NANOMODIFICATION OF A NATURAL CLINOPTILOLITE ZEOLITE

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Abstract. Clinoptilolite, a common natural zeolite was chemically modified with HCl and Si to enable the sequestration of Cs and Sr isotopes, in both water and some types of solid waste (nuclear industry residues, for instance). The method reported allows to preserve the crystalline structure of the zeolite, thus maintaining its advantageous textural characteristics, while incorporating the adequate surface moieties for various applications, including trapping of polluting ions in water.

1. INTRODUCTION

Zeolites are natural porous crystalline aluminosilicates, consisting of SiO_4 and AlO_4 tetrahedra linked by oxygen atoms [1-3]. In the zeolite structure, each aluminum atom contributes one negative charge which must be balanced by an exchangeable cation (Ca^{2+}, Mg^{2+}, Na^+, K^+, etc.), located in the channels and cavities throughout the structure [2]. These cations are coordinated with a defined number of water molecules, and are bound to the aluminosilicate structure by weak electrostatic bonds, allowing the intercalation of small aggregates within the particles [3]. These cations play a very important role in determining the adsorption and thermal properties of the zeolites [2]. Clinoptilolite, one of the most commonly occurring natural minerals, is a member of the heulandite zeolite group [1]. It is created as weathering product of volcanic glass [4]. Its microporous structure and may have a specific surface area as large as 500 m^2/g. It is a very good adsorbent for cations, notably ammonium, and noncharged but polar organic compounds. It has recently successfully utilized for the removal of heavy metals [5,6].

Interestingly, the detailed chemical structure, i.e., the chemical groups available on its surface, of clinoptilolite dictates its selectivity towards competing ions [7], which represents and attractive venue for tailored functionalization. Clinoptilolite has a relatively small Cation-Exchange Capacity (CEC) of 2.25 meq/g, but its cation selectivity is:

$Cs^{+1} > Rb^{+1} > K^{+1} > NH^{+4} > Ba^{+2} > Sr^{+2} > Na^{+1} > Ca^{+2} > Fe^{+2,+3} > Al^{+3} > Mg^{+2} > Li^{+1}$.

Clinoptilolite and natural chabazite have been already used to extract Cs and Sr from nuclear wastes and fallout [7], so it represents a potential cost-effective source for pollution remediation technologies, provided a control of its chemical selectivity and efficiency can be controlled. Accordingly, in this

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present work clinoptilolite was treated with HCl and Si, which would enable it to filter the Cs and Sr isotopes, which are common (and dangerous) pollution ions in water and nuclear waste materials.

2. EXPERIMENTAL

Natural Clinoptilolite (*NC*) was mined in the Puebla State, in Central México, where it is very common. The *NC* was ion-exchanged by heating at 50 °C in an aqueous solution of HCl (0.1 N). It was placed inside a cooling bath and kept in these conditions for one week. By this method, the *NC* was converted to the Acidic Clinoptilolite (*AC*). Afterwards, *AC* samples were chemically-modified on its surface by adding the following amounts of silicon: 0.2, 0.6, 1, and 1.5 mL in presence of peroxide and heptane at 70 °C. Thus, a series of Acidic Modified Clinoptilolites (*AMC*) were obtained, identified in this work as *AMC1*, *AMC2*, *AMC3*, and *AMC4* respectively.

A SEM, Model JSM 300 was used to determine the crystallite size, both before and after ion-exchange. The crystal structures of zeolites *NC*, *AC*, and *AMC* were determined with X-ray powder diffraction by using a RIGAKU MiniFlex II diffractometer with CuK_α (λ = 1.5418 Å) radiation. X-ray diffraction data were collected within the 2θ range from 5 to 90, at a scan rate of 0.02°/sec. HRTEM samples were sonicated in isopropanol and deposited on carbon grids and analyzed in a JEOL 2010 F microscope equipped with a Schottky-type field emission gun, an ultra-high-resolution pole piece, operating at 200 kV. XPS analyses were carried out on a modified laser ablation system Riber LDM-32. The pressure in the analysis chamber was approximately 10^{-10} Torr and 10^{-9} Torr at the sample-loading chamber. The X-ray AlK_α line at 1486.6 eV was utilized. The binding energies were calibrated with reference to Cu$2p_{3/2}$ and Ag$3d_{5/2}$ at 932.67 eV and 368.26 eV, respectively. The maximum resolution attained with this set up was 1.1 eV measured for the graphite C1s signal. The spectra were collected by acquiring the data every 0.2 eV with an energy resolution of 0.8 eV. For each sample, XPS spectra were obtained by scanning from 1486.6 to 0 eV. Then, narrow scans were performed in the high resolution mode for the Si2p, O1s, Al2p, and C1s windows. Also, narrow windows were taken for Mg2p, Na1s, Fe2p, Ca2p, and S2p, which accounts for impurities within the zeolite system. Binding energies (BE) were referenced with respect to the C1s signal at 284.5 eV after taking measurements, in order to correct induced charge-effects. Surface

Table 1. Chemical analysis data of natural clinoptilolite zeolite (NC)[a].

Components	Wt.%	Ion contents in the elemental cell	
SiO_2	62.36	Si	28.18
Al_2O_3	13.14	Al	7.01
CaO	2.72	Ca	1.32
Na_2O	3.99	Na	3.50
K_2O	1.20	K	0.69
Fe_2O_3	1.63	Fe	0.55
FeO	-	-	-
MgO	0.92	Mg	0.62
TiO_2	0.39	Ti	0.13
H_2O[b]	8.32	H_2O	20.57
H_2O[c]	5.33	O	72.0

[a]Clinoptilolite: $Na_{3.50}K_{0.69}Mg_{0.62}Ca_{1.32}[(Al_{7.0}1Fe_{0.55})(Si_{28.18}Ti_{0.13})O_{72.0}].20.57H_2O$.
[b] Crystallization water.
[c] Extra water which is present in clinoptilolite mineral and does not form its crystal structure.

stoichiometries were calculated from the peak area ratios. Synthetic zeolite ZSM5 (MFI) was taken as a reference (standard). It was assumed an ideal SiO_2 tetrahedral arrangement where the oxygen to silicon ratio atomic concentration is C(O1s)/C(Si2p) = 2. From XPS O1s and Si2p transitions taken from the standard, and by assuming the ideal ratio of 2, it was obtained that oxygen to silicon ratio sensitivity factors were about of S(O1s)/S(Si2p)=3.6, which were very similar to the ones already reported [8].

The core level spectra of Si2p and O1s narrow scans were performed by using a non-linear fit of Gaussian-Lorentzian functions. Gaussian-Lorentzian proportion of 0.9-0.1 was kept constant. The intensity ratio of Si$2p_{3/2}$ and Si$2p_{1/2}$ transitions was kept 2:1 and BE at a constant separation of 0.61 eV [9]. It and the full-width-half-maximum (FWHM) were allowed to change.

3. RESULTS AND DISCUSSION

The chemical composition of the natural clinoptilolite zeolite is summarized in Table 1. This composition gave Si/Al ratio of 4.74, similar to the ratio reported by Breck [10].

The bulk structure of *AC* and *AMC* was confirmed by XRD analysis identified as clinoptilolite. The chemically modified *AMC* with silicon layers did not display changes in their crystalline structures, as can be seen from Fig. 1.
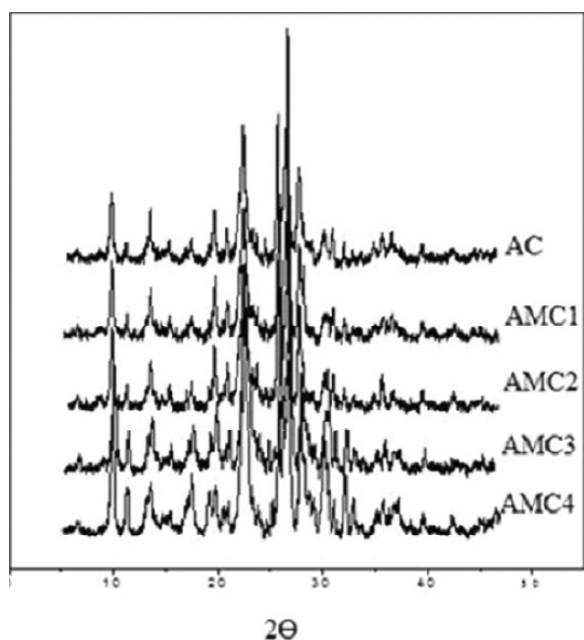
Fig. 1. X-ray diffraction patterns of acid treated (AC) and acidic modified clinoptilolites (AMC).

Fig. 2. SEM image displaying the morphology of natural clinoptilolite (NC).

The SEM of Fig. 2 corresponds to natural clinoptilolite zeolite (*AC*). This zeolite presented a crystal size in the range of about 2 to 15 μm. This range of crystal size was also observed approximately for AC and AMC zeolites.

Fig. 3 presents the XPS spectra for Si and O windows, where their respective fitting is included for sample MFI (the structure designation defined by IZA for synthetic zeolite ZSM5). The envelope of the Si window consists of a convolution of Si2p3/2
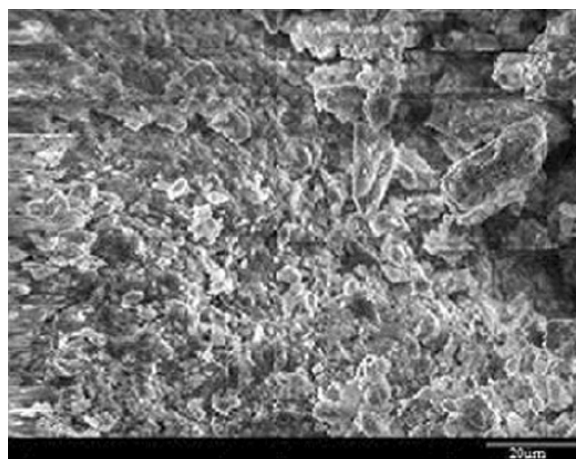
and Si2p1/2 -oxide and a Si2p3/2 and Si2p1/2 -metallic transitions. The envelope of the O window consists of a convolution of O1s related to a tetrahedral bonding to Si, and an O1s related to a signal coming from contamination or impurities. Atomic concentrations were calculated from the peak areas of Si2p-oxide and O1s curve fit components and reported sensitivity factors [8]. Photoionization cross sections σ were also used as an additional method for calculation of atomic concentrations, where results were very similar. In this case, oxygen to silicon ratio was about of $\sigma(O1s)/\sigma(Si2p) = 3.3$; where $\sigma 1S = 63.54$ and $\sigma Si2p = 19.14$ [13], very similar to the ratio found for the case of oxygen to silicon sensitivity factors. Table 2 includes the calculated atomic concentrations.
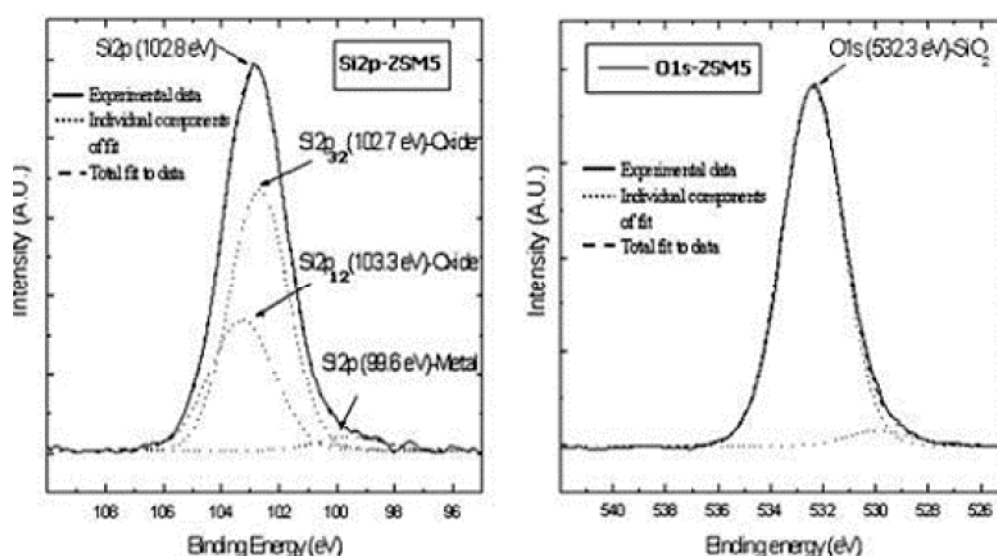

Fig. 3. High resolution XPS spectra for (a) Si and (b) O window corresponding to the synthetic zeolite ZSM-5, which was utilized as a standard for quantification. Atomic concentrations were calculated from the peak areas of the Si2p and O1s curve-fit components. The same procedure was followed for all the samples, whose calculated atomic concentrations are shown in Table 1.

Table 2. Calculated atomic concentration for different samples. Atomic concentrations were calculated from the peak areas of the Si2p and O1s curve-fit components. See Fig. 1, where Si and O windows spectra for the standard sample (ZSM5) are displayed.

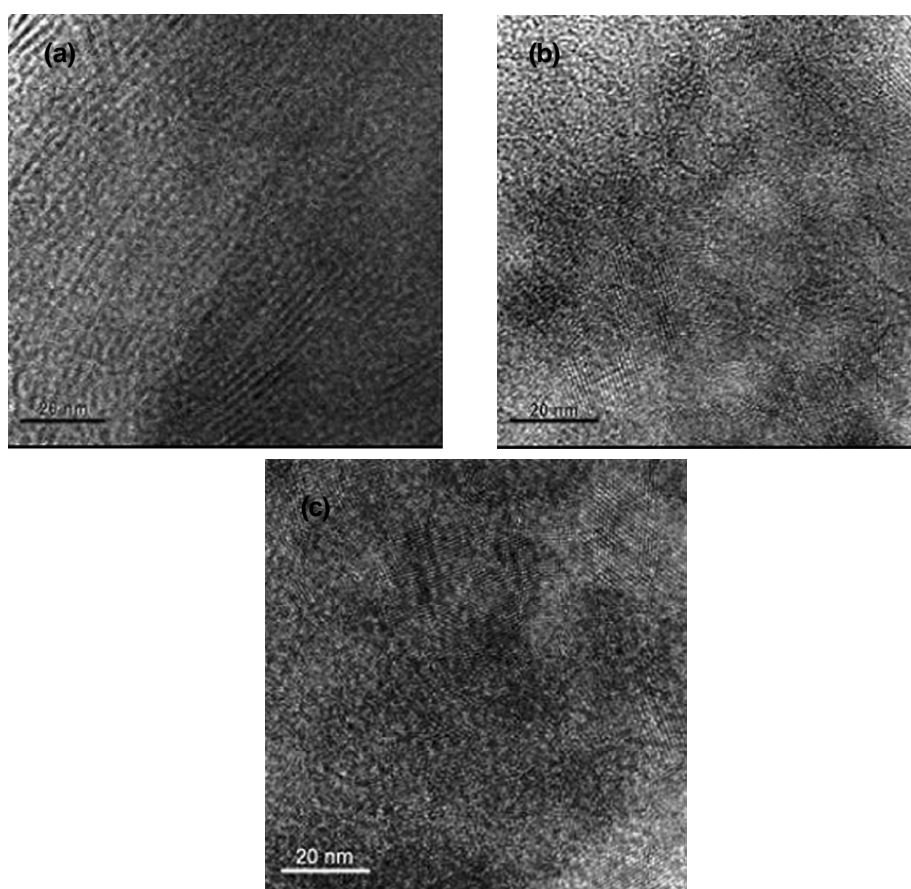| Sample	Atomic concentration (%)		
	O	Si	C (O)/C (Si)
ZSM5	71.0	29.0	2.44
NC	69.3	30.0	2.26
AC	70.0	30.0	2.33
AMC1	68.1	31.8	2.14
AMC2	69.4	30.5	2.27
AMC3	67.4	32.5	2.07
AMC4	66.1	34.0	1.94

Fig. 4. HRTEM images of clinoptilolite zeolites, show the comparison between acid clinoptilolite-zeolite AC (A) with acidic modified clinoptilolites AMC3 (B), and AMC4 (C), which have more quantity of silicon over each surface respectively. They revealed how the silicon layers were deposited with certain crystalinity at nanometric scale on the surface of AC, forming AMC respectively.

It may be observed from Table 2, that there is slight increase in the silicon atomic concentration for samples from *AMC1* to *AMC4* as a result of the treatment with silicon. This increase is from 30% for sample *AMC2* to almost 34% for sample *AMC4*; note that for the standard sample (*ZSM5*) it is 29%.

In all samples, there were not changes in the values of BE's, as long Si2p-oxide (102.8 eV) as O1s-SiO2 (532.3 eV). The added silicon atoms were attached to the structure of the sample with no change in the nature of the Si-O bonding in SiO_2. We can conclude, supported by the XPS measurements, that the

nature of the Si-O bonding remains in all the samples very close to the SiO_2 stoichiometry, which in the ideal case is the tetrahedral-type [14].

The silicon formed nanocrystals the surface of AC, forming AMC as may be observed in the HRTEM images of Fig. 4. This nanocrystallinity represents a very important finding, since it can help to improve the mechanical properties of the filters [3] and so allowing a more robust material for the treatment of samples with Cs and Sr isotopes pollutants.

4. CONCLUDING REMARKS

A series of acidic modified clinoptilolites (AMC) were obtained by a functionalization method designed ad-hoc. The resulting materials preserve the original crystalline structure of the zeolite while having the chemical surface groups enabling to sequester Cs, Sr and other dangerous ions in water and some types of solid waste (specifically, nuclear byproducts). The technological application of this method is currently under way and will reported separately.

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