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Development of Superior Sorbents for Separation of CO_2 from Flue Gas at a Wide Temperature range during Coal Combustion

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No patentable subject matter is disclosed in this report.

Abstract

A number basic sorbents based on CaO were synthesized, characterized with novel techniques and tested for sorption of CO_2 and selected gas mixtures simulating flue gas from coal fired boilers. Our studies resulted in highly promising sorbents which demonstrated zero affinity for N_2, O_2, SO_2, and NO very low affinity for water, ultrahigh CO_2 sorption capacities, and rapid sorption characteristics, CO_2 sorption at a very wide temperature range, durability, and low synthesis cost. One of the "key" characteristics of the proposed materials is the fact that we can control very accurately their basicity (optimum number of basic sites of the appropriate strength) which allows for the selective chemisorption of CO_2 at a wide range of temperatures. These unique characteristics of this family of sorbents offer high promise for development of advanced industrial sorbents for the effective CO_2 removal.

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Executive Summary

A number basic sorbents based on CaO were synthesized, characterized with novel techniques and tested for sorption of CO_2 and selected gas mixtures simulating flue gas from coal fired boilers. Our studies resulted in highly promising sorbents which demonstrated zero affinity for N_2, O_2, SO_2, and NO very low affinity for water, ultrahigh CO_2 sorption capacities, and rapid sorption characteristics, CO_2 sorption at a very wide temperature range, durability, and low synthesis cost. One of the "key" characteristics of the proposed materials is the fact that we can control very accurately their basicity (optimum number of basic sites of the appropriate strength) which allows for the selective chemisorption of CO_2 at a wide range of temperatures. These unique characteristics of this family of sorbents offer high promise for development of advanced industrial sorbents for the effective CO_2 removal.

1. INTRODUCTION

The availability of clean, affordable energy is essential for the prosperity and security of United States and the world in the 21st century. About 85 percent of U.S. energy is derived from fossil fuels, and continued reliance on these fuels is fore cast well into the 21st century. 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 Earth's population over the last decades combined with the improvement of quality of life is directly related with the dramatic increase of man made CO_2 concentrations, since both of the above reasons are linearly related with the production and consumption of energy primarily obtained from fossil fuels (nuclear energy consists of a small percentage of the energy used). Increased deforestation due to fires or need to use more land for agricultural needs results in a major decrease of CO_2 removal due to the photosynthesis performed by plants and trees. Finally, a significant amount of CO_2 is released to the atmosphere by oceans. While for the latter three sources of CO_2 humans have no means of controlling directly or collecting the CO_2 emitted, all the activities utilizing fossil fuels can in principle lead to collection 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 (maybe with the exception of automobiles and aircrafts) 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. Hence, the invention of novel methods/processes for transformation of CO_2 to some other "harmless" species will be of unique value for minimizing global warming.

CO_2 is used for the production of chemicals such as acetone, urea, salicylic acid, cyclic carbonates and polycarbonates. However, since these chemicals constitute a very small percentage of the amount produced annually, the reduction of carbon dioxide via the chemical transformation to chemicals or specialty chemicals has low potential for success. Hence, one should consider other ways for reducing CO_2 emissions to the atmosphere via chemical transformation. A significant amount of effort has been devoted among others to investigate catalytic approaches to utilize CO_2. The efforts were identified after the Kyoto Conference (Japan), which was held in December 1997 and

brought together scientists and ideas from every place on Earth. The papers presented at that meeting were published (Inui et al., 1998) and constitute a good collection of helpful ideas and scientific information.

The first step in carbon sequestration is the CO_2 separation and removal from the flue gas leaving which commonly contains relatively large concentrations of water, oxygen, nitrogen and lower concentrations of nitrogen and sulfur oxides, trace metals (Hg, As, Se), particulates, and other gases such as carbon monoxide, etc. Of course, the composition of flue gas may vary significantly depending on operating conditions and type of coal(s). In addition, for the development of novel CO_2 sorbents one should consider that they should be able to perform effectively for other applications (i.e. coal gasification, production of high purity hydrogen from WGS etc.) which mandates that they offer large level of versatility in operation with gaseous streams with variable composition. 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. 650 ^oC).

High aluminum content zeolites have been used extensively for separations of gases including carbon dioxide from gas mixtures. The relation between the properties of various zeolites and their CO_2 adsorption behaviors in PSA was presented in an early study by Inui et al., (Inui et al., 1988a; Innui et al., 1998b). It was concluded that chabazite and 13X zeolite were the most proper selections for this process while the next best candidates were erionite and 4A zeolite. 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 to 300 ^oC thus limiting the process for separation at relatively high temperatures. It should be also noted that some zeolites possessed a low and a high temperature desorption peak in the above temperature range. The patent of Ojo et al., (Ojo et al., 1996) has recently received considerable attention for removal of carbon dioxide from gas mixtures at low temperatures (ranging from 5 to 50 ^oC). This separation is based on Al-rich X faujasite (or formaly LSX which stands for low silicon X faujasite) which is exchanged with various monovalent, divalent or trivalent ions selected from Groups IA, IIA and IIIA of the Periodic Table. However, according to the patent description the process of this invention can only be used to

purify any gases which are less polar that CO_2. If the gas is more or equally polar than CO_2 it will co-adsorb on the sorbent and occupy a significant part of the available sites thus decreasing the selectivity for the separation and the operating time of the cycle before regeneration is required. This characteristic automatically limits its use for cases where the gas stream contains others compounds such as SO_2, H_2O. Moreover, the process designed based on these sorbents is supposed to remove only relatively low concentrations of CO_2 (being an impurity) from gas streams. This process cannot be used at elevated temperatures, something that would be ideal for high temperature CO_2 separations in purifying flue gas from coal utilization or other related areas. High aluminum zeolite based sorbents will deactivate irreversibly due to steam dealumination in the presence of water at elevated temperatures.

Moreover, it should be noted that numerous sorbents are based on Li-exchanged systems which render the sorbents unable to operate at relatively high temperatures because lithium sublimes. Others (Suzuki et al., 1997) utilized hydrophobic zeolites for the removal of CO_2 in order to avoid the problem of co-adsorbing water. Experiments comparing hydrophilic 5A with hydrophobic Y faujasite showed that the latter one can preserve its sorption characteristics even at relatively high moisture contents. Of course, the performance of the sorbent decreases with the increase of the moisture level. In contrast, 5A loses its sorption characteristics immediately even with traces of moisture. An interesting study for separation of dilute mixtures of CO_2 and NO_2 was performed by Wang et al., (Wang et al., 1998). It was concluded that there is competitive adsorption of NO_2 and CO_2 and it depends not only on the surface polar sites but also on the zeolite pore geometry and dimensions. Adsorption of CO_2 was correlated with the polarity of the zeolites as a result of dominant adsorption via interaction of the quadrupole moment and the polar surface sites. From the results presented in that work (all experiments were performed at 60 ^oC) one can observe that in general CO_2 adsorbs faster than NO_2 (CO_2 is more polar than NO_2) while it desorbs much faster than the latter molecule, rendering these sorbents as effective systems for separation of these gases.

A computer simulation of a novel adsorber for CO_2 recovery from flue gas was performed by Pugsley et al., (Pugsley et al., 1994). They introduced an elegant model for

a circulating fluidized bed pressure-temperature swing adsorber (CFB-PTSA) which demonstrated numerous advantages over existing PSA systems. For that study a competitive adsorption model for CO_2, N_2 and O_2 over X zeolite was used. Another interesting approach in removing CO_2 comes from the Tokyo Electric Power Company (Ishibashi et al., 1996). These researchers combined the use of Ca-exchanged X faujasite in a more advanced method than PSA, namely Pressure and Temperature Swing Adsorption (PTSA). For the PTSA process the addition of a temperature swing for the gas introduced to the adsorption column was applied. A 20% improvement over previous approaches and time stability for extended periods of operation was observed. An interesting observation is that the Al_2O_3 bed used as desiccant in a primary phase of the process to capture sulfuric acid in the form of aluminum sulfate thus preserving the integrity of the CO_2 sorbent. A comparison between 13X and activated carbon for recovery of CO_2 from a simulant flue gas by PSA was performed by Cho and coworkers (Chue et al., 1995). It was found that the 13X zeolite produces higher purity of CO_2 than the activated carbon due to its significantly higher selectivities for this separation. Finally, potassium hydrotalcite have been tested as CO_2 sorbent at 400 ^oC to simulate separations of CO_2 from other gases including water at relatively elevated temperatures (i.e. steam methane reforming). This study identified the complexities of CO_2 adsorption on hydrotalcite. Among other characteristics it should be noted that preadsorption of molecules such as water or carbon dioxide may alter significantly the capacity of the material and even generate adsorption sites for physisorption.

As is well appreciated, the utilization of coal or in general any fossil fuels is associated with CO_2 emissions and is going to be severely constrained by regulations aiming at decreasing the *Green House Gases*. The Vision-21 program which deals with the design of future power plans with significantly higher efficiencies and practically no environmental problems, as well as many other initiatives associated with production of energy, synthesis chemicals and fuel cells, mandates the development of novel sorbents for removal of CO_2 under a very broad range of operating conditions. In this study an attempt has been made to develop the high capacity alkali metals doped alkaline metal oxide sorbents for removal of carbon dioxide from industrial flue gas.

2. EXPERIMENTAL

Sorbents Preparation

Various loadings of alkali metals doped calcium oxide sorbents were synthesized by wet impregnation method using Aldrich (99.9%) CaO as the source of calcium oxide. The precursors used for the 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), potassium hydroxide for potassium; rubidium chloride and rubium hydroxide (Aldrich) for rubidium; cesium chloride (Aldrich), cesium hydroxide (Aldrich), cesium carbonate (Fisher) for cesium. All the sorbents were prepared by mixing the alkali metal precursor and calcium oxide such that the weight concentration of alkali metal is 10 and 20-weight percentage (based on alkali metal and CaO only). The appropriate amounts of alkali metal precursor in distilled water and calium oxide were mixed vigorously under heating. The distilled water added to form the slurry was in proportion to 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 dried further in an oven at 125 ^oC overnight and subsequently calcined in oxygen or helium atmosphere at 750 ^oC for 5 h. After calcinations, the sorbents were stored in a glove box under inert atmosphere.

Sorption Experiments

The adsorption desorption experiments on the above prepared sorbents along with pure calcium oxide were carried out in a Perkin Elmer PYRIS-1 thermogravimetric analyzer apparatus. The TGA balance can measure accurately up to 1 μg. 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 in order to remove any pre-adsorbed atmospheric carbon dioxide and/or water vapor then tested at different adsorption temperature such as 50, 450, 600 and 650 C in order to find out the good sorption capacity. The temperature profile used for these experiments was 10 C up and 15 C down. The highest saturation capacity of CO_2 was selected at 600 C and total desorption temperature was selected at 725 C. Sorbents with

high saturation capacity and selectivity for CO_2 and relatively rapid adsorption was selected as the best candidates. The desorption curve to be an important piece of information to determine the rapidness of the cycle. During the adsorption step the sorbents was allowed to reach equilibrium while the desorption step was performed in an inert carrier gas. The detailed adsorption and desorption study was explained in the results and discussion section.

BET surface areas

BET surface area of these sorbents was measured by nitrogen adsorption at –196 C using an 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 suing approximately six values of relative pressure ranging from 0.05 to 0.99.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy was used to analyse the atomic surface concentration on Cs/CaO before and adsorption of carbon dioxide. The XPS analyses were conducted on a Perkin-Elmer Model 5300 X-ray photoelectron spectrometer with MgK_{α} radiation at 300W. Typically, 89.45 and 35.75 –eV pass energies were used for survey and high-resolution spectra respectively. The effects of sample charging were 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 catalysts were calculated via the XPS results using the total integrated peak areas of the Cs 4s, Ca 2p, O 1s and C 1s regions.

3. RESULTS AND DISCUSSIONS

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 rubidium oxide. The adsorption equilibrium isothernms of carbon dioxide on MgO, CaO, and RbO at 600 C are shown in Figure 1. The results showed that

the amount of CO_2 adsorbed on MgO and RbO is very low, where as the adsorption of CO_2 on CaO is nearly 12 wt.% during one-hour equilibrium process. The difference of the adsorption capacity between CaO to MgO and RbO is very high, which means that the surface area of MgO and RbO becoming lower when the adsorption temperature is increasing to 600 C. The adsorption equilibrium results indicated that the adsorption CO_2 on MgO and RbO sorbent supports is more difficult at this temperature without any chemical modification. The adsorption behavior of CaO, MgO and RbO 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 on the principal factors determining overall reacitivity (Karatepe et al., 1998). Therefore, selection of CaO as the sorbent support is good idea for further study.

A set of CO_2 adsorption experiment on 10-15 mg of the commercial CaO was performed at different temperature 50, 450 and 600 °C working with a gas containing pure CO_2 (99.99%), and with gas flow rate 20 ml min^{-1} in order to find out the good adsorption temperature. Prior to the adsorption, the sorbent was pretreated at 750 C for 3 h under helium atmosphere. Once the desired adsorption temperature reached, the helium flow switched to 99.99% CO_2. The increase in weight with time was recorded and the adsorption of CO_2 on CaO was calculated form the increase in weight. The data obtained at different temperature was shown in Figure 2. As shown in Figure 2, the adsorption CO_2 equilibrium on CaO increased with increase of temperature, larger adsorption equilibrium was observed at 600 °C. Similar observation was found (Steciak et al., (1995) in their study about SO_2 removal by sorbent injection at high temperatures.

Boreardt et al. (Boreardt and Bruce, 1986) reported that the gas-solid heterogeneous reaction of CaO with SO_2 and H_2S, depends on the available surface area of the solid, in contrast to these studies (Tantet et al., 1995) suggested that the basic property of sorbent also increases the adsorption capacity of SO_2 even at lower temperatures. Therefore, we have got an inspiration for development of a new family of sorbents such as alkali metals doped alkaline earth metal oxide sorbents for separation of CO_2 from flue gas. In fact, these types of systems are highly basic and have been used extensively for many catalytic transformations in the petrochemica/refining and chemical

production industries. These materials being basic will be ideal to attract CO_2, which can be considered to be weak acid. The basicity (number and strength of sites) of this type of materials can be modified very accurately in an attempt to synthesize systems with desired properties. Surprisingly, nobody used these materials as sorbents since practically all the efforts are concentrated in utilizing zeolites as sorbents due to their large cation exchange capabilities and their sieving effects (Ojo et al., 1996). Li- zeolites are the most common sorbents used for production of production of O_2 and N_2 from air, CO_2 separation. However, these sorbents cannot withstand at relatively high temperatures because lithium sublimes beyond 550 °C.

Figure 3 shows the CO_2 adsorption capacity of 20wt.% alkali metal (Li, Na, K, Rb, and Cs) loaded CaO for mixture of 20 vol.% CO_2 in Helium at 50 °C. One should note that the performance of Li/CaO is even worse than that of CaO. One can observe that Cs/CaO adsorbs the highest amount of CO_2, actually more than double than the second best performing sorbent (Rb/CaO). This remarkable observation carries unique potential for development of superior sorbents for removal of CO_2 and deserves to be investigated further. Any alkali metal loaded CaO, with an exception of Li, leads to improvement of the sorption characteristics of the sorbent due to increase of the number of basic sites on the surface (Tantet et al., 1995). A general increase of the sorption capacity with the increase of atomic radii of the alkali metal (Li<Na<K<Rb<Cs) is observed.

CO_2 adsorption experiments of alkali metals doped CaO were performed at 450 ^oC (See Figure 4). The adsorption trend is similar to that we observed at 50 ^oC. However, the adsorption capacity of sorbents other than Li/CaO increased 20 times higher than that they adsorbed at 50 ^oC within 5 minute. It clearly indicates that the alkali metals doped CaO sorbents adsorbs carbondioxide very fast at higher temperatures. One can note that the Cs/CaO sorbent was adsorbing higher carbon dioxide than the other alkali metal doped CaO, which suggest that the bigger particle size and higher basicity is the main reason for the higher CO_2 adsorption capacity. All the sorbents that we used in the above mentioned study was prepared by using the alkali metal chloride as the precursors for the alkali metals doping.

Different Cs precursor doped CaO oxide sorbents was tested by CO_2 adsorption study at 450 ^oC. As shown in Figure 5, the adsorption equilibrium isotherms of cesium hydroxide and cesium carbonated doped CaO showed similar adsorption capacity, where as the cesium chloride doped CaO showed lower adsorption capacity than Cesium hydroxide and cesium carbonate doped CaO. This behavior is closely related to the dispersion of alkali metal on the support and nature of the products formed during the CO_2 adsorption and to the higher basicity of the sorbent. Therefore, we decided to use cesium hydroxide doped CaO as a sorbent for further study, because hydroxide precursor deposited CaO showing higher adsorption capacity than all other alkali metal precursors doped CaO materials.

Figure 6 shows the effect of Cs loading on CaO for CO_2 adsorption equilibrium study at 450 ^oC. The adsorption equilibrium capacity increased with increasing cesium loading up to 20 wt.%, then it started going down. The main reason for reducing the adsorption at higher loadings Cs may be due to the formation of crystalline Cs on the surface of the sorbent beyond 20 wt.%. Though Cs is highly basic and larger atomic size, the adsorption capacity at higher Cs loadings decreasing drastically, it may be due to the formation of paracrystalline Cs deposition on CaO support.

The performance of the 20 wt.% of alkali metal hydroxide deposited CaO sorbents at 600 ^oC is presented in the Figure 7. Prior to adsorption of CO_2 gas, the sorbents were pretreated at 750 ^oC for 3 h under 20 ml/min helium flow. Once the temperature reached at 600 C the gas flow system was switched to 99.99% CO_2. The adsorption equilibrium isotherms was measured with respect time versus wt.% increase. One can clearly see from Figure 7, 90% of the CO_2 adsorption takes place in first 5 minutes of adsorption isotherm, after five minutes, the adsorption increase very slowly with time. A general trend in increase of the adsorption capacity was observed with respective to ionic radii and the basicity of the alkali metal metal (Li<Na<K<Rb<<Cs). It should be noted that 20%Cs/CaO had adsorbed 52% of CO_2 in 5 h, indicates that the Cs deposited CaO sorbents are highly active and very stable at higher temperature. Therefore, these sorbents can be very useful for capturing CO_2 from flue gas power plants. In contrast to recent results (Gupta and Fan (2002) our sorbents are completely

different, moreover, we used commercial CaO as support material, which adsorbs five times less than our highly active 20%Cs/CaO sorbent at 600 ^{o}C.

The carbon dioxide adsorption capacities in the presence of 50 vol% air, 10 vol% water, and 40 vol% carbon dioxide were obtained at adsorption temperature of 600 C and these results were compared with the single CO_2 adsorption capacities on 20%Cs/CaO sorbent (Figure 8). From Figure 8, one can undoubtedly observe that there is very small (less than 2%) difference between the adsorption capacity of the sorbent with respect to 99.99% CO_2 and mixture of 40 vol%CO_2, 50 vol% air and 10 vol% water. The dynamic adsorption capacity of the sorbent did not reduce even in the presence of 10 vol% water especially at higher temperature. The rate of adsorption of the sorbent also stable in the presence of 10 vol% water. Resulting the adsorption sites of the sorbents preferable adsorb only CO_2, which is less polar than water. Therefore, the sorbents that we prepared are highly hydrophobic in nature. Suzuki et al (Suzuki et al., 1997) have observed CO_2 adsorption on hydrophobic zeolite under high moisture conditions, but the adsorption capacity of these zeolites are very less compared to 20%Cs/CaO. Therefore, our sorbent is far better than any other sorbent for the adsorption of CO_2 in presence of water vapor reported in the literature.

The sorbent 20wt.%Cs/CaO after three different experiments such as pretreatment at 750 ^{o}C for 3 h under helium flow, CO_2 adsorption at 600 ^{o}C for 1 h, and CO_2 desorption at 725 ^{o}C for 1h were characterized by XPS technique. It should be mentioned that prior to XPS analysis, all the above three materials were collected after their experiment and stored in vacuum oven. Analogous 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 O1s, Ca 2p and Cs 3d core levels are depicted in Figure 9, 10 and 11, respectively. 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 2.

The O 1s profile, as shown Figure 9, is due to the overlapping contribution of oxygen from CaO and Cs_2O in the case of sorbent after pretreatment and after CO_2

desorption, and 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 2, 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 (Wagner et al., 1978) while the minor component denoted as O1s from $CaCO_3$ and Cs_2CO_3 was found at 530.4 eV with sole exception of CO_2 adsorption (see Table 2). The binding energy values of two different types of O 1s peaks can be judged from the difference in the electronegativity of the elements (Imamura et al., 1993). It should be noted that only one oxygen photoelectron peak at 530.4 eV that belong to CaO and Cs_2O was observed in the case of pure 20%Cs/CaO and 20%Cs/CaO after CO_2 adsorption. The peak intensity of O 1s corresponding to CaO and Cs_2O decreased with appearance of new peak corresponds to carbonates after CO_2 adsorption. This clearly indicates that the 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 adsrotpion at 600 ^oC. Therefore, sorbents that we used for this study is very stable sorbents at elevated temperatures.

The photoelectron peak of Ca 2p for three different samples of 20%Cs/CaO sorbent are shown in Figure 10. The binding energy values of Ca 2p core level for all three samples are presented in Table 2. From the data presented in Figure 10 and Table 2, one can be noted that the binding energy value of Ca 2p varied between 347 and 347.4 eV. This can be explained by the fact that the binding energy was found in above range typically of $CaCO_3$ and CaO respectively. These values are in perfectly agreement with the values reported in the literature (Fujimori, 1983), moreover, the binding energy of $CaCO_3$ was also confirmed by an own reference measurement. As shown in Figure 10, the binding energy value of Ca 2p peak for the samples 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 intensity of Ca 2p core level peak is also reduced after CO_2 adsorption and increased to same height after desorption clearly indicates that some amount of sorbent support also react with CO_2 and forms into $CaCO_3$, at higher temperature CO2 liberates from the support and reappear as CaO. However, the support itself is not acting as sorbent for removal of CO_2 from flue gas.

Figure 11 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 with 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 the Cs is in the Cs_2O form. The binding energy value decreased from 724.0 to 723.7 eV (see Table 2) after CO_2 adsorption. The decrease of binding energy and increase of peak intensity of Cs 3d predicts that the Cs_2O reacts with CO_2 and form Cs_2CO_3. Moreover, the binding energy value of Cs $3d_{5/2}$ at 723.7 eV is correspond to the Cs_2CO_3 (Briggs, and Shah, 1990). After CO_2 desorption at 725 C for 1 h, the binding energy and the peak intensity of Cs $3d_{5/2}$ is observed similar to that of the sample before CO_2 adsorption. This obviously explains that the CO_2 preferably reacts with 20% doped Cs than support materials (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 12 and Table 2. As can be noted from Figure 13, the ratio between Cs $3d_{5/2}$/Ca 2p is higher for the sample after CO_2 adsorption than sample before CO_2 adsorption than sample after CO_2 desorption, which indicates large amount of Cs deposited in the pores of CaO was segregating out from the pores of CaO and reacted with CO_2, deposited as Cs_2CO_3 on the surface of support material. However, The ratio between Cs/Ca reduced after desorption of CO_2 at 725 C for 1h, Cs again going into the pores of CaO. The ratio between Cs $3d_{5/2}$/C 1s and Ca 2p/C 1s observed the same trend in both the cases. The ratios between Cs $3d_{5/2}$/C 1s and Ca 2p/C 1s is decreased five times less in both the cases after adsorption of CO_2 at 600 C for 1h, which clearly indicates that the CO_2 reacting with both active component (Cs) and support material (CaO). However, the adsorption CO_2 is very fast and very high with respect to active component (Cs) than suppport material (CaO). That is the reason why; the ratio between Cs $3d_{5/2}$/Ca 2p is very after adsorption CO_2. The present XPS measurements provide strong evidence that the 20%Cs/CaO is very stable sorbents even at elevated temperature. Additionally, XPS results also point out that the adsorbed CO_2 preferably chemisorb with Cs than CaO.

4. CONCLUSIONS

The PI and coworkers have initiated work involving mono- and bialkali combinations of alkali metals on rare earth oxides. Among others, we found that from all alkali metals, Cs results in the most promising sorbents under identical operating conditions. It is remarkable to note that the sorption capacity at 600 ^{o}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, only with rather dilute CO_2 streams and show low selectivity due to coadsorption of polar molecules. We found that the CO_2 desorption was fully reversible from these sorbents by increasing the temperature about 50 ^{o}C above the adsorption temperature. In addition to the high sorption observed over the Cs/CaO sorbents, one can note that the rate of sorption for these sorbents is very high as well. More specifically, within the first 100 minutes the sorption over Cs/CaO jumps to 40 wt.% CO_2/wt sorbent which is a very large number at a rather short time on stream. This characteristic is of unique value because 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 the Cs/CaO sorbents is their very high affinity towards 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). These results are given with the straight lines being parallel to the Time axis with intersect at 0 wt.% increase. Flue gas from conventional coal-fired power plants contains approximately 13% CO_2, 73% N_2, 3% O_2, 10% H_2O and about 1% other gases. It is remarkable to note that Cs/CaO does not adsorb any N_2 or O_2 at 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 (dashed curve) at compositions similar to that of typical flue gas was employed, this sorbent reproducibly did 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 60/1. This shows that this sorbent possesses relatively low affinity for water, a characteristic which can be improved further. It is also remarkable to note that from independent experiments(not shown here) we have shown reproducibly that this sorbent does not adsorb any SO_2 and NO at a wide temperature range (including 600 ^{o}C), which indicates that the latter gases have zero affinity for the surface of the sorbents.

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Table 1: BET surface areas of various supports and sorbents.

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

Table 2: Binding energy values and surface atomic ratios for selected sorbents determined by XPS

Sorbent	Binding energy (eV)			Cs $3d_{5/2}$ /Ca 2p	Cs $3d_{5/2}$ /C 1s	Ca 2p /C 1s
	Cs $3d_{5/2}$	Ca $p_{3/2}$	O 1s			
20%Cs/CaO (after calcinations)	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]O1s peak from metal carbonates.

Table 3: Ratio Between Adsorption Wt.% of CO_2 and other Gases

Adsorbed gases	Wt.% rations
CO_2/N_2	∞
CO_2/O_2	∞
CO_2/H_2O	82

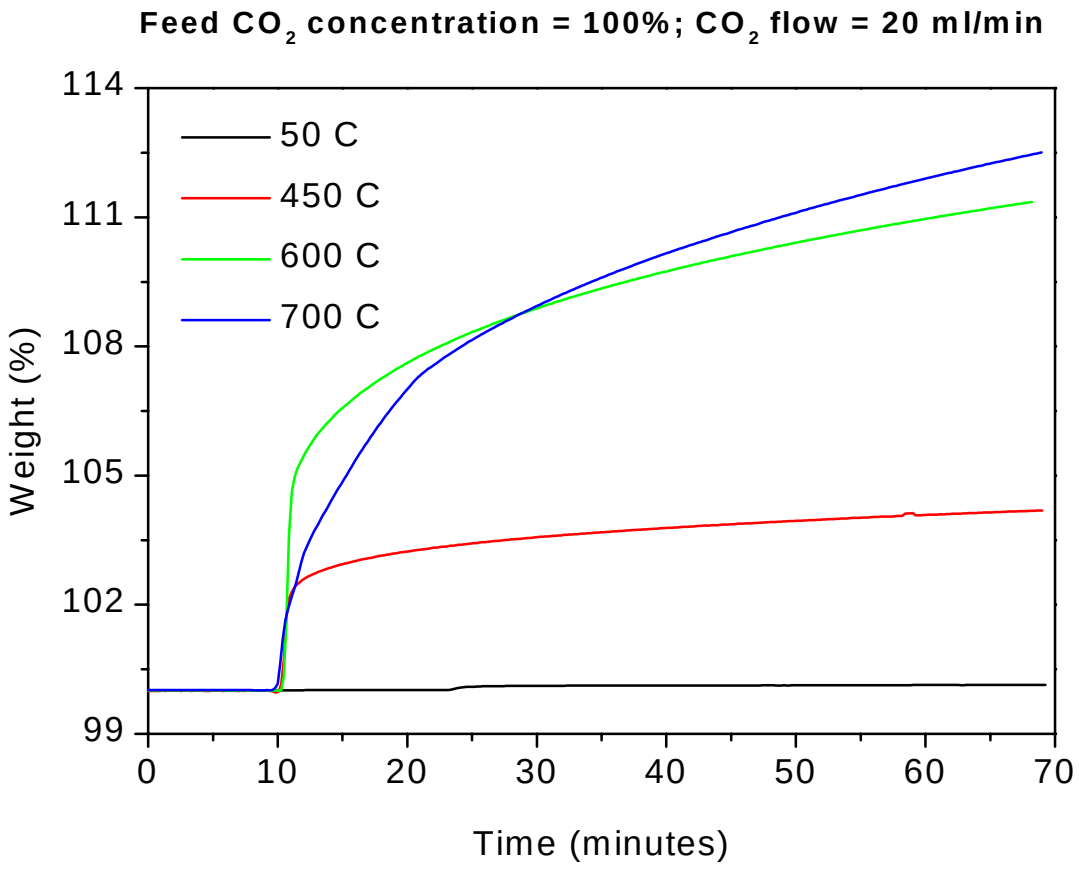

Figure 1: Effect of Temperature on CO_2 Adsorption over CaO

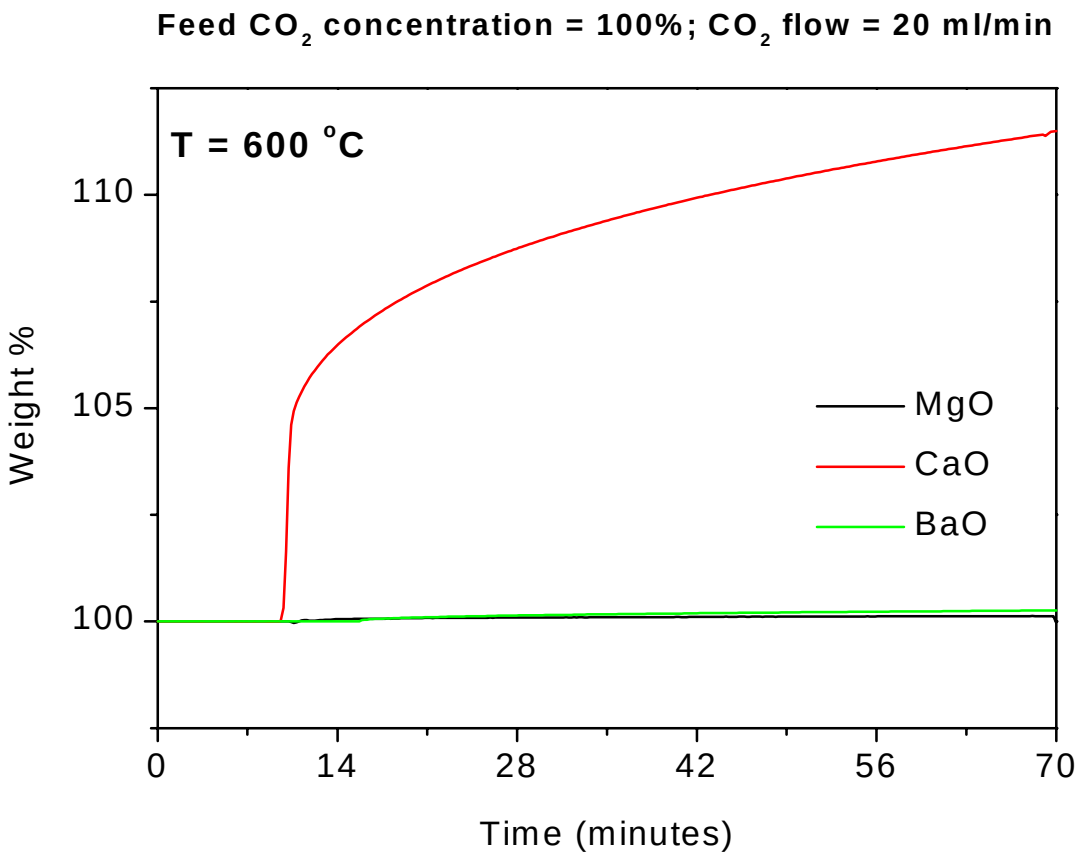

Figure 2: CO_2 Adsorption on Different Supports at 600 ^oC

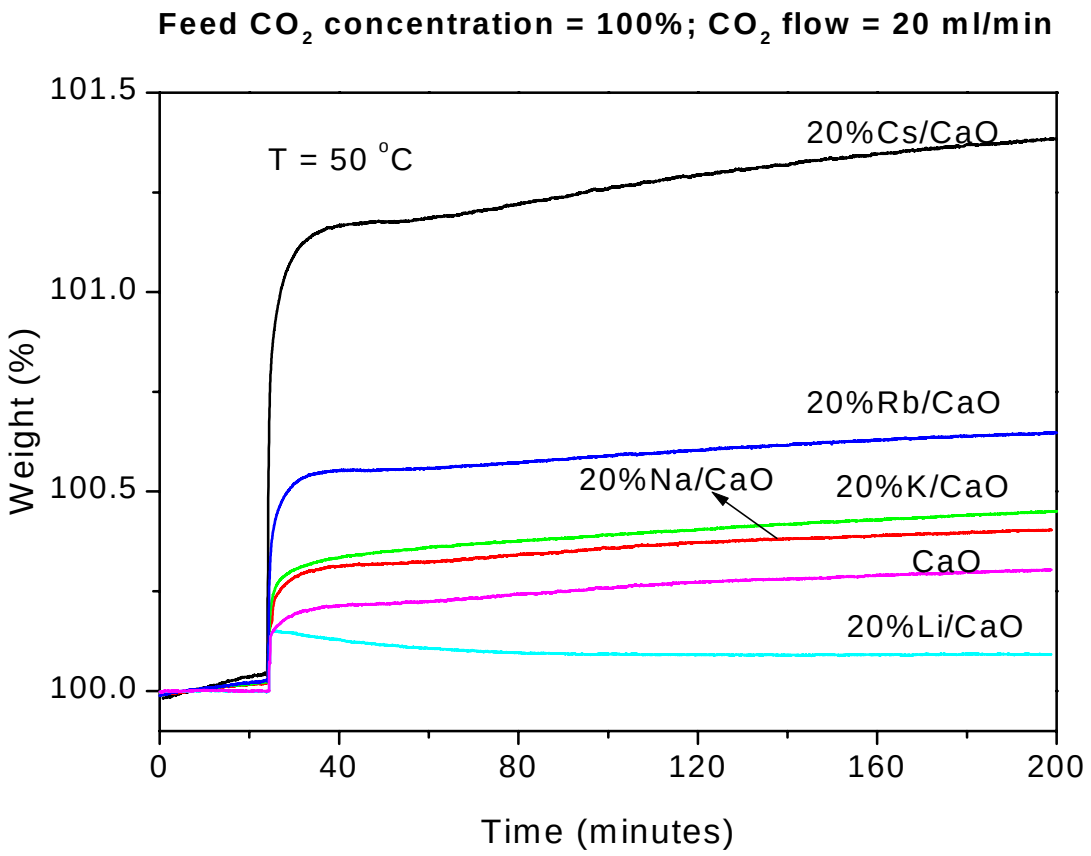

Figure 3: CO_2 Adsorption on CaO Doped with Alkali Metal Chlorides at 50 ^{O}C

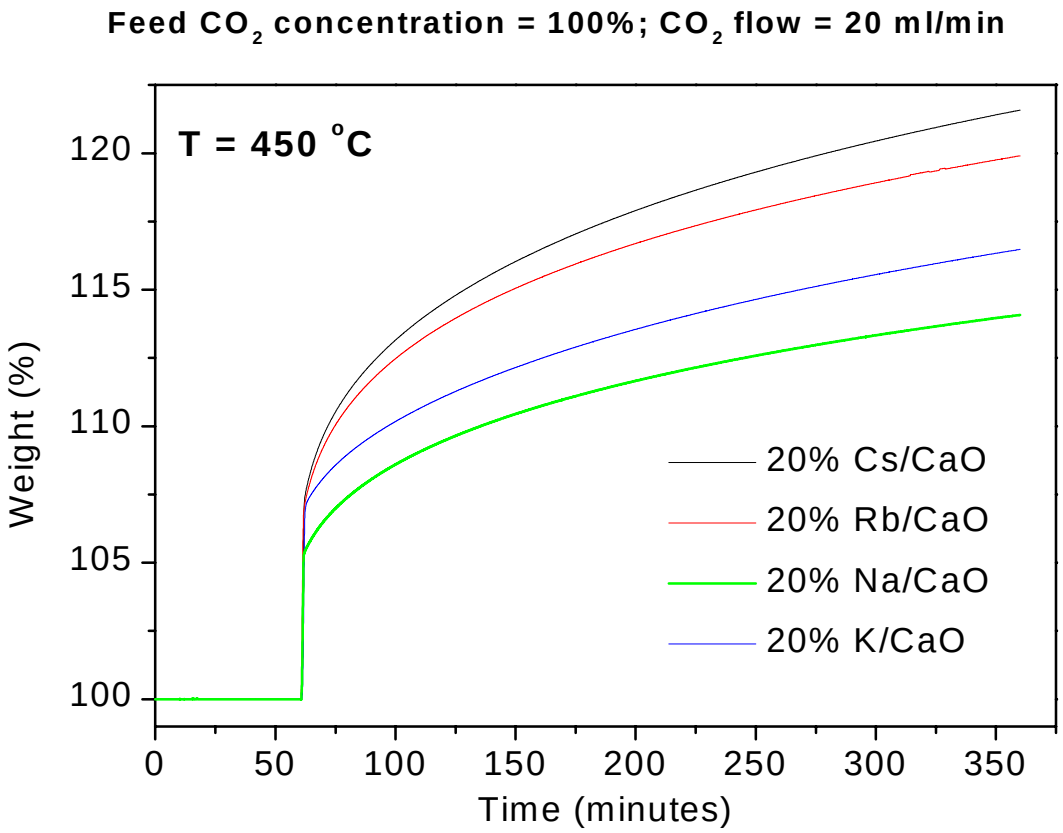

Figure 4: CO_2 Adsorption on CaO Doped with Alkali Metal Chlorides at 450 ^{o}C

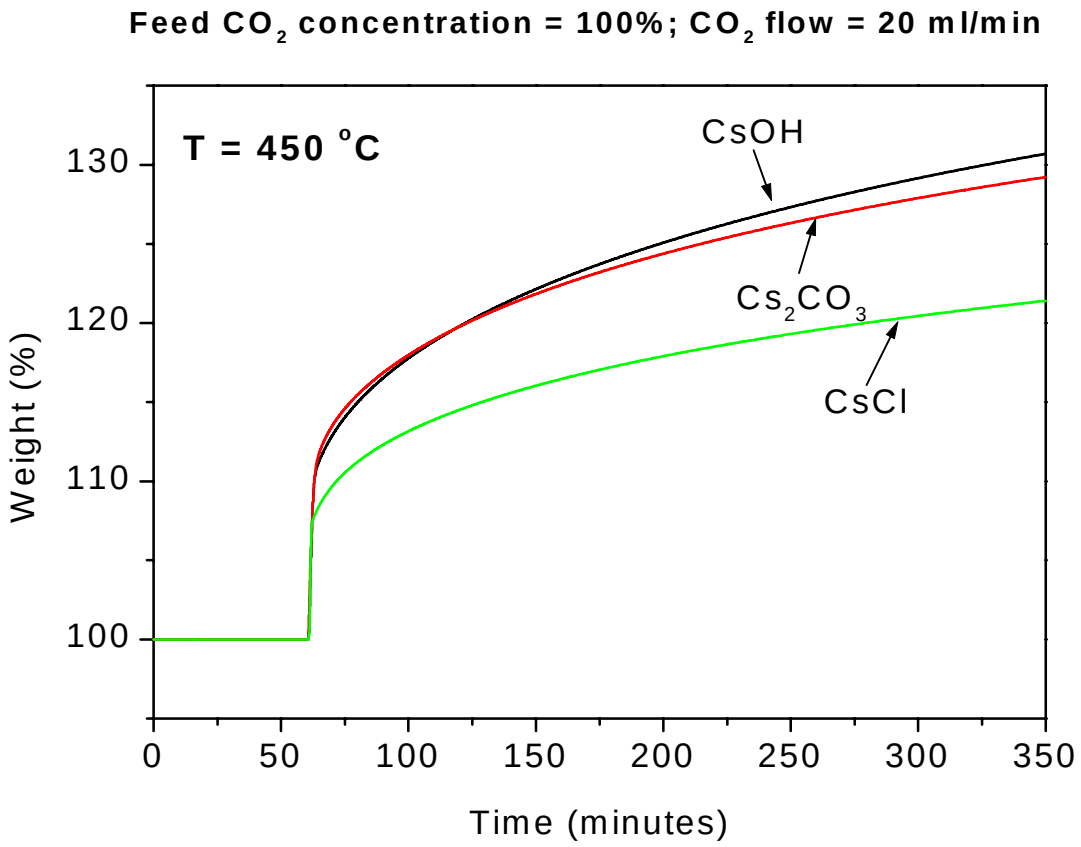

Figure 5: CO_2 Adsorption on 20%Cs/CaO Prepared using Different Precursors of Cesium oxide

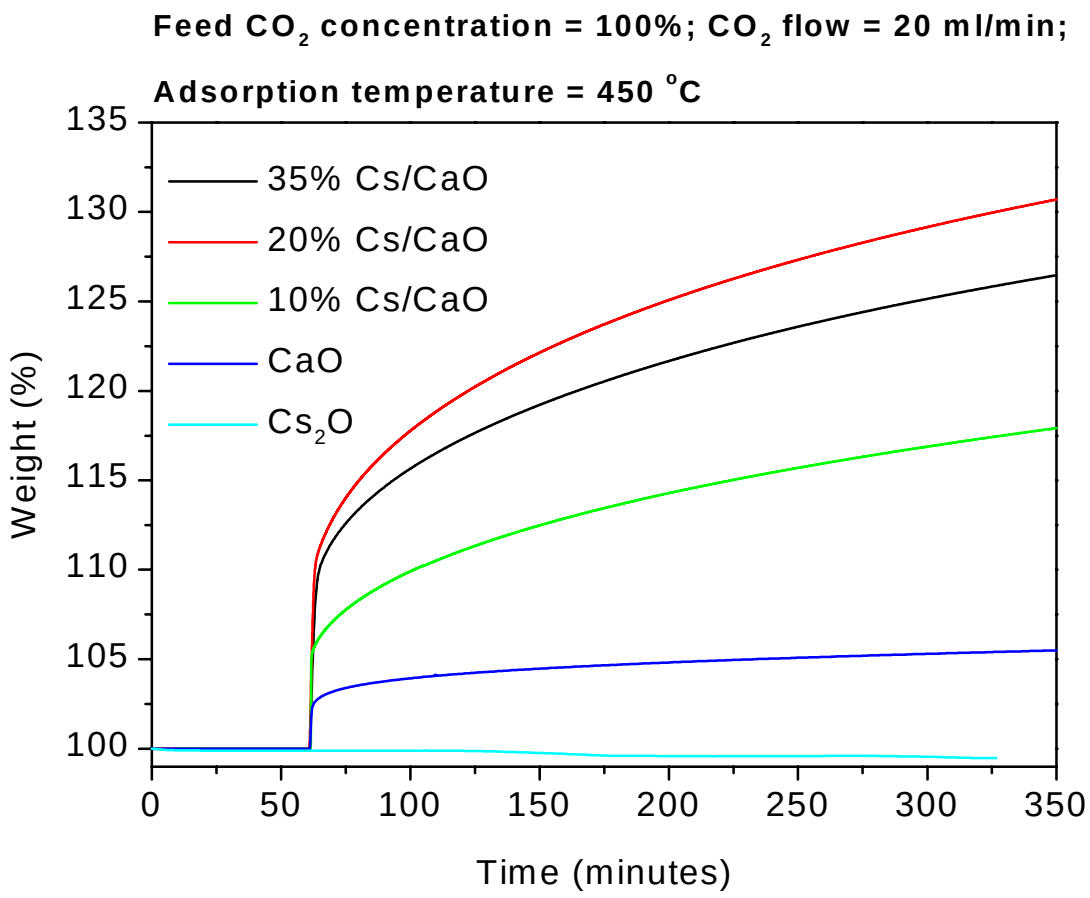

Figure 6: Effect of Cs Loading on CaO (CsOH used as Cs precursor during the synthesis)

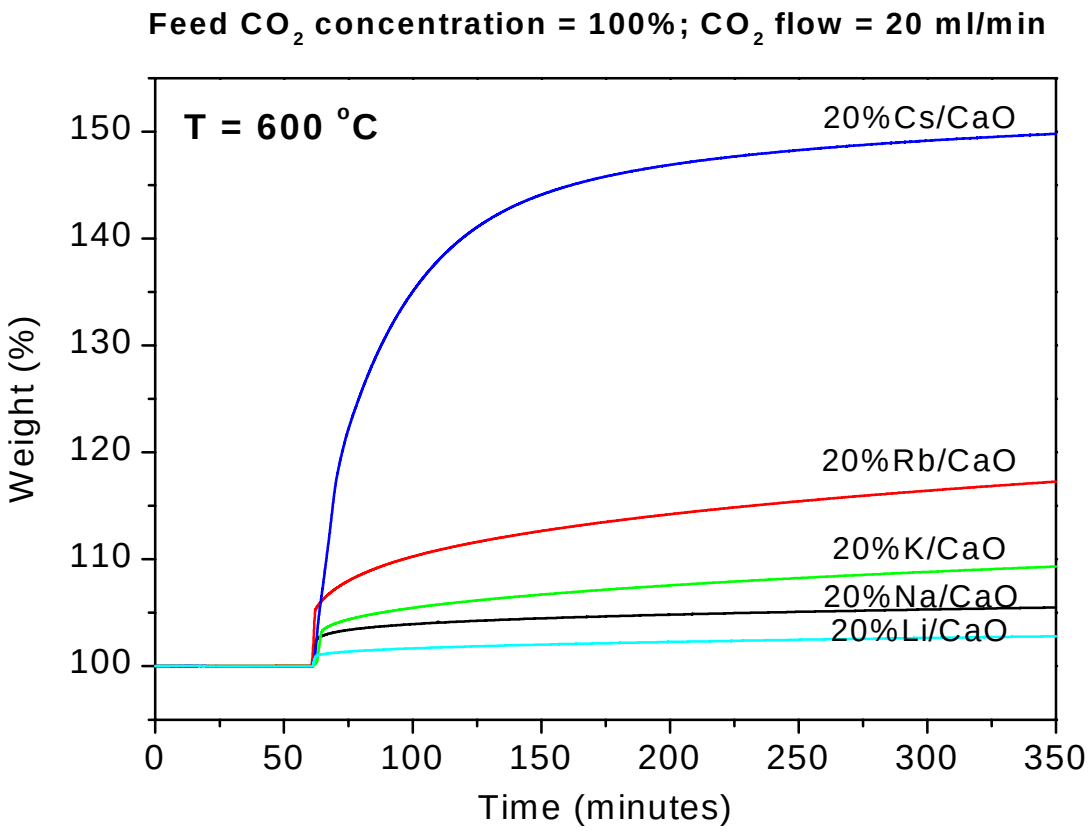

Figure 7: CO_2 Adsorption on CaO Doped with Alkali Metal Hydroxides at 600 ^{O}C

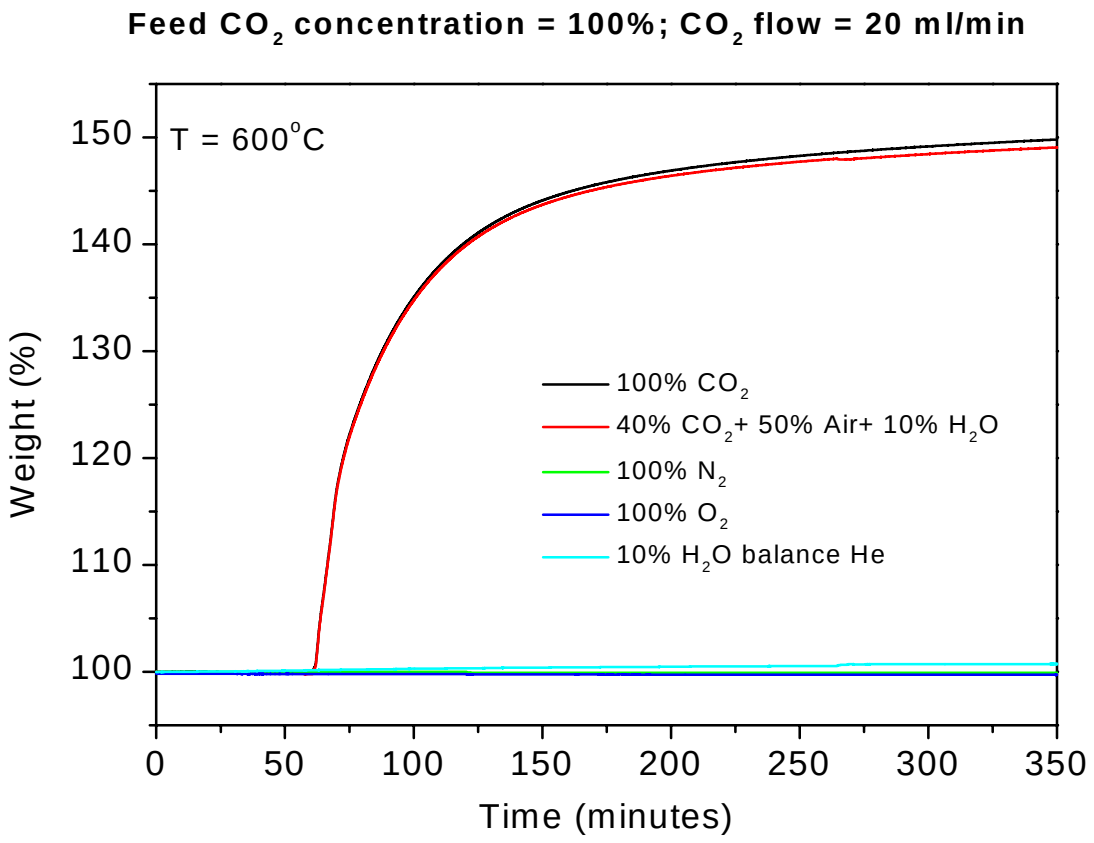

Figure 8: Adsorption of other gases on 20%Cs/CaO

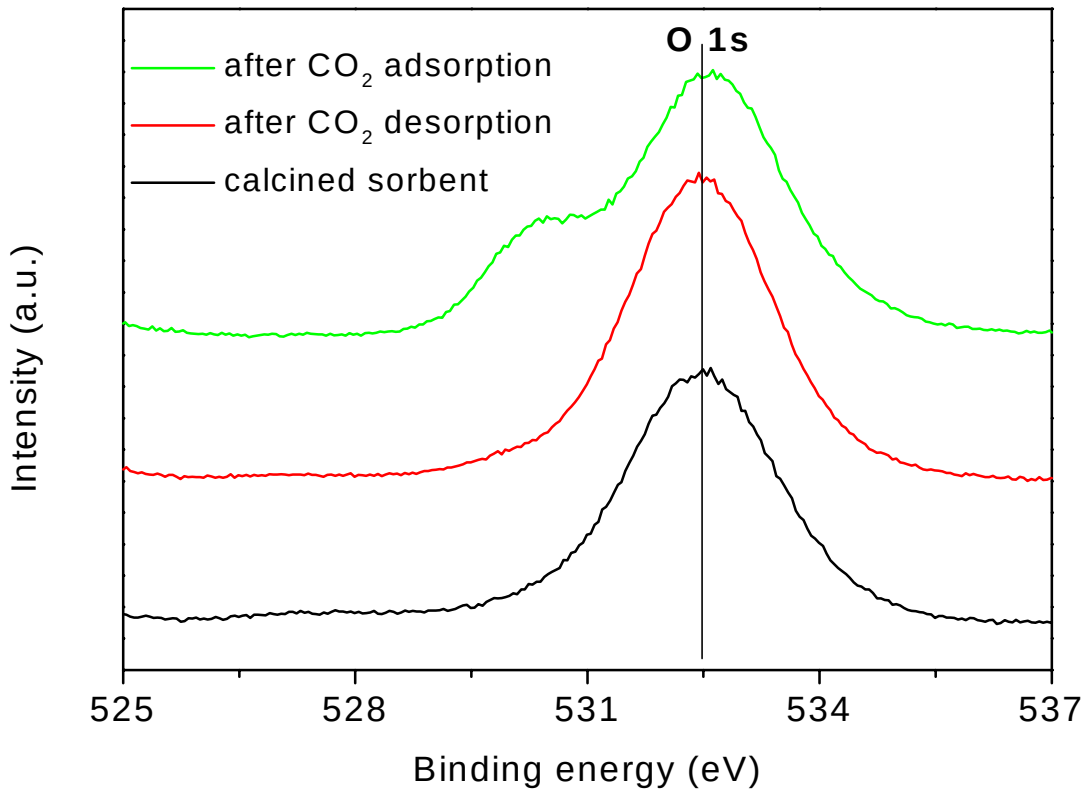

Figure 9: XPS spectra of O 1s core level peak.

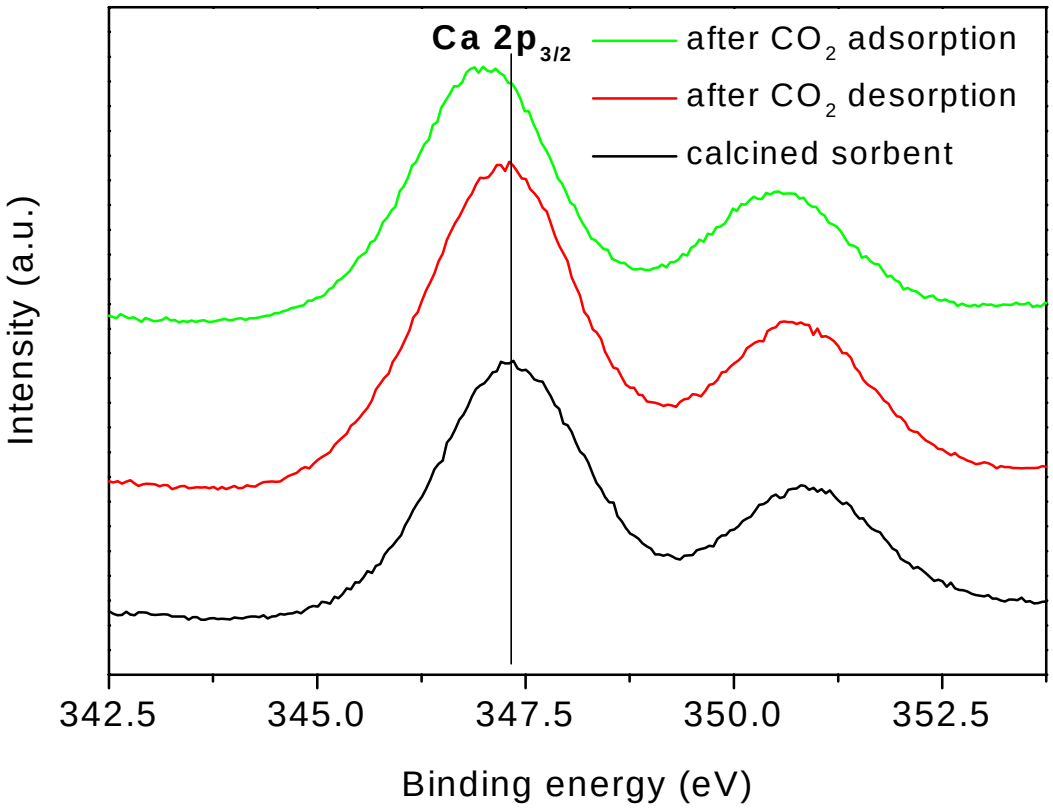

Figure 10: XPS spectra of Ca 2p core level peak

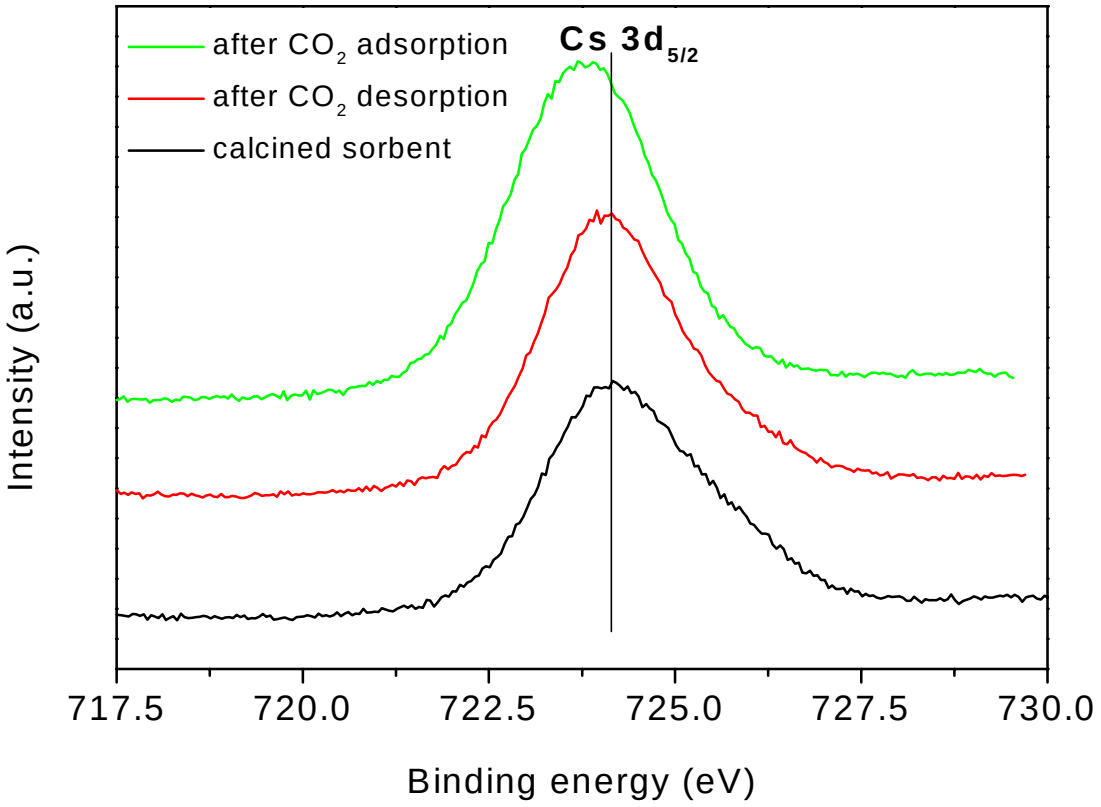

Figure 11: XPS Spectra for Cs 3d core level peak

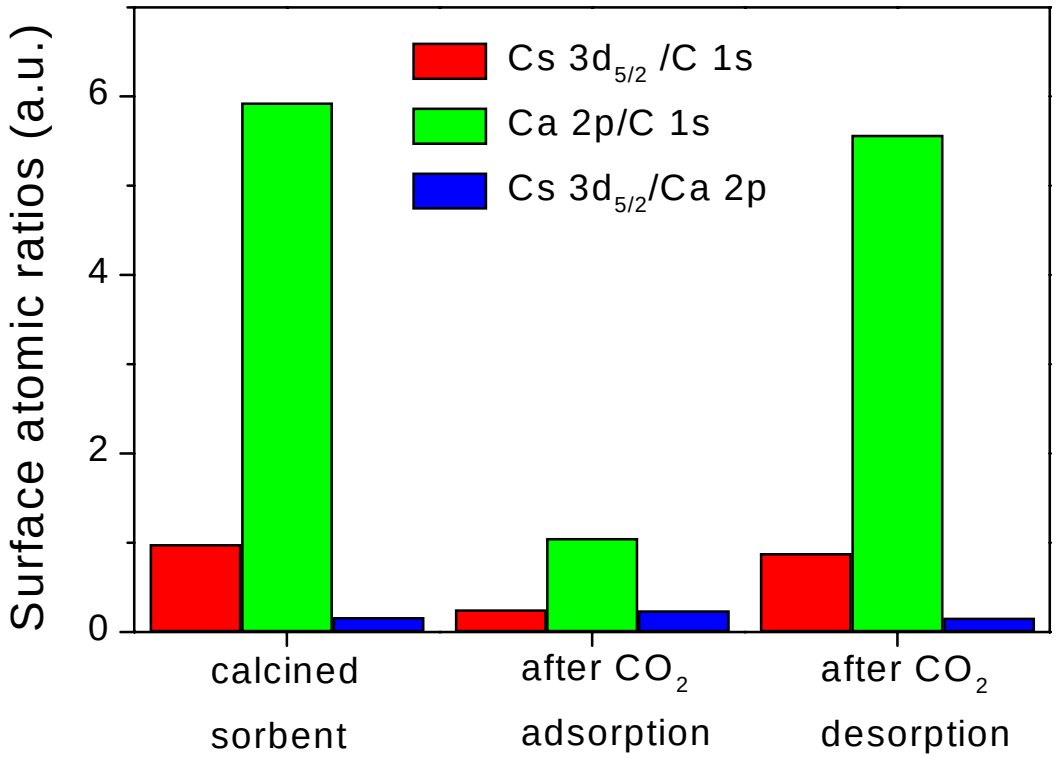

Figure 12: Surface Atomic Ratios Determined by XPS

US Patent Applications, Refereed Articles, Presentations, and Students Receiving Support from the Grant

US Patent Applications

1) Smirniotis. P.G., and P.E. Reddy, *Title*: Novel Sorbents for Separation of CO_2 at a Wide Temperature Range, Invention disclosure for US patent (UC case 101-020).

Journal Articles (peer reviewed)

1) Reddy, P. E. and P.G. Smirniotis, "Sorption of CO2 by Alkaili Metals doped CaO Sorbents", **Gas Separation and Durification**, *submitted* 2002.

2) Reddy, P. E., S. Gopal, and P.G. Smirniotis, "Novel Sorbents for adsorption of CO_2 from Gas Mixtures at High Temperatures", **Chemical Communications**, *submitted* 2002.

Conference Presentations

This work was presented only at the 2002 Annual Contractors Meeting in Pittsburgh, PA in June 2002.

Students received support from the grant.

Graduate Students:

1) Mr. Srikant Gopal, graduate (Ph.D.) student in Chemical Engineering

2) Mr. Kyesang Yoo, graduate (Ph.D.) student in Chemical Engineering