Structural incorporation of nitrogen into zeolites, and alpos: ab initio molecular orbital calculations on stability and basicity

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Abstract

Ab initio molecular orbital calculations (HF/6-31G∗) are used to obtain thermodynamical information on the possibility to form NH-bridging or NH_2-terminal groups in amorphous and crystalline materials containing Si–O–Si and Al–O–P structures, such as for instance, zeolites and aluminophosphates. We have employed dimeric model clusters Si–O–Si and Al–O–P which contain NH_2-terminal groups or an oxygen atom substituted by a NH bridging unit. The Brönsted basicity and the softness–hardness of these structures have been determined using the proton affinity and the HOMO energy, respectively. The obtained results indicate that for both Si–O–Si and Al–O–P linkages and from a thermodynamic standpoint, the formation of a NH_2 terminal group is the most favorable process being exothermic by 6–7 kcal mol^{-1}, whereas the substitution of a bridging oxygen by a NH group is endothermic by 27–28 kcal mol^{-1}. Therefore, it appears that at lower temperatures one should preferentially form NH_2-terminal groups and the NH-bridging will be formed when increasing the temperature. The calculated proton affinities indicate the following order for Brönsted basicity of the nitrogen systems: dimethylamine > $H_3SiOSiH_2NH_2$ > $H_3SiNHSiH_3$ > $H_3AlOPH_2NH_2$, and that the bridged and terminal systems can be classified as strong bases. The calculation of NH stretching frequencies allows to distinguish between NH-bridging will be formed and NH_2-terminal groups because the NH stretching on substituted NH-bridging and NH_2-terminal Si–O–Si and Al–O–P linkages differ by 100 cm^{-1} and 50 cm^{-1}, respectively. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Zeolites are a class of aluminium silicates with large cavities (cages) linked by pores. Acid sites distributed over the large internal surface activate chemical bonds and thus are responsible for a catalytic function of zeolites [1]. The typical acid centers of zeolites are Brönsted acid sites which compensate the negative charge as-sociated to the tetrahedrally coordinated framework Al. The acid strength of those sites has been obtained by calculating the proton affinity (P.A.) or protonation energy of an anionic cluster [2–4]. Also, the properties of zeolites have been analyzed in terms of their softness and hardness, as introduced by Klopman [5], Salem [6], Pearson [7] and Fleming [8] (H.S.A.B. principle), and the parameters which control these properties have been established [9].

Other molecular sieves are synthesized containing Al and P in the framework and they

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have been denoted as ALPOs [10]. These are no acidic, and Brönsted acidity is developed when Si is introduced in the framework generating the so called SAPO's molecular sieves [11].

With respect to the basicity of zeolites, this is of Lewis type and it is associated to framework oxygens [12], the strength depends on the nature of the charge compensating cation, being the largest for the alkali series and increasing when decreasing the charge to radius ratio [12]. In any case the basicity of zeolites and even ALPOs is weak in strength [13]. It would appear that this basicity could be increased if framework and terminal-oxygens in zeolites and AlPOs could be exchanged by nitrogen.

In this way, Stein et al. [14] tried to substitute bridging oxygens by NH-bridging in AlPO-5 and HY zeolite at elevated temperatures, but the experiments did not result in the formation of Si–N or Al–N bonds. These authors gave qualitative references which indicate that silicates glasses and gels [15–18] may incorporate some nitrogen when treated with ammonia at elevated temperatures. Kerr and Shipman [19] described an amido zeolite Y, which they tried to obtain by the reaction of the hydrogen zeolite Y with ammonia at elevated temperatures and 760 Torr of pressure, converting $SiO_3(OH)$ into $SiO_3(NH_2)$ sites, which were detected using infrared and thermogravimetric techniques. Schnickd et al. [20] had synthesized a sodalite structure with phosphorus–nitrogen framework, which was analysed by XRD. The authors showed that in order to balance the P–N–P bond a Cl^- ion surrounded by tetrahedrally arranged Zn^{2+} ions was placed into the center of each β cage.

More recently [21], it has been presented that an amorphous aluminophosphate can form Al–N–P bonds when it is heated with NH_3 at high temperature. The formation of Al–N–P and Al–O–P–NH$_2$ has been demonstrated [22], and the resultant materials are more basic than zeolites.

The present paper describes a theoretical study using ab initio molecular orbital calculations and model clusters to obtain thermody-

namical information on the formation of NH-bridging or NH$_2$-terminal groups in amorphous and crystalline materials containing Si–O–Si and Al–O–P structures such as for instance zeolites and aluminophosphates. The Brönsted and Lewis base strength, and softness–hardness of the possible NH-bridging and surface NH$_2$ groups have been obtained. The Brönsted basicity has been determined by calculating the proton affinity of dimeric clusters [Si–O–Si] and [Al–O–P] which contain NH$_2$-terminal groups and oxygen-bridging atoms substituted by a NH-bridging unity. The Lewis basicity or donor capacity is determined using the HOMO (Highest Occupied Molecular Orbital) energy of the model clusters. Finally the I.R. stretching frequencies of the NH groups in the different clusters have been calculated.

2. Models and methodology

Calculations were carried out at the Hartree–Fock self-consistent field with a 6-31G∗ basis set [23–25] (HF/6-31G∗) which has polarisation functions (*d*-type) on non hydrogen atoms. The Berny analytical gradient [26] method was used for the optimization of the geometry of the cluster structures. These ab initio calculations were performed on IBM RS/600 workstations using both Gaussian 92 [27] and Gaussian 94 [28] package programs. In our calculations we have used the model cluster approximation, since it has been successfully used to explain a large number of amorphous silicates and zeolite properties [29]. The dimeric model clusters selected are shown in Fig. 1 and can be classified in two groups. The first one represents clusters with a NH-bridging, i.e, $H_3SiNHSiH_3$ and $H_3AlNHPH_3$. The second type of clusters contain a NH$_2$-terminal group, $H_3SiOSiH_2NH_2$ and $H_3AlOPH_2NH_2$, and can be used to simulate the existence of a NH$_2$ linked to the terminal atoms. In order to preserve the correct charge and spin multiplicity of
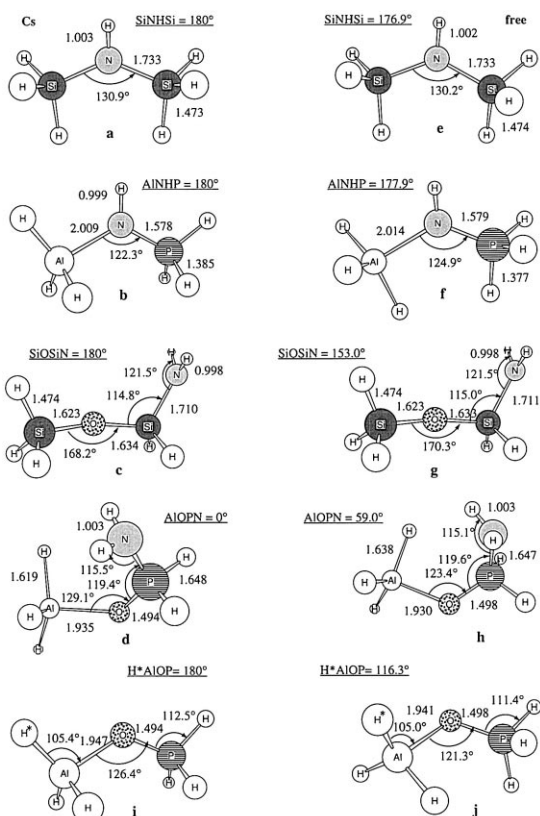
Fig. 1. 6-31G∗ optimized parameters for the dimeric clusters obtained using Cs and no symmetry (free) restrictions. (a) and (e) $H_3SiNHSiH_3$, (b) and (f) $H_3AlNHPH_3$, (c) and (g) $H_3SiOSiH_2NH_3$, (d) and (h) $H_3AlOPH_2NH_3$, (i) and (j) H_3AlOPH_3.

the models, the 'dangling' bonds that would connect the model with the rest of the solid were saturated by hydrogen atoms [29,30]. In this paper we do not use OH groups to saturate the 'dangling' bonds, to prevent the formation of intramolecular hydrogen bonds and/or structures with chemical meaning [29,31,32], because preliminary calculations show the existence of these problems.

Besides, calculations of Blaszowski and Van Santen [33] and Blaszowski et al. [34,35] show that the utilization of OH groups instead of H atoms does not change the results of the studied mechanisms. Also, Sauer [31] and Brand et al. [36,37] are shown that the OH groups produce an exaggerated electrostatic results. The

Brönsted basicity of the clusters was determined by calculating the proton affinities of the clusters. The geometry of the localized protonated clusters are shown in Fig. 2. The optimization of the geometry of the protonated and neutral clusters was carried out using both Cs and no symmetry (free) restrictions. As a reference base, we have also calculated the neutral and protonated dimethylamine at HF/6-31G∗ level to compare the basicity of the nitrogen containing materials with that of a well known basic molecule such as the dimethylamine. In order to evaluate the Lewis basicity and 'softness' character of these clusters we have chosen the energy of the HOMO. The structures of the neutral clusters and dimethylamine were characterized by calculating the Hessian matrix and analyzing the vibrational normal modes.
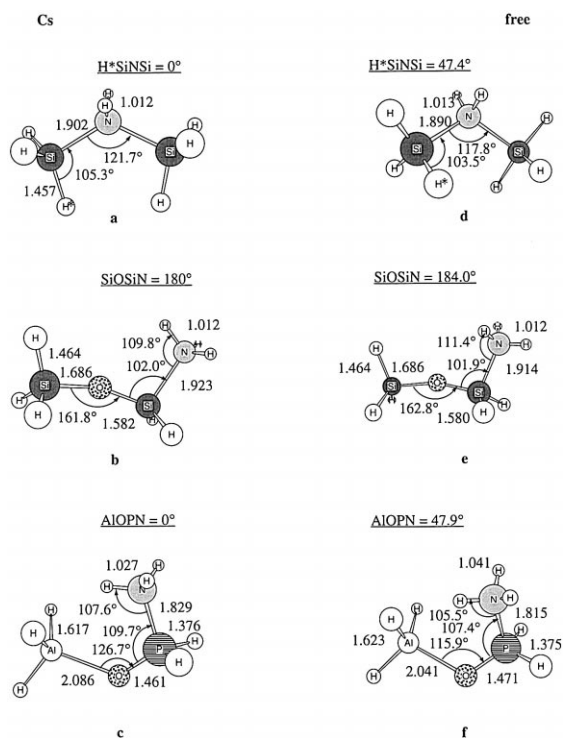

Fig. 2. 6-31G∗ optimized parameters for the protonated dimeric clusters obtained using Cs and no symmetry (free) restrictions. (a) and (d) $H_3SiNH_2SiH_3$, (b) and (e) $H_3SiOSiH_2NH_3$, (c) and (f) $H_3AlOPH_2NH_3$.

3. Results and discussion

3.1. Geometrical parameters of the clusters

The geometrical parameters obtained by the optimization with Cs symmetry and without constrains (free) for the neutral clusters are shown in Fig. 1. In the $H_3SiNHSiH_3$ cluster, the bond distances and the Si–N–Si angle are practically the same for the structure with Cs symmetry and for the fully optimized one (see Fig. 1a and e), being the only difference a little deformation of planarity of Si–NH–Si. The comparison of the obtained values for the SiO distance (1.733 Å) and the Si–N–Si angle ($\sim$ 130–131°), with the values corresponding at HF/6-31G$*$ of the disiloxane molecule ($H_3SiOSiH_3$) [38] (1.626 Å and 170.1°), indicate that the replacement of a oxygen-bridging with a NH-bridging group produces an increase in the distance of the silicium to the nitrogen atom by ca 0.11 Å, and a decrease of the Si–N–Si angle by ca 40°. Contrarily, one observes that the geometry of the $H_3SiNHSiH_3$ cluster is analog to the calculated for $H_3SiOHAlH_3$ (Si–O–Al = 131.9° and 131.0°, and Si–N distance = 1.702 Å and 1.721 Å, at HF/6-31G$*$ and MP2/6-31G$*$ [39], respectively). These data lead to suppose that the geometry of a silicon zeolite with a NH-bridging group is not much different to the corresponding zeolite containing framework Al and bridging OH groups. In other words, the geometrical modifications introduced by the exchange of some oxygen by nitrogen can be perfectly stabilized owing to long range effects of the zeolite structure.

The geometrical conformations of the H_3Al-$NHPH_3$ optimized cluster (Fig. 1b and f) with Cs symmetry and without symmetry are slightly different. In relation with the fully optimized conformation, the AlH_3 group and the PH_3 group have rotated $\sim$ 60° around the Al–N and P–N bonds, respectively, respect to the Cs conformation. The Al–N and P–N bond distances have practically the same values in the two conformations, $\sim$ 2.01 Å (Cs) and $\sim$ 1.58 Å (free), there is a little difference (approx. 2–3°) in the Al–N–P angle between the fully optimized cluster (124.9°) and the restricted optimized cluster. These values are different to the distances of the linkages, Al–O (1.74 Å), P–O (1.52 Å) and the Al–O–P bond angle (143.0°) which are the standard values employed on the calculation of the silicoaluminophosphates [40]. Comparison of the $H_3AlNHPH_3$ and H_3AlOPH_3 geometries (see Fig. 1) shows that the substitution of an oxygen-bridging by a NH-bridging causes a lengthening of Al–O and N–P bond distances, $\Delta r \approx 0.073$ Å and $\Delta r \gg 0.081$ Å, respectively. Unfortunately, we have not found experimental values for Al–N–P system to be able to verify our calculated values. However, the trends are in good agreement with the mean experimental values determined in zeolites AlPO-n ($n = 11$ [41], 16 [42], 18 [43], 31 [44] and 41 [45]) where the $\langle Al$–$O\rangle$ and $\langle P$–$O\rangle$ observed distances are (1.65 Å–1.85 Å) and (1.54 Å–1.58 Å) respectively, and the observed $\langle AlOP\rangle$ angles are in the range 125°–180°. Moreover, the experimental values of AlPO-31 are similar with the calculated structural parameters.

The geometries of the $H_3SiOSiH_2NH_2$ cluster with Cs and free symmetry (Fig. 1c and g) are practically the same, though the fully optimized cluster presents a dihedral angle Si–O–Si–N of 153.0°, which means that the planarity of the framework with Cs symmetry is broken. In both conformations the distances r_{SiO}, r_{SiN} and r_{NH} are practically identical, but nevertheless it exists a small difference of ca 2° in the Si–O–Si angle. These geometrical parameters are nearly identical to the obtained values for disiloxane at HF/6-31G$*$ level [38], but the inclusion of a NH_2 terminal group increases the Si–O bond distance, in the (O–SiH_2–NH_2) moiety by (0.01 Å. The Si–O–Si angle (170.3°) is always greater than the experimental value (144.1°) of disiloxane [46]. This is due to the flexibility of the Si–O–Si angle, which requires a high level calculation to obtain an accurate
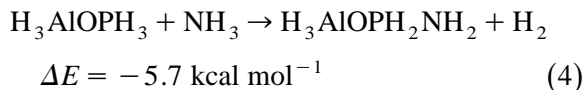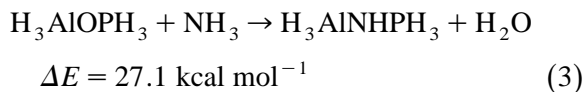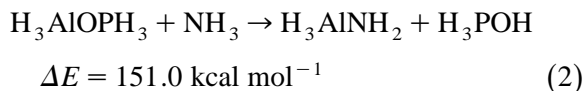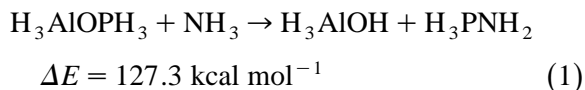
value [38]. The geometry of the $H_3AlOPH_2NH_2$ cluster is shown in Fig. 1d and h. The structures of Cs and fully optimized conformations have a dihedral angle Al–O–P–N of 0° and 59.0°, respectively, and thus the Al–O–P bond angle changes from convex to concave. In both conformations, the bond distances are nearly identical, Al–O $\sim$ 1.93 Å, O–P $\sim$ 1.49 Å, and N–P $\sim$ 1.65 Å, but the Al–O–P angle is smaller in the free conformation (123.4°) than in the Cs conformation (129.1°). Also, in both conformations, the AlH_3 group is nearly planar.

The geometries of the protonated clusters with Cs symmetry and fully optimized conformations are shown in Fig. 2. The structure of the protonated $H_3AlNHPH_3$ is not shown because by using the 6-31G∗ basis set and basis sets of greater size and quality, a stationary point has not been localized. The effect of the protonation in the geometrical parameters of the $H_3SiNHSiH_3$ produces an increase of 0.16 Å–0.17 Å in the Si–N distance and a decrease in the Si–N–Si angle of ca 9–12°. For the $H_3SiOSiH_2NH_2$ cluster, the protonation leads to an increase of ca 0.06 Å for SiO distances of (H_3SiO^-) moiety, and a decrease of ca 0.05 Å in the OSi distance of $(-OSiH_2NH_2)$ part, while the Si–O–Si angle decrease by ca 6–7°. The protonated $H_3AlOPH_2NH_2$ cluster follows the same trend, the AlO bond distance increase (0.11 Å–0.15 Å, and the Al–O–P angle diminishes $\sim$ 7°.

3.2. Analysis of the thermodynamic stability: process of formation of NH-bridging and NH_2-terminal groups

One of the aims of this work is to evaluate, from a thermodynamic point of view, the existence of NH-bridging and NH_2-terminal (NH_2 linked to the surface) groups on systems with [Al–O–P] and [Si–O–Si] linkages. Therefore, we have calculated firstly the variation of energy for the hypothetical process represented by Eqs. (1)–(4). The thermodynamical data enables to characterize the four different processes which

may occur with an aluminium phosphate when contacted with ammonia:

$$H_3AlOPH_3 + NH_3 \rightarrow H_3AlOH + H_3PNH_2$$

$$\Delta E = 127.3 \text{ kcal mol}^{-1} \qquad (1)$$

$$H_3AlOPH_3 + NH_3 \rightarrow H_3AlNH_2 + H_3POH$$

$$\Delta E = 151.0 \text{ kcal mol}^{-1} \qquad (2)$$

$$H_3AlOPH_3 + NH_3 \rightarrow H_3AlNHPH_3 + H_2O$$

$$\Delta E = 27.1 \text{ kcal mol}^{-1} \qquad (3)$$

$$H_3AlOPH_3 + NH_3 \rightarrow H_3AlOPH_2NH_2 + H_2$$

$$\Delta E = -5.7 \text{ kcal mol}^{-1} \qquad (4)$$

The first process represents the breaking of the linkage (Al–O–P) followed by the protonation of the terminal Al and the ammonolysis of the terminal P. The second process involves the protonation of P and the ammonolysis of the terminal Al after breaking the (Al–O–P) linkage. The third process corresponds to the substitution of the oxygen by a NH-bridging group. The fourth process simulates the formation of surface NH_2 groups linked to the aluminium phosphate. The clusters H_3AlOPH_3, $H_3AlOPH_2NH_2$ and $H_3AlNHPH_3$ have been calculated in free and Cs conformations, and the other molecules involved in these processes have been optimized without symmetry constraints. In our opinion, the Cs symmetry is more adequate to simulate crystalline type structures, whereas the free structures can be used to better simulate amorphous materials. The values obtained for the reaction energies are similar for both Cs and free conformations, being for the above processes the difference in energy lower than $\sim$ 1 kcal mol^{-1} (Table 1). The results of the processes (1), (2), (3) are thermal by 127.3 kcal mol^{-1}, 151.0 kcal mol^{-1}, and 27.1 kcal mol^{-1} respectively, whereas process (4) is exothermic by -5.7 kcal mol^{-1}. These data indicate the high stability of Al–O–P bridges, something which is in agreement with the results of Derouane et al. [40] who indicated that an Al–O–P bridge is more stable than Si–O–Al or Si–O–P. From a thermodynamic point of
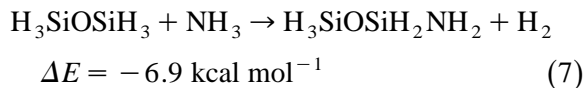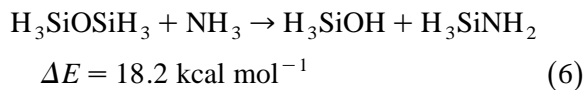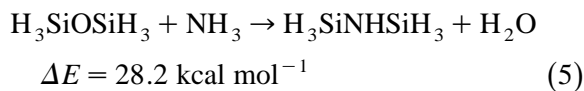
Table 1
HF/6-31G* absolute energies, proton affinities (P.A.) and HOMO energy from different clusters and dimethylamine

CLUSTER	Energy, u.a.		Proton affinities, kcal mol^{-1}		HOMO Energy, eV	
	Cs	Free	Cs	Free	Cs	Free
$H_3SiNHSiH_3$	−636.3876655	−636.3876772	−216.27	−218.49	−10.62	−10.63
$H_3AlNHPH_3$	−641.0992800	−641.1018281	−	−	−12.01	−12.08
$H_3SiOSiH_2NH_2$	−711.3274916	−711.3274828	−223.54	−224.12	−11.23	−11.22
$H_3AlOPH_2NH_2$	−716.0353994	−716.036977	−180.27	−183.14	−113.42	−13.36
Dimethylamine	−134.2299845	−134.2388493	−240.68	−235.12	−8.95	−9.84

view, it appears that the formation of a NH_2-terminal group on the surface of zeolite, is the most favorable process followed by the formation of Al–NH–P bridges. In this way, it appears that at lower temperatures one should preferentially form Al–O–P–NH_2 groups upon treatment of crystalline or amorphous alumino phosphates by NH_3. When increasing the reaction temperature Al–NH–P groups should be formed, and only at very high reaction temperatures one could expect to form Al–NH_2 and H_3–P–NH_2 species.

The possible reactions involved when contacting with NH_3 crystalline or amorphous materials containing Si–O–Si groups are:

$$H_3SiOSiH_3 + NH_3 \rightarrow H_3SiNHSiH_3 + H_2O$$

$$\Delta E = 28.2 \text{ kcal mol}^{-1} \qquad (5)$$

$$H_3SiOSiH_3 + NH_3 \rightarrow H_3SiOH + H_3SiNH_2$$

$$\Delta E = 18.2 \text{ kcal mol}^{-1} \qquad (6)$$

$$H_3SiOSiH_3 + NH_3 \rightarrow H_3SiOSiH_2NH_2 + H_2$$

$$\Delta E = -6.9 \text{ kcal mol}^{-1} \qquad (7)$$

Eq. (5) represents the substitution of an oxygen by a NH-bridging in a Si–O–Si bridge. Eq. (6) involves the hydrolysis of a Si–O bond, followed by ammonolysis to form H_3SiNH_2 species. Finally, Eq. (7) considers the formation of a NH_2 surface group bonded to a terminal silicon. These data show that the required energy for the substitution of an oxygen in a Si–O–Si bridge by a NH-bridging (28.2 kcal mol^{-1}) is similar to the case in which a [Al–O–P] species was considered. However, as in the [Al–O–P] structure, the most probable process

(-6.9 kcal mol^{-1}), is the formation of a NH_2 surface group without the breaking of the Si–O–Si bridge (process 7). The comparison of [Si–O–Si] and [Al–O–P] linkages indicates that the process of substitution of an oxygen-bridging by a NH-bridging is practically the same, regardless that we consider a pure silicate or an aluminium phosphate. Also, the most favorable process in both linkages is the formation of a NH_2 surface group without the breaking of the respective bridge. Furthermore, we note that the energy of the processes calculated by imposing Cs restrictions and without restrictions are of the same order, and indicate the same probability to occur in crystalline or amorphous systems. The experimental results of Corma et al. [13], where he tried to incorporate nitrogen in AlPO-5 molecular sieves, and in HY zeolite, showed no formation of Si–N or Al–N bonds. Stein described the reaction of the nitrogen in AlPO-5 by three possible mechanisms, first the formation of a five coordinate Al, secondly a formation of a six coordinate Al, and finally, a P–NH_2 terminal group, after the breaking of the Al–O–P linkage. The results of Stein were supported by X-ray diffraction (XRD), Infrared spectroscopy (I.R.), high resolution solid state Nuclear Magnetic Resonance (^{27}Al, ^{31}P, ^{1}H and ^{15}N), working at temperatures until 1173 K.

3.3. Theoretical calculation of basicities

We have attempted to evaluate the Brönsted and Lewis basicity of the NH-bridging and NH_2-terminal groups of the $H_3SiNHSiH_3$,

H_3AlNPH_3, $H_3SiOSiH_2NH_2$, and $H_3AlOPH_2NH_2$ clusters by comparing the calculated proton affinities and the HOMO energy of these systems. In Table 1 the absolute energies of the neutral structures are listed along with the resulting proton affinities and the HOMO energy of the neutral systems. As a reference value on basicity, we have also calculated, at the HF/6-31G∗ level, the proton affinity and the HOMO of a reference molecule such as dimethylamine, and the values are listed in Table 1. We can see that the calculated proton affinity (P.A.) on dimethylamine (235.1 kcal mol^{-1}) is not too far from the value (221.3 kcal mol^{-1}) calculated by Smith and Radom [47] at G2 level, and the experimental values, of 220.6 and 227.8 kcal mol^{-1}, reported in the scales of Lias et al. [48], and Mautner and Sieck [49], respectively. The HOMO energy has been used to calculate the Lewis basicity, but in the $H_3AlOPH_2NH_2$, and H_3AlNPH_3 clusters the highest energy occupied orbital does not correspond to the highest occupied orbital centered on nitrogen atom, and since we are interested by the donor character of the nitrogen atom, we have used as the active HOMO or frontier orbital the highest occupied orbital which has its mean component on the nitrogen active site [50]. This fact can be due to the geometry of these clusters, which have Al–O and Al–N distances very large, therefore weak Al–O and Al–N bonds, which cause that the highest occupied orbital is not centered on the nitrogen atom but on atoms such as Al and P. The calculated proton affinities indicate the following order for the Brönsted basicity of the nitrogen clusters: dimethylamine > $H_3SiOSiH_2NH_2$ > $H_3SiNHSiH_3$ > H_3AlNPH_3 > $H_3AlOPH_2NH_2$. The HOMO energy of these systems gives from the point of view of soft–hard basicity or Lewis basicity the order: dimethylamine > $H_3SiNHSiH_3$ > $H_3SiOSiH_2NH_2$ > H_3AlNPH_3 > $H_3AlOPH_2NH_2$. Comparison of the calculated P.A. with the theoretical scale of Smith and Radom [47] and the experimental scales [48,49] shows that these clusters are placed on the top of the scales, above systems such as PH_3, CH_3CN, through CS, CH_2CO, NH_3,..., until dimethylamine which is the most basic molecule. Therefore, the bridged and terminal nitrogenated structures studied were can be classified as strong bases. The calculated P.A. and HOMO basicities of systems follows a similar trend, but there is a discrepancy between silicium clusters.

3.4. NH stretching

Finally, we have calculated the vibrational frequencies of the NH stretching of the various clusters, because these frequencies can be used in Infrared spectroscopy of zeolites to distinguish between NH-bridging and NH_2-terminal groups. Harmonic vibrational frequencies have been obtained by diagonalizing the Hessian matrix and by analyzing the vibrational normal modes. In the systems with Cs symmetry appear one or two negative frequencies, small in absolute value, and generally, lesser than 100 cm^{-1}, except for the dimethylamine Cs, that has a negative frequency of 700 cm^{-1} associated with the pyramidization of the nitrogen atom. All fully optimized clusters presents positive frequencies. The $H_3SiOSiH_3NH_2$ cluster presents a very small negative frequency associated to the distortion of planarity of the framework of the cluster and with the displacement of equatorial hydrogen atoms bonded to the silicium atoms. The $H_3SiNHSiH_3$, $H_3AlNHPH_3$, and $H_3AlOPH_2NH_2$ clusters present two negative frequencies, the first frequency corresponds to the breaking of the planarity of the framework of the cluster, which in the $H_3SiNHSiH_3$ and $H_3AlNHPH_3$ clusters is very small while in the $H_3AlOPH_2NH_2$ cluster the distortion is large as can be seen in the full optimized geometrical conformation of the cluster. The second negative frequency corresponds generally to the rotation of the SiH_3, AlH_3 or NH_2 groups around of the single bonds to which these groups are linked. The vibrational frequencies of the NH

Table 2
Calculated ab initio harmonic frequencies of NH stretching (cm^{-1}) from different clusters, dimethylamine and ammonia in Cs and free symmetries with HF/6-31G∗ basis set

Cluster	νNH (cm^{-1})	
	Cs	Free
$H_3SiNHSiH_3$	3464	3476
$H_3AlNHPH_3$	3530	3495
$H_3SiOSiH_2NH_2$	3495/3582	3494/3581
$H_3AlOPH_2NH_2$	3462/3552	3450/3541
dimethylamine	3631	3462
NH_3	3402/3516	3402/3516

Reported frequencies obtained by multiplying the calculated harmonic frequencies by scale factor of 0.92 [38,51].

bond stretching calculated at HF/6-31G∗ level are scaled by a factor of 0.92, because ab initio calculations give values too large and are typically scaled to more properly reproduce experimental results [51]. The choice of this scale factor is due to the fact that the calculated frequencies for NH_3 at HF/6-31G∗ level are obtained using a scale factor of 0.92 [38,51], which is in accord with the scale factor used for the molecule of disiloxane [38] at HF/6-31G∗ level. These scaled calculated frequencies are listed in Table 2. The whole corrected frequencies vary for the fully optimized geometrical conformations between 3460 and 3580 cm^{-1}. These values are in the range of the experimental NH stretching ($\sim$ 3300–3500 cm^{-1}) for primary and secondary amines [52]. These calculated frequencies allow to distinguish between NH-bridging and a NH_2-terminal groups because the NH stretching of substituted NH-bridging and NH_2-terminal Si–O–Si and Al–O–P linkages differ by 100 cm^{-1} and 50 cm^{-1}, respectively.

4. Conclusions

In this work we have carried out ab initio molecular orbital calculations to obtain thermodynamical information on the possibility to form NH-bridging or NH_2-terminal groups in amorphous and crystalline materials containing Si–

O–Si and Al–O–P structures, such as for instance, zeolites and aluminophosphates. In these calculations we have employed dimeric model clusters Si–O–Si and Al–O–P which contain NH_2-terminal groups or an oxygen atom substituted by a NH-bridging unit. The Brönsted basicity and the Lewis basicity and 'softness' character of these structures have been determined using the proton affinity and the HOMO energy, respectively. The optimization of the geometry of the neutral and protonated clusters was carried out using both Cs and no symmetry restrictions.

The calculated geometry of the $H_3SiNHSiH_3$ cluster is similar to the $H_3SiOHAlH_3$ and this result allows to suppose that the geometry of a silicon zeolite with a NH-bridging group is not much different to the corresponding zeolite containing framework Al and bridging OH groups.

The energetic of the possible reactions involved when contacting NH_3 with $H_3SiOSiH_3$ and H_3AlOPH_3 clusters indicate that from a thermodynamic standpoint the formation of a NH_2 terminal group on the surface of zeolite is the most favorable process, being exothermic by 6–7 kcal mol^{-1}. The substitution of an oxygen in Si–O–Si and Al–O–P linkages by a NH-bridging has the same energy, and it is endothermic by 27–28 kcal mol^{-1}. Therefore, it appears that at lower temperatures one should preferentially form NH_2-terminal groups, and the NH-bridging will be formed when increasing the temperature. Furthermore, the energy of the process calculated by imposing Cs restrictions and without restrictions are of the same order of magnitude, and indicate the same probability to occur in crystalline or amorphous systems.

The calculated proton affinities are compared to that of dimethylamine, which is used as a reference molecule, and the obtained results indicate the following order for Brönsted basicity: dimethylamine > $H_3SiOSiH_2NH_2$ > $H_3SiNHSiH_3$ > $H_3AlOPH_2NH_2$, and consequently the nitrogenated clusters can be considered as strong bases which are located on the

top of the theoretical and experimental proton affinity scales.The HOMO energy of these systems gives from the point of view of soft–hard basicity the order: dimethylamine $> H_3SiNHSiH_3 > H_3SiOSiH_2NH_2 > H_3AlNPH_3 > H_3AlOPH_2 NH_2$.

Finally, the calculated NH stretching frequencies allow to distinguish between NH-bridging and NH_2-terminal groups because the NH stretching of NH-bridging and NH_2 terminal groups differ by 100 cm^{-1} on Si–O–Si linkages, and 50 cm^{-1} on Al–O–P linkages.

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