μg. To maintain TGA balance accurately, 30 mL min^{-1} constant helium flow was used as a purge gas. For the sorption experiments, relatively small amounts of sorbent (ranging from 8 to 25 mg depending on the type of experiment) was placed in a platinum boat. Each sorbent was first pretreated at 750 °C for 3 h under total helium flow of 50 mL min^{-1} (20 mL from gas station + 30 mL of purge gas) in order to remove any preadsorbed atmospheric carbon dioxide and/or water vapor then tested at different adsorption temperatures such as 50, 450, 600, and 700 °C by using a gas flow of 50 mL/min (20 mL of CO_2 (99.999%) from gas station + 30 mL of purge gas). The temperature profile used for these experiments was 10 °C up and 15 °C down. The highest saturation capacity of CO_2 was found at 600 °C, and the total desorption temperature was selected at 725 °C. The rate of desoroption at 600 °C was very slow when compared to the higher temprature. Therefore, we selected 725 °C to perform the desorption study. Sorbents with high saturation capacity and selectivity for CO_2 and relatively rapid adsorption were selected as the best candidates. The desorption cycle was an important piece of information to determine the effectiveness of the sorbent. During the adsorption step the sorbents were allowed to reach equilibrium, whereas the desorption step was performed in an inert gas until it reaches the original weight of the sorbent. The detailed adsorption and desorption experiments were discussed in the results and discussion section.

2.3. Sorbent Characterizations. *BET Surface Areas.* BET surface areas of these sorbents were measured by nitrogen adsorption at −196 °C using a Gemini (Micromeretics) instrument. Prior to the analysis, ~0.5 g of sorbent was degassed at 400 °C for 2 h. The adsorption isotherms of nitrogen were collected at −196 °C using approximately six values of relative pressure ranging from 0.05 to 0.99.

Average Particle Size Analysis. Average particle size analysis of the sorbents was done by using Mastersizer S Version 2.15, Malvern Instrument. The average particle size of the sorbents is 150 μm, which was determined by the above-mentioned instrument.

X-ray Photoelectron Spectroscopy (XPS). X-ray photoelectron spectroscopy was used to analyze the atomic surface concentration of Cs/CaO before and after the adsorption of carbon dioxide. The XPS analyses were conducted on a Perkin-Elmer model 5300 X-ray photoelectron spectrometer with MgK_α radiation at 300 W. Typically, 89.45 and 35.75 eV pass energies were used for survey and high-resolution spectra, respectively. The effect of sample charging was eliminated by correcting the observed spectra for a C 1s binding energy value of 284.6 eV. The sorbents were mounted onto the sample holder and were degassed overnight at room temperature and pressures on the order of 10^{-7} Torr. The binding energies and atomic concentrations of the sorbents were calculated via the XPS results using the total integrated peak areas of the Cs 3d, Ca 2p, O 1s, and C 1s regions.

3. Results and Discussion

The BET surface area of various alkaline-earth-metal oxides and cesium-doped calcium oxide sorbents before and after CO_2 adsorption were depicted in Table 1. As shown in Table 1, the BET surface area of commercial calcium oxide is higher than magnesium oxide and barium oxide. The general observation is that the BET areas of the materials under consideration are relatively low. In this study commercially available supports were utilized. The adsorption equilibrium isotherms of carbon dioxide on MgO, CaO, and BaO at 600 °C are presented in Figure 1 in order to compare them under identical conditions. The results reveal that the amount of CO_2 adsorbed on MgO and BaO is very low, where as on CaO it is nearly 12 wt % during a 1-h equilibrium process. The adsorption equilibrium results further indicate that the adsorption of CO_2 on MgO and BaO sorbent supports is practically negligible at this temperature without any chemical modification of the surface. The adsorption behavior of MgO, CaO, and BaO is closely related to the nature of the product formed during the adsorption and to the surface area. The surface area of a solid sorbent is a very important parameter in the solid gas adsorption process and may be one of the principal factors determining overall reactivity.[5] Therefore, the selection of CaO as the sorbent support is the obvious choice for further studies.

A set of CO_2 adsorption experiments on CaO were performed at different temperatures, namely 50, 450, 600, and 700 °C with

TABLE 1: BET Surface Areas of Various Supports and Sorbents after Calcination, after CO_2 Adsorption, and after CO_2 Desorption

sorbent	BET surface area (m^2/g)
MgO (Aldrich)	9.8
CaO (Aldrich)	20.0
BaO (Aldrich)	2.1
20% Cs/CaO (after calcination)	7.4
20% Cs/CaO (after adsorption)	2.3
20% Cs/CaO (after desorption)	7.1

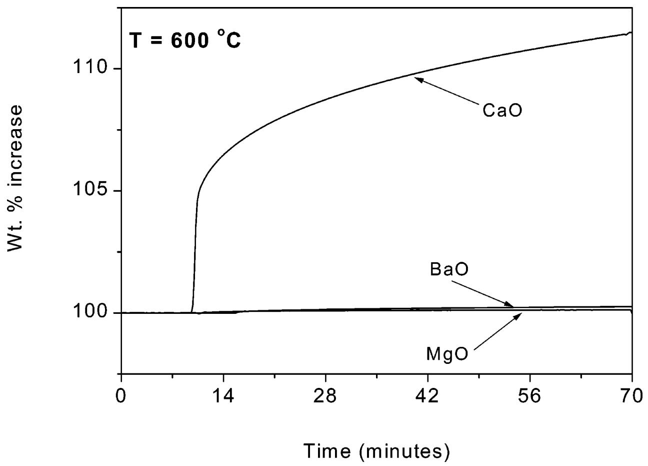

Figure 1. CO_2 adsorption on different supports at 600 °C. Conditions: concentration of $CO_2 = 99.999\%$; flow = 50 mL min^{-1} (20 mL of 99.999% + 30 mL of He as purge as gas).

a gas containing pure CO_2 (99.999%) and at a gas flow rate of 50 mL min^{-1} (20 mL of pure CO_2 (99.999%) from gas station + 30 mL of He as a purge gas). Prior to the adsorption, the sorbent was pretreated at 750 °C for 3 h under 50 mL min^{-1} (20 mL of He from gas station + 30 mL of He as a purge gas) flow of helium. Once the desired adsorption temperature reached, the helium flow from the gas station was switched to CO_2 stream. The increase in the weight of sample with time was recorded and the adsorption of CO_2 on CaO was calculated from the increase in its weight. The data obtained at different temperatures are presented in Figure 2 in order to understand the optimum adsorption temperature for further studies. As can be noted from Figure 2, the adsorption of CO_2 on CaO increased monotonically with the temperature, and a large adsorption equilibrium was observed at 700 °C. In contrast to the traditional sorption, which is carried out at low temperatures and is based on physisorption, the present systems are based on chemisorption of the adsorbate on the surface of the sorbent support. Evidently, the amount of CO_2 chemisorbed increases with increase in temperature, and it is favored by the basic nature of the sorbent support since CO_2 is a weak acid. The desorption was performed at 725 °C, which indicate that the chemisorption of CO_2 on the CaO support is practically reversible and follows the following reactions.

Chemisorption:

$$CaO + CO_2 \rightarrow CaCO_3 \tag{1.1}$$

Desorption:

$$CaCO_3 \rightarrow CaO + CO_2 \tag{1.2}$$

It should be noted that we did not attempt to modify or optimize the basicity as well as the surface properties and morphology of these materials for this study. The results and data that will be presented below indicate that when chemisorption is the controlling mechanism, the amount of CO_2 adsorbed will be significantly higher than the case of physisorption. Of course, the need for a relatively high separation temperature determines the mechanism of sorption.

The effect of promoting the surface with alkali metals was examined. It is well-known that loading alkali metals on alkaline-earth-metal oxides leads to basic or superbasic surfaces.[6] Figure 3 shows the CO_2 adsorption capacity of 20 wt % alkali metal (Li, Na, K, Rb, and Cs) loaded CaO for a mixture of 20 vol % CO_2 in helium at 50 °C. One should note that the

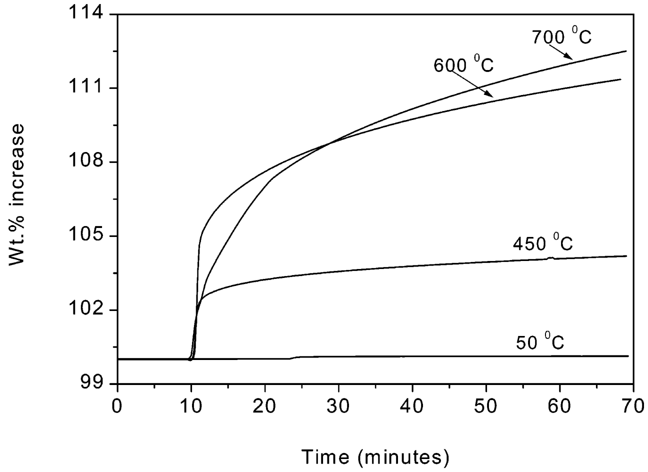

Figure 2. Effect of temperature on CO_2 adsorption over CaO. Conditions: concentration of $CO_2 = 99.999\%$; flow = 50 mL min^{-1} (20 mL of 99.999% + 30 mL of He as purge as gas).

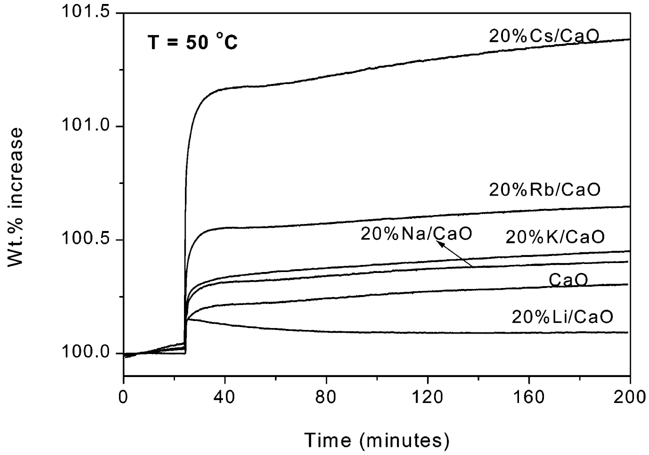

Figure 3. CO_2 adsorption on CaO doped with alkali-metal chlorides at 50 °C. Conditions: concentration of $CO_2 = 99.999\%$; flow = 50 mL min^{-1} (20 mL of 99.999% + 30 mL of He as purge as gas).

performance of Li/CaO is even worse than that of CaO, because of the sublimation of lithium on the surface of CaO at higher temperatures. One can observe that Cs/CaO adsorbs the highest amount of CO_2. This interesting observation carries unique potential for the development of superior sorbents for removal of CO_2 and deserves to be investigated further. Any alkali metal loaded CaO, with the exception of Li, leads to improvement of the sorption characteristics of the sorbent due to an increase in the number of basic sites on the surface.[7] A general increase of the sorption capacity with the increase of atomic radii of the alkali metals ($Li < Na < K < Rb < Cs$) is observed. This trend follows exactly the change of electropositivity of the alkali metals, which increase from top to bottom in the periodic table. Cesium is the most electropositive alkali metal used in this study and leads to the highest uptakes of CO_2. Evidently, this feature of Cs, which is directly related to its basicity characteristics, is responsible for the behavior that we observed.

CO_2 adsorption experiments on alkali-metal-doped CaO were performed at 450 °C and are presented in Figure 4. The adsorption trend with respect to various alkali metals is similar to that was observed at 50 °C. However, the adsorption capacity of sorbents other than Li/CaO increased significantly in comparison with what we observed when the experiments were performed at 50 °C under identical conditions. This clearly indicates that the alkali-metal-doped CaO sorbent adsorbs carbon dioxide very fast at higher temperatures. One can note that the

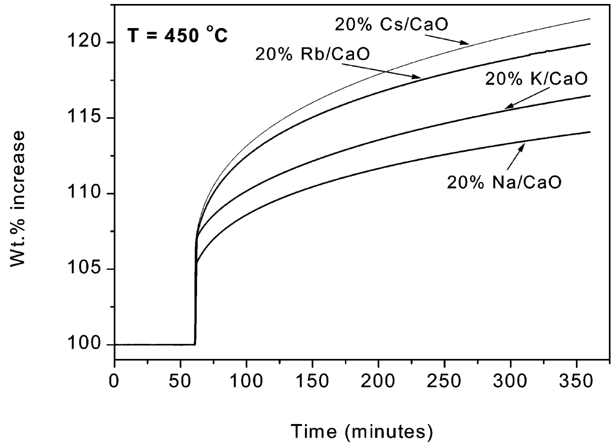

Figure 4. CO_2 adsorption on CaO doped with alkali-metal chlorides at 450 °C. Conditions: concentration of CO_2 = 99.999%; flow = 50 mL min^{-1} (20 mL of 99.999% + 30 mL of He as purge as gas).

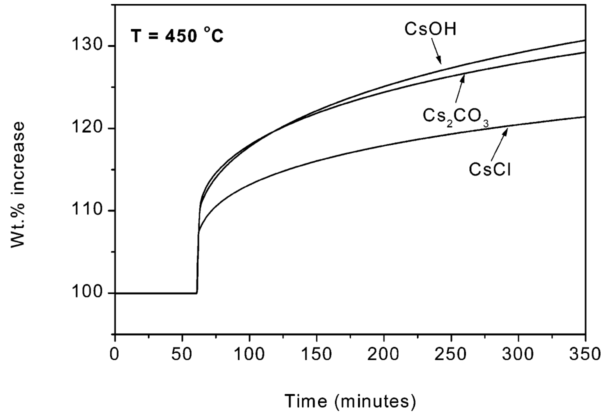

Figure 5. CO_2 adsorption on 20% Cs/CaO prepared using different precursors of cesium oxide. Conditions: concentration of CO_2 = 99.999%; flow = 50 mL min^{-1} (20 mL of 99.999% + 30 mL of He as purge as gas).

Cs/CaO sorbent demonstrated the highest uptake of carbon dioxide than the other alkali-metal-doped CaO sorbents, which suggests that the higher basicity of Cs loaded on CaO is responsible for the observed behavior.

All the sorbents that we used in the above-mentioned studies were prepared by using an alkali-metal chloride as the precursor for the alkali-metal doping. Since Cs was observed to be the most effective dopant, we decided to examine the effect of the anionic part of the precursor.

Different Cs-precursor-doped CaO sorbents were tested for CO_2 adsorption at 450 °C. As shown in Figure 5, the adsorption equilibrium isotherms of cesium hydroxide and cesium carbonate doped CaO showed practically similar adsorption characteristics. In contrast, the cesium chloride doped CaO sorbent showed lower adsorption capacity than the other two samples. The better performance of the sorbents synthesized from CsOH and Cs_2CO_3 precursors is due to the fact that during calcination under inert atmosphere these precursors decompose to Cs_2O, which is the active surface species for the uptake characteristics that were observed. In contrast, when CsCl is used as the precursor, its decomposition under identical conditions leads to significant amounts of cesium metal. This claim was validated (not shown) by our XPS experiments. Therefore, we decided to use cesium hydroxide doped CaO as the sorbent for the remaining studies, since the hydroxide precursor resulted in the best sorbents. Moreover, the use of the hydroxide precursor is more advantageous from environmental point of view since the gases resulting from the decomposition of the precursor during the synthesis steps do not require any further treatment.

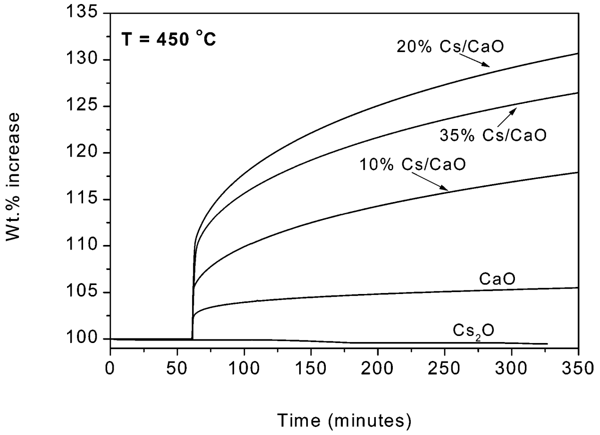

Figure 6. Effect of Cs loading on CaO (CsOH used as Cs precursor during the synthesis). Conditions: concentration of CO_2 = 99.999%; flow = 50 mL min^{-1} (20 mL of 99.999% + 30 mL of He as purge as gas).

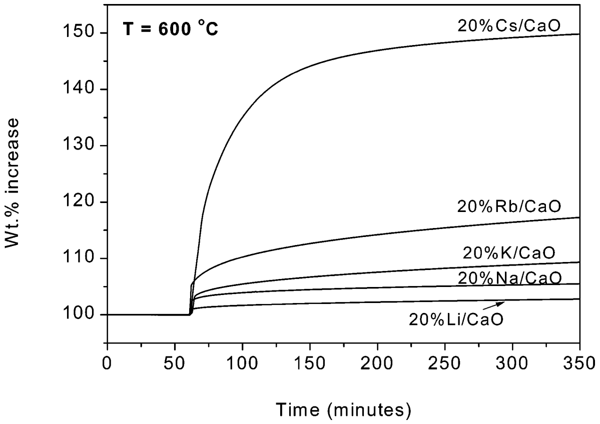

Figure 7. CO_2 adsorption on CaO doped with alkali metal hydroxides at 600 °C. Conditions: concentration of CO_2 = 99.999%; flow = 50 mL min^{-1} (20 mL of 99.999% + 30 mL of He as purge as gas).

Figure 6 shows the effect of Cs loading on CaO for CO_2 adsorption equilibrium study at 450 °C. The adsorption equilibrium capacity increased with increasing cesium loading up to a level of about 20 wt %. For higher cesium loadings the uptake of carbon dioxide decreases. The main reason for reducing the adsorption at higher Cs loadings is the formation of crystalline Cs_2O on the surface of the sorbent beyond 20 wt %. Though Cs is highly basic, the adsorption capacity at higher Cs loadings decreases significantly. This is due to the formation of paracrystalline Cs_2O deposition on CaO support, which is favored by the relatively higher Cs concentration.

The performance of 20 wt % of alkali-metal hydroxide deposited CaO sorbents for CO_2 adsorption at 600 °C is presented in Figure 7. Prior to admitting CO_2 gas, the sorbents were pretreated at 750 °C for 3 h under 50 mL min^{-1} (20 mL from gas station + 30 mL of purge gas) helium flow. Once the temperature reached to 600 °C, the 20 mL min^{-1} gas flow system in the gas station was switched to 99.999% CO_2. One can clearly observe from Figure 7 that about 80% of the CO_2 adsorption occurs within the first 40 min. A general trend of increasing adsorption capacity was observed with respective to ionic radii and the basicity of the alkali metal ($Li < Na < K < Rb \ll Cs$). It should be noted that 20% Cs/CaO sample adsorbed about 50 wt % of CO_2 within 5 h. Therefore, these sorbents are very promising for capturing of CO_2 from numerous applications

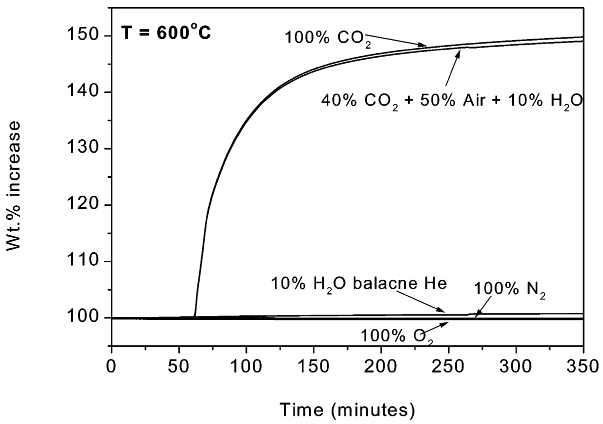

Figure 8. Adsorption of other gases on 20% Cs/CaO: Gas flow is same in all the cases. i.e., 50 mL min^{-1} (20 mL of mixture of gases + 30 mL of He as purge gas).

TABLE 2: Ratio between Adsorption Weight Percentages of CO_2 vs Other Gases

adsorbed gases	wt % rations
CO_2/N_2	∞
CO_2/O_2	∞
CO_2/H_2O	82

related to power generation or production of chemicals. In contrast to recent studies where the emphasis was directed toward optimizing the CaO supports,[8] in our study we gave emphasis on promoting the surface of a rather "average" CaO support in order to find distinct differences from the effects of dopants.

To examine the selectivity of the Cs/CaO sorbent for CO_2 with respect to a mixture of gases commonly found in practical applications, we studied the uptake of this sorbent in the presence of 40 vol % CO_2, 50 vol % air, 10 vol % water, and He (purge gas) at 600 °C (Figure 8). These results were compared with the results of 20% Cs/CaO sorbent using pure CO_2 + He (purge gas). One can undoubtedly observe that there is very small (less than 2%) difference between the adsorption capacity of this sorbent between the case where pure CO_2 + He (purge gas) (top curve) and the case where the mixture of 40 vol % CO_2, 50 vol % air, 10 vol % water, and He (purge gas) (second from the top curve) were used. It is also worth noting that the dynamic sorption characteristics (rate) of this sorbent did not decrease for the case where the mixture of gases was used. In other words, from the kinetic point of view, we observed that the rate of adsorption of the sorbent was practically unchanged in the presence of 10 vol % water. This indicates that these sorbents are very selective for CO_2, which is less polar than water. The relative hydrophilic or hydrophobic character of the sorbents depends on the polarity of adsorbate, in the present case CO_2, H_2O, N_2, and O_2. Naturally, CO_2 is a linear molecule and its dipole moment is zero; therefore, the polarity of CO_2 is less than the polarity of water. Suzuki et al.[4] have studied the CO_2 adsorption on hydrophobic zeolites under high moisture conditions at ambient temperature, but the adsorption capacity of those zeolites are much less when compared to 20% Cs/CaO. To understand further about these sorbents under operation in the presence of water, we performed another experiment where only 10% of water in helium was supplied to the sorbent. By comparison, we found that the CO_2 uptake on this sorbent is 82 times higher than that for water (Table 2). This sorbent also shows no affinity for nitrogen and oxygen. We performed independent experiments where pure N_2 and O_2 were admitted individually, and we found that neither of these gases adsorb on the surface. These characteristics are ideal for sorbents to remove carbon dioxide from flue gas and/or gas effluents resulting from utilization of fossil fuels.

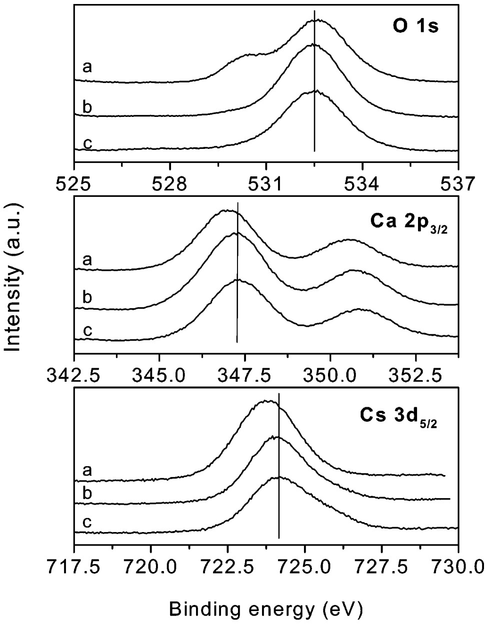

Figure 9. XPS spectra of Cs 3d, Ca 2p and O 1s core level peaks for 20 wt % Cs/CaO sorbent: (a) after adsorption at 600 °C; (b) after desorption at 725 °C; (c) after temperature 750 °C.

The most effective sorbent (20 wt % Cs/CaO) was characterized by XPS in order to study its surface characteristics. These studies were performed after three different pretreatment steps, namely heating at 750 °C for 3 h under helium flow, CO_2 adsorption at 600 °C for 1 h, and CO_2 desorption at 725 °C for 1 h. It should be mentioned that, prior to the XPS analysis, all the sorbents were collected after their experiment and stored in a vacuum oven. Analogs of two C 1s signals could be discerned in all spectra (not shown). The intensity of C 1s core level is very predominant in the case of sorbent after CO_2 adsorption. Hence, C 1s at 284.5 eV was considered to be a good reference for binding energy calibration. The XPS bands of O 1s, Ca 2p, and Cs 3d core levels are depicted in Figure 9. The binding energy values of O 1s, Ca 2p, and Cs 3d photoelectron peaks and Cs 3d/Ca 2p, Cs 3d/C 1s, and Ca 2p/C 1s surface atomic concentration ratios as determined by XPS of the above-mentioned sorbents are summarized in Table 3.

The O 1s profile, as shown in Figure 9, is due to the overlapping contribution of oxygen from CaO and Cs_2O in the case of the sorbent after pretreatment and after CO_2 desorption and to the overlapping contribution of oxides and carbonates of Ca and Cs in the case of sorbent after CO_2 adsorption. As shown in Figure 9, and Table 3, from the XPS spectra of O 1s corresponding to sorbent after CO_2 adsorption, one can clearly detect that there are two types of O 1s peaks. The major component, denoted as O 1s from CaO and Cs_2O had a binding energy of 532.5 eV[9] while the minor component denoted as O 1s from $CaCO_3$ and Cs_2CO_3 was found at 530.4 eV with sole exception of CO_2 adsorption (see Table 3). The binding energy values of two different types of O 1s peaks can be judged from the difference in the electronegativity of the elements.[10] It should be noted that only one oxygen photoelectron peak at 530.4 eV that belongs to CaO and Cs_2O was observed in the case of pure 20% Cs/CaO, and 20% Cs/CaO after CO_2 after desorption. The peak intensity of O 1s corresponding to CaO and Cs_2O decreased with the appearance of a new peak corresponding to carbonates after CO_2 adsorption. This observation clearly indicates that the

TABLE 3: Binding Energy Values and Surface Atomic Ratios for Selected Sorbents Determined by XPS

	binding energy (eV)					
sorbent	Cs $3d_{5/2}$	Ca $p_{3/2}$	O 1s	Cs $3d_{5/2}$/Ca 2p	Cs $3d_{5/2}$/C 1s	Ca 2p C 1s
20%Cs/CaO (after calcination)	724.01	347.45	532.5	0.166	0.985	5.93
20%Cs/CaO (after CO_2 absorption)	723.75	346.9	532.5 530.4[a]	0.242	0.254	1.053
20%Cs/CaO (after CO2 desorption)	724.0	347.4	532.5	0.16	0.886	5.57

[a] O 1s peak from metal carbonates.

sorbents before CO_2 adsorption and after CO_2 desorption are in the similar phase. The structural behavior of the sorbent does not change even after CO_2 desorption at 725 °C. Therefore, the sorbents that we used for this study are very stable at elevated temperatures.

The photoelectron peak of Ca 2p for three different samples of 20% Cs/CaO are shown in Figure 9. The binding energy values corresponding to Ca 2p core level for all three samples are presented in Table 3. From the data presented in Figure 9 and Table 3, one can note that the binding energy of the Ca 2p varied between 347 and 347.4 eV. This can be explained from the fact that the binding energy that was found in above range typically corresponds to $CaCO_3$ and CaO, respectively. These values are in perfect agreement with the values reported in the literature.[11] Moreover, the binding energy of the $CaCO_3$ was also confirmed by a measurement that was performed as a reference. As shown in Figure 9, the binding energy value of the Ca 2p peak after pretreatment and after CO_2 desorption was observed at 347.4 eV, while in the case of sample after CO_2 adsorption the binding energy value reduced to 347.0 eV. The fact that the intensity of Ca 2p core level peak is also reduced after CO_2 adsorption and increased to the same height after desorption clearly indicates that part of the sorbent support also reacts with CO_2 to form $CaCO_3$. At higher temperatures during regeneration, the CO_2 is liberated from the support and reappears as CaO. However, the support itself is not acting as a sorbent for removal of CO_2 from flue gas.

Figure 9 shows the core level of the Cs $3d_{5/2}$ region recorded with three different samples of 20% Cs/CaO sorbent. A significant increase in the intensity and broadening of the Cs $3d_{5/2}$ peak is observed for the sample after CO_2 adsorption. The broadening of the XPS peak can be attributed to the formation of Cs_2CO_3. The binding energy of Cs $3d_{5/2}$ at 724 eV is observed for the sample before CO_2 adsorption, which is due to Cs that is in the Cs_2O form. The binding energy value decreased from 724.0 to 723.7 eV (Table 3) after CO_2 adsorption. The decrease of binding energy and increase of peak intensity of the Cs 3d indicates that the Cs_2O reacts with CO_2 and forms Cs_2CO_3. In fact, the binding energy value of Cs $3d_{5/2}$ at 723.7 eV corresponds to Cs_2CO_3.[12] After CO_2 desorption at 725 °C for 1 h, the binding energy and the peak intensity of the Cs $3d_{5/2}$ was observed to be similar to that of the sample before CO_2 adsorption. This observation obviously explains that the CO_2 preferably reacts with Cs than the supporting material (CaO).

The Cs $3d_{5/2}$/Ca 2p, Cs $3d_{5/2}$/C 1s, and Ca 2p/C 1s surface atomic ratios, as determined by XPS, for three different 20% Cs/CaO samples are shown in Figure 10 and Table 3. As can be noted that the ratio between Cs $3d_{5/2}$ and Ca 2p is higher for the sample after CO_2 adsorption than for the sample before CO_2 adsorption and after CO_2 desorption, which indicates that large amounts of Cs deposited in the pores of the CaO segregate out from the pores and react with CO_2, leading to the deposition of Cs_2CO_3 on the surface of the support material. However, the Cs/Ca ratio decrease after desorption of CO_2 at 725 °C for 1 h, indicating that the Cs again going back into the pores of CaO. The ratio between Cs $3d_{5/2}$/C 1s and Ca 2p/C 1s revealed to have the same trend in both cases. The ratio between Cs $3d_{5/2}$/C 1s and Ca 2p/C 1s has decreased five times less in both cases after adsorption of CO_2 at 600 °C for 1 h, which clearly indicates that the CO_2 is reacting with both active component (Cs) and the support material (CaO). However, the adsorption of CO_2 is very fast and very high with respect to active component (Cs) than the support material (CaO). That is the reason the ratio between Cs $3d_{5/2}$/Ca 2p is very high after adsorption of CO_2. Thus, the present XPS measurements provide strong evidence that the 20% Cs/CaO sorbent is very stable even at elevated temperatures. Additionally, XPS results also point out that the adsorbed CO_2 preferably chemisorbs on Cs than CaO.

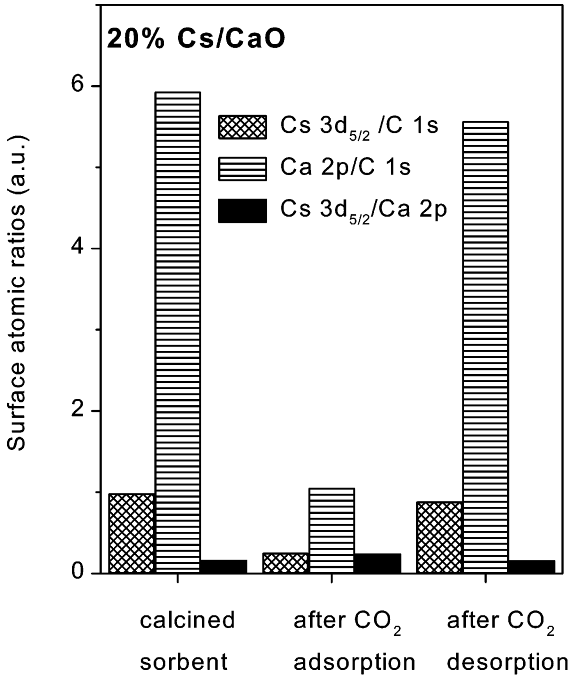

Figure 10. Surface atomic ratios of Cs $3d_{5/2}$, Ca 2p, and C 1s core levels for 20 wt % Cs/CaO sorbent determined by XPS.

4. Conclusions

We found that Cs supported on CaO results in the most promising sorbents for CO_2. It is remarkable to note that the sorption capacity at 600 °C over 20% Cs/CaO is about 50 wt % CO_2/wt sorbent. This sorption capacity is a tremendous improvement over existing industrial systems, which operate at significantly lower temperatures, with rather dilute CO_2 streams and show low selectivity due to coadsorption of polar molecules. We found that the CO_2 desorption is reversible from these sorbents by increasing the temperature about 100 °C above the adsorption temperature. In addition to a high sorption observed over the Cs/CaO sorbent, it can be noted that the rate of sorption for these sorbents is also very high. More specifically, within first 40 min the sorption over Cs/CaO jumps to

40 wt % CO_2/weight percent of sorbent, which is a very large number at a rather short time on stream. This unique characteristic feature has immense significance since it can lead to very rapid pressure swing cycles, thus improving tremendously the performance of the separation process.

One of the most important features of Cs/CaO sorbents is their very high affinity toward CO_2. This sorbent was subjected to independent sorption experiments under identical operating conditions in the presence of pure N_2 or O_2 or H_2O (90% in helium) or a mixture containing all these gases. It is remarkable to note that Cs/CaO reportedly does not adsorb any N_2 or O_2 under these conditions, which indicates that the latter gases have zero affinity for the surface of the sorbents. This is indeed the most desirable situation because one can effectively separate CO_2 from N_2 and O_2 thus maximizing the separation factor. When a mixture of CO_2, air and H_2O at compositions similar to that of typical flue gas was employed, this sorbent does not adsorb any N_2 and O_2 while at the end of the sorption step the CO_2/H_2O molar ratio on the sorbent was 82/1. This shows that this sorbent possesses low affinity for water, a characteristic feature that can be improved further.

The surface atomic ratios of Cs 3d/C 1s, and Ca 2p/C 1s determined by XPS indicated that the adsorption of CO_2 is preferably taking place on Cs_2O rather than CaO. The XPS analysis further showed that the surface atomic ratio between Cs $3d_{5/2}$ and Ca 2p core levels appreciably increase for the sorbents prepared with $\sim$ 20 wt % loading of Cs on CaO after CO_2 adsorption. For higher Cs loadings the performance did not improve further due to the formation of paracrystalline Cs_2O on the CaO support surface. CsOH- and Cs_2CO_3-doped CaO sorbents provided significantly higher adsorption of CO_2 than CsCl mainly due to the formation of a highly dispersed Cs_2O on the CaO support.

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