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Enhancement of the CO₂ Retention Capacity of Y Zeolites by Na and Cs Treatments: Effect of Adsorption Temperature and Water Treatment

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Adsorption of carbon dioxide on parent and alkaline-modified Y zeolites was investigated by temperature-programmed desorption (TPD) analysis of these materials previously saturated with CO₂ at different temperatures (50–200 °C). Parent zeolite was treated with different sodium and cesium aqueous solutions, using both carbonates and hydroxides as precursors. Morphological, crystallographic, and chemical properties of these materials were determined by nitrogen physisorption, X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, inductively coupled plasma (ICP), X-ray photoelectron spectroscopy (XPS), and NH₃-TPD. Slight desilication phenomena were observed when hydroxides were used as precursors, whereas the treatment with Cs salts leads to higher crystallinity losses. Several successive adsorption–desorption cycles were carried out in order to check the stability of the adsorbents. Both Cs treatments lead to an enhancement of the retention capacity when adsorption is carried out at the highest temperatures (100–200 °C), whereas Na treatments hardly affect adsorption properties of the parent material. The evolution of the retention capacity of carbon dioxide after water adsorption–desorption was also studied. It was observed that water pretreatment enhances the adsorption capacity of the Cs-treated zeolites.

1. Introduction

Carbon dioxide, mainly emitted from combustion processes and industrial plants, is the major contributor to global warming. Carbon dioxide sequestration is considered the only real possibility for a tight control of the CO₂ emissions. This sequestration involves three different steps: separation or capture, transportation, and storage. Among these steps, the separation processes are the most expensive.¹ Therefore, the development of CO₂ separation technologies is currently a key issue in environmental and chemical engineering.

Nowadays, the most common method for carbon dioxide capture is gas absorption, monoethanolamine (MEA) being the most usual solvent. However, this operation has important drawbacks: degradation of the solvent at process conditions and the large amounts of energy required for regeneration (energy demands are estimated to be 330–340 kWh/ton CO₂ recovered).^{2,3} Adsorption processes can overcome these drawbacks, because of its low energy requirement, cost advantage, and easiness of applicability over a relatively wide range of temperatures and pressures.⁴ Activated carbons, and especially activated carbons with increased basic character, have been successfully used for carbon dioxide adsorption due to their high surface area and pore volume.⁵ They present high adsorption capacity at low CO₂ concentration and fast intraparticle mass transfer.⁶ However, activated carbons are not stable at the relatively high temperatures (>200 °C)⁷ at which the adsorption of CO₂ from off-gases should be carried out. Zeolitic materials could be an interesting alternative for these purposes. Thus, several works in the literature dealt with CO₂ adsorption over different types of zeolites: X,^{8–13} Y,^{9,14,15} A,^{8,9} and other natural zeolites. Na–Y zeolite has been suggested because of its easier regenerability.¹⁵ In a previous work,¹⁶ we have found that, at low temperatures (50 °C), X zeolite performs better than Y zeolite, but the retention capacity strongly decreases as tem-

perature increases, and the presence of water severely inhibits the adsorption of CO₂.

It must be also considered that the cation incorporated to the zeolite structure can largely modify the chemical properties of the material. The addition of Cs to other materials, such as calcium oxides, has shown to largely increase the CO₂ adsorption capacity,¹⁷ whereas the exchange of Na–X zeolite with this metal has shown to increase the basic character of these zeolites for base-catalyzed reactions.¹⁸ On the other hand, the treatment of zeolites in aqueous alkaline media (such as solutions of group I metal hydroxides) can lead to a partial desilication of the zeolites, altering their morphology (development of additional mesoporosity, increasing the accessibility of the active sites) and surface reactivity (increasing their hydrophilic character). This effect is widely described in the literature for high Si/Al ratio zeolites,^{19,20} but not for zeolites with lower Si/Al ratio, such as the Y zeolites.

So, the scope of this work was to carry out a systematic study of the effect of the modification of Y zeolites by Cs addition on the adsorption properties, testing two of the most conventional precursors: hydroxide and carbonate.¹⁷ To separate the potential effects of the change of the electronegative of the counteraction and the potential desilication, parallel treatment of the Y zeolite with sodium hydroxide and carbonate was also carried out. Comparison of the materials was made in terms of total adsorption capacity after two adsorption–desorption cycles at 50, 100, and 200 °C and performance after water desorption.

2. Experimental Section

Materials Preparation. The commercial zeolite (Na–Y) used in this study was purchased from Zeolyst Corp. The alkaline treatment of the zeolites was carried out at 70 °C for 2 h, followed by drying at 100 °C for 12 h and calcination at 650 °C for 4 h (Cs₂CO₃ decomposes at 612 °C, and Na₂CO₃ at 400 °C). Alkali metal solutions (0.5 M) were prepared by dissolving CsOH or Cs₂CO₃ (both from Avocado) into distilled water. In each case, 2 g of zeolite was suspended into 100 mL

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of the Cs⁺ solution. The modified zeolites were recovered by filtration and repeatedly washed with distillate water. Another set of Na–Y zeolite samples has been treated in the same way but using NaOH and Na₂CO₃ instead of the cesium precursors. Prepared zeolites will be referred to as Cs–Y-a or Na–Y-a, where a refers to the cesium or sodium precursor (h for hydroxide precursor and c for carbonate precursor).

Materials Characterization. Bulk chemical composition of all the samples was determined by inductively coupled plasma-mass spectrometry (ICP-MS), using an octapole HP-7500c. The samples were dissolved in 1% HNO₃ (1:250), and Rh was used as internal standard.

Nitrogen adsorption–desorption isotherms were obtained at –196 °C on a Micromeritics ASAP 2000 instrument. Previously, the samples were outgassed at 200 °C for 6 h in high vacuum. The Brunauer–Emmett–Teller (BET) equation was used for calculating the specific surface area of the materials from nitrogen adsorption isotherms. The micropore surface area and the micropore volume were determined by applying the *t*-plot method.

Acidity strength studies were carried out by NH₃-TPD (TPD = temperature-programmed desorption), in a Micromeritics TPD-2900 apparatus connected to a Glaslab 300 mass spectrometer using He as the carrier gas. For this purpose, 0.25 g of adsorbent sample was saturated in ammonia–stream of 10/90 NH₃/He—at 50 °C during 30 min and then heated from 50 to 650 °C at 10 °C/min in a stream of pure He with a flow rate of 50 cm³/min.

Powder X-ray diffraction (XRD) was performed with a Philips PW1710 diffractometer, working with the Cu K α line (λ = 0.154 nm). Measurements of the samples were carried out in the 2 θ range of 5–85°, at a scanning rate of 2° in 2 θ min^{–1}. The surface species were characterized by X-ray photoelectron spectroscopy (XPS; VG-Microtech Multilab 3000). The binding energies were referenced to the C 1s band at 285 eV. Infrared spectra were recorded on a Nicolet Nexus FTIR instrument with a resolution of 2 cm^{–1} using the KBr pellet technique.

Adsorption Experiments. Adsorption experiments were conducted in the aforementioned Micromeritics apparatus. 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 620 °C for 1 h, with a heating rate of 10 °C/min from room temperature. After being cooled to the temperature at which the adsorption will be carried out (50, 100, or 200 °C), the adsorbent material was contacted with the gaseous feed (pure CO₂) for 20 min. The reversibly adsorbed carbon dioxide was removed by treatment of the sample in He flow for 1 h at the adsorption temperature. 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 °C/min until 620 °C in a constant He flow. MS signal was integrated in order to obtain amounts of CO₂ desorbed, calibrating the device with the decomposition of known amounts of pure CaCO₃.

To study the regenerability of the adsorbents, after holding the sample temperature at 620 °C during 1 h, the temperature is decreased to the initial value and the adsorption–desorption cycle repeated. The adsorption of CO₂ after the presence of steam is studied by saturating the sample at 50 °C with water, by successive injection of water pulses, and then the desorption process is carried out until 620 °C according to the previously described method. Once the sample is cooled to 50 °C, it is saturated with CO₂ in order to evaluate its adsorption after the water adsorption–desorption.

Table 1. Chemical Composition of the Studied Zeolites^a

| zeolites | Si/Al | wt % | | atomic ratio | | | |
|----------|-------|--------|--------|----------------------|----------------------|----------------------|----------------------|
| | | Cs (%) | Na (%) | (Si/Al) _b | (Si/Al) _s | (Cs/Al) _b | (Cs/Al) _s |
| Na–Y | 2.97 | — | 0.47 | 2.87 | — | — | — |
| Cs–Y-h | 2.84 | 23.92 | 0.12 | 2.74 | 2.14 | 0.84 | 0.77 |
| Cs–Y-c | 3.00 | 18.74 | 0.11 | 2.89 | 2.65 | 0.78 | 0.86 |
| Na–Y-h | 2.64 | — | 0.56 | 2.54 | — | — | — |
| Na–Y-c | 3.00 | — | 0.50 | 2.92 | — | — | — |

^a Bulk composition determined by ICP-MS and surface composition by XPS.

3. Results and Discussion

Properties of the Adsorbents. The chemical compositions of the modified zeolites are summarized in Table 1. The treatment with CsOH results in a percentage of cesium (in the bulk) of around 24%, whereas the modification with Cs₂CO₃ leads to a cesium loading of 19%. Since the increase of cesium concentration and the decrease of sodium concentration are not correlated, it is inferred that a fraction of this metal is not directly exchanging the sodium of the parent zeolites. In the case of the analogous treatment with sodium compounds, sodium concentration does not vary significantly for Na–Y-c, whereas Na–Y-h presents an increase of sodium of about 9%. Concerning the Si/Al ratio, it is observed that it is hardly affected by the treatment with carbonates, whereas a slight decrease in this Si/Al ratio has been observed for the zeolites treated with hydroxides, especially in the case of NaOH treatment. Si/Al and Cs/Al atomic ratios, in the external surface region, are compared, for the cesium-treated zeolites, to Si/Al and Cs/Al bulk ratios (Table 1). The Si/Al atomic ratio derived from XPS is significantly lower than the bulk ratio for alkaline treatment, suggesting that the desilication takes place mainly on the surface. Concerning the Cs/Al ratio, the Cs–Y-h zeolite, which has the higher cesium content, presents a lower amount of cesium in the surface than the zeolite treated with carbonate. Therefore, the desilication could help to extend homogeneously the cesium into the structure. The desilication of zeolites in alkaline solutions is reported in the literature for high Si/Al ratio zeolites, such as MFI, BEA, MOR, and FER,^{19,20} but, to the best of our knowledge, not for either low Si/Al ratio zeolites, such as Y zeolites, or for cesium-treated zeolites.

The Cs 3d_{5/2} binding energies decreased from 724.0 eV for Cs–Y-h, to 723.7 eV for Cs–Y-c. The first value is due to the Cs in the Cs₂O form, and the former one corresponds to Cs atoms surrounded by less electronegative atoms, as in the case of Cs as exchanged cation in the zeolite framework.^{21,22} It was suggested that O 1s BE of the zeolite is directly correlated to the basicity of the framework oxygen, whose basic strength increases with decreasing O 1s BE,²³ rather than to zeolite composition (Si/Al ratio and cation). Sodium treatments, as well as cesium alkaline treatment, do not modify the basic strength of the oxygen framework, since in all cases O 1s BE is invariable (531.8 eV). The zeolite treated with cesium carbonate presents the most basic framework oxygen (531.5 eV). Similar values and interpretations were given by Okamoto and Kubota²³ for the original Na–Y zeolite and for Cs-treated Na–Y zeolites (531.8 eV for the untreated and 531.6 eV for the Cs-treated).

Figure 1 shows representative XRD patterns of the modified zeolites. XRD patterns showed the characteristic peaks of a FAU framework. The intensity of the signal decreases for the Cs-treated zeolites, suggesting loss of crystallinity. No differences are observed in the loss of crystallinity for the Cs-treated zeolites between hydroxide and carbonate precursors. This behavior was observed in the literature for cesium-exchanged and -impreg-

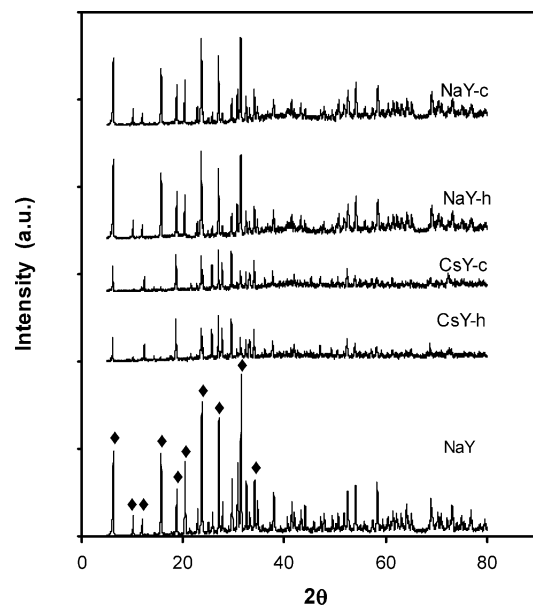


Figure 1. X-ray diffractograms of the zeolites tested. Marks show reflections corresponding to faujasite.

Table 2. Textural Properties and NH_3 -TPD Results of Parent and Modified Zeolites

| zeolites | S_{BET}^a (m^2/g) | V_{total}^b (cm^3/g) | V_{micro}^c (cm^3/g) | V_{meso} (cm^3/g) | av pore diam (\AA) | NH_3 peak temp ($^\circ\text{C}$) |
|----------|---|--|--|---|----------------------------------|---|
| Na-Y | 811 | 0.46 | 0.40 | 0.06 | 15.4 | 189 |
| Cs-Y-h | 473 | 0.21 | 0.26 | 0.04 | 15.8 | 269 |
| Cs-Y-c | 473 | 0.21 | 0.26 | 0.04 | 15.8 | 168 |
| Na-Y-h | 854 | 0.42 | 0.33 | 0.09 | 17.8 | 229 |
| Na-Y-c | 697 | 0.29 | 0.24 | 0.05 | 15.5 | 203 |

^a BET method. ^b $V_{\text{total}} = V_{\text{ads}} P/P_0 = 0.99$. ^c t -plot method.

nated zeolites,²⁴ and, as in that case, no evidence of the presence of other crystalline phases were observed. The sodium-treated zeolites show higher crystallinities than the Cs-exchanged, being more crystalline the zeolite resulting from hydroxide precursor. The markedly higher loss of crystallinity of the carbonate-treated zeolite can be tentatively explained by the effect of the CO_2 released during the calcinations of the material. This reduction was not linked to the collapse of the structure as shown in IR analysis (not shown), where the intensity of the characteristic bands of the FAU framework (1158, 795, and 580 cm^{-1}) are retained with respect to the parent zeolite.²⁶

Cesium and sodium treatments also affect the morphological properties of the materials, such as surface area and pore volume. The main textural properties of the samples are shown in Table 2, whereas the adsorption–desorption isotherms are shown in Figure 2. Although in all cases the materials show a combination of mesoporous and microporous structure, there are important differences in the porous structure. N_2 adsorption measurements on the parent zeolite, cesium-modified zeolites, and Na–Y-c showed a type I isotherm (typical for a microporous material with low mesoporosity²⁷). Both cesium precursors lead to important decreases, both in microporous and mesoporous volume (about 50%), in accordance with the loss of crystallinity in the zeolite structure that could be justified by the incorporation of Cs ions to the structure, also revealed by XPS in the case of the carbonate precursor. Na–Y-c also presents an important loss of the surface area (higher than 10%), corresponding this decrease to the loss of microporous structure. In the case of Na–Y-h zeolite, the isotherm presents both type I and type IV behavior with hysteresis loop. There is a step increase in the amount of nitrogen adsorbed when the relative pressure was

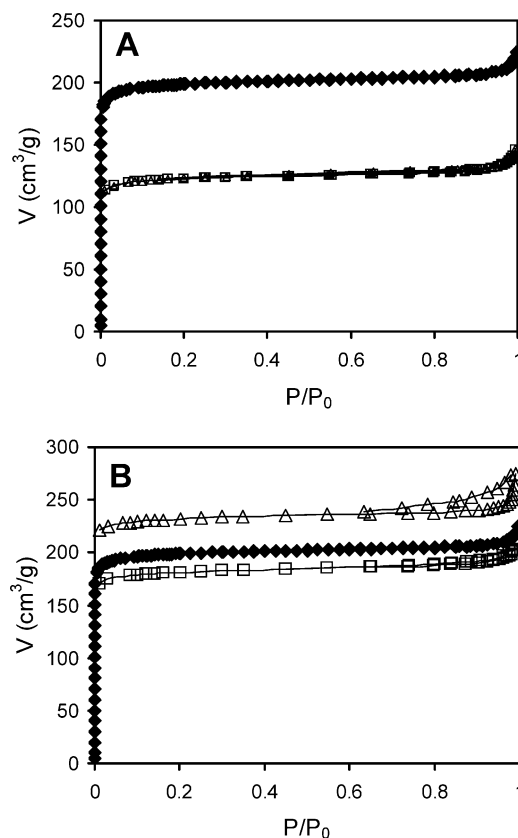


Figure 2. N_2 adsorption isotherms: (A) zeolite Na–Y and cesium derivatives; (B) zeolite Na–Y and sodium derivatives [parent zeolite (\blacklozenge), hydroxide precursor (\triangle), and carbonate precursor (\square)]. Filled symbols, adsorption; open symbols, desorption.

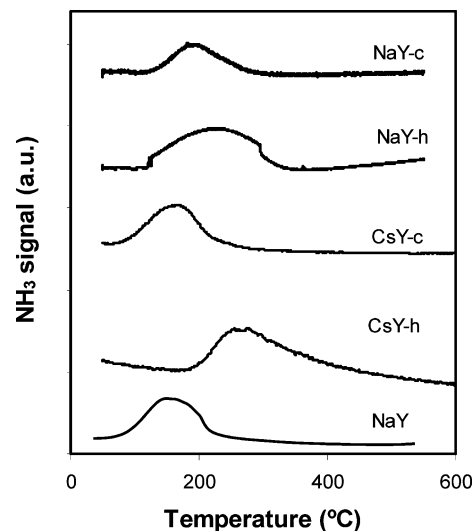


Figure 3. NH_3 -TPD patterns of the zeolites studied in this work.

higher than 0.7. These features indicate the presence of both micropores and mesopores in the zeolite structure. Similar behaviors are reported in the literature for other zeolites,^{20,25} desilication being proposed as a method to develop mesoporosity in microporous zeolites.

The observed physicochemical changes after the studied treatments are also reflected in the acidity of the treated zeolites. Ammonia adsorption profiles (NH_3 -TPD) are shown in Figure 3, whereas the maxima of desorption peaks are summarized in Table 2. As a general trend, the number of acid sites in the alkaline-treated zeolites (both with NaOH and CsOH) increases, in good agreement with the lower Si/Al ratio (Table 1). The

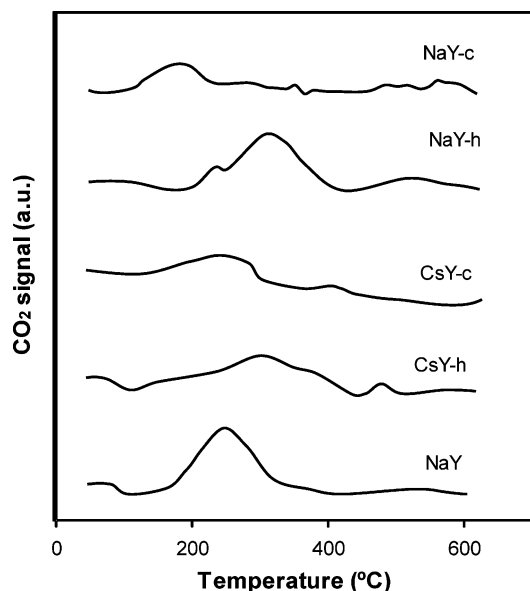


Figure 4. CO₂-TPD profiles of the zeolites after the second cycle of adsorption at 50 °C.

Table 3. CO₂-TPD Results for the Zeolites Tested (CO₂ Adsorption at 50 °C)

| zeolites | | first desorption peak | | second desorption peak | | total CO ₂ desorbed (mg/g) |
|----------|--------------|-----------------------|---------------------------------|------------------------|---------------------------------|---------------------------------------|
| | | <i>T</i> (°C) | CO ₂ desorbed (mg/g) | <i>T</i> (°C) | CO ₂ desorbed (mg/g) | |
| Na-Y | first cycle | 290 | 2.70 | | | 2.70 |
| | second cycle | 208 | 2.36 | | | 2.36 |
| Cs-Y-h | first cycle | 298 | 2.42 | | | 2.42 |
| | second cycle | 300 | 2.22 | | | 2.22 |
| Cs-Y-c | first cycle | 279 | 0.91 | 610 | 0.85 | 1.76 |
| | second cycle | 264 | 0.80 | | | 0.80 |
| NaY-h | first cycle | 234 | 2.52 | | | 2.52 |
| | second cycle | 245 | 2.43 | | | 2.43 |
| Na-Y-c | first cycle | 249 | 2.14 | | | 2.14 |
| | second cycle | 197 | 0.87 | | | 0.87 |

acid strength shows a slight increase, as it is deduced from the displacement of the NH₃ peak toward higher temperatures. The zeolites treated with carbonate as precursor present both the same strength (Table 1) and the same number of acid sites as the parent zeolite (Figure 3).

Adsorption Studies. (a) Comparison of the Adsorption Capacity Measured by TPD of the Materials. Retention of CO₂ over the studied materials were carried out by successive saturation of the material with pure CO₂ at a given temperature, followed by a TPD up to 620 °C in order to ensure the total absence of CO₂ in the material, either adsorbed or as carbonates (temperatures of carbonates decomposition are 400 °C for Na₂CO₃ and 612 °C for Cs₂CO₃). Previous TPD experiments without saturation with CO₂ did not show any CO₂ release peak. To take into account the chemical modification of the material during the adsorption-desorption cycles, two consecutive cycles were performed. As a general trend, important differences were observed between these cycles, these differences being negligible between the second and the subsequent cycles. Results obtained for the saturation of the samples at 50 °C are shown in the Figure 4 (second cycle), whereas the main results are summarized in Table 3. The desorbed amount of carbon dioxide detected in the TPD experiment is a function of the number of adsorption sites available in the adsorbent surface (evaluated as milligrams of CO₂ per gram of adsorbent), whereas the temperature of the peak is a measurement of the strength of the adsorbate-

adsorbent interactions. As a general trend, desorption takes place on the interval of 200–400 °C (depending on the considered material). However, in some cases, a second desorption peak appears at temperatures around 500–600 °C, a peak that is tentatively associated with the decomposition of alkaline carbonates, whereas the former one is caused by the desorption of adsorbed CO₂.

The proposed treatments largely affect the CO₂ trapping capacity. The parent zeolite shows a relatively low adsorption capacity (2.7 mg/g), decreasing to 2.36 mg/g in the second cycle. For a conventional activated carbon, the total retention capacity (measured by the same procedure) is of about 11 mg of CO₂/(g of sorbent).

The treatment of the parent zeolite with sodium hydroxide solution hardly affects the trapping capacity of the parent material, whereas the treatment with Na₂CO₃ even leads to a marked decrease of the adsorption capacity after the second adsorption cycle. Concerning the Cs-treated zeolites, their retention capacity is lower than that for the parent zeolite: 2.42 mg/g for the hydroxide-treated zeolite and 1.76 mg/g for the carbonate-treated one. For both Cs- and Na-treated zeolites, the CO₂ adsorption capacity measured by TPD remains almost constant in the first and second adsorption cycles for the hydroxide-treated zeolite, whereas it strongly decreased for carbonate precursor. However, in the case of the Cs-Y-c sample, the decrease in the trapping capacity is due to the loss of the desorption peak at high temperature, the low-temperature one remaining constant. Thus, zeolite decarbonation could take place during the first cycle, probably due to the presence of residual CO₂ from the material preparation in the zeolite framework. In the case of the hydroxide precursor, the total retention capacity is higher than 2 mg/g, a value considerably lower than that corresponding to activated carbons (about 11 mg/g). Therefore, modifications of the parent Na-Y zeolite with both sodium and cesium treatments do not enhance significantly the performance of the zeolite as adsorbent at 50 °C, neither as capacity of adsorption nor as the strength of the interaction (since the temperatures of desorption peaks are very similar).

(b) Effect of the Temperature on the Adsorption Capacity Measured by TPD. Adsorption-desorption cycles were carried out by performing the adsorption at higher temperatures (100 and 200 °C) in order to evaluate the effect of the adsorption temperature in the retention capacity. This behavior is a key point for the industrial application of the adsorbents, since off-gases of combustion processes are usually at high temperatures and activated carbon-based adsorbents are unable to adsorb CO₂ at temperatures higher than 75 °C. The results for these experiments are summarized in Figure 5, whereas the total retention capacities in the first and second adsorption-desorption cycles are reported in Tables 4 and 5.

No significant differences between CO₂ desorbed in the first and second cycles can be observed, with the exception of the lower adsorption capacity observed for adsorption at 100 °C. In all cases, the amount of CO₂ retained tends to decrease as the temperature increases, suggesting—in good agreement with the negligible desorption at temperatures above 500 °C—that the retention is controlled by the adsorption (an exothermic process) rather than by caustification reactions (endothermic).

The behaviors of the parent, the Na-treated, and the Cs-treated zeolites are quite different. The parent zeolite shows a continuous decrease of the retention capacity with the temperature, the total adsorption capacity at 200 °C being about 0.2 mg/g in the second cycle. In the case of both Na-treated zeolites, the amount of adsorbed CO₂ also decreases with the temperature, although

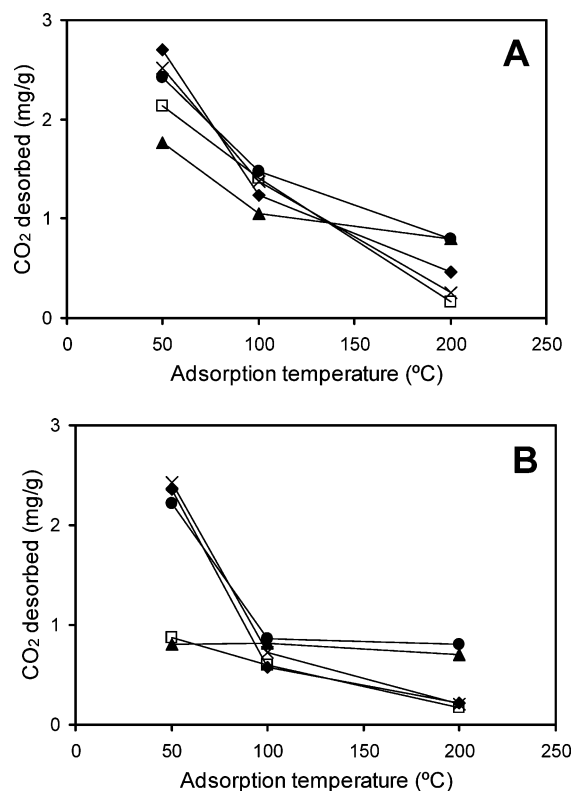


Figure 5. Influence of temperature on the capacity of adsorption: (A) CO₂ desorbed in the first cycle and (B) CO₂ desorbed in the second cycle [Na–Y (◆), Cs–Y–h (●), Cs–Y–c (▲), Na–Y–h (×), and Na–Y–c (□)].

Table 4. CO₂-TPD Results for the Zeolites Tested (CO₂ Adsorption at 100 °C)

| zeolites | | first desorption peak | | second desorption peak | | total CO ₂ desorbed (mg/g) |
|----------|--------------|-----------------------|---------------------------------|------------------------|---------------------------------|---------------------------------------|
| | | T (°C) < 475 °C | CO ₂ desorbed (mg/g) | T (°C) > 475 °C | CO ₂ desorbed (mg/g) | |
| Na–Y | first cycle | 287 | 1.24 | | | 1.24 |
| | second cycle | 168 | 0.58 | | | 0.58 |
| Cs–Y–h | first cycle | 276 | 1.07 | 571 | 0.41 | 1.48 |
| | second cycle | 260 | 0.86 | | | 0.86 |
| Cs–Y–c | first cycle | 282 | 0.90 | 501 | 0.15 | 1.15 |
| | second cycle | 290 | 0.82 | | | |
| Na–Y–h | first cycle | 232 | 1.37 | | | 1.37 |
| | second cycle | 237 | 0.72 | | | 0.72 |
| Na–Y–c | first cycle | 221 | 1.51 | | | 1.41 |
| | second cycle | 236 | 0.60 | | | 0.60 |

the amount of CO₂ retained at 100 °C is slightly higher than in the case of the parent zeolite. Furthermore, no significant differences are observed either between both sodium precursors (carbonate and hydroxide) or between the sodium-treated zeolites and the parent one.

Concerning to the Cs-treated zeolites, the behavior of both materials is different. The zeolite treated with Cs hydroxide presents a marked decrease—in the second cycle—on the retention capacity in the step from 50 to 100 °C, whereas there are no appreciable differences on the retention capacity at 200 °C. Carbonate-treated zeolite decreases considerably the amount of CO₂ retained in the second cycle due to the decrease of the retention at temperatures above 500 °C (caustification processes). However, the retention capacity of this zeolite remains almost constant as temperature increases. So, at the highest studied temperature, this solid presents the highest retention capacity, followed by the zeolite treated with CeOH. The morphological properties (surface area and pore volume)

Table 5. CO₂-TPD Results for the Zeolites Tested (CO₂ Adsorption at 200 °C)^a

| zeolites | | first desorption peak | | total CO ₂ desorbed (mg/g) |
|----------|--------------|-----------------------|---------------------------------|---------------------------------------|
| | | T (°C) < 475 °C | CO ₂ desorbed (mg/g) | |
| Na–Y | first cycle | 295 | 0.46 | 0.46 |
| | second cycle | 266 | 0.22 | 0.22 |
| Cs–Y–h | first cycle | 283 | 0.80 | 0.80 |
| | second cycle | 287 | 0.80 | 0.80 |
| Cs–Y–c | first cycle | 250 | 0.80 | 0.80 |
| | second cycle | 245 | 0.70 | 0.70 |
| Na–Y–h | first cycle | 262 | 0.25 | 0.25 |
| | second cycle | 251 | 0.21 | 0.21 |
| Na–Y–c | first cycle | 234 | 0.16 | 0.16 |
| | second cycle | 229 | 0.17 | 0.17 |

^a No desorption peaks were detected above 475 °C.

are not responsible of the improved behavior on the retention capacity of CO₂ at 100 and 200 °C, since sodium-treated zeolites present higher surface area and microporous and mesoporous volume than cesium ones. In the same way, the desilication is not the only cause of the highest retention capacity at high temperature of Cs–Y–h, since the Na–Y–h zeolite has the lowest aluminum content.

If the behavior of both Cs-treated zeolites is compared, it is observed that they perform similarly, in spite of their different properties. It should be noted that although the chemical properties (basic character according to XPS and TPD) of the carbonate-treated zeolites are more favorable for CO₂ adsorption, the content of Cs is lower than that corresponding to the hydroxide-treated ones, this Cs being more homogeneously distributed in the zeolite structure. It must be considered that Cs participates in the CO₂ retention, but the formation of surface carbonates could hinder the adsorption of CO₂ on the zeolite surface. Furthermore, from XPS data, it was inferred the existence of crystalline Cs₂O on the surface of hydroxide-treated zeolite, which is suggested to be an active species for the CO₂ uptake.¹⁷

(c) Effect of Water on the Adsorption of CO₂. Water is an important component of flue gas and can compete with CO₂ to react with active adsorption sites of the zeolite. Furthermore, it has a detrimental effect on the stability of the adsorbent. Therefore, the influence of water on the adsorption of CO₂ was investigated at 50 °C according to the procedure outlined in the Experimental Section. Figure 6 compares the capacity of adsorption of CO₂ measured by TPD after water desorption, with the retention without water adsorption over the zeolite in the second cycle. The parent zeolite presents a marked decrease in the carbon dioxide retention after the treatment with water. However, the Na–Y–h zeolite exhibits an enhancement in of the CO₂ retention capacity of 12%—respecting the second cycle—after water desorption. In the case of cesium-treated zeolites, especially in desorption at relatively low temperatures, a promoting effect on the adsorption of CO₂ by the preadsorbed moisture is observed. The amount of carbon dioxide desorbed at temperatures below 400 °C increases in 9% for Cs–Y–h and 24% for Cs–Y–c. The presence of CO₂ desorption is also observed in the high-temperature zone, although it supposes a very low fraction of the total retained CO₂ (less than 10%).

From NH₃-TPD experiments, it was deduced that the number of acid sites after alkaline treatments (both CsOH and NaOH) increased, as well as the acid strength. This increase in the strong acidity reveals that part of the Al does not remain tetrahedrally coordinated,²⁰ but this nonframework aluminum could generate strong Lewis acid sites²⁸ that in the presence of water would

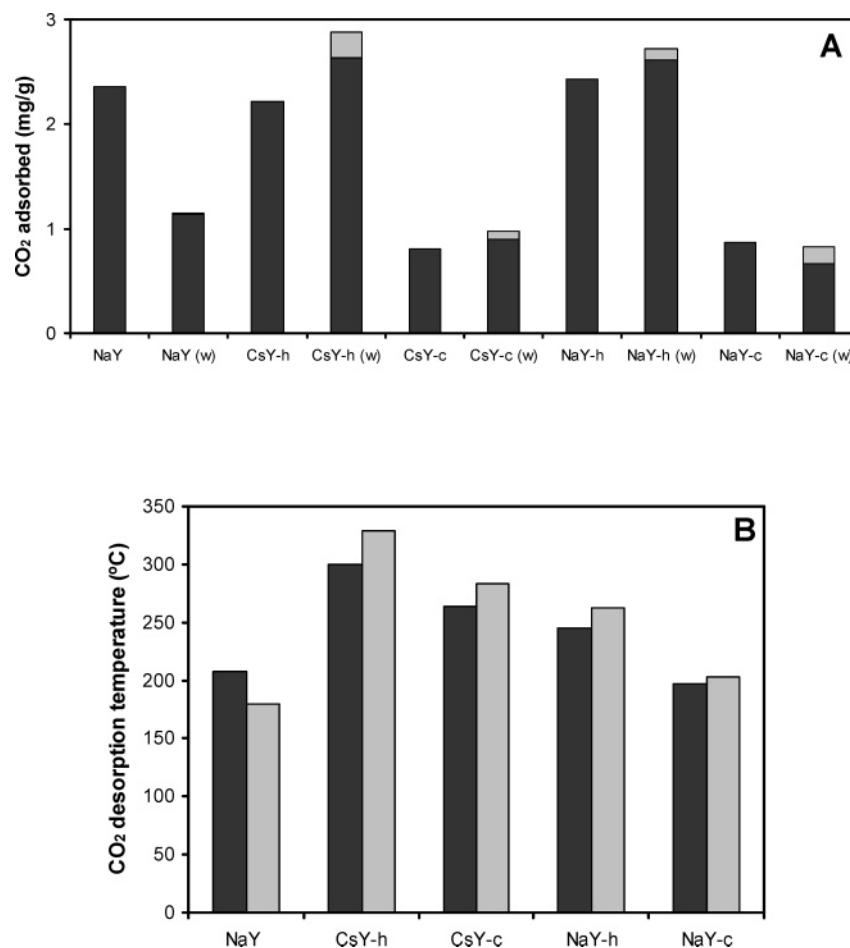


Figure 6. Influence of the previous adsorption–desorption of water in the CO₂ adsorption properties for the studied zeolites: (A) adsorbed amount (black columns correspond to CO₂ desorbed in the first peak and gray in the second peak); (B) main desorption temperature (black, without water treatment; gray, after water treatment).

generate Bronsted acid sites. In this way, Kustov and Sachtler²⁹ studied the effect of the presence of water during the reduction of Pt, Pd–Na–Y and Pt, Pd–H–Y catalysts following the characteristic bands, in IR spectra, of Lewis sites by the interaction with CO molecules. They observed that the presence of water before or during the reduction removed strong Lewis acid sites in decationized zeolites (no Lewis sites were detected in the sodium form). Presumably water was strongly adsorbed on these sites, and it was not desorbed under the conditions of reduction and further with helium. Water molecules coordinated to Lewis sites could create new Bronsted acid sites. This enhancement in the Bronsted acidity would increase the capacity of adsorption of CO₂ for the alkaline-treated zeolites, since the hydroxyl groups of the Bronsted acids could be the responsible of the formation of bicarbonates.³⁰ In the same way, Inui et al.⁸ verified that the Bronsted acidity enhanced the physisorption of CO₂.

However, it is remarkable that the increase in the retention capacity of CO₂ after water treatment is more important for cesium alkaline treated zeolite than for a sodium one. Thus, add to the Bronsted acidity creation in the alkaline-modified zeolites the incorporation of cesium into the zeolitic structure has an effect on the CO₂ retention capacity. It is known that the presence of steam can affect the acidic properties of the zeolites via alteration of aluminum ordering in the framework.³¹ The water molecules create the first hydrogen bonds with oxygen atoms coordinated with the alkali cations in the pores. According to Schenkel et al.,³² who studied the interaction of several molecules with alkali metal exchanged zeolites, the

hydrogen bonds between OH groups and zeolite oxygen are weaker on Cs–X than on Na–X, since the size of Cs⁺ cations reduces the formation of ordered hydrogen bonds with the lattice oxygen. Thus, the grade of alteration of aluminum framework should be less important for the cesium-modified zeolites than for the sodium ones. Furthermore, the presence of cesium in the structure induces changes in the carbon dioxide adsorption, since the main desorption peak of carbon dioxide is displaced toward higher temperatures (Figure 6). Gallei and Stumpf³³ attributed this displacement to the shift in the temperature of formation either of the free carbonate or monodentate carbonate to higher temperatures in presence of water.

4. Conclusions

Treatment of Y zeolites with Cs solutions leads to promising materials for CO₂ adsorption processes at relatively high temperatures. Cs treatment modifies the crystallographic structure, the morphological properties, and the surface chemistry of the parent material, because of both the Cs–Na ion exchange and the zeolite framework desilication.

Although the adsorption capacity of the materials is very similar to that of parent and Na-treated zeolites at 50 °C, at the highest temperatures studied, Cs-treated zeolites perform clearly better.

Concerning the effect of a previous adsorption–desorption of water on adsorbents performance, the Cs treatment seems to completely change the behavior of the adsorbent. Thus, whereas the retention capacity of the parent zeolite decreases after this

treatment and of the Na-treated ones remains almost unaltered, the retention capacity of the Cs-treated materials increases after this treatment.

Acknowledgment

The authors acknowledge M. A. G. del Cura (Laboratorio de Petrología Aplicada, Unidad Asociada CSIC-UA, Alicante, Spain) for her kind help in the determination of surface compositions of the samples.

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Received for review May 15, 2007

Revised manuscript received October 15, 2007

Accepted October 19, 2007

IE070685C