ADSORPTION OF CARBON DIOXIDE ON ALKALI METAL EXCHANGED ZEOLITES

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Introduction

The increasing atmospheric CO_2 concentration, mainly caused by fossil fuel combustion, have become an important concern for global warming because the atmospheric CO_2 concentrations increased significantly in the last century and rises continuously at a faster rate. Carbon dioxide is produced in large quantities by many important industries such as fossil-fuel-fired power plants, steel production, chemical and petrochemical manufacturing, cement production, and natural gas purification. The reasons for the CO_2 removal are traditionally technical and economical concerns. Carbon dioxide present in natural gas will reduce the heating value of the gas and as an acid component it has the potential to cause corrosion in pipes and process equipment and also to cause catalyst poisoning in ammonia synthesis (1). In the past decades, CO_2 removal from flue gas streams started as a potentially economic source of CO_2, mainly for enhanced oil recovery operations. Moreover, CO_2 was also produced for other industrial applications such as carbonation of brine, welding as an inert gas, food and beverage carbonation, dry ice, urea production, and soda ash industry (2). However, environmental concerns, such as the global climate change, are now focused as one of the most important and challenging environmental issues facing the world community, and have motivated intensive research on CO_2 capture and sequestration. Carbon dioxide as one of the greenhouse gases (GHG) is currently responsible for over 60 % of the enhanced greenhouse effect, methane (CH_4) contributes 20 %, and the remaining 20 % is caused by nitrous oxide (N_2O), a number of industrial gases, and ozone. Scientific evidence now strongly suggests that increased levels of GHG may lead to higher temperature, and cause climate change on a global scale. Various climate models estimate that the global average temperature may rise by about 1.4 – 5.8 ºC by the year 2100 (3).

The standard method to removal CO_2 break down the whole system into its component parts: capture, transport, and storage. The capture and ulterior storage in a geologic reservoir is, nowadays, the technique more useful to reduce the CO_2 concentration in the atmosphere. However, the total amount of antrophogenic carbon dioxide that is captured is lower than 19 Mt/year. The reason is because the capture is only possible for large stationary sources of CO_2, like power plants or cement fabrics. The large stationary sources produce around 60 % of the total carbon dioxide, which is 14 Gt CO_2/year.

Below, each of these components is defined:

- Capture, is the production of a CO_2 stream that is ready for transport and storage. CO_2 from large industrial sources is usually part of a stream composed of several gases. In general, the CO_2 is separated as a fairly pure stream (90-99% pure) and then compressed to over 100 atm. While power plants are the largest single source of CO_2 (over a third of all CO_2 emissions), other industrial operations (e.g., ammonia plants, refineries, natural gas processing) also provide attractive targets. In most cases,

capture (including compression) is by far the largest cost component (typically 80% of the costs for power plants) (4), Table 1.

- Transport is moving CO_2 from the capture site to the storage site. For moving large amounts of CO_2, pipeline transport is almost always the preferred mode. Small amounts of CO_2 can be transported via truck, while tanker ships are being considered for some circumstances.
- Storage is comprised of injecting CO_2 into a reservoir. Monitoring and verification fall under this component.

Table 1. Costs and cost drivers for capture, transportation and storage of CO_2 (5)

Segment	Costs	Common cost drivers	Specific costs drivers
Capture	4 – 73 €/ t CO_2	• Volume of CO_2 • Location • Onshore/ offshore	• Type of source • Retrofit or new build
Transportation	0 – 16 €/ t CO_2		• Distance from sink / market • Existing infrastructure • Ship versus pipeline
Storage	1 – 10 €/ t CO_2		• Existing infrastructure • Size of storage field • Monitoring requirements

Some processes (e.g. acid gas processing, hydrogen and ammonia production) produce point sources of highly concentrated or pure CO_2. The process already includes CO_2 separation therefore these sources typically only require compression and dehydration for CO_2 capture and therefore the capture cost is relatively low (4-8 €/t CO_2). However, these sources are typically dispersed and small scale with the total current worldwide, estimated to be around 120 Mt/year. The power sector represents the largest opportunity for capture and storage. In the power sector, capture using existing technologies such as post-combustion amine systems have a current costs in the range of 32-48€/t CO_2, avoided for new build projects using pulverised coal or natural gas combined cycle generation (2,6). Integrated gasification combined cycle (IGCC), an emerging coal or coke-based technology for power generation offers the lowest cost of capture for power at 12-20€/t CO_2 as the CO_2 stream is already concentrated (7).

Thus, it is evident that the fact of obtaining an economically technique to capture the cabon dioxide is of prime concern.

Types of techniques for capture of CO_2

There are three main techniques for capture of CO_2 in power plants: pre-combustion capture, oxy-fuel combustion and post-combustion capture.

In pre-combustion capture, fuel is reacted with oxygen or air, and in some cases steam, to give mainly carbon monoxide and hydrogen. This process is known as gasification, partial oxidation or reforming. The mixture of mainly CO and H_2 is passed through a catalytic reactor, called a shift converter, where the CO reacts with steam to give CO_2 and more H_2. The CO_2 is separated and the H_2 is used as fuel in a gas turbine combined cycle plant. The process is, in principle, the same for coal, oil or natural gas, but when coal or oil are used there are more stages of gas purification, to remove particles of ash, sulphur and nitrogen compounds and other minor impurities. The CO_2 concentration and pressure are both higher in pre-combustion capture than in post-combustion capture, so the CO_2 capture equipment is much smaller and different solvents can be used, with lower energy penalties for regeneration.

The oxy-fuel combustion consists on increasing the concentration of CO_2 in flue gas by using concentrated oxygen instead of air for combustion, either in a boiler or gas turbine. The oxygen would be produced by cryogenic air separation, which is already used on a large scale, for example in the steel industry. If fuel is burnt in pure oxygen, the flame temperature is excessively high, so some CO_2-rich flue gas would be recycled to the combustor to make the flame temperature similar to that in a normal air-blown combustor. The advantage of oxygen-blown combustion is that the flue gas has a CO_2 concentration of over 80%, so only simple CO_2 purification is required. Another advantage is that NO_X formation is suppressed, and the volume of gas to be treated in the flue gas desulphurization plant is greatly reduced. Additionally, other than a need for flue gas desulphurization, oxyfuel combustion relies mainly on physical separation processes for O_2 production and CO_2 capture thereby avoiding the use of any reagents and/or solvents that contribute to operating costs and the environmental disposal of any related solid or liquid wastes. The main disadvantage of oxyfuel combustion is that a large quantity of oxygen is required, which is expensive, both in terms of capital cost and energy consumption.

Post-combustion capture involves separating CO_2 from the flue gas produced by fuel combustion. A variety of techniques can be used for this separation:

- <u>Absorption</u>: is the most employed method for the removal of CO_2. The most common solvent is monoethanolamine (MEA). Prior to CO_2 removal, the flue gas is cooled and particulates and other impurities are removed as far as possible. It is then passed into an absorption vessel where it comes into contact with the chemical solvent, which absorbs much of the CO_2 by chemical reactions to form a loosely bound compound. The CO_2– rich solvent taken from the bottom of the absorber is passed into another vessel (stripper column) where it is heated with steam to reverse the CO_2 absorption reactions. CO_2 released in the stripper is compressed for transport and storage and the CO_2–free solvent is recycled to the absorption vessel. CO_2 recovery rates of around 85-95% capture are normally proposed and product purity can be in excess of 99% (8). The main concerns with MEA and other amine solvents are corrosion in the presence of O_2 and other impurities, high solvent degradation rates from reaction with SO_X and NO_2 and the large amounts of energy required for regeneration.

- <u>Membranes</u>: gas separation membranes rely on differences in physical or chemical interactions between gases and a membrane material, causing one component to pass through the membrane faster than another. Although there are various types of membrane are currently available, any of them achieve high degrees of separation, so multiple stages and/or recycle of one of the streams is necessary. This leads to increased complexity, energy consumption and costs. There is also a gas absorption membranes hybrid system (9). The CO_2 diffuses through the membrane and is removed by an absorption liquid such as amine, which selectively removes certain components. In contrast to gas separation membranes, it is the absorption liquid, not the membrane that gives the process its selectivity.
- <u>Cryogenics</u>: CO_2 can be separated from other gases by cooling and condensation. Cryogenic separation is widely used commercially for purification of CO_2 from streams that already have high CO_2 concentrations (typically >90%) but it is not normally used for more dilute CO_2 streams. A major disadvantage of cryogenic separation of CO_2 is the amount of energy required to provide the refrigeration necessary for the process, particularly for dilute gas streams. Another disadvantage is that some components, such as water, have to be removed before the gas stream is cooled, to avoid blockages. Cryogenic separation has the advantage that it enables direct production of liquid CO_2, which is needed for ship transport.
- <u>Solid sorbents</u>: sorbents such as calcium or lithium based oxides can react with CO_2 to form carbonates and the carbonates can be regenerated to oxides by heating to a higher temperature (10). These processes have the potential to reduce efficiency penalties compared to wet absorption processes. A weak point of processes that use natural solid sorbents (limestone and dolomite) is that they deactivate rapidly and a large make-up flow of sorbent is needed, although the deactivated sorbent may find application in the cement industry. Lithium based sorbents are much more durable but they are intrinsically expensive materials.
- <u>Adsorption</u>: some solid materials with high surface areas, such as zeolites and activated carbon, can be used to separate CO_2 from gas mixtures by adsorption. Gas is fed to a bed of solids that adsorbs CO_2 and allows the other gases to pass through. When a bed becomes fully loaded with CO_2, the feed gas is switched to another clean adsorption bed and the fully loaded bed is regenerated to remove the CO_2. In *pressure swing adsorption* (PSA), the adsorbent is regenerated by reducing the pressure. In *temperature swing adsorption* (TSA), the adsorbent is regenerated by raising its temperature and in *electric swing adsorption* (ESA) regeneration takes place by passing a low-voltage electric current through the adsorbent.

  PSA and TSA are used commercially for gas separation and are used to some extent in hydrogen production and in removal of CO_2 from natural gas, but ESA is poorly explored and tested at present. Adsorption is not yet considered attractive for large-scale separation of CO_2 from flue gas because the capacity and CO_2 selectivity of available adsorbents is low (11). However, it may be successful in combination with another capture technology. Adsorbents that can operate at higher temperatures in the presence of steam with increased capacity and improved selectivity are needed.

Activated carbons have been widely used as carbon dioxide adsorbents due to their high surface area, which confers them high adsorption capacity. However, this high capacity

of adsorption is limited at room temperatures. Przepiorski et al. (12) have tested activated carbons in the capture of CO_2 at 25 and 36 ºC, observing an important decrease in the capacity of adsorption in only 9 ºC. For this reason, in this work, we have selected zeolites as adsorbents for carbon dioxide capture. High aluminium (or low silicon) content zeolites have been extensively used for separation of gases including carbon dioxide from gas mixtures. Inui et al. (13) studied the relation between the properties of various zeolites and their CO_2 adsorption behaviours, concluding that 13X zeolites were the most proper choice. Likewise, Kumar et al. (14) established that NaY zeolite could be a substitute of 13X zeolite due to its easier regenerability. Furthermore, in order to improve the capacity of adsorption of these zeolites, treatments with Cs were carried out, since it is the most electropositive metal of the periodic table. The effect of temperature, as well as the regenerability of these zeolites, both after CO_2 desorption and after water desorption, was tested.

Experimental section

Zeolites NaX (Alltech) and NaY (Zeolyst Corporation) are used as received. The alkaline treatment of the zeolites was carried out at 70 ºC for 2 h, followed by drying at 100 ºC 12 h and calcination at 650 ºC for 4 h. Alkali metal solutions (0.5 M) were prepared disolving CsOH (Avocado) or Cs_2CO_3 (Avocado) into distilled water. In each case, 2 g of zeolite were suspended into 100 mL of the Cs^+ solution. The modified zeolites were recovered by filtration and repeatedly washed with distillate water to remove the impurities completely. The resulting zeolites were pretreated at 650 ºC in an oven for 4h in order to remove the moisture and other contaminants prior to the experiments. Prepared zeolites will be referred to as Cs*A-B*, where *A* is the type of zeolite (X or Y) and *B* refers to the cesium precursor (*OH* for CsOH and *c* for Cs_2CO_3).

Adsorption experiments were carried out in a Micromeritics TPD-2900 apparatus connected to a Glaslab 300 mass spectrometer using He as the carrier gas. Before each TPD experiment, 50 mg of sample was introduced in a quartz tube and outgassed in a He flow of 30 mL/min by thermal treatment at 600 ºC for 1 hour, with a heating rate of 10 ºC/min from room temperature. After being cooled to 50 ºC, the adsorbent material was contacted with the gaseous feed (pure CO_2) for 20 min. The reversibly adsorbed carbon dioxide was the removed by treatment of the sample in He flow for 1 h at 50 ºC. The completion of this desorption process was confirmed by the recovery of the baseline of the mass spectrometer. The TPD tests were carried out by heating the sample with a ramp of 10 ºC/min between 50 ºC and 600 ºC with constant He flow. In order to study the regenerability of the adsorbents, after keeping the latter temperature constant for 60 min, the sample is cooled to 50 ºC and the adsorption process repeated. The selectivity for CO_2 adsorption in presence of water vapour is studied saturating the sample at 50 ºC with water, by successive injection of water pulses, and then the desorption process is carried out according to the previous described method. Once the sample is cooled to 50 ºC, it is saturated with CO_2 in order to evaluate its adsorption after the water adsorption.

Nitrogen adsorption-desorption isotherms were obtained at –196 ºC on a Micromeritics ASAP 2000 instrument. Previously, the samples were outgassed at 200 ºC for 6 h in high vacuum. Acidity strength studies were carried out by NH_3-TPD, in the Micromeritics instrument aforementioned. Powder X-ray diffraction (XRD) was performed with a Philips

PW1710 diffractometer, working with the Cu Kα line (λ = 0.154 nm). The unit cell chemical composition of all samples was determined by ICP-MS, using an octapole HP-7500c.

Results and discussion

Physico-chemical properties of both, parent and treated zeolites are shown in Table 2. The treatment with CsOH results in a percentage of cesium between 18 and 19 %, whereas the modification with Cs_2CO_3 obtains a cesium load of 16-18 %. As it could be expected, the treatment with alkaline solutions leads to a displacement of ammonia desorption peak to lower temperatures. Nitrogen physisorption data reveal a decrease in the microporous volume and the surface area after the treatment.

Table 2. Chemical composition and morphological properties of the zeolites studied

Zeolites	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	Cs (%)	Cs/Al	NH$_3$-peak temperature (ºC)
NaX	432	0.17	-	-	306
CsX-OH	387	0.14	18.9	2.75	156
CsX-c	404	0.14	16.2	2.83	164
NaY	1064	0.4	-	-	227
CsY-OH	474	0.21	17.9	4.38	169
CsY-c	473	0.18	18.1	4.36	171

According to the experimental procedure, during the TPD stage, the carbon dioxide interacting directly with the adsorption sites is desorbed by the increase of the temperature. Table 3 compares the results obtained from the CO_2–TPD curves with Cs-zeolites, carrying out the adsorption at 50 ºC.

This desorption takes place in reverse order of the strength of the adsorption sites and the adsorbate-adsorbent affinity. The desorbed amount of carbon dioxide detected in TPD experiment is a function of the number of adsorption sites available in the adsorbent surface (evaluated as mg CO_2/g adsorbent), whereas the temperature of the peak can be considered as a relative measurement of the strength of the adsorbate-adsorbent interactions. Depending on the adsorbent, one or several peaks can be observed in the TPD curves. For NaX zeolite only one desorption peak was detected, which indicated that there is only one type of adsorption site for CO_2. For the other zeolites, there are in all cases two desorption peaks.

Table 3. CO_2-TPD results for the zeolites tested (CO_2 adsorption at 50 ºC)

Zeolites	1st desorption peak		2nd desorption peak		Total CO_2 desorbed (mg/g)
	T (ºC)	CO_2 desorbed (mg/g)	T (ºC)	CO_2 desorbed (mg/g)	
NaX	364	14.0	-	-	14.0
CsX-OH	415	9.0	554	0.5	9.5
CsX-c	427	0.7	612	8.1	8.8
NaY	157	0.5	570	0.3	0.8
CsY-OH	277	0.9	572	0.3	1.2
CsY-c	279	0.6	610	0.3	0.9
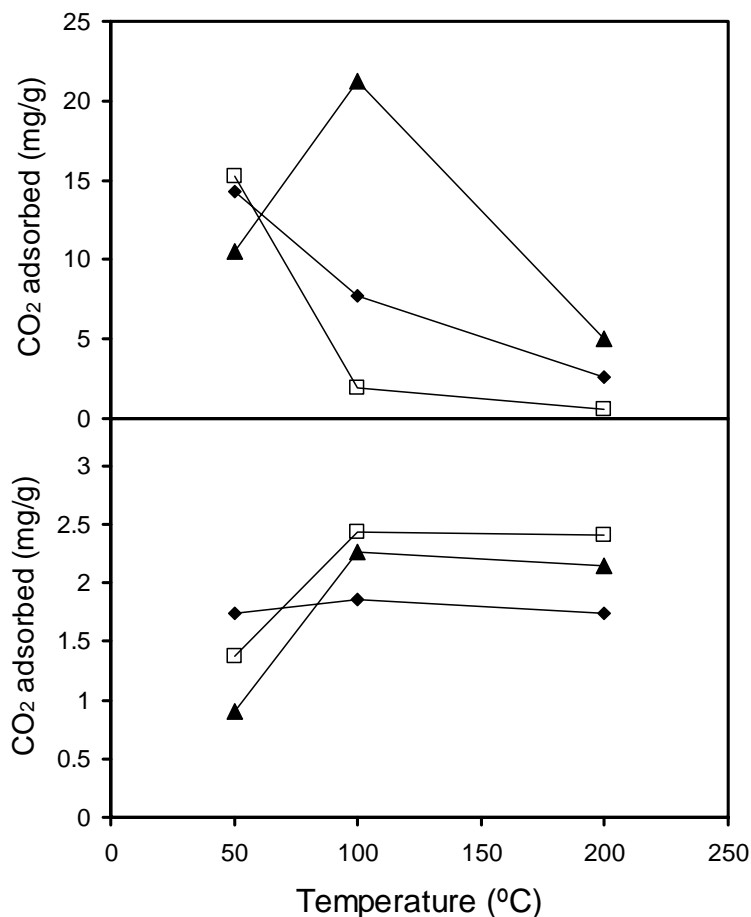
Figure 1. Influence of temperature on the capacity of adsorption of (a) X-zeolites and (b) Y-zeolites [parent (♦), CsOH modified zeolite (□) and Cs_2CO_3 treated zeolite (▲)]

In general, desorption temperature is displaced to higher temperatures after Cs treatment. Apart of this generality, X and Y zeolites present different behaviours. CsX-OH desorbs 15.3 mg/g divided into two desorption peaks, at 415 and 554 °C. Likewise, CsY-OH zeolite shows an improved performance after the modification, however, its capacity of adsorption is very poor. In the case of carbonate treated zeolites, also two behaviours are observed. CsX-c zeolite, although with a total adsoption capacity lower than NaX, presents an important desorption peak at high temperature (612 °C), whereas for the CsY-c zeolite, the size of the desorption peak at the highest temperature is quite small. It is important to point out that cesium carbonate decomposes at 610 °C, so the peaks evolved at around 600 °C involves chemical reaction instead a simple adsorption. Likewise, the regenerability of the adsorbents, studied according to the procedure described in the experimental section, improves after the alkaline treatment over both types of zeolites.

In order to test the influence of adsorption temperature in the capacity of adsorption of CO_2, adsorption experiments were repeated at 100 and 200 °C. The results are presented in Fig. 1. NaX zeolite exhibits a decrease in the capacity of adsorption with the temperature, whereas NaY zeolite –with a poorer performance- remains its capacity of adsorption. As general trend there are two types of behaviours corresponding to two different mechanisms: adsorption and chemical reaction.

The experiments of adsorption of CO_2 after desorption of water reveal that although alkaline-treated zeolites adsorb more water than NaX and NaY, they improve their performance after Cs treatment retaining larger amounts of carbon dioxide than before the water presence.

Conclusions

Adsorption of carbon dioxide on alkaline modified X and Y zeolites was investigated by means of a thermal programmed desorption technique. NaX and NaY were modified with cesium hydroxide and cesium carbonate. Add to the adsorption capacity of the adsorbents, resistance to water and the effect of the temperature were also tested. Two different mechanisms were detected in the carbon dioxide adsorption: physical adsorption and chemical reaction (carbonatation). Adsorption capacity of the modified zeolites is lower than the parent ones at 50 °C, however with the increase of the temperature, and in the cases where chemical reaction is implied, the amount of carbon dioxide retained also increases. Regarding the effect of water in the CO_2 adsorption, although the water adsorption over NaX zeolite unable the further adsorption of CO_2, in the case of the cesium treated zeolites, its capacity of adsorption for CO_2 is improved after water desorption.

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