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Silica nanoboxes from alumina rich zeolites: thermal and chemical stability of the monomodal and bimodal materials

R. Le van Mao,* L. Lu, N. T. Vu, Q. Zhao, H. T. Yan, and N. Al-yassir

Industrial Catalysis Laboratory, Department of Chemistry & Biochemistry, Concordia University, 7141 Sherbrooke West, SP 275-09, Montreal, Quebec Canada H4B 1R6

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Silica nanoboxes synthesized from alumina-rich zeolites, showed two distinct categories of nano-structured materials. Entirely mesoporous nanoboxes (monomodal Al-nanoboxes) were highly thermally and chemically resistant even in the acidic form whereas calcination at high temperature of materials still containing some zeolite remnants (bimodal Al-nanoboxes), resulted in dramatic loss of surface area and pore volume. Pore closure by mobile and amorphous aluminic species was believed to occur. The high thermal and chemical stability of the monomodal Al-nanoboxes was found to be related to the highly siliceous character of the mesopore walls which contained isolated tetrahedral Al atoms linked to tetrahedral Si atoms. Treatment of the acid form of the bimodal nanoboxes with La or Ce containing solutions resulted in quite thermally stable materials owing to the reduction of the number of protonic sites by the rare-earth metal ions.

KEY WORDS: silica nanoboxes from Al-rich zeolites; thermal stability; monomodal; bimodal pore size distribution; structure of the cavity walls.

1. Introduction

Novel mesoporous materials, silica nanoboxes [1], were synthesized by controlled dealumination of alumina-rich zeolites (X and A types). In contrast with the synthetic MCM-41 materials [2] which show relatively low thermal and chemical stability [3], the new silica nanoboxes could withstand a temperature of at least 700 °C or the loading of triflic acid – a superacidic compound – up to 20–25 wt without undergoing significant structural collapse [1].

Silica nanoboxes were obtained by pore enlargement of zeolite materials using ammonium hexafluorosilicate (AHFS) in buffered solution which "selectively" removed some zeolite walls in the way that the newly created nanometer-sized cavities exhibited a quite narrow pore size distribution (monomodal Al-nanoboxes) [1]. However, if some zeolite "clusters" were left in these cavities (bimodal Al-nanoboxes), the material underwent a rapid pore closure upon activation at high temperature, resulting in a dramatic decrease in surface area and pore volume.

In the present paper, we report the results of our investigations on the chemical composition and structure of the walls of the mesoporous cavities of the monomodal Al-nanoboxes. We also report that in the bimodal Al-nanoboxes, the "mobile" aluminic species resulting from the thermal degradation of the (left-over) zeolite clusters are the cause of the pore closure. Finally, some methods are proposed in order to improve the thermal stability of the bimodal Al-nanoboxes, such as ion-exchange with rare-earth metal ions (La^{3+} or Ce^{3+}) [4].

2. Experimental

2.1. *Secondary synthesis of Al-nanoboxes*

These materials were prepared by controlled dealumination of the NaX zeolite using a solution of AHFS in a manner similar to that reported in ref. [1]. In particular, the (m)Al-nanoboxes and the (b)Al-nanoboxes which were the monomodal and the bimodal materials, were obtained by secondary synthesis from the NaX using preferably the following procedures.

2.1.1. *(m)Al-nanoboxes*

10.0 g of NaX zeolite (Linde, powder form, dried at 120 °C overnight) were placed in a glass beaker containing 414 cm^3 of 0.8 M ammonium acetate aqueous solution. Then, 46 cm^3 of an aqueous solution of 0.5 mol dm^{-3} of AHFS, freshly prepared, were added under moderate stirring. After 30 min of reaction at room temperature, the beaker was placed in a water bath heated at 50 °C and left there for 1 h. The solid was then rapidly separated by filtration and washed on the filter with 2,000 cm^3 of warm water (50 °C). The obtained material was subsequently immersed in 2,000 cm^3 of boiling water and refluxed for 1 h.

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*To whom correspondence should be addressed.
E-mail: lvmao@alcor.concordia.ca

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After filtration and washing with 300 cm^3 of distilled water, the solid was dried at 120 °C overnight (weight = 7.0 g). This sample was called (m)Al-nanoboxes because it showed upon calcination at 600 °C for 3 h a sharp peak of pore size distribution in the mesopore region (monomodal pore texture).

2.1.2. (b)Al-nanoboxes

10.0 g of NaX zeolite (Linde, powder form, dried at 120 °C overnight) were placed in a glass beaker containing 200 cm^3 of 0.8 M ammonium acetate aqueous solution. Then, 25.0 cm^3 of an aqueous solution of 0.5 mol dm^{-3} of ammonium hexafluorosilicate, freshly prepared, were added under vigorous stirring, using a syringe on an infusion pump at a rate of 0.9 cm^3 min^{-1}. The slurry was left at room temperature for other 2 h. The solid was then separated by filtration and washed on the filter with 600 cm^3 of hot water. The sample, called (b)Al-nanoboxes, was finally dried at 120 °C overnight.

The obtained nanobox materials, the (m)Na-deal X and the (b)Na-deal X, respectively, showed the textural properties reported in table 1.

2.2. Preparation of the NH_4 and the acidic forms of the Al-nanoboxes

The ammonium forms, namely (m)NH_4-deal X and (b)NH_4-deal X respectively, were obtained by ion-exchange with ammonium ions [1]. Subsequent calcination at 600 °C resulted in (m)H-deal X and (b)H-deal X samples, respectively.

2.3. Preparation of the (b)LaH-deal X and (b)CeH-deal X samples

10 g of (b)NH_4-deal X were placed in a beaker containing 100 cm^3 of an aqueous solution of 5 wt of La (III) nitrate hexahydrate (Strem Chemicals) and the suspension was mildly stirred at room temperature for 2 h. The solid was filtrated, washed with distilled water, dried at 120 °C overnight and finally activated at 700 ° C for 3 h. The obtained sample, which contained 1.3 wt of La, was called (b)LaH-deal X.

The same treatment of (b)NH_4-deal X with Ce (III) nitrate hexahydrate aqueous solution was carried out. The solid, similarly dried and activated, was called (b)CeH-deal X. Its content in Ce was 1.2 wt.

2.4. Characterization of the solid materials

Some of the techniques used to characterize the materials comprising the atomic absorption spectroscopy (AAS) for the determination of the Si/Al ratio, X-ray powder diffraction (in particular at small angle), BET for the determination of textural properties, thermogravimetric (TGA) and differential thermal (DTA) analyses performed in Ar flow, were already described in detail in the previous work [1]. In particular with the technique of X-ray diffraction at small angles, great cares were taken in order to eliminate eventual optical artefacts. In addition, our investigation procedure and results were constantly compared to those used and obtained in the characterization of MCM-41 materials with increasing Al content [5]. La and Ce contents were measured using an inductively couple plasma emission spectrometer (Agilent 7500 ICP-MS). Other characterization techniques included (single-pulse) ^{27}Al and ^{29}Si magic angle spinning (MAS) NMR which were performed on a Bruker DSX300 machine, operating at 7 T (300.13 MHZ ^{1}H frequency). Samples were packed in 4 mm o.d. rotor, spinning at 12–14 and 6 kHz for ^{27}Al and ^{29}Si experiments, respectively. For ^{27}Al experiments, between 240 and 8000 scans were accumulated with 1 s repetition time, whereas between 1100 and 3000 scans with 20 s repetition time were necessary for ^{29}Si experiments. Aluminum chloride hexahydrate and 2,2-dimethyl-2-silapentane-5-sulfonate sodium salt (DSS) were used as external references for ^{27}Al and ^{29}Si chemical shifts, respectively.

3. Results and discussion

3.1. Concepts for the production of silica nanoboxes by secondary synthesis from zeolites

Synthetic zeolites, crystalline aluminosilicates, possess networks of pores (cavities and/or channels) whose

Table 1

Pore characteristics of the (m)Al-nanoboxes studied in this work

Sample	Temp. (° C)	BET surface area (m^2 g^{-1})			Sorption vol (cm^3 g^{-1})			Average mesopore diameter (nm)
		S_t	S_{mes}	S_{mic}	V_t	V_{mes}	V_{mic}	
Parent NaX (Si/Al = 1.2)	250	740	35	696	0.31	0.03	0.28	n.a.
(m)Na-deal X (Si/Al = 3.2)	250	451	451	0	0.54	0.53	0	4.6
(m)Na-deal X	600	252	252	0	0.38	0.37	0	4.7
(m)NH_4-deal X	250	443	443	0	0.57	0.56	0	4.7
(m)H-deal X (Si/Al = 3.9)	600	328	328	0	0.43	0.42	0	4.5

n.a. = not applicable.

size is smaller than 1 nm. Alumina-rich zeolites, such as A and X types, have frameworks made of tetrahedral silicon and aluminum atoms, a Si/Al atom ratio equal to or (slightly) higher than 1.0, a pore size ranging from ca. 0.3 to 0.8 nm, a total surface area which may exceed 600 m^2 g^{-1}. On the other hand, silica-rich zeolites, such as the pentasil ZSM-5, have a quite high Si/Al atom ratio (sometimes close to 1,000) and a system of micropores with size smaller than 1.0 nm.

Zeolites have important commercial applications, particularly in catalysis. However, for catalytic processes dealing with bulky molecules, it is necessary to have materials with pores larger than the nanometer. One important achievement in the synthesis of the nanostructured materials is the development of the silica-containing MCM-41 structure [2]. Unfortunately, these materials are not very thermally and chemically stable.

One of the objectives of our research laboratory is the development of porous materials whose size is in the range of a few nanometers. Our approach is to use an already (structurally) organized materials like zeolites and to carry out the enlargement of their small pores by submitting them to a very mild and gradual leaching operation. Such approach is similar to that of the (selective) removal of some walls of small-sized apartments of a building in order to obtain larger apartments, without obviously provoking a total collapse of the building.

Pore walls of alumina-rich zeolites are predominantly made of Al: thus, a pore enlargement has to be carried out by an acid leaching or similar process (dealumination). On the other hand, the pore enlargement of silica-rich zeolites must involve a silica leaching medium (desilication) which is usually a base.

These operations are not easy at all because a serious structural damage or collapse is always possible around the corner. Therefore, the key for a successful production of nanoboxes consists of a good choice of leaching parameters to ensure a selective and gradual Al or Si removal, and a set of quite severe criteria of selection to warranty the physical and chemical properties of the obtained materials.

3.2. Dealumination of X and A zeolites

Methods of Al removal from zeolite framework are well-known [6]. However, if a very dilute mineral acid solution is used as Al leaching medium, it is quite difficult to obtain nanoboxes with no micropores, no apparent crystallinity, new mesopores showing a sharp pore size distribution, and (still) significant surface area (higher than 300 m^2/g from a value of 740 m^2/g for the NaX) and pore volume (at least of 0.4 cc/g) [1]. With dilute acid solutions, the probability of success to obtain the wanted nanoboxes does not usually overcome 10 and the materials obtained are not very thermally and chemically resistant. Surprisingly, the production of nanoboxes (from Na-X zeolite) having the characteristics as previously defined, is much easier (success rate of 80 and higher) by using as dealuminating agent the ammonium hexafluorosilicate in buffered solution.

In the following, the results of this work will be used to explain these surprising characteristics (thermal and chemical resistance).

3.3. Structure of the walls of the monomodal nanoboxes

The solid state ^{27}Al and ^{29}Si -NMR spectra of the parent Na-X zeolite are shown in figures1 and 2, respectively. This (quite well crystallized) zeolite has all its Al atoms in tetrahedral configuration as seen in the ^{27}Al spectrum (figure1.1) while the ^{29}Si spectrum of its Si atoms shows several peaks corresponding to different environments, i.e corresponding to the number of Al atoms linked, through oxygen atoms, to them : Si (nAl) [7a](figure 2.1). The ^{27}Al and ^{29}Si -NMR spectra of the H-deal X sample (m) Al-nanoboxes) (figures 1.2 and 2.2, respectively) are very similar to those recorded for the (thoroughly) dealuminated zeolite NaY using $SiCl_4$ vapor and repeatedly washed [7b]. Thus, this nanobox material shows only one peak for the ^{29}Si–NMR spectrum which is located at a chemical shift normally assigned to the Si (0Al) environment (Figure2.2) while its ^{27}Al spectrum suggests that these Al atoms are predominantly in tetrahedral configuration with a few ones having a (probably distorted) octahedral configuration (figure1.2). The existence of these Al tetrahedral sites is confirmed by DTA/TGA. In fact, there is a weight loss of circa 6.4 wt (average value of several runs) within the temperature range of 300 °C and 450 °C (TGA curve, not included), which corresponds to the weight loss due to the decomposition of the ammonium ions (DTA curve, not included). By taking into account that the decomposition of ammonium ions results in the release of a proton in accordance with the following equation: $[NH_4^+ \Longrightarrow (NH_3) + H^+]$, this weight loss allows us to calculate the density of the Al tetrahedral sites: $[Al]_{tet} = 3.8 \times 10^{-3}$ mol g^{-1}. This value is perfectly in agreement with the Si/Al ratio of 3.2 as determined by AAS for the (m) Na-deal X (table1).

At first, the highly siliceous character of the walls of the newly formed cavities (Table 1) is said to provide the new nanoboxes with a higher thermal and chemical stability, allowing them to withstand high-temperature treatments or corrosive actions of very acidic species such as concentrated sulphuric acid or triflic acid [1]. Distorted configurations of Al sites are also seen as the causes of the stability of many modified or "non-normally" synthesized zeolitic or mesoporous aluminosilicates such as the AlMCM-41 materials, as recently reported [8].

Our NMR data (figures 1 and 2) allows the following interpretation. The treatment of the Na-X with AHFS in buffered medium effectively results in a non-homogeneous dealumination process, i.e. starting with the

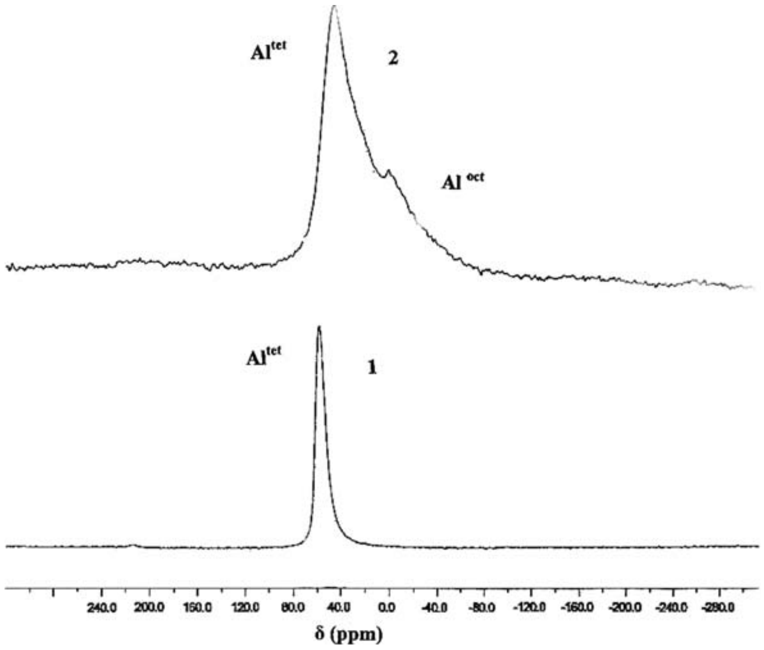

Figure 1. MAS ^{27}Al–NMR spectra of : 1) parent Na-X ; 2) (m)H-deal X (activated at 700 °C). Al^{oct}: octahedral Al; Al^{tet}: tetrahedral Al.

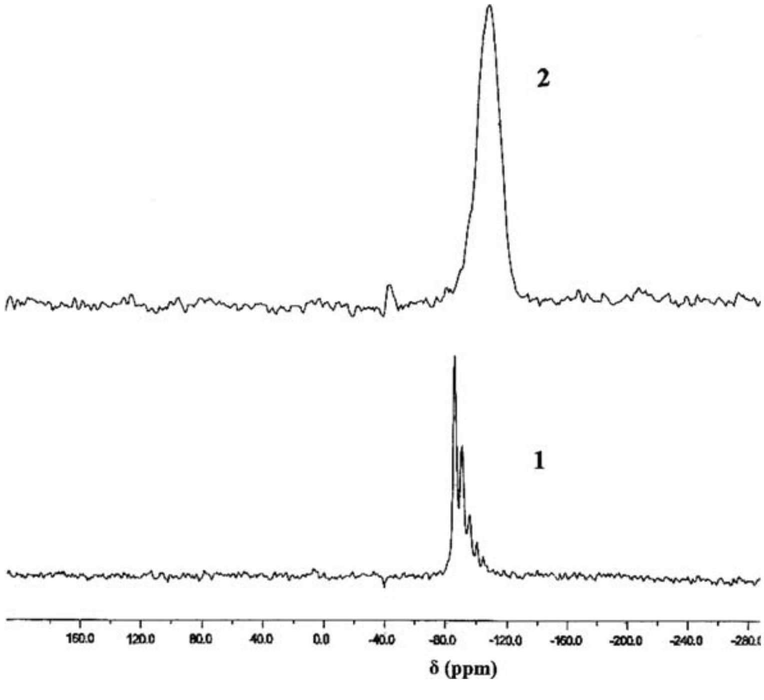

Figure 2. MAS ^{29}Si–NMR spectra of: 1) parent Na-X ; 2) (m)H-deal X (activated at 700 °C).

extraction of Al atoms accompanied by their replacement by Si atoms, through an exchange Al-Si reaction, as hypothesized by Skeel and Breck [9]. The corrosive action of AHFS only stops when the remaining Al atoms are in well isolated positions. In fact, these Al atoms are predominantly in the tetrahedral configuration (figure 1.2) and show an environment which can be depicted as Al (4 O-Si), as evidence by the ^{29}Si NMR spectrum of figure 2.2. Thus, new mesopores are created, which have silica rich pore walls made of tetrahedral Si atoms and in which tetrahedral Al atoms are inserted in largely dispersed manner. We believe that the stability of the new nanoboxes is closely related to their unique and solid wall structure.

3.4. *The bimodal nanoboxes*

As reported in table 2, the bimodal nanoboxes [(b) deal-X] when activated at high temperatures, lose almost all their surface areas. However, it does not appear that

Table 2
Pore characteristics of the (b) Al-nanoboxes [(b) deal X] studied in this work

Sample	Temp. (° C)	BET surface area (m^2 g^{-1})			Sorption vol (cm^3 g^{-1})			Average mesopore diameter (nm)
		S_t	S_{mes}	S_{mic}	V_t	V_{mes}	V_{mic}	
(b)Na-deal X	250	363	230	133	0.38	0.33	0.05	5.4
(b)NH_4-deal X	250	234	190	45	0.39	0.36	0.02	6.9
(b)NH_4-deal X	300	261	166	95	0.37	0.33	0.04	7.7
(b)NH_4-deal X	350	174	160	14	0.35	0.34	0.01	7.3
(b)NH_4-deal X [(b)H-deal X]	400	152	152	0	0.32	0.32	0.00	8.0
(b)NH_4-deal X [(b)H-dealX]	450	118	118	0	0.30	0.30	0.00	9.6
(b)NH_4-deal X [(b)H-deal X]	500	71	71	0	0.24	0.24	0.00	12.5
(b)NH_4-deal X [(b)H-deal X]	550	9	9	0	0.03	0.03	0.00	n.a.
(b)H-deal X	600	7	6	0	0.02	0.02	0.00	n.a.
(b)LaH-deal X	700	163	130	36	0.24	0.22	0.02	6.0
(b)CeH-deal X	700	145	120	25	0.26	0.23	0.02	7.3

n.a. = not applicable.

these materials have undergone a complete structural collapse. In fact, the diffraction pattern of the (b) deal-X material (figure3.2) indicates that the mesoporous cavities (estimated diameter : 6.0 nm) are there along with some zeolite remnants. These nano-sized cavities are quite similar to those obtained with the monomodal nanoboxes [1]. However, the (presumably amorphous) aluminic species resulting from the action of the protons on the zeolite remnants, move towards the cavity openings during the calcination. This leads to the closure of the pore openings, resulting in a dramatic decrease in surface area, as also observed elsewhere [6].

To evidence the phenomena of motion of aluminic species under the effect of high temperature heating, the (b) NH_4-deal X was investigated with the TGA/DTA and BET techniques. As with the (m) NH_4-deal X sample, the bimodal sample exhibited a weight loss (of circa 4.7 wt) between 300 °C and 450 °C due to the thermal decomposition of ammonium ions. BET surface area measurement done on the (b) NH_4-deal X sample, having been activated at different temperatures (table 2), allowed us to follow up the phenomenon of pore closure. At 300 °C, when ammonium ions started to decompose into protons, the zeolite component as revealed by the surface area of the micropores (S_{mic}, table 2), experienced a rapid structural collapse so that at 400 °C, all the zeolite clusters were destroyed by the well known "proton attack''. The mesoporous component which could be represented by its surface area S_{mes} (table 2), offered a better resistance to this proton attack. However, at 550 °C, even the surface area corresponding to these mesopores, became nil (table 2). To interpret the last phenomena, we have to consider the following facts:

i) Small angle X ray diffraction pattern of the (b) NH_4-deal X [or (b) H-deal X] , activated at 700 °C (figure 3) still clearly showed the presence of the

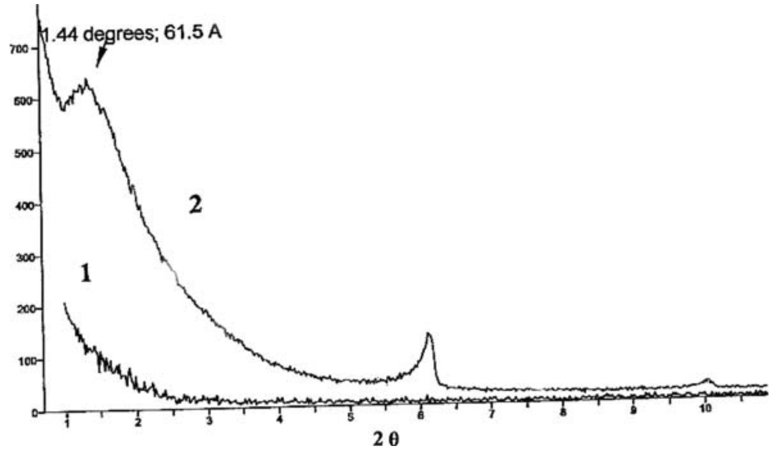

Figure 3. 1)Pattern 1 is that obtained with empty sample holder. 2) small angle X-ray pattern of the (b)H-deal X (activated at 700 °C).

mesoporous cavities similar to those of the monomodal nanoboxes [1].

ii) The walls (of the cavities) of the bimodal nanoboxes were not different from those of the monomodal nanoboxes: if the latter could withstand high temperature treatment, why did the former "structurally'' collapse?

iii) The key problem seemed to be the zeolite remnants in the bimodal nanoboxes: once the ammonium ions were decomposed into protons, the latter started to extract Al as octahedral Al, so that these amorphous aluminic species were now free to move on the internal surface of the mesoporous cavities. Moreover, at high temperatures, the natural tendency of these aluminic species was to move towards the outside region of the cavities which finally led to a gradual closure of the pore openings, as evidenced by a dramatic decrease in surface area and sorption volume (table 2).

Another piece of experimental evidence of this hypothesis of pore closure upon calcination was provided by ion-exchanging the ammonium ions of the bimodal nanoboxes with La^{3+} or Ce^{3+} ions, prior to their high temperature treatment. In fact, it was shown that treatment of the bimodal Al-nanoboxes (ammonium forms) with La^{3+} or Ce^{3+}ions containing aqueous solution stabilized the zeolite remnants, thus preventing the structure damaging effect of protons at high temperatures (table2). This is probably due to the replacement of some ammonium ions, sit on the tetrahedral Al atoms of the remaining zeolite clusters, by these lanthanide cations, so that there are less protons (generated by the thermal decomposition of ammonium ions) to "attack'' the zeolite component. This stabilizing phenomenon by La^{3+}ions was previously observed with ammonium X, Y and desilicated Y [4].

Some enhanced stability of the bimodal Al-nanoboxes was also observed by incorporation (into the cavities) of some Al alkoxides or silicon containing species prior to the thermal treatment [9].

Finally, silica nanoboxes could be produced from silica-rich zeolites (example: ZSM-5) this time by selective desilication, so that it is now possible to have two categories of nanoboxes, Si-nanoboxes and Al-nanoboxes, corresponding to the two categories of parent zeolites used, Si-rich and Al-rich zeolitic materials, respectively [9]. The (quite large) surfaces of these novel materials are hydrophobic and hydrophilic, respectively.

4. Conclusion

Silica nanoboxes which were synthesized from alumina-rich zeolites, showed two distinct categories of nano-structured materials: entirely mesoporous nanoboxes (monomodal Al-nanoboxes) and nanoboxes still containing some zeolite remnants (bimodal Al-nanoboxes). In contrast with the monomodal material, the ammonium form of the bimodal material, when heated at high temperature, experienced dramatic losses of surface area and pore volume. The cause of such textural changes was clearly identified as pore closure owing to the mobility of the aluminic species produced by protons attacking the zeolite component.

Treatment of the ammonium form of the bimodal nanoboxes with La or Ce containing solutions resulted in quite thermally stable materials, probably due to the reduction of the number of protonic sites upon ion-exchange with the rare-earth metal ions (III_b cations).

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