Microporous and Mesoporous Materials 135 (2010) 187–196

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Step-wise dealumination of natural clinoptilolite: Structural and physicochemical characterization

Yunier Garcia-Basabe [a,b], Inocente Rodriguez-Iznaga [c], Louis-Charles de Menorval [d,**], Philip Llewellyn [e], Guillaume Maurin [d], Dewi W. Lewis [f,***], Russell Binions [f], Miguel Autie [g], A. Rabdel Ruiz-Salvador [a,*]

[a] Zeolite Engineering Laboratory, Institute of Materials Research and Engineering (IMRE), University of Havana, Havana 10400, Cuba
[b] Department of Physics, Faculty of Mechanical and Chemical Engineering, University of Matanzas, Matanzas 40100, Cuba
[c] Materials Technology Laboratory, Institute of Materials Research and Engineering (IMRE), University of Havana, Havana 10400, Cuba
[d] Institut Charles Gerhardt Montpellier, CNRS, Université Montpellier 2, Place E. Bataillon, 34095 Montpellier cedex 05, France
[e] Laboratoire Madirel UMR CNRS 6121, Université de Provence, Centre St Jérôme, 13397 Marseille cedex 20, France
[f] Department of Chemistry, University College London, 20 Gordon St., London WC1H 0AJ, UK
[g] Molecular Engineering Laboratory, Institute of Materials Research and Engineering (IMRE), University of Havana, Havana 10400, Cuba

ARTICLE INFO

Article history:
Received 20 March 2010
Received in revised form 16 July 2010
Accepted 17 July 2010
Available online 22 July 2010

Keywords:
Clinoptilolite
Heulandite
Dealumination
Al vacancy
Silanol nest

ABSTRACT

The step-wise dealumination of a natural clinoptilolite has been achieved through a new milder treatment, comprising cycles of aqueous solutions of hydrochloric acid with washing steps. The course of the dealumination was monitored by XRD, FTIR, TGA, UV–vis-DRS and NMR. The XRD patterns show a contraction of cell volume during progressive dealumination steps and a decrease in crystallinity after the third dealumination cycle. The framework and OH vibrations in FTIR spectra show progressive extraction of aluminum atoms from zeolite framework and consequently the formation of silanol nests. ^{27}Al MAS NMR indicates that low levels of octahedral aluminum species are created during the treatments.

1. Introduction

By modifying the chemical composition of the framework, the properties of a zeolite can be fine tuned [1–3]. Such modifications can be brought about during synthesis – for example by varying the synthesis gel, particularly Si/Al, or by inclusion of other species which will isomorphously substitute into the framework, such as iron or titanium. Alternatively, changes can be made post-synthesis and the main route here is to remove Al from the framework, with replacement by Si possible. The most important example is that of dealumination of synthetic faujasite structured materials, where the hydrophilic zeolite X (Si/Al ~1.5) can be converted into hydrophobic zeolite Y (with far greater Si/Al). These modifications to the framework, which do not modify the topology, can have significant impact on both the chemical and physical properties of zeolites. From a chemical point view, most of the changes in catalytic and sorption properties can be considered as being the result of the variation in the overall electronegativity of the solid, as discussed by Mortier and co-workers [4–6]. But another important result of such treatments are physical changes, such as to the thermal stability and pore volume, which result from both the changes to the framework and also to concomitant formation of extra-framework species [7,8]. Of course, where natural zeolites are concerned, only post-synthesis treatments are applicable!

Dealumination is most commonly achieved by the hydrolysis of Al–O bonds by acid leaching or through hydrothermal treatment in the presence of water vapors [9–11]. Dealumination leads not only to the breaking of Al–O bonds – making the Al available for extraction by very diluted acid leaching – but can also result to a loss of crystallinity, particularly where low Si/Al materials are treated. Thus, milder methods for dealumination are sought.

Clinoptilolite is the most common natural zeolite, which whilst isotypic with heulandite has a higher Si/Al: clinoptilolites having Si/Al > 4 and and heulandites Si/Al < 4 [12]. The abundance, low extraction cost and high chemical stability of clinoptilolite make this zeolite a very attractive material for adsorption and environmental applications. In this type of applications it is known that usually the performance of the zeolites are very dependent of Si/Al ratio. The framework of clinoptilolite (IZA code HEU), constructed of 4-4-1 secondary building units, consists of three chan-

---

* Corresponding author. Tel.: +53 7 8780903; fax: +53 7 8794651.
** Corresponding author. Tel.: +33 467143341; fax: +33 467143304.
*** Corresponding author. Tel.: +44 20 76794779; fax: +44 20 76797463.
E-mail addresses: lcdemenorval@univ-montp2.fr (L.-C. de Menorval), d.w.lewis@ucl.ac.uk (D.W. Lewis), rabdel@imre.oc.uh.cu (A.R. Ruiz-Salvador).

1387-1811/$ - see front matter © 2010 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2010.07.008

nels connected in two dimensions: two of them formed of 8-membered rings and the third of 10-membered rings. The 10-membered channel (A) and one of the 8-membered channels (B) runs parallel to the crystallographic axis *c*, with the second 8-membered (C) parallel to the *a* axis (Supplementary Fig. S1 in Electronic Supporting Information). The HEU topology also feature layers joined by reticularly rigid oxygen bridges. It is well known that a significant proportion of the Al resides in the tetrahedral sites (T2 following the notation of Alberti [13]) that form the interlayer links (Fig. 1a); the T2 site is about 40% occupied by Al, depending of zeolite sample [13–15]. Thus, it is clear that extensive Al removal can cause interlayer disconnection and consequent breakdown of the zeolite structure (Fig. 1b). Furthermore, it would be expected that only ~50% of the Al can be extracted without destroying the zeolite. However, appropriate hydrothermal treatments can result in migration of Si to fill the Al vacancies and thus stabilize the otherwise depillared structure. This appears to be the mechanism that explains the pioneering results of Barrer and Makki who treated natural clinoptilolite with hydrochloric acid of different strengths, obtaining a series of highly crystalline solids with progressive changes in adsorption properties [9]. More recently, clinoptilolite and heulandite dealumination has been considered by a number of authors, following similar or related treatments [16–20]. In these studies the acid treatments are performed on natural cationic forms of the zeolites, where decationization (ion exchange between compensation cations in the zeolites and the H_3O^+ ions in the acid solution) and the dealumination process can occur simultaneously in a competitive way. Moreover, these studies also showed that in order to remove more than 30% of the aluminum from the clinoptilolite framework it is necessary to use a high acid concentration ($\geqslant$1 M), which of course will also result in a significant reduction in the crystallinity.

In this work, using a natural Cuban clinoptilolite, we have developed a step-wise dealumination methodology, using milder conditions than previously considered, whose aim is to minimize loss of crystallinity and porosity upon Al removal. The progress of the dealumination is followed through different spectroscopic techniques and X-ray diffraction.

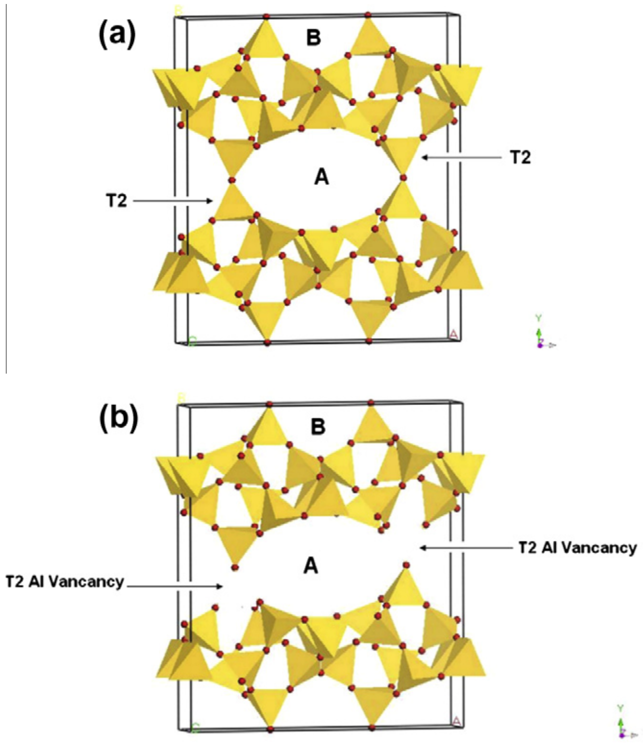

Fig. 1. The clinoptilolite framework view perpendicular to *c* axis. (a) Aluminum atoms in tetrahedral site T2. (b) Aluminum vacancies in T2 site.

2. Experimental

2.1. Starting materials

The clinoptilolite used in this work is the main phase present in the zeolitic rock (the raw mineral) from the Caimanes deposit, Moa (Cuba). In addition, Mordenite, Quartz, Feldspar and Montmorillonite are present. The raw mineral was ground and sieved to 32–90 μm grains and then purified by washing with distilled water in a fluidized bed process [21] to remove the non-zeolitic mineral phases. In addition, the denser and lighter fractions were discarded as they often contain feldspar and clays to obtain a material more rich in clinoptilolite phase [22]. After vacuum filtration and drying, this resulted in a mixture of about 87% clinoptilolite, 8.5% quartz and 4.5% Mordenite [23]. Herein this sample is referred to as purified zeolite or natural clinoptilolite (NZ). The chemical composition of the NZ sample is showed in Table 1.

The ammonia form of the natural clinoptilolite zeolite (denoted NH_4Z) was obtained by ion exchange with aqueous 1 M NH_4Cl solution at 100 °C for 40 h. The solid:liquid ratio was 1 g of solid: 10 ml of solution following a methodology described elsewhere [24]. The solution was changed every 8 h. The NH_4Z was washed with distilled water until no Cl^- was detected in the wash water by a $AgNO_3$ test, and then dried at 60 °C overnight. The acid form of this material, denoted HZ, was obtained by air calcining NH_4Z by heating at a rate of 5 °C min^{-1} to 400 °C and maintaining this temperature for 16 h.

2.2. Dealumination procedures

In order to minimize framework damage we use a lower concentration of HCl than that in many previous procedures [9,17,19,20,25]. Since one of the main effects of hydronium ions in zeolites is to also exchange with the extra-framework cations, this is avoided by the use of the acid form of the zeolite. Thus, HZ was treated with a 0.6 M HCl solution. The temperature and time of reaction was 100 °C and 2 h, respectively. The solid:liquid ratio was 1 g of solid: 10 ml of solution. After this treatment the zeolite was washed 3 times in an ultrasonic bath for 15 min each time with a dilute solution of 0.05 M of HCl at 70 °C. The solid:li-

Table 1
Chemical compositions and distance between tetrahedral sites-oxygen of the zeolite framework <TO> of the natural and modified zeolites.

% Atomic	NZ	HZ	HZD1	HZD3	HZD5
O	65.2(1)	66.1(2)	65.3(1)	65.6(4)	65.1(2)
Al	5.41(3)	6.15(4)	4.18(2)	3.94(1)	3.09(2)
Si	24.2(5)	26.7(4)	29.3(3)	29.8(4)	30.9(2)
Fe	0.98(9)	0.72(4)	0.89(6)	0.40(5)	0.23(3)
K	0.74(9)	0.34(8)	0.33(9)	0.25(4)	0.19(6)
Ca	2.58(5)	–	–	–	–
Mg	0.79(7)	–	–	–	–
Si/Al	4.48	4.34	7.00	7.55	10.00
Si/Fe	24.69	37.08	32.92	74.50	134.35
Al per unit cell	6.57	6.37	4.21	3.9	3.57
Vacancy per unit cell	0	0.11	2.36	2.67	3.62
<TO>/Å	1.647	1.647	1.645	1.644	1.643

The values in parenthesis are the standard deviations for atomic percentage in each element.
Vacancy per unit cell is the number of vacancies in tetrahedral framework and is calculated from: $\mathrm{Vacancy_{uc}} = 36 - \mathrm{Si_{nat}} - \frac{\mathrm{Al}}{\mathrm{Si}} * \mathrm{Si_{nat}}$, where $\mathrm{Si_{nat}}$ is the Silicon atoms by unit cell in natural zeolite and Al/Si is the aluminum/silicon ratio of the sample.
Mean tetrahedral atom to oxygen distance $< \mathrm{TO} >= \frac{n_{\mathrm{Si}}1.605+n_{\mathrm{Al}}1.72+n_{v}1.68}{36}$.