

Study of the Adsorption Space of Modified Clinoptilolites

Rolando Roque-Malherbe, Alba N. Costa-Hernandez, Christymarie Rivera-Maldonado, Frances N. Lugo-Alvarado and Ramon Polanco-Estrella

Institute for Physical Chemical Applied Research, School of Science, University of Turabo, Gurabo, PR 00778-3030, USA

Received: February 14, 2013 / Accepted: March 15, 2013 / Published: May 25, 2013.

Abstract: Carbon dioxide (CO₂) adsorption is an important adsorbent characterization method and a significant industrial process. In separation and recovery technology, the adsorption of the CO_2 is important to reduce the concentration of this gas considered as one of the greenhouse gases. Natural zeolites, particularly clinoptilolite, are widely applied as adsorbents. In this regard, in the present research, the structure, composition and morphology of modified with hexafluorosilicate (HFSi) and orthophosphoric acid (H₃PO₄) clinoptilolites were investigated by characterizations and measurements made with, X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDAX) and gravimetric adsorption. Additionally, the surface Chemistry of the modified clinoptilolites was analyzed by applying diffuse reflectance fourier transform infrared spectrometry (DRIFTS). Further, the interaction of CO₂ within the adsorption space of these modified clinoptilolites and a synthetic ZSM-5 zeolite was studied with the help of adsorption measurements. After all, an appropriate theoretical methodology for the analysis of the XRD and adsorption data was applied. The calculated cell parameters of the tested are similar to those reported for a typical clinoptilolite of: a = 17.662 Å, b = 17.911 Å, c = 7.407 Å and $\beta = 116.40$ The resolution of the TGA derivative profiles indicated the presence of two steps for water release, one of them represents the loss of majority of the water present in the micropores. This was evidenced as a broad peak centered at about 50 °C for the CSW-HFSi-0.1, but at 100 °C for the samples CSW-HFSi-0.4. The SEM micrographs corresponding to the modified clinoptilolites, was evidenced that the CSW zeolite shows secondary particles exhibiting diameters from 3 to 40 µm, formed by primary clinoptilolite crystallites showing a crystallite size, $\Phi = 40$ nm. The EDAX elemental analysis it can be demonstrated that the exchange process replaced about 85% of the charge compensating ions. The DRIFT spectra of the modified clinoptilolites, specifically, CSW-HFSi-0.1, show a narrow band at about: 3,740 cm⁻¹ corresponding to terminal silanol groups (Si-OH) and a band 3,600-3,650 cm⁻¹ resulting from extra-framework Al-OH. With the precision of the measured micropore volumes related to the excellent fitting of the adsorption data by the D-R isotherm equation, it can be affirm that carbon adsorption took only place in the micropore region. The isosteric heat of adsorption calculated for the modified clinoptilolites was greater than those values reported of ZSM-5 zeolite, particle packing silica, dealuminated Y zeolite (DAY) Cd, Zn and Ni-nitroprussides and Cu-nitroprusside and a Ni-MOF. With the obtained result it can be concluded that the modified clinoptilolites with HFSi showed a quality as adsorbent comparable to commercial synthetic zeolites.

Key words: Natural zeolites, modification, clinoptilolite, carbon dioxide, adsorption space, surface chemistry.

1. Introduction

Adsorption is a very important industrial process, and it is the source of many methods for the study of the adsorption space of adsorbents [1-5]. Natural zeolites are significant materials as adsorbents [6-12] and other uses such as, ion exchangers [13, 14], catalysts [15, 16], catalyst supports [17, 18], ion conductors [19, 20], the production of porous [21] and hard ceramics [22]. These minerals are mined from deposits, where the zeolitic phases are mixed, principally, with montmorillonite, quartz, calcite, feldspars, magnetite and volcanic glass [8, 9]. However, in some cases it is possible to find highly pure

Corresponding author: Rolando Roque-Malherbe, professor, research fields: physical chemistry of materials, energy and pollution abatement applications. E-mail: rroque@suagm.edu and rrqoeumalh@aol.com.

materials, to be precise, more than 90 wt% of a single zeolitic phase in the mineral [11, 21]. In this regard, the main reason to conduct this research is the modification of a highly pure natural zeolite adsorbent to produce an adsorbent comparable to synthetic zeolite. In other word, the modification of a powdered clinoptilolite rock to produce a functional adsorbent.

For gas-phase applications commercial zeolites are applied as adsorbents in different bound forms, composed of the zeolite and a binder to produce a reliable adsorption bed and prevent an extreme pressure drop [23]. Typically the zeolite content of the bound form is, in general, around 85-90 wt.% [2]. Clinoptilolite, the most abundant natural zeolite could be found with a zeolite content in the rock up to 85-90 wt.% [9, 21]. Besides, natural zeolite rocks are harder than commercial zeolite bound forms [22]. Further, if natural zeolites are properly crushed, approximately spherical particles, with a diameter 1-10 mm, could be obtained. If these particles are modified by ion exchange and chemical and heat treatments we consider that will be produced materials with more zeolite per weight and with a quality as adsorbent comparable in many applications to commercial zeolites.

The character of the zeolite micropore surface is strongly affected by the nature of their surface sites. In this sense, a zeolite exchanged with ammonium cations, expressed as follow:

 $Na - Zeolite + NH_4^+ \leftrightarrow NH_4 - Zeolite + Na^+$

It can be transformed into an acid zeolite by the thermal decomposition of the exchanged ammonium cations, as follows:

 NH_4 – Zeolite \xrightarrow{heat} H – Zeolite + NH_3

In this situation, protons are connected to the zeolite oxygen atoms forming OH bridged groups. These sites are responsible for the Brönsted acidity of natural and other aluminosilicate zeolites. The hydroxyl bridged groups have been widely studied by, IR spectrometry [24], microcalorimetry [25], nuclear magnetic resonance [26], and other methods [27, 28]. Between other conclusions, it was proposed that the acidity of these sites is related with the ease of the proton to be released, i.e., if the interaction between the proton and the oxygen is weaker the Brönsted site should be more acid and the zeolite more active as an acid catalyst [24-29]. This inference, however, is not totally exact, since other effects, influences the properties of these acid sites [28]. In this regard, sorption effects are responsible for changes in the reaction rates of paraffin cracking, a reaction catalyzed by acid zeolites [30, 31].

One of the methods to increase the acidity of acid zeolites is dealumination. This process can be done for example: by hydrothermal treatments (steaming), acid leaching, or with treatments in flowing silicon tetrachloride (SiCl₄) or hexafluorsilicates ((NH₄)₆SiF₆) [24]. These dealumination methods could increase the amount of zeolite in the sample, eliminate charge compensating cations to open the zeolite channels, create mesopores and increase the adsorption field. All these improvements could lead to a useful adsorbent.

To show that a material is a good adsorbent, carbon dioxide adsorption could provide very useful information about the adsorption space of microporous materials [32], where, the adsorption space, is the three dimensional location, where molecules are subjected to the adsorption force fields [33].

One of the important applications of carbon dioxide adsorption as a characterization tool is the measurement of the: micropore volume, the most important parameter for the geometrical characterization of the adsorption space of microporous materials. Usually, these measurements are carried out with the help of nitrogen adsorption isotherms measured at -196 °C [3, 5]. But at such a low temperature, the transport kinetics of the nitrogen molecules through the micropores is very slow in pores smaller than 0.7 nm. But, in the case of carbon dioxide adsorption, at 0 °C the higher temperature of adsorption applied cause that the carbon dioxide molecules have a bigger kinetic energy; subsequently, they are capable to go into the microporosity for pores of sizes less than 0.7 nm [32]. Therefore, an experimental solution for this difficulty is the use of carbon dioxide adsorption at 0 °C instead of nitrogen at -196 °C, in order to apply the Dubinin adsorption isotherm to describe carbon dioxide adsorption. The obtained data can be used for the determination of the micropore volume and the calculation of the isosteric heat of adsorption in order to qualify the geometry and the nature of the interaction between carbon dioxide and the zeolite framework, allowing, in sum, the characterization of the geometry and the interactions within the adsorption space [5, 10].

Carbon dioxide adsorption is not only an important adsorbent characterization method but it is an important industrial application of adsorbents. In this regard, the separation and recovery of carbon dioxide is a very important research problem; since it is a greenhouse gas which contributes to global warming and a reactant in significant industrial processes; as for example the Solvay process for the production of NaHCO₃ [35-37]. Independently of the molecular carbonaceous adsorbents, sieves, alumina or silica gel can be applied for carbon dioxide separation. The activated alumina is currently considered the most suitable sorbent for removing carbon dioxide from air in the pressure swing adsorption (PSA) process [37]. Nevertheless, cheap and environmentally friendly natural zeolite materials, with high micropore volume and strong surface interaction with the carbon dioxide molecule have potential applications in carbon dioxide separations [38].

In these research the structure, composition and morphology of clinoptilolites modified with hexafluorosilicate (HFSi) and orthophosphoric acid (H₃PO₄), with measurements and characterizations by means of, X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDAX) and gravimetric adsorption measurements.

Further, was studied the surface chemistry of the modified clinoptilolites and the interaction of carbon dioxide with the framework of the modified clinoptilolites, two synthetic ZSM-5 zeolites used for comparison and data previously obtained for the adsorption of carbon dioxide in amorphous silica and a dealuminated Y zeolite [34], a metal organic framework [39], and four nitroprussides [40, 41] by applying diffuse reflectance Fourier transform infrared spectrometry (DRIFTS) and adsorption measurements with the help of an automatic adsorption analyzer. Finally an appropriate theoretical methodology for the analysis of the X-ray diffraction profiles and the adsorption data was applied [5, 34, 39-41]. As far as we know the modification of clinoptilolite with HFSi to improve their adsorption properties had not been previously attempted.

2. Experiments

2.1 Materials and Modification Procedures

All the consumable chemicals were analytical grade without additional purification. The water used in the synthesis process was bi-distilled.

The natural zeolite studied in the present research was a clinoptilolite mined in the deposit located in Sweetwater, Wyoming, USA. The sample was provided by ZeoponiX Inc., Louisville, Colorado. This natural zeolite was labeled Clinoptilolite Sweetwater (CSW). The measured mineralogical composition of this material was, clinoptilolite, 90 ± 5 wt.%, and the rest, montmorillonite (2 wt.%), quartz (2 wt.%), calcite (2 wt.%), feldspars (1 wt.%), magnetite (1 wt.%).

A powdered sample of CSW clinoptilolite of 30 to 40 meshes (0.4-0.6 mm) was modified by an ion exchange treatment with a 1 M ammonium chloride solution (NH₄Cl) to get the sample NH₄-CSW [13]. This solution was prepared with 13.40 g of ammonium chloride in 250 mL of deionized water (DDW). 25 g of natural zeolite were exchanged in

reflux five times with the 1 M NH₄Cl solution at 100 °C, each exchange had a duration of 3 h. This treatment produced an ammonium clinoptilolite that was identified as NH4-CSW. This zeolite was thereafter filtered, washed exhaustively with bi-distilled water and dried in an oven at 70 °C. Further, the ammonium clinoptilolite was dealuminated with a 0.1 M solution of ammonium hexafluorosilicate (HFSi), explicitly: (NH₄)₆SiF₆ [24]. This solution was prepared with 0.05 g of (NH₄)₆SiF₆ in 500 mL of DDW. Another 0.4 M solution was prepared with 0.20 g of (NH₄)₆SiF₆ in 500 mL of DDW. A sample of 10 g of ammonium zeolite was refluxed for four h with 500 mL of 0.1 M (NH₄)₆SiF₆ at 80 °C. The same treatment was given to another 10 g of ammonium zeolite but with a 0.4 M solution of (NH₄)₆SiF₆. Following this treatment, each sample was filtered, washed exhaustively and dried in an oven at 70 °C. Finally each sample was calcined at 500 °C for a period of 2 h. The calcined sample prepared with 0.1 M HFSi was identified as CSW-HFSi-0.1 and the calcined sample prepared with 0.4 M of HFSi was identified as CSWHFSi-0.4.

The natural clinoptilolite was also dealuminated with orthophosphoric acid. To be precise, 20 g of natural clinoptilolite was refluxed with a 4 M solution of orthophosphoric acid (H_3PO_4) at 100 °C, for a period of 20 min. After the treatment with H_3PO_4 the sample was washed and dried in an oven at 70 °C. This treatment resulted in the clinoptilolite dealumination by isomorphous replacement of aluminum atoms by phosphorus atoms [18]. The samples dealuminated with orthophosphoric acid were identified as CSW-H₃PO₄-20 and CSW-H₃PO₄-40.

To compare our data were tested three synthetic zeolites, H-ZSM-5 (CBV-3020, $SiO_2/Al_2O_3 = 32$) and H-ZSM-5(CBV5020, $SiO_2/Al_2O_3 = 53$), both provided by the PQ Corporation and one Na-X, provided by Laporte [12]. Additionally, was studied a homoionic sodium natural clinoptilolite from the deposit located in Castillas, Havana, Cuba,

labeled Na-HC [17]. The mineralogical composition of this zeolite rock labeled HC was clinoptilolite 85 \pm 5 wt.%, and the rest montmorillonite (5-6 wt.%), quartz (3-4 wt.%), calcite (1-2 wt.%), feldspars (1-2 wt.%), magnetite (0-1 wt.%) and volcanic glass (1-2 wt.%) [9]. The HC zeolite was exchanged with a 1 M sodium chloride solution in reflux, five times at 100 °C, for a period of three h to get the Na-HC sample [17]. Finally, the CSW zeolite was exchanged with sodium, following the process applied in the case of the HC sample, to produce the homoinic zeolite Na-CSW [21].

2.2 Characterization Methods.

X-ray diffraction tests were carried out with a Bruker D8 Advance system in a Bragg- Brentano vertical goniometer configuration. The angular measurements were made with a (Theta/2Theta) of \pm 0.0001 reproducibility, by applying steps of 0.01° from 5° to 40° to get XRD profiles that could be accurately resolved by least square methods. The X-ray radiation source was a ceramic X-ray diffraction Cu anode tube type KFL C 2 K of 2.2 kW, with long fine focus.

A variable computer-controlled motor driven divergence slit with 2.5° Soller slits were included to allow kept the irradiated area on the sample surface constant. A Ni filter was placed, prior to the detector, to eliminate Cu-Kß radiation. А LynxEyeTM detector one-dimensional was employed. This detector is based on a Bruker AXS compound silicon strip technology and increases measured intensities, without sacrificing resolution and peak shape. This together with the use of small scanning step resulted in high quality XRD profiles suitable for mathematical treatment [39-41].

The TGA testing process was carried out with a TA, Q-500 equipment. To make the TGA test, the samples were placed into a ceramic sample holder, which is suspended from an analytical balance. Then, the sample holder was heated according to a

predetermined thermal cycle, that is: the temperature was linearly scanned, from 27 to 350 °C, at a heating rate of 5 °C/min, in a flow of 100 mL/min of the purge gas that is pure N₂. The data collection, the temperature control, the programmed heating rate, and the gas flow control, were automatically controlled by the software of the TA, TQ500 TGA. The TGA data was collected as a weight percent W(t) versus T (°C) profile, where: $W(T) = (M(T)/M_0) \times 100$, is the per-cent ratio of the sample mass during the thermal treatment, M(T), and the initial mass of the sample M_0 .

Elemental chemical analysis of the tested samples were performed using an energy dispersive X-ray (EDAX) spectrometer coupled to a JEOL Model JSM-6360 scanning electron microscope (SEM), equipped with an energy dispersive X-ray analysis detector and with a JEOL JLSM-6000 SEM and EDAX analysis system. The acceleration of the electron beam was 20 kV in both cases. The sample grains were placed on a carbon tape, and then introduced into the sample-holder. In order to guarantee, that we were testing a sample with a homogeneous distribution within the sample, different spots were analyzed. Together with the EDAX analysis scanning electron micrographs of the tested samples were obtained.

To get the diffuse reflectance infrared Fourier transform spectra, was applied a Thermo Scientific Nicolet iS10 FTIR spectrometer with the Smart Collector for diffuse reflectance analysis and the environmental chamber for the smart collector. The spectra were collected with a resolution of 4 cm⁻¹ and were made 100 scans per sample. To get the spectra in the case of the dehydrated samples, a background with KBr (FTIR pure, provided by Nicolet) located in the sample holder of the environmental chamber was made by applying the same conditions used to get, later, the sample spectra. To dehydrate the samples, it were heated, at 300 °C, under N₂ (Praxair, 99.99%) flow at a rate of 50 cc/min for a duration of 2 h. Lastly, the spectra of the dehydrated zeolite were obtained

with the sample inside the environmental chamber, at room temperature, under N_2 (Praxair, 99.99%) flow at a rate of 50 cc/min.

Water adsorption was measured gravimetrically at atmospheric pressure in air containing water vapor at different partial pressures [10, 11]. To study carbon dioxide adsorption, isotherms were collected, in an upgraded Quantachrome Autosorb-1 automatic physisorption analyzer, the adsorption isotherms of CO2 at 0 °C were collected for samples degassed at 300 °C for a period of three h in high vacuum (10^{-6}) Torr). In this case since the carbon dioxide vapor pressure, P_0 , at 0 °C, is high, to be precise, $P_0 =$ 26,141 Torr, subsequently, we will be working in the following relative pressure range: 0.00003 < P <0.03. The experience indicates that the adsorption process in this range is very well described by the Dubinin adsorption isotherm equation [42]. The Dubinin-Astakhov (D-A) adsorption isotherm equation can be represented in a log-log scale as follows [43]:

$$\ln(n_a) = I(N_a) - \left(\frac{RT}{E}\right)^n \ln\left(\frac{Po}{P}\right)^n \tag{1}$$

This relation, describes the relation between the amount adsorbed, *n a*, and the inverse of the relative pressure, i.e., P/P_0 . Where, E, is a parameter named the characteristic energy of adsorption, Na, is the maximum amount adsorbed in the volume of the micropore, and, n (1 < n < 5) is an empirical parameter. This equation is a very powerful tool for the description of the experimental data of adsorption in microporous material [42, 43]. The fitting process of Eq. (1) allowed us to calculate the best fitting parameters, i.e., N_a , E, and n. If, n= 2, we get the Dubinin-Radushkevitch (D-R) equation that was the equation applied here. Then, with the help of the CO₂ adsorption isotherms and Eq. (1) with: n = 2, the micropore volume, $W_{MP} =$ $N_a V_L$ (where V_L is the molar volume CO₂ at 0 °C) and the characteristic energy of adsorption, E (kJ/mol) were measured [5, 39-41].

3. Results and Discussion

In Fig. 1a, it is shown that the XRD profiles of the modified samples and in Figs. 1b and 1c the details of the patterns corresponding to the samples, NH4-CSW, CSW-HFSi-0.1 and CSW-H₃PO₄-20. The search carried out with the PDF-2, 2009 release database, created by the International Center for Diffraction Data produced a match of the XRD profile of the modified samples with the profiles of clinoptilolite. The clinoptilolite framework type is HEU; whose maximum space group (SG) symmetry is the monoclinic, C2/m (SG No. 12) [44]. The cell parameters data reported for a representative clinoptilolite are: a = 17.662 Å, b = 17.911 Å, c =7.407 Å and $\beta = 116.40$ [45]. We calculated the cell parameters, of the modified clinoptilolite samples by fitting the XRD profiles of these materials with mathematical functions simulating XRD patterns by applying the Pawley method [46]. These calculations were concretely made supposing the C12/m1 (No. 12) space group. In Table 1, are reported the calculated cell parameters for this space group alongside the Gaussian crystallite size (Φ). The TOPAZ software together with the Pawley calculations made the corrections to separate instrumental and strain effects from the crystallite size by applying the Williamson-Hall method [47]. The calculations were made by assuming a spherical shape for the Gaussian crystallite size (Φ). Further, in Fig. 2 is reported one of the fitted profiles as an illustration of the performed process. The calculated parameters are similar to those reported for a typical clinoptilolite [45]. But, a variation of the values of these parameters throughout the dealumination process was observed (Table 1 and Fig. 1b). These differences could be linked to the ionic radius of Al³⁺ and Si⁴⁺ in tetragonal coordination (0.39 Å for Al^{3+} and, 0.26 Å for Si^{4+} [48]).

The state of the zeolitic water is also important for the structural characterization of these materials. TGA data can be applied as a means for the study of the state of water in porous materials, since in the hydrated state the TG profile of these materials, from



Fig. 1 XRD profiles of the modified natural clinoptilolites (a) detail of samples NH₄-CSW, CSW-HFSi-0.1, CSW-HFSi-0.4 and CSW-H₃PO₄-20.

Group and Gaussian crystanice size (*).							
Sample	a (Å)	b (Å)	c (Á)	β (degree)	$V(\text{\AA}^3)$	<i>ф</i> (nm)	
CSW-NH ₄	17.693 (4)	17.959 (4)	7.404(6)	116.01 (1)	2,114 (1)	40 (1)	
CSW-HFSi-0.1	17.659 (4)	17.858 (3)	7.394 (5)	116.34 (1)	2,089 (1)	39 (1)	
CSW-HFSi-0.4	17.688 (5)	17.965 (3)	7.403 (1)	116.31 (1)	2,108 (1)	39 (1)	
CSW-H ₃ PO ₄ -20	17.672 (4)	17.975 (6)	7.416 (6)	116.33 (1)	2,111 (1)	37 (1)	
CSW-H ₃ PO ₄ -40	17.695 (8)	17.99 (1)	7.411 (2)	116.18 (1)	2,116 (1)	29 (1)	

Table 1 Cell parameters for the treated clinoptilolite samples calculated with the Pawley method assuming the C2/m space group and Gaussian crystallite size (Φ).



Fig. 2 XRD profile of the CSW-HFSi-0.1 sample fitted with the Pawley method for the *C2/m* space group (c).

30 to 300 °C, is merely a water thermo-desorption profile (Fig. 3). During the TG analysis, the process of water thermo-desorption occurs by the release of water adsorbed in different sites of the zeolite tunnels. In Fig. 4, the resolved TGA derivative profiles corresponding to the modified natural clinoptilolites: CSW-HFSi-0.1, CSW-HFSi-0.4, CSW-H₃PO₄-20 and

the ZSM-5 (CBV-3020) are shown. These profiles were resolved by fitting a theoretical profile, computed as the sum of two Lorentzian functions, to the experimental data by applying the peak separation and analysis software Peak Fit (Seasolve Software Inc., Framingham, Massachusetts) based on the least square procedure. The experimental profile is the continuous line, this profile is fitted by the theoretical function illustrated by the dashed line, further, the two peaks employed to compute the calculated profile are shown also as dashed curves (Fig. 4).

The resolution of the TGA derivative profiles indicated the presence, essentially, of two steps for water release. During the first, was lost the majority of the water present in the micropores. This thermal effect



Fig. 3 TGA profiles of the modified natural clinoptilolites: (a) the ZSM-5 (CBV-3020), (b) CSW-HFSi-0.1, (c) CSW-H₃PO₄-20 and (d) CSW-HFSi-0.4.



Fig. 4 TGA derivative profiles of the modified natural clinoptilolites: (a) ZSM-5 (CBV-3020), (b) CSW-HFSi-0.1, (c) CSW-H₃PO₄-20 and (d) the CSW-HFSi-0.4.

was evidenced as a broad peak centered at about 50 °C for the samples ZSM-5 (CBV-3020) and CSW-HFSi-0.1, but at 100 °C for the samples CSW-HFSi-0.4 and CSW-H₃PO₄-20. The second effect was placed at around 75 °C for the sample ZSM-5 (CBV-3020), but at 125 °C for CSW-HFSi-0.1, 150 °C for CSW-HFSi-0.4 and 175 °C for CSW-H₃PO₄-20 (Fig. 4). The first process characterized the release of physically adsorbed water from an energetically heterogeneous adsorbent as a zeolite [10], to be precise, since water was released at different temperatures, these fact means that it was linked with different adsorption energies to the framework. The second peak was related to the removal of coordinated water.

Fig. 5 is reported the DRIFTS spectrum of the difference spectra of the modified natural clinoptilolite CSW-HFSi-0.1 after a treatment at 250 °C under nitrogen flow by two h and after the same treatment at 500 °C. To get this spectrum the sample located in the sample holder of the environmental chamber was dehydrated at 250 °C, under N₂ (Praxair,

99.99%) flow at a rate of 50 cc/min for a duration of 2 h and then the temperature was lowered to room temperature. A DRIFT spectrum was taken at that moment and saved as background. Later, the spectrum of the sample at room temperature after a treatment inside the environmental chamber, at 500 °C, under N₂ (Praxair, 99.99%) flow at a rate of 50 cc/min was collected. The resulting spectrum is difference spectrum shown in Fig. 5. This DRIFTS profile indicated that all the water contained in the studied zeolite was removed after the first treatment at 250 °C. This result was coincident with the TGA data (Fig. 3), which indicated that water was totally released from the modified sample CSW-HFSi-0.1 at 250 °C. Consequently, these samples were, totally dehydroxylated during the modification treatment. As a result all the water released during the TGA process was only located in the adsorption space of the zeolite CSW-HFSi-0.1.

In sum, the TGA and DRIFTS data previously discussed indicated that all the water was released up to 250 °C in two steps. These steps can be related, in



Fig. 5 DRIFTS spectrum of the difference spectra of the modified natural clinoptilolite CSW-HFSi-0.1 after a treatment at 250 °C under nitrogen flow by two h and after the same treatment at 500 °C.

sequence, to the removal of water physically adsorbed on the micropore and coordinated water, respectively [41].

Fig. 6 shows the SEM micrographs corresponding to the modified clinoptilolites, CSW-NH₄, CSW-HFSi-0.1 and CSW-HFSi-0.4. In the reported micrographs was evidenced that the CSW zeolite shows secondary particles exhibiting diameters from 3 to 40 μ m, formed by primary clinoptilolite crystallites showing a crystallite size, $\Phi = 40$ nm. Additionally, in Fig. 7 are displayed the SEM micrographs of the modified clinoptilolites: CSW-NH₄, CSW-HFSi-0.1, CSW-HFSi-0.4 and CSW-H₃PO₄-20 at higher magnification. These last micrographs evidenced the lath morphology of the primary clinoptilolite crystallites.

The elemental analysis of the clinoptilolite samples Na-CSW [21], Na-HC [17] and CSW-NH₄, CSW-HFSi-0.1, CSW-HFSi-0.4 and CSW-H₃PO₄-20 determined was by EDAX elemental analysis. These results are reported in Table 2. These results demonstrated that the exchange process replaced about 85% of the charge compensating ions, to be precise, the Na⁺, K⁺, Ca²⁺ and Mg²⁺ present in the natural material were exchanged by Na⁺ or in the produced homoinic clinoptilolites [17], to produce the Na-CSW and NH₄-CSW homoinic samples. In the case of the samples treated with orthophosphoric acid, together with the dealumination process the Na^+ , K^+ , Ca^{2+} and Mg²⁺ located in the micropores of the natural clinoptilolite were exchanged by protons [18]. In addition to the ion exchange was evidenced a slight increase in the Si/Al relation during the dealumination



Fig. 6 SEM micrographs corresponding to the samples NH_4 -CSW, CSW-HFSi-0.1 (bar = 5 μ m) and CSW-HFSi-0.4 (bar = 10 μ m).



Fig. 7 SEM micrographs corresponding to the samples NH_4 -CSW, CSW-HFSi-0.1, CSWHFSi-0.4 and CSW-H₃PO₄-20 (bar = 2 μ m).

Sample	Si	Al	0	Na	K	Ca	Mg	Fe	Si/Al
Na-CSW	37.4	9.3	45.2	5.5	0.9	0	0.7	1.1	4.0
Na-HC	37.5	9.4	45.4	5.8	1.0.	0	0.4	0.5	4.0
CSW-NH4	40.8	10.3	45.5	0.3	1	0	0.7	1.4	4.0
CSW-HFSi-0.1	41.4	9.6	46.3	0.1	0.9	0	0.3	1.0	4.3
CSW-HFSi-0.4	45.4	9.5	43.1	0.1	0.8	0	0.3	0.8	4.8
CSW-H3PO4-20	40.1	6.6	50.8	0.6	0.9	0	0.0	1.0	6.1

 Table 2
 EDAX elemental analysis of the natural and modified samples in wt.%.

process. All this facts indicated a change in the zeolite chemistry that must be reflected in the adsorption properties of the modified clinoptilolites.

With the help of water adsorption, we studied the morphology of the tested clinoptilolites. Water vapor adsorption in a complex porous systems as natural zeolites occurs something like that [5, 10]: initially micropore filling, where the adsorption behavior is dominated nearly completely by the interactions of the adsorbate, and the pore wall; after that, at higher pressures, external surface coverage, consisting of monolayer, and multilayer adsorption on the walls of mesopores, and open macropores, and at last capillary condensation in the mesopores. In Fig. 8, are reported the water adsorption isotherms at 27 °C in Na-CSW, Na-HC and Na-X zeolites. During this adsorption process, water vapor at low pressures filled the micropores as was evidenced by the plateau in the following range of relative pressure: $0.2 < P/P_0 <$ 0.4, at higher pressures $P/P_0 > 0.5$ the external surface was covered and finally near $P/P_0 = 1$ capillary condensation in the mesopores takes place. The previously described adsorption processes, indicated the existence of micropores, mesopores and

macropores [49], or simply a primary porosity, that is, the cavities and channels which constitute the zeolite framework and a secondary porosity describing the macroporosity and the mesoporosity developed between the zeolite crystals [8].

Fig. 9 is shown these DRIFT spectra, in the range between: 3,200-3,800 cm⁻¹. Between, the bands present in the recorded DRIFTS spectra, the most important are the OH stretching vibrations related to the hydroxyl functionalities, specifically: silanol groups: Si-OH that is, terminal hydroxyl groups showing low acidity bridged hydroxyl groups: Si-OH-Al in which the proton shows Brönsted acid character and non-acidic extra-framework hydroxyl groups [50]. In the specific case of the DRIFTS spectrum corresponding to the ZSM-5, reported in Fig. 9, were evidenced three bands caused by the O-H stretching vibrations, to be precise: a band around: 3,590 cm⁻¹ corresponding to the Brönsted acid sites, 3,660 cm^{-1} band at related another to extra-framework, Al-OH, that is: positively charged extra-framework aluminum, and a peak located at 3,740 cm⁻¹ related to terminal silanol groups [26]. the case of the modified clinoptilolites, In



Fig. 8 Adsorption isotherms of water at 27 °C on: Na-CSW, Na-HC and Na-X.



Fig. 9 DRIFTS spectra of the modified natural clinoptilolites: (a) CSW-HFSi-0.1 and CSWH₃PO₄-20 and (b) the ZSM-5 (CBV-5020).

specifically, CSW-HFSi-0.1, a narrow band at about: 3,740 cm⁻¹ corresponding to terminal silanol groups (Si-OH) was evidenced; in the rest of the OH stretching vibration range, i.e., 3,000-3,700 cm⁻¹; was only evidenced a band 3,600-3,650 cm⁻¹ resulting from extra-framework Al-OH. The CSW-H₃PO₄-20 DRIFTS profile didn't show peaks in the range between: 3,200-3,800 cm⁻¹. The explanation that can be given to this profile should be related to dehydroxilation; since this process, in zeolites [6] and silica [51], produces the condensation of the OH groups. In the particular case of zeolites is generally accepted that during the process of dehydroxylation at temperatures up to 500 °C, bridged hydroxyls condenses to produce water and left behind the zeolite framework negatively charged [52], trigonal aluminum [53] and different types of positively charged extra-framework aluminum [54], at higher temperatures a dehydrogenation process is as well produced [55]. Thereafter, the modification process made to produce the sample CSW-HFSi-0.1 created a framework charged with positive and negative charges, where the charge compensating cations of the zeolite were removed, making available an open adsorption

space where adsorbed molecules are subjected to electrostatic interactions with the framework. This surface Chemistry is appropriate for adsorption, since this adsorption space is open. Besides, the electrostatic field, created by the negative and positive charge of the framework produces electrostatic interactions between the adsorbed molecule and the adsorbent.

Fig. 10 is reported the Dubinin plots of the adsorption isotherms of carbon dioxide at 0 °C on the modified zeolites CSW-HFSi-0.1 and CSW-HFSi-0.4. For comparison was as well reported the isotherm of CO₂ adsorption at 0 °C on the ZSM-5 (CBV-5020) zeolite [34]. The values of the micropore volume measured with the help of carbon dioxide adsorption, W_{MP}^{CO2} , are reported in Table 3. This parameter was measured by fitting Eq. (1), with: n = 2, to the reported adsorption data (Fig. 10).

The precision of the measured micropore volumes is related to the excellent fitting of the adsorption data by the D-R isotherm equation, the appropriate relative pressure range tested ($0.00003 < P/P_0 <$ 0.03) and the big amount of adsorption points produced during the adsorption test. All these facts allowed us to affirm that carbon adsorption took only

 Table 3 Micropore volume and zeolitic phase amount calculated with the Dubinin Radushkevish isotherm equation.

Samples	N _a (mmol/g)	W_{MP}^{CO2} (cm ³ /g)	<i>f</i> (wt.%)
ZSM-5-3020	3.55 ± 0.01	0.169 ± 0.001	94
CSW-HFSi-0.1	3.13 ± 0.01	0.149 ± 0.001	93
CSW-HFSi-0.4	2.81 ± 0.01	0.134 ± 0.001	84



Fig. 10 Dubinin-Radushkevitch (D-R) plots of the adsorption isotherms of carbon dioxide at 0 °C on: CSW-HFSi-0.1, CSW-HFSi-0.4 and the ZSM-5 (CBV-5020).

place in the micropore region; consequently, the adsorption of carbon dioxide at 0 °C clearly evaluated the micropore volume of the studied zeolite samples.

With the help of the micropore volume, WMP, of the zeolite present in the natural zeolite rock or in a bound form of a commercial zeolite and the micropore volume of the corresponding pure phase, W_{phase}^{pure} , of the same zeolite, we can determine the amount f, of zeolitic phases in wt.% (whenever it is the only zeolitic phase present), with the help of the equation: f = $W_{MP}^{CO2}/W_{phase}^{pure}$. It is very well known that the micropore volume for pure clinoptilolite $W_{HEU} \approx 0.16$ cm³/g [12] and the microporous volume of the MFI framework of pure H-ZSM-5 is $W_{MFI} \approx 0.18 \text{ cm}^3/\text{g}$ [58]. Subsequently, with the help of these data the amount f_{i} of the zeolitic phase present in the modified clinoptilolites and the H-ZSM-5 used for comparison were calculated (Table 3). Further, the X-ray diffraction data (Figs. 1b and 1c) allowed the calculation of the phase composition of the modified clinoptilolites by means of standards [21] by applying a previously developed methodology [56, 57]. In the present case the standard was the sample NH₄-CSW.

Table 4 shows the results obtained applying this methodology. These results indicated that the modification increased the amount of clinoptilolite, in the case of the sample CSW-HFSi-0.1.

This was one of the aims of the treatments to produce an adsorbent comparable to commercial zeolites. However, in the case of samples CSW-HFSi-0.1 was observed a decrease in the amount of clinoptilolite in the sample and for the sample CSW-H₃PO₄-20 a big decrease (Figs. 1b and 1c). These results indicated that the increase in the concentration of $(NH_4)_6SiF_6$ and the treatment with orthophosphoric acid are not useful to achieve the proposed goals.

Is knowed in general, if a molecule contact the surface of a solid adsorbent, it become subjected to diverse interaction fields, such as: the dispersion energy, repulsion energy, polarization energy, field dipole energy, field gradient quadrupole energy, and as well some specific interactions, as the acid-base interaction, ϕ_{AB} , and the adsorbate-adsorbate interaction energy [59]. Dispersion and repulsion forces are present during physical adsorption in all adsorbents.

 Table 4 Phase composition of the modified clinoptilolites.

Sample	Clinoptilolite (wt.%)	Others (wt.%)
CSW-NH ₄	91 (5)	9 (5)
CSW-HFSi-0.1	95 (5)	5 (5)
CSW-HFSi-0.4	72 (5)	28 (5)
CSW-H ₃ PO ₄ -20	41 (5)	59 (5)

The electrostatic interactions between the adsorbed molecule and the adsorbent framework, depend on the structure and composition of the adsorbed molecule and the adsorbent itself [1-5]. That is, the interaction between the adsorbent and molecules with, for example, a noticeable quadrupolar moment, like the carbon dioxide molecule ($Q_{CO2} = -4.3 \times 10^{-42} \text{ C} \cdot \text{m}^2$) give raise to specific interactions, where the combination of the dispersive and electrostatic attractive interactions are normally stronger than merely the dispersion interactions. In the case of interest here it is accepted that carbon dioxide interacts with surfaces through their dispersive and quadrupole moment interactions [1].

The parameters calculated with the D-R adsorption isotherm equation not only allowed us to evaluate the micropore volume of the sample, but also the adsorption interaction between the adsorbate and the adsorbent. To evaluate this interaction was used the characteristic energy of adsorption, calculated by fitting Eq. (1), with: n = 2, to the data reported in Fig. 10 (Table 3). The accuracy of the measured characteristic energy is related to the same arguments previously discussed for the micropore volume.

The quantitative evaluation of the interaction between carbon dioxide and the zeolite will be carried out with help of the isosteric heat of adsorption, q_{iso} [1-5]. In this regard, it is possible to calculate, q_{iso} , in an original way using only one isotherm as follows [42]:

In which:

$$\Delta G = RT \ln\left(\frac{P}{Po}\right)$$

 $q_{iso}(\theta) = -\Delta G + EF(T, \theta)$

$$F(T, \ \theta) = \frac{\alpha T}{2} \left(In[1/\theta] \right)^{\left(\frac{1}{n}\right) - 1}$$
(3)

where: $\theta = n_a/N_a$; $\alpha = -dlnN_a/dT$ and *E*, and *n*, are the parameters of the Dubinin adsorption equation (in our case: n = 2, and *E* is reported in Table 5). It is also possible to assert that: $E = \Delta G(1/e)$, where: $\theta = 1/e$, in which, $e \approx 2.71828183$ is the base of the Napierian logarithm system. Now with the help of Eqs. (2) and (3), for $\theta = 1/e \approx 0.37$ is possible to get the following equation [34]:

$$q_{iso}(0.37) = -\Delta G(0.37) + EF(T, 0.37) = E[F(T, 0.37) - 1]$$
(4)

To calculate, F(T, 0.37), with the help of Eq. (4) was used trustworthy experimental calorimetric data reported in literature, i.e, $q_{iso} = 22$ kJ/mol for the adsorption of carbon dioxide at 27 °C in the range: 0.1 < $n_a < 0.7$ mmol/g in MCM-41 [58] and the characteristic energy of adsorption, E, calculated by fitting Eq. (1), with: n = 2, to carbon dioxide adsorption on MCM-41 previously reported, E = 19 kJ/mol [34]. Consequently, it was possible to estimate that: $F(T, 0.37) \approx 2.16$. Thereafter, with the relation:

$$q_{iso}(0.37) = 1.16 E$$

were calculated the isosteric heat of adsorption (Table 5). The results reported indicated that the tested modified zeolites shows similar values for the measured isosteric heat of adsorption; but greater than those value of the isosteric heat of adsorption reported also in the present paper for the ZSM-5 zeolite, also larger than those reported for a particle packing silica and a dealuminated Y zeolite (DAY) [34], Cd, Zn and Ni-nitroprussides [41] and Cu-nitroprusside [40] and a Ni-MOF [39] (Table 6), as well bigger than experimental isosteric adsorption heats measured for the adsorption carbon dioxide on MCM-41- [58], silicalite [59], Na clinoptilolite

 Table 5
 Parameters calculated with the Dubinin-Radushkevish isotherm equation.

Sample	$N_a (\text{mmol/g})$	E_{2}^{CO} (Kj/mol)	q_{iso}^{CO2} (Kj/mol)
ZSM-5-3020	3.55 ± 0.01	33 ± 1	38 ± 2
CSW-HFSi-0.1	3.13 ± 0.01	40 ± 1	46 ± 2
CSW-HFSi-0.4	2.81 ± 0.01	43 ± 1	50 ± 2

(2)

Sample	$E^{\rm CO2}$ (Kj/mol)	q ^{CO2} _{iso} (Kj/mol)	N_a (mmol/g)	$W_{\rm MP}^{\rm CO2}~({\rm cm}^3/{\rm g})$	Reference
P-68-Silica	24 ± 1	28 ± 1	3.57 ± 0.01	0.170 ± 0.001	Ref. [26]
Cd-NP	21 ± 1	25 ± 1	2.67 ± 0.01	0.127 ± 0.001	Ref. [33]
Cu-NP	20 ± 1	24 ± 1	3.23 ± 0.01	0.154 ± 0.001	Ref. [34]
DAY	17 ± 1	20 ± 1	6.93 ± 0.01	0.331 ± 0.001	Ref. [26]
Ni-MOF	16 ± 1	18 ± 1	1.68 ± 0.01	0.080 ± 0.01	Ref. [32]
Zn-NP	12 ± 1	14 ± 1	5.08 ± 0.01	0.242 ± 0.001	Ref. [33]
Ni-NP	9 ± 1	11 ± 1	5.78 ± 0.01	0.275 ± 0.001	Ref. [33]

Table 6 Parameters Calculated with the Dubinin-Radushkevish Equation for a particle packing silica, Cd, Zn, Cu and Ni-nitroprussides (NPs), dealuminated Y zeolite (DAY) and a Ni MOF.

and K-clinoptilolite [60], Na-A [61] and Na-X and MOF-5 [62] and MOF-508b [63], but similar to measured isosteric heats of adsorption for the adsorption of carbon dioxide on sodium ferrerite (Na-FER) [64].

The previously described adsorption data indicated that the interaction of the carbon dioxide molecule with the modified zeolites is strong. Subsequently, these materials could be very useful in gas separations. One of the causes of adsorption selectivity, are adsorption interactions. In this regard, the electrostatic interactions between the adsorbed molecule and the adsorbent framework, which depends on the structure and composition of the adsorbed molecule and the adsorbent itself, have an important role in adsorption selectivity. For example, for molecules such as: H₂O, H₂S, SO₂ and NH₃ with a high dipole moment and CO₂ a molecule with a high quadrupole moment, the electrostatic interactions are stronger than the dispersion plus repulsion interactions when are adsorbed in an aluminosilicate zeolite as the modified clinoptilolites. Dispersion and repulsion are forces present in all the adsorption couples. In the case of: H₂, Ar, CH₄, N₂ and O₂; given that, the dipole moments of these molecules is cero, the quadrupole moment is very low or absent, and the polarization effect will be only noticeable in the case of adsorbents with high electric fields, then dispersion forces are the only interaction present during the adsorption process of these gases. [5, 10, 12]. Thereafter, these gases are less strongly adsorbed in aluminosilicate zeolites and related materials than those showing electrostatic interactions. Consequently, the adsorption of H2O, H2S, SO2 and NH3 in aluminosilicate zeolites is very strong and those of CO_2 relatively strong; then these zeolites will remove these gases selectively in mixtures with: H₂, Ar, CH₄, N₂ and O₂. These interactions are, as well, responsible for the high regeneration temperatures needed by zeolites to be applied; fact that oblige to spend a large quantity of energy for their regeneration.

As was above commented, the elemental chemical analysis of the modified clinoptilolites shown in table 2 indicated that ammonium exchanged about 90% of the charge compensating ions present in the natural zeolite. Thereafter, since the modified clinoptilolites CSW-HFSi-0.1 and CSW-HFSi-0.4 were further treated with (NH₄)₆SiF₆ and finally calcined, both zeolites were practically completely dehydroxylated producing a framework negatively and positively charged. The previously discussed energetic factor is very important for a precise description of the adsorption space. However, the geometrical factor is as well decisive. In this sense, the experimental evidence accumulated by us indicated that CSW natural clinoptilolite didn't adsorb nitrogen at 77 K. However, it adsorbs carbon dioxide at 0 °C. The structure of clinoptilolite, HEU framework type, show 3 channels; i.e., one 8-MR channel along [100], with an access of 2.6×4.7 (Å)2; two parallel channels along [001] one 8-MR with a window of access with 3.3 Å \times 4.6 Å, and a 10-MR with an access of 3.0 Å \times

Table 7 Kinetic diameter (σ) of some gases [6, 67].

Gas	σ (Å)	Gas	σ (Å)	
N ₂	3.64	H ₂ O	2.64	
O ₂	3.46	N_2O	3.17	
CO_2	3.3	H_2S	3.4	
CH ₄	3.76	NH_3	3.1	

7.6 Å [37]. Additionally, the kinetic diameter of: carbon dioxide is 3.4 Å and those of nitrogen 3.6 Å (Table 7) [6, 67]. We can conclude from the previous discussion that the effective access window of the modified clinoptilolite could be estimated to be around 3.5 Å, value that was as well reported by other authors [23]. This is an optimum value for the application of these modified clinoptilolites in bio-gas and natural gas cleaning, carbon dioxide recovery and gas drying. Since, the kinetic diameter of: water, hydrogen sulfide indicates that it can be fitted into the clinoptilolite pores, on the other hand those of oxygen and methane don't fit (Table 7).

Consequently, the modified clinoptilolites, like other microporous crystalline materials could be successfully applied for removing of H₂O, NH₃, NO₂, SO₂, SH₂, CO₂, and other impurities from gas streams.

4. Conclusions

In the research reported here was studied the structure, composition and morphology of modified clinoptilolites with, XRD, TGA, SEM-EDAX and gravimetric adsorption measurements. With the obtained data were calculated, the cell parameters, was measured the elemental and phase composition, studied the state of water and the morphology of the tested materials. The calculated cell parameters were similar to those reported for a typical clinoptilolite, but a variation of the values of these cell parameters during dealumination, was observed. To be precise, a small diminution of the cell volume was observed. The resolution of the TGA derivative profiles denoted the presence of two steps for water release. The first process was the desorption of physically adsorbed water from an energetically heterogeneous adsorbent as a zeolite and the second peak was related to the release of coordinated water. The water adsorption processes denoted the existence of micropores and mesopores in the CSW sample. The elemental analysis of the tested clinoptilolite samples determined with EDAX elemental

analysis demonstrated that the exchange process replaced about 85% of the original zeolite charge compensating ions, by Na⁺ or in the produced homoinic clinoptilolites. For the samples treated orthophosphric acid together with the with dealumination process the Na⁺, K^+ , Ca²⁺ and Mg²⁺ located in the micropores of the natural clinoptilolite are exchanged by protons. Besides, it was evidenced a slight increase in the Si/Al relation during the dealumination process. As well, the CSW-HFSi samples were, practically, completely dehydroxylated during the modification treatment. All this facts indicated a change in the zeolite chemistry that must be reflected in the adsorption properties of the modified clinoptilolites. The surface chemistry of the modified clinoptilolites utilizing DRIFTS was studied. Besides, the interaction of carbon dioxide within the adsorption space of the modified clinoptilolites and two synthetic ZSM-5 zeolites were studied with the help of an automatic physisorption analyzer. Finally, an appropriate theoretical methodology for the analysis of the XRD and adsorption data was applied.

These results indicated that the modification process augmented the amount of clinoptilolite in the sample CSW-HFSi-0.1, but diminished it in the rest of the modified samples. The modification created an open adsorption space, since the charge compensating cations of the zeolite were removed. Additionally, a framework charged with positive and negative charges was produced in the samples treated with HFS. In this adsorption space, adsorbed molecules are subjected to strong electrostatic interactions with the framework. Additionally, the pore size of the obtained material only allow the adsorption of small molecules, subsequently these materials could be very useful in gas separations. Thereafter, the treatments produced adsorbents comparable to commercial zeolites.

The modification of clinoptilolite with HFSi to improve their adsorption properties had not been previously attempted.

Acknowledgments

The authors acknowledge the financial support provided by the US Department of Energy through the Massey Chair project at the University of Turabo. We also recognize the support of the National Science Foundation under the project CHE-0959334. We are also grateful to the Department of Mathematics and Physics of the University of Puerto Rico-Cayey Campus for the help provided during the SEM-EDAX analysis. As well we recognize the help provided by Mr. Carlos Muñiz, Mr. Raul Perez, and the Puerto Rico Energy Center in some of the SEM-EDAX tests.

References

- R.M. Barrer, Zeolites and Clay Minerals as Sorbents and Molecular Sieves, Academic Press, London, 1978, p. 497.
- [2] D.M. Ruthven, Principles of Adsorption and Adsorption Processes; John Wiley and Sons, New York, 1984, p. 62.
- [3] F. Rouquerol, J. Rouquerol, K.S.W. Sing, Adsorption by Powder Porous Solids, Academic Press, New York, 1999, p. 93.
- [4] M. Thommes, Nanoporous Materials: Science and Engineering, Imperial College Press, London, 2004, p. 317.
- [5] R. Roque-Malherbe, Adsorption and Diffusion in Nanoporous Materials, Boca Raton, Florida, CRC Press, 2007, p. 57.
- [6] D.W. Breck, Zeolite Molecular Sieves, J. Wiley, and Sons, New York, 1974, p. 593.
- [7] R. Roque-Malherbe, A. Berazain, J.A. del Rosario, Calorimetric measurement of ion exchange heats in homoinic heulandite and mordenite, J. Thermal Anal. 32 (1987) 949.
- [8] C.de las Pozas, R.L. Cordero, J.A. González-Morales, N. Travieso, R.R. Malherbe, A comparative study of MeAPO molecular sieves with AFI structure type Zeolites, J. Mol. Catal. 83 (1993) 145.
- [9] M. Fuentes, J. Magraner, C. de las Pozas, R.R. Malherbe J.P. Pariente, A. Corma, Cyclization of citronellal to isopulegol by zeolite catalysis, App. Catal. 47 (1989) 367.
- [10] C. de las Pozas, R.L. Cordero, C.D. Aguilas, M. Cora, R.R. Malherbe, Location and reducibility of Ni ions in HEU type zeolite, J. Sol. State Chem. 114 (1995) 108.
- [11] F.A. Mumpton, Natural Zeolites, Occurrence,

Properties, Use, Pergamon Press, New York, 1978, p. 3, Natural Zeolites: Occurence, Properties, Uses of Natural Zeolites, Akademiai Kiado, Budapest, 1988, p. 333.

- [12] G.V. Tsitsisvili, T.G. Andronikashvili, G.N. Kirov, L.D. Filizova, Natural Zeolites, Ellis Horwood, New York, 1992, p. 295.
- [13] R. Roque-Malherbe, Handbook of Surfaces and Interfaces of Materials, Volume 5, H. Academic Press, New York, 2001, p. 495.
- [14] R. Roque-Malherbe, Physical Chemistry of Materials: Energy and Environmental Applications, Boca Raton, Florida, CRC Press, 2009, p. 63.
- [15] R. Roque-Malherbe, L. Lemes, L. López-Colado, A. Montes, Zeolites '93 Full Papers Volume. International Committee on Natural Zeolites Press, Brockport, New York, 1995, p. 299.
- [16] R.R. Malherbe, Complementary Approach to the Volume Filling Theory of Adsorption, Mic. Mes. Mat. 41 (2000) 227.
- [17] R.R. Malherbe, W. del Valle, J. Ducongé, E. Toledo, Lead, cooper, cobalt and nickel removal from water solutions by dynamic ionic exchange in LECA zeolite beds, Int. J. Env. & Pollution 31 (2007) 292-303.
- [18] C. de las Pozas, W. Kolockiewics, R.R. Malherbe, Modification of clinoptilolite by orthophosphoric acid leaching, Mic. Mat. 5 (1996) 325.
- [19] R.R. Malherbe, M.H. Vélez, Foundations of thermodielectric analysis: Part 1. Cationic polarization, J. Thermal Anal. 36 (1990) 1025.
- [20] R.R. Malherbe, Handbook of Surfaces and Interfaces of Materials, Volume 2, Academic Press, New York, Chapter 13, 2001, p. 509.
- [21] R.R. Malherbe, R. Roque-Malherbe, W. del Valle, F. Marquez, J. Duconge, M.F.A. Goosen, Synthesis and characterization of zeolite based porous ceramic membranes, Separation Sci. & Tech. 41 (2006) 73.
- [22] M.H. Vélez, O. Raymond, A. Alvarado, A. Jacas, R.R. Malherbe, New materials obtained from high temperature phase transformations of natural zeolites, J. Mater. Sci. Letters 14 (1995) 1653.
- [23] S. Sircar, A.L. Myers, Handbook of Zeolite Science and Technology, Marcell Dekker Inc., New York, 2003, p. 1063.
- [24] G.H. Kühl, Catalysis and Zeolites, Fundamentals and Applications, Springer-Verlag, Berlin, 1999, p. 81.
- [25] N.C. Martinez, J.A. Dumesic, Applications of Adsorption Microcalorimetry to the Study of Heterogeneous Catalysis, Adv. Catal. 38 (1992) 149.
- [26] W.E. Farneth, R. Gorte, Method for characterizing zeolite acidity Chem. Rev. 95 (1995) 615.
- [27] H.G. Karge, M. Hunger, H.K. Beyer, Catalysis and

Zeolites. Fundamentals and Applications, Springer-Verlag, Berlin, 1999, p. 198.

- [28] C. Li, Z. Wu, Handbook of Zeolite Science and Technology, Marcell Dekker Inc., New York, 2003, p. 423.
- [29] C. delas Pozas, C. Díaz-Aguila, E. Reguera-Ruiz, R. Roque-Malherbe, Mössbauer study of the hydrothermal transformation of clinoptilolite in faujasite, J. Solid State Chem. 93 (1991) 215.
- [30] L. Yang, K. Trafford, O. Kresnawahjuesa, J. Sepa, R. J. Gorte, D. White, An Examination of Confinement Effects in High-Silica Zeolites, J. Phys. Chem. B, 105 (2001) 1935.
- [31] R. Roque-Malherbe, F. Diaz-Castro, Calculation of the energy of adsorption of *n*-paraffins in nanoporous crystalline and ordered acid catalysts, and its relationship with the activation energy of the monomolecular catalytic cracking reaction, J. Mol. Catal. A 280 (2008) 194.
- [32] D.C. Amoros, J.A. Monge, M.A. de la Casa-Lillo, A.L. Solano, A CO₂ as an Adsorptive to characterize carbon molecular sieves and activated carbons, Langmuir 14 (1998) 4589.
- [33] C. Muñiz, J. Duconge, R. Roque-Malherbe, Paranitrophenol liquid-phase adsorption in dealuminated Y zeolite, J. Coll. Int. Sci. 329 (2009) 11-16.
- [34] R.R. Malherbe, R. Polanco, F.M. Linares, Study of the interaction between silica surfaces and the carbon dioxide molecule, J. Phys. Chem. C 114 (2010) 17773.
- [35] C. Knöfel, C. Martin, V. Hornebecq, P.L. Llewellyn, Study of carbon dioxide adsorption on mesoporous aminopropylsilane-functionalized silica and titania combining microcalorimetry and in situ infrared spectroscopy, J. Phys. Chem. C 113 (2009) 21726.
- [36] M.T. Ho, G.W. Allinson, D.E. Wiley, Reducing the Cost of CO₂ Capture from Flue Gases Using Pressure Swing Adsorption, Ind. Eng. Chem. Res. 47 (2008) 4883-4890.
- [37] S. Deng, Encyclopedia of Chemical Processing; Taylor and Francis: Boca Raton, FL, USA, 2006, p. 2825.
- [38] R.V. Siriwardane, M.S. Shen, E. P. Fisher, Adsorption of CO₂, N₂, and O₂ on Natural Zeolites, Energy & Fuels 17 (2003) 571.
- [39] A. Rios, C. Rivera, G. Garcia, C. Lozano, P. Fierro, L.F. Cobas et al., Synthesis, structure, adsorption space and magnetic properties of Ni-oxalate porous molecular magnet, J. Mat. Sci. & Eng. A 2 (2012) 284.
- [40] R.R. Malherbe, O.N.C. Uwakweh, C. Lozano, R. Polanco, A.H. Maldonado, P. Fierro, et al., Structural Effects and Interactions of Carbon Dioxide Molecules Adsorbed on Ni, Zn, and Cd Nitroprussides, J. Phys. Chem. C 115 (2011) 15555.
- [41] R.R. Malherbe, C. Lozano, R. Polanco, F. Marquez, F.

Lugo, A.H. Maldonado et al., Study of carbon dioxide adsorption on a Cu nitroprusside polymorph, J. Sol. State Chem. 184 (2011) 1236.

- [42] B.P. Bering, M.M. Dubinin, V.V. Serpinskii, On thermodynamics of adsorption in micropores, J. Coll. Int. Sci. 38 (1972) 185-194.
- [43] M.M. Dubinin, Physical adsorption of gases and vapors in micropores, Prog. Surf. Memb. Sci. 9 (1975) 1.
- [44] C.H. Baerlocher, W.M. Meier, D.H. Olson, Atlas Zeolite Framework Type, 5th ed., Elsevier, Amsterdam, 2001, p. 156.
- [45] M.M. Treacy, J.B. Higgins (eds.), Collection of Simulated XRD Powder Patterns for Zeolites, Elsevier, Amsterdam, 2001, p. 186.
- [46] G.S. Pawley, Unit-cell refinement from powder diffraction scans, J. Appl. Cryst. 14 (1981) 357.
- [47] G.K. Williamson, X-ray line broaden-ingfromjiled aluminium and wolfram, W.H. Hall. Acta Metallurgica 1 (1953) 22-31.
- [48] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Acta. Cryst. A 32 (1976) 751.
- [49] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pirotti, J. Rouquerol, et al., Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity, Pure App. Chem. 57 (1985) 603.
- [50] P. A. Jacobs, Acid zeolites: An attempt to develop unifying concept, Catal. Rev. Sci. Eng. 24 (1982) 415.
- [51] R. Mueller, H.K. Kammler, K. Wegner, S.E. Pratsinis, OH surface density of SiO₂ and TiO₂ by thermogravimetric analysis, Langmuir 19 (2003) 160.
- [52] J.B. Uytterhoeven, L.G. Christner, W.K. Hall, Studies of the hydrogen held by solids: VIII. The decationated zeolites, J. Phys. Chem. 69 (1965) 2117.
- [53] J.A. van Bokhoven, A.M.J. van der Eerden, D.C. Koningsberger, Three-coordinate aluminum in zeolites observed with *in-situ* X-ray absorption near-edge spectroscopy at the Al K-edge: Flexibility of aluminum coordinations in zeolites, J. Am. Chem. Soc. 125 (2003) 7435.
- [54] G. Catana, D. Baetens, T. Mommaerts, R.A. Schoonheydt, B.M. Weckhuysen, Relating structure and chemical composition with lewis acidity in zeolites: A spectroscopic study with probe molecules, J. Phys. Chem. B 105 (2001) 4904.
- [55] M.J. Nash, A.M. Shough, D.W. Fickel, D.J. Doren, R.F. Lobo, High temperature dehydrogenation of bronsted acid sites in zeolites, J. Am. Chem. Soc 130 (2008) 2460.
- [56] C. Gonzales, R.R. Malherbe, E.D. Shchukin, Theoretical principles for quantitative x-ray analysis in

systems with high microabsorption, J. Mater. Sci. Letters 6 (1987) 604.

- [57] C. Gonzales, R.R. Malherbe, Optimization of quantitative X-ray phase analysis by Monte Carlo methods, Acta Crystall. A 43 (1987) 622
- [58] C. Kladis, S.K. Bhargava, K. Foger, D.B. Akolekar, Effects of air pollutants on the cerium exchanged high silica zeolite catalyst: a Fourier transform infrared study, J. Mol. Cat. A 171 (2001) 243.
- [59] J.N. Israelachvili, Intermolecular and Surface Forces 3rd ed., Elsevier, Amsterdam, 2011, p. 9.
- [60] Y. He, N.A. Seaton, Heat of adsorption and adsorption heterogeneity for methane, ethane and carbon dioxide in MCM-41, Langmuir 2 (2006) 1150.
- [61] J.A. Dunne, M. Rao, S. Sircar, R.J. Gorte, A.L. Myers, Calorimetric heats of adsorption and adsorption isotherms:
 2. O₂, N₂, Ar, CO₂, CH₄, C₂H₆, and SF₆ on NaX, H-ZSM-5, and Na-ZSM-5 zeolites, Langmuir 12 (1996) 5896.
- [62] S.U. Rege, R.T. Yang, M.A. Buzanowski, Sorbents for

air, prepurification in air separation, Chem. Eng. Sci. 55 (2000) 4827.

- [63] A.R. Perez, G. Aguilar-Armenta, Adsorption kinetics and equilibria of carbon dioxide, ethylene, and ethane on 4A(CECA) zeolite, J. Chem. Eng. Data 55 (2010) 3625.
- [64] D. Saha, S. Deng, Adsorption equilibria and kinetics of carbon monoxide on zeolite 5A, 13X, MOF-5 and MOF-177, J. Chem. Eng. Data 54 (2009) 2245.
- [65] L. Bastin, P.S. Barcia, E.J. Hurtado, J.A.C. Silva, A.E. Rodrigues, B. A microporous metal-organic framework for separation of CO₂/N₂ and CO₂/CH₄ by fixed-bed adsorption, Chen, J. Phys. Chem. C 112 (2008) 1575.
- [66] A. Pulido, P. Nachtigall, A. Zukal, I. Domínguez, J. Cejka, Adsorption of CO₂ on sodium-exchanged ferrierites: The bridged CO₂ complexes formed between two extraframework cations, J. Phys. Chem. C 113 (2009) 2928.
- [67] R.W. Baker, Membrane Technology and Applications 2nd ed., J. Wiley and Sons, New York, 2004, p. 531.