

Study of the Temperature-Programmed Desorption of Carbon Dioxide (CO₂) on Zeolites X Modified with Bivalent Cations

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Abstract

Study of physisorbed and chemisorbed carbon dioxide (CO₂) species was carried out on the NaX zeolite modified by cationic exchanges with bivalent cations (Ca²⁺ and Ba²⁺) by temperature-programmed desorption of CO₂ (CO₂-TPD). Others results were obtained by infrared to complete the study. The results of this research showed, in the physisorption region (213 - 473 K), that the cationic exchanges on NaX zeolite with bivalent cations increase slightly the interactions of CO₂ molecule with adsorbents and/or cationic site. Indeed, the desorption energies of physisorbed CO₂ obtained on the reference zeolite NaX (13.5 kJ·mol⁻¹) are lower than that of exchanged zeolites E-CaX and E-BaX (15.77 and 15.17 kJ·mol⁻¹ respectively). In the chemisorbed CO₂ region (573 - 873 K), the desorption energies related to desorbed species (bidentate carbonates: CO_3^{2-}) on the exchanged zeolites E-CaX and E-BaX are about 81 kJ·mol⁻¹, higher than the desorbed species (bicarbonates: HCO₃) on the reference R-NaX (62 kJ·mol⁻¹). In addition, the exchanged E-BaX zeolite develops the secondary adsorption sites corresponding to bicarbonates species with desorption energies of 35 kJ·mol⁻¹ lower to desorption energies of bicarbonates noted on the reference zeolite NaX.

Keywords

Adsorption, Faujasite X, Chemisorbed and Physisorbed CO₂, Exchanged Zeolites, Bivalent Cations, Temperature-Programmed Desorption (TPD), Infrared

1. Introduction

Nowadays, about 80% of annual emissions of greenhouse gases are attributed to carbon dioxide (CO₂). And these emissions of CO₂ have rapidly increased in the atmosphere during the last 200 years [1] [2] [3]. This increase of CO₂ concentrations is due to anthropic activities such as the fluid catalytic cracking, combustion processes and other industrial activities which are responsible to many environmental problems [4] [5]. Therefore, it is a great urgency to reduce the CO₂ concentration from the atmosphere.

Technologies including membrane separation, absorption with solvent and adsorption using adsorbents porous have been successful for the trapping of CO2 from flue gas [6] [7] [8] [9] [10]. In that way, processes for CO_2 trapping from gas stream based on the adsorption/desorption using porous basic materials such as natural or synthetic faujasite-type zeolites, have shown promising results [1]. Zeolite-types adsorbents are widely used as compound for gas separation and purification, ion exchange, and catalysis [11]. According to literature, the experimental results when using faujasite X-type zeolites as adsorbents for CO₂ are better that to others zeolites such as faujasite Y-type zeolites and other zeolites [12] [13] [14]. More recently, several experiments have been conducted on CO_2 adsorption using X-type zeolites exchanged with monovalent or bivalent cations to evaluate the effects of the crystal structure and the nature of the ion on the capacities CO₂ adsorption [11] [12] [15] [16]. Moreover, experiments on infrared spectroscopy by Fourier transformation infrared (FTIR) and CO₂ temperature-programmed desorption (TPD) on X-type zeolites have shown two types of adsorption onto the surface: a physisorption attributed to adsorbed CO₂ linearly linked onto cationic sites and a chemisorption attributed to adsorbed CO_2 as bicarbonates (HO-CO₂⁻ or HCO₃⁻), and unidentate or bidentate carbonates species (CO_3^{2-}) [17] [18]. As previously published by our team, study on the physisorbed CO₂ by TPD-CO₂ further concludes that the addition of small amounts of magnesium oxide on faujasite zeolites of X-type improved the interactions of physisorbed CO_2 without noticeable increase of the chemisorptions [18].

In this work, we studied sodium cation exchange (Na^+) by bivalent cations $(Ba^{2+} \text{ and } Ca^{2+})$ to increase the strength of the basic sites and thus the interactions between CO₂ and the cation and/or with porosity (adsorbent). Then, we have evaluate the influence of barium and calcium on the capacities of CO₂ adsorption of CO₂ physisorbed and chemisorbed species and it's desorption energies at low and high temperature using the CO₂ temperature-programmed desorption as the primary technique. Infrared analysis was carried out in complement for the identification of adsorbed species on adsorbents.

2. Experimental

Zeolite used as reference adsorbent is a faujasite type zeolite NaX (Axens: Si/Al ratio = 1.2). The exchange of the sodium cations by calcium and barium cations has been

obtained by cationic exchange using $CaCl_2$ and $Ba(NO_3)_2$ from Sigma-Aldrich (purity > 99%) and Pro-Lab (purity > 96%) respectively.

2.1. Cationic Exchanges

Protocol for cationic exchanges is the same used in recent studies [16] [18]. 3 g of NaX zeolite were placed under agitation in 250 mL during 24 hours (h) in an aqueous solution containing 0.02 mol·L⁻¹ of the metal nitrate or chloride ([Ba²⁺] = [Ca²⁺]). The samples was then filtered, then washed with an ultrapure water (3 × 40 mL) to eliminate the free nitrate or chloride ions into the adsorbents. The solids was then dried during 24 h at 373 K in a furnace. Exchanged zeolites were been sieved to have a particle size between 0.2 and 0.4 mm. In this study, all samples obtained by cationic exchanges and the reference will be designated respectively by letters E and R. For example R-NaX (Reference NaX) and E-CaX and E-BaX (Exchanged zeolites by the calcium and Barium).

2.2. Adsorbents Characterizations

Characterization techniques and protocols used in this work are the same as those applied in recent studies [16] [18].

Thermal stability and mass losses of samples were obtained using an SDT-Q-600 TA instrument with a stream of dry argon (100 mL·min⁻¹) in a temperature range between 298 and 873 K, with a 5 K·min⁻¹ ramp.

The specific surface area and pore volumes were obtained using a Micromeritics TRISTAR 3000 instrument with automatic injection of nitrogen, where about 100 - 150 mg of sample was pre-treated during 1 h at 363 K then at 623 K during 10 h.

The N_2 physisorption isotherms were carried out at 77 K. The specific surface area was determined by the BET method, and the micropore volume was estimated through the t-plot method, applied to a layer thickness between 5 and 7 Å, and the Dubinin-Raduskevitch method. Therefore, the mesopore volume was determined by the difference between the total pore volume, determined at 0.97 P/P₀, and the total porous volume obtained by the Dubinin-Raduskevitch method.

X-ray diffraction (XRD) patterns were registered at room temperature using a Siemens D5005 low-resolution diffractometer using Cu K*a* monochromatic radiation ($\lambda = 0.154050$ nm). The samples were scanned in the 3° - 70° (θ) range with a 0.01 (θ) step and a scanning speed of $0.1^{\circ}(\theta)$ /min. Structural Rietveld refinements were carried out using the Fullprof program.

2.3. CO₂ Adsorption/Desorption

Protocols on carbon dioxide thermal desorption (CO₂-TPD) measurements are the same used by T. Belin *et al.* [18].

2.4. Infrared Experiments

Protocols of Fourier transformed infrared (FTIR) measurements are the same

used by T. Belin et al. [18].

2.5. Theoretical Aspects

Desorption energies of CO_2 on adsorbents were calculated using the method of Cvetanovic *et al.* [19]. The assumptions are that no readsorption occurs and no diffusional limitations of the desorbed species within the porosity during the process. Values were derived from the following equation [18]:

$$2\ln(T_m) - \ln(\beta) = \frac{E_{des}}{RT_{max}}$$

where T_{max} (or T_m) is the temperature at the peak maximum (*K*), β is the heating rate (K·min⁻¹), E_{des} is the desorption energy (J·mol⁻¹) and *R* is the perfect gas constant (J·mol⁻¹·K⁻¹). Desorbed quantities of CO₂ are determined using a calibration curve, previously established, and representing the TCD signal in function of known CO₂ amounts.

3. Results and Discussion

3.1. Ion Exchange

In **Table 1** are reported the ionic radius of Ca^{2+} , Ba^{2+} and Na^+ , cationic exchange percentages and the global Si/Al molar ratio. The cationic exchange percentage is close to 100% after replacement. The same order of magnitude as those obtained for Chabazite, Beta, X and Y in the preparation of adsorbents for the elimination of CO_2 [16] [20] [21]. Cations are considered as centers of adsorption for CO_2 and that is why their numbers and distribution will have a direct influence on their performances [16] [22].

In contrast, the exchange of monovalent cations by divalent cations results in a decrease in the number of cations and of the electronic density in the cationic supercage [8] [16] [23]. This would cause a loss of the adsorption amounts of carbon dioxide onto zeolites modified with the divalent cations [16] [24].

3.2. DTA-TGA Analysis

Dehydration temperatures of adsorbents are determined by thermal gravimetric and differential analysis (TGA-TDA) and **Figure 1** shows the curves obtained. On the three adsorbents, most of the weight is lost between 300 and 600 K related to the loss of water adsorbed into the pores of the zeolites [16] [24] [25].

 Table 1. Ionic radius of alkali-earth and the cationic exchange percentage obtained on exchanged zeolites.

Adsorbents	Ionic radius (nm)	Ion exchanged (%mol)	Si/Al molar ratio
R-NaX	0.102	-	1.2
E-CaX	0.100	>97.0	1.4
E-BaX	0.135	>98.9	1.2

After 600 and 1023 K, the weight losses are very low. The ratio between the total mass lost in 623 and 1073 K was calculated and the results are shown in **Table 2**. This ratio is very high as it is between 92% and 96%. Compared to reference zeolite NaX and E-CaX. The exchanged E-BaX zeolite shows a ratio more important.

This result is in line with those of Moïse *et al.* [25] who showed that the amount of water adsorbed on MgX zeolite was higher than that adsorbed on NaX zeolite. The author attributed this behaviour to the radius of the cation Mg^{2+} which is higher than that of Na⁺ resulting in a radius of hydration higher for Mg^{2+} .

Thus, for all adsorbents, the minimal required temperature for the activation of exchanged zeolites is of about 623 K [16]. At this temperature, an average of 85% of the adsorbed species have already been desorbed. Then, before each experiment, an outgassing thermal treatment will be carried out in two steps as indicated by T. Belin *et al.* [18].

3.3. N₂ Physisorption

 N_2 adsorption/desorption isotherms obtained on R-NaX and the exchanged zeolites (E-CaX and E-BaX) are shown in **Figure 2**. According to IUPAC norms, the shape of the isotherms is of Type I for all the adsorbents indicating that they can be considered as microporous zeolites. A strong adsorption is observed at low $P/P_{saturation}$ (less than 0.2) followed by a plateau at higher pressure indicating that



Figure 1. TGA curves of NaX reference and exchanged zeolites (heating rate of 5 K·min⁻¹).

 Table 2. Results of structural characteristics and TGA-DTA study obtained on the NaX reference and on exchanged zeolites.

Adsorbents	А _{вет} (m².g ⁻¹)	V _{total pore} (cm ³ .g ⁻¹)	V _{microporous} (cm ³ .g ⁻¹)	mass loss up to 623 K (wt%)	mass loss up to 1073 (wt%)	623 K/1073K Ratio (wt%)
R-NaX	590	0.317	0.300	22.05	23.93	92.14
E-CaX	492	0.285	0.274	16.93	18.05	92.16
E-BaX	349	0.200	0.193	16.21	16.72	96.95



Figure 2. Isotherms of N_2 physisorption obtained on the reference zeolite NaX and onexchanged zeolites.

no more adsorption occurs. From these isotherms, BET surface areas and microporous and total porous volumes have been calculated (**Table 2**). Discussions of its results on the reference NaX and exchanged BaX have been widely discussed on previous studies [16] [18].

However after cationic exchange, there is a decrease of BET surface areas and the microporous volumes. It seems that the main cause of these losses BET surface areas and the microporous volumes is the decrease of cationic density into supercage of faujasite X or to a plugging of the porosity as indicated by Chandwadkar *et al.* in these studies [20] [21]. These losses are also related to the quality of cationic exchange. They increase when the cationic exchange rate is important (**Table 1** and **Table 2**).

Ammoudi [20] also made the same observations during cationic exchanges of Cu^{2+} on zeolite X with different rates. However, since the CO_2 adsorption occurred mainly into the micropores, a significant decrease in the accessible pore volume would result in a loss of CO_2 amounts adsorbed into exchanged zeolites [18].

3.4. XRD Analysis

Results of this analysis do not show amorphous phase on these diffractograms. The crystalline structure of the faujasite X does not seem to be modified after cationic exchange since the significant XRD peaks of reference NaX remain visible for the XRD spectrum of the exchanged zeolite (**Figure 3**).

Moreover, the data of these XRD spectra indicates the absence of parasite phase and/or impurities within the detection limit of the apparatus (~2%) for E-BaX and E-CaX. On the other hand contrary to E-CaX, the diffractogram of the E-BaX zeolite shows some peaks more intense in the region between 10° and 45°. This is probably due to new arrangement of cationic sites within of the X zeolite structure [16].

3.5. FTIR Analysis

The FTIR analysis of all adsorbents was performed in the range between 4000 and 1000 cm⁻¹. Hydroxyl groups (HO⁻), the linearly adsorbed CO₂ on the cationic sites (CO₂-Na⁺), the bicarbonates (HCO₃⁻), the unidentate and bidentate carbonates (CO₃²⁻) are the species studied in this region [18] [26].

The spectra obtained at 373 and 473 K on the reference zeolite (R-NaX) and exchanged zeolites (E-CaX and E-BaX) are shown in Figure 4. Differences



Figure 3. XRD patterns of the reference zeolite NaX and exchanged zeolites (Cu Ka = 0.154050 nm).





between the samples are visible and two main domains are studied: 2400 - 2200 cm⁻¹ and 1800 - 1000 cm⁻¹. These regions are respectively attributed to the physisorbed and chemisorbed CO₂ species [18] [23] [27] [28]. In the domain of the physisorbed CO₂ at 323 K (**Figure 4(a)**) all adsorbents show a band of physisorbed CO₂. These zeolites present the adsorption sites of CO₂ at this temperature. However, the intensity of the absorption band of exchanged E-CaX remains higher than that of two others adsorbents (**Figure 4(a)**). The amounts of physisorbed CO₂ are thus more important on this adsorbent at 373 K, which can translate strong interactions CO₂/cation.

At 473, a quasi-disappearance of the band of physisorbed CO₂ is observed on zeolites R-NaX (**Figure 4(b)**). Exchanged zeolites E-CaX and E-BaX show a band of low intensity. Bonenfant *et al.* [12] explained that a loss of the CO₂ adsorbed capacities is generally expected on the NaX zeolite when the temperature increases, due to the thermal agitation in the zeolite pores. Thus, a decrease of the microporous volume is only sufficient to explain the intensities of this band whatever the modification process [18]. However, the absorption band obtained on E-BaX is more intense than that of E-CaX (**Figure 4(b**)), which indicates an amount of physisorbed CO₂ more important present at this temperature. This remains in conformity with the basic force of exchanged cation (Ba²⁺ > Ca²⁺). It seems in this case, that a reinforcement of the alkalinity of the cationic sites in the reference zeolite NaX would increase the trapping of physisorbed CO₂ at high temperatures on the cationic sites.

In the chemisorbed CO₂ domain (1800 - 1200 cm⁻¹), R-NaX zeolite shows three bands well defined at 373 and 473 K. These bands are identified as unidentate carbonates at 1691 and 1360 cm⁻¹ ($CO_3^{2-}: v_{as}OCO$ et v_sOCO respectively) and as water or bicarbonates at 1642 cm⁻¹ ($HCO_3^{-}: v_{as}OCO$ ou $v_{as}H_2O$) [18] [28] [29]. The presence of bands due to carbonate groups revealed that the framework oxygen atoms surrounding the cations in the reference NaX zeolite behave as stronger basic centers [30]. Contrary to R-NaX, at 373 K, exchanged E-CaX shows only the presence of monodentate and bidentate carbonates (1672 cm⁻¹ and 1628 cm⁻¹) and on the exchanged E-BaX, only the bicarbonates are show (1650 cm⁻¹). It seems that at 373 K (Figure 4(b)) the bicarbonates and bidentate carbonates are majority on exchanged zeolites (E-BaX and E-CaX respectively).

At 473 K, there is the appearance of two bands at 1480 cm⁻¹ and 1420 cm⁻¹ on reference R-NaX corresponding to bidentate carbonates. A decrease intensity of bicarbonates (1642 cm⁻¹) is observed. The monodentate carbonates (1700 and 1350 cm⁻¹) are always present. However, the amount of the carbonates is reduced by the temperature as evidenced with the slight decrease of bands intensities. The spectra obtained on exchanged E-BaX (**Figure 4(b)**) indicate that the bicarbonates (1642 cm⁻¹) are majority, in front of bidentate carbonates (1360 cm⁻¹). For the exchanged E-CaX, the majority species remain are the bidentate carbonates (1628 cm⁻¹). We will tend to associate the energies desorption of each type of CO₂ species.

3.6. CO₂ Thermal Desorption: CO₂-TPD

The thermal desorption curve obtained show two regions (Figure 5) which are attributed to physisorbed (200 - 400 K) and chemisorbed CO_2 species (above 600 K) [18] [31]. For each region, these curves associated with the desorbed amount are deconvoluted using Gaussian functions and the peaks are indexed. These peaks represent the minimum number to avoid the errors between experimental and theoretical profile [18] in its study of physisorbed CO_2 on NaX zeolite. It was then possible to estimate the temperature of maximum desorption, to calculate the amounts and the desorption energies of physisorbed and chemisorbed species of adsorbed CO_2 .

Table 3 recapitulates the total amounts adsorbed and desorbed of CO_2 obtained after exploitation of thermal desorption curves to 2, 4, 6 and 10 K·min⁻¹ for R-NaX and of exchanged zeolites. The amounts of adsorbed and desorbed CO_2 on reference R-NaX zeolite (4.041 and 3.103 mol·g⁻¹ respectively) are higher than exchanged zeolites (**Table 3**). On the other hand, it is interesting to note



Figure 5. Thermal desorption curve of CO₂ obtained on R-NaX at 4 K·min⁻¹ in a temperature range between 213 and 873 K.

Table 3. Total amounts adsorbed and desorbed of CO_2 obtained after exploitation of thermal desorption curves to 2, 4, 6 and 10 K·min⁻¹ with the reference NaX and of exchanged zeolites.

Adsorbed CO ₂ amounts (mol·g ⁻¹)		desorbed CO2 amounts (mol·g ⁻¹)			Ratio (% mol)	
Samples	Total	Total	Physisorbed	Chemisorbed	$\underline{CO_2}$ desorbed CO_2 adsorbed	<u>CO2</u> desorbed CO2 adsorbed
R-NaX	4.041	3.103	2.874	0.229	76.8	8.0
E-CaX	3.523	2.627	2.206	0.421	74.6	19.1
E-BaX	2.885	2.774	2.473	0.301	96.2	12.2

that the CO_2 desorbed percentage increases with the alkalinity of the cation (**Table 3**). This must be also close to the specific loss of surface and to microporous volume observed during textural analysis.

The total amount adsorbed decreases with the reduction of porous volume but the difference between adsorbed and desorbed amount is also reduced. This observation must be relativized by the observation of the relationship between amounts desorbed and adsorbed.

For example, approximately 77% of the species are desorbed on the zeolite of R-NaX reference. The residue seems be irreversibly adsorbed. A decrease of physisorbed CO₂ amounts is also observed on exchanged zeolites E-CaX and E-BaX. These results also can be explained by the fact that the cationic density is decreased in the supercage during the cationic exchanges with bivalent cations $(2Na^+ \text{ for } 1M^{2+})$ [10] [12] [32] and that specific surface is decreased. Desorbed amounts of chemisorbed CO₂ on exchanged zeolites are higher than those obtained on the R-NaX reference. This seems related to the basic character of the cations Ca²⁺ and Ba²⁺ which is higher than Na⁺. However, exchanged zeolite E-BaX shows a total desorbed amount near to 100% at 873 K (**Table 3**) and an average proportion of chemisorbed absorbed species ($\approx 12\%$), contrary to E-CaX which shows an average proportion of 19.1 with a total desorbed amount (about 75%) near to reference R-NaX zeolite (**Table 3**). For the adsorption /desorption processes, the exchanged zeolite E-BaX can be interesting.

In CO₂ physisorbed region (210 K - 450 K), the deconvoluted curves using Gaussian functions obtained to 2 K·min⁻¹ on exchanged E-BaX, E-CaX zeolites and on R-NaX are show on **Figure 6**. The maximum desorption temperature T_m determined is also indicated.

Desorption energies calculated for the CO_2 physisorbed (and chemisorbed) to the maximal desorption temperature (T_m) after exploitation of curves to 2, 4, 6 and 10 K·min⁻¹ des adsorbents studied are recapitulated in **Table 4**. Reference NaX zeolite indicates a desorption energy of CO_2 physisorbed equal to 13.47



Figure 6. Physisorbed region of R-NaX, E-BaXand E-CaXthermal desorption curvesafter deconvolution using Gaussian functionsat 4 K·min⁻¹.

	CO ₂ desorption energies (kJ·mol ⁻¹)			
	Physisorbed	Chemisorbed		
Adsorbents	CationCO ₂	HCO_3^-	CO ₃ ²⁻	
R-NaX	13.47	62.34	u.d	
E-CaX	15.77	u.d	81.06	
E-BaX	15.17	35.27	80.82	

Table 4. The desorption energies of physisorbed CO_2 correlated to the maximum desorption after exploitation the thermal (CO₂-TPD) desorption curves to 2, 4, 6 and 10 K·min⁻¹.

u.d: undefined.

kJ·mol⁻¹. These obtained on exchanged zeolites E-CaX and E-BaX are comparable (15.77 and 15.07 kJ·mol⁻¹ respectively) and higher than those obtained on R-NaX.

It seems that the cationic exchanged with bivalent cations (Ba²⁺ and Ca²⁺) increase CO₂ interactions at low temperature with adsorbents. This slight increase of energy can be attributed to basic character of the cation (Na⁺ < M²⁺ or M = alkaline earth metal ions) [12]. CO₂ molecule will be, in cases, linked more strongly on the cation most basic. In addition, a study realizes by Aguilar *et al.* on the CO₂ adsorption on the clinoptilolite has indicated that the substitution of Na⁺ and K⁺ by Ca²⁺ caused a rise of the basicity of the framework oxygen acting as basic center [33]. Others studies carried out by Krista *et al.* [11], on the CO₂ adsorption by X and Y zeolites exchanged with alkaline metal, have shown an increase of CO₂/zeolite when the cation size increases. And according to them, this is related with an increase of basicity of the framework compared to the smaller cation forms.

Contrary to desorption profiles obtained in physisorbed region, the desorption profiles in CO_2 chemisorbed region between 523 - 813 K of exchanged zeolites (E-BaX and E-CaX) are very different compared to that obtained on reference NaX zeolite (**Figure 7**). In the region of the exploited temperatures, the desorption profile of R-NaX shows one massif with a maximal desorption temperature (T_{m1}) about 673 K.

The E-BaX desorption profile shows two massifs. One with a maximal desorption temperature (T_{m1}) belong 673 K and another with temperature (T_{m2}) above 673 K. This adsorbent seems developed of adsorption sites, at high temperature, lower than those of reference NaX in the temperature region studied. On exchanged E-CaX zeolite, one massif only is observed with a maximal desorption temperature (T_{m1}) higher to that determined on R-NaX and comparable to that determined on E-BaX zeolite (**Figure 7**).

The infrared spectra results at 473 K (Figure 4(b)) for the exchanged E-CaX, the majority species remain mainly the bidentate carbonates with the CO_2 adsorption sites more homogeneous on the surface than other exchanged. It



Figure 7. Chemisorbed region of thermal desorption curves obtained after deconvolution using Gaussian functions on (a) reference zeolite NaX and the exchanged zeolites (b) E-BaX and (c) E-CaX at $4 \text{ K} \cdot \text{min}^{-1}$.

appears therefore that the species of CO₂ chemisorbed to peak of maximal temperature desorption ($T_m > 673$ K), on exchanged E-CaX and E-BaX zeolites ($T_{m\,1}$ and $T_{m\,2}$ respectively) are bidentate carbonates (Figure 7). Thus, desorption energies related of these species on E-CaX and E-BaX zeolites are about 81.1 and

80.8 kJ·mol⁻¹ respectively (**Table 4**). It seems that cationic exchanges no change the desorption energies of bidentate carbonates on faujasite X zeolites.

The infrared spectra obtained on exchanged E-BaX (Figure 4(b)) indicate that the bicarbonates are majority, in front of bidentate carbonates on the surface of the zeolite. Thus, CO₂ chemisorbed species with a maximal temperature desorption belong to 623 K ($T_{m\,1} < 623$ K) correspond to bicarbonates (Figure 4(b)) and the associated energies on E-BaX are about 35.3 kJ·mol⁻¹, corresponding to secondary adsorption sites (Table 4). On reference NaX zeolite, related energies bicarbonates are about of 62.3 kJ·mol⁻¹. Compared to R-NaX zeolite, on E-BaX zeolite a decrease of CO₂ desorption energy of bicarbonates is observed (35.27 kJ·mol⁻¹). It seems that the desorption energies of bicarbonates decrease and depending on the type of exchanged cation.

On other hand, in the literature, the isosteric heat of adsorption (Q_{st}) varies between 40 and 46 kJ·mol⁻¹ [10] [32].

Desorption energy of bicarbonate does not correspond to the Q_{st} value found in the literature, but seems to be near. Then, the determination of Q_{st} value on NaX zeolite will be principally assigned to chemisorbed species. Amine khelifa *et al.* [10] have also observed a decrease of Q_{st} values when Na⁺ is exchanged with Mg²⁺ cation within the NaX zeolite.

4. Conclusions

The faujasite NaX was used as reference for the cationic exchanges with bivalent cations (Ca^{2+} and Ba^{2+}) to study the influences of the cations on physisorbed and chemisorbed carbon dioxide (CO_2) species by temperature-programmed desorption of CO_2 (CO_2 -TPD). Infrared analysis was carried out in complement for the identification of adsorbed species on adsorbents.

The analysis of infrared spectra at 473 K showed that the majority adsorbed species on reference NaX are mainly the bicarbonates, the unidentate and bidentate carbonates. On exchanged zeolites (E-CaX and E-BaX) the mainly species are the bicarbonates and the bidentate carbonates. The linearly adsorbed CO_2 on the cationic sites is also present but very small proportion at this temperature. However compared to other adsorbents, the exchanged E-BaX zeolite shows the highest proportions.

As expected with the CO_2 -TPD experiments, the profiles of CO_2 desorption on zeolites revealed two distinct zones. A CO_2 physisorbed region (213 - 373 K) and other CO_2 chemisorbed region (573 - 873 K). The CO_2 adsorbed and desorbed amounts and the CO_2 desorption energies which are associated to the physisorbed and chemisorbed species were calculated.

The amounts of CO₂ adsorbed obtained on R-NaX (4.041 mol·g⁻¹) are higher than those obtained on exchanged E-CaX and E-BaX zeolites (3.523 and 2.885 mol·g⁻¹ respectively). The influence of the microporous volume of the zeolite is clearly evidenced on the experimental CO₂-TPD. The total amounts of CO₂ desorbed on R-NaX (2.874 mol·g⁻¹) are also higher to E-CaX and E-BaX (2.627 and 2.774 mol·g⁻¹). On the other hand, the exchanged zeolite E-BaX shows a total desorbed amount near to 100% at 873 K, unlike R-NaX and E-CaX zeolites where the total desorbed amounts are evaluated at about 75%. It seems that on its two adsorbents, carbon dioxide is irreversible adsorbed.

In the CO₂ physisorbed region, the CO₂ desorbed amount obtained on R-NaX is 2.874 mol·g⁻¹ and the desorption energies related to physisorbed species at the maximal temperature desorption are 13.43 kJ·mol⁻¹. The amounts obtained on E-CaX and E-BaX (2.206 and 2.473 mol·g⁻¹ respectively) are lower compared to R-NaX. On the other hand, the CO₂ desorption energies related to CO₂ physisorbed obtained on exchanged E-CaX and E-BaX zeolites are 15.77 and 15.17 kJ·mol⁻¹ respectively, higher than that of the reference R-NaX zeolite (13.47 kJ·mol⁻¹). Thus, it appears that the cationic exchanges carried out do not improve the adsorption capacities of carbon dioxide physisorbed but increase the interactions of CO₂/cation or CO₂/adsorbent in the low temperatures region (213 - 373 K).

In the CO₂ chemisorbed region (573 - 873 K), the desorbed amounts of CO₂ chemisorbed species of exchanged E-CaX (0.421 mol·g⁻¹) and E-BaX (0.301 mol·g⁻¹) zeolites are higher than those obtained on the reference R-NaX (0.229 mol·g⁻¹). The desorption energies related to desorbed species (bidentate carbonates: CO_3^{2-}) on E-CaX and E-BaX are about 81 kJ·mol⁻¹, higher than the desorbed species (bicarbonates: HCO_3^-) on the reference R-NaX (62 kJ·mol⁻¹). However, the exchanged E-BaX zeolite develops the secondary adsorption sites corresponding to bicarbonates species with desorption energies of 35 kJ·mol⁻¹ lower to desorption energies of bicarbonates noted on R-NaX. The exchanged E-BaX zeolite can be used in the processes of CO₂ adsorption/desorption for the carbon dioxide recovery. It desorbs near to 100% of CO₂ species at 873 K and has low energies CO₂ adsorption sites at high temperature (573 - 873).

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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