ENTRAPPING MOLECULES IN ZEOLITES NANOCAVITIES: A THERMODYNAMIC AND *AB-INITIO* STUDY

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Abstract. Adsorption enthalpies of Ar, N_2, CO, H_2O, CH_3CN and NH_3 on H-BEA and H-MFI zeolites and on Silicalite, have been measured calorimetrically at 303K in order to assess the energetic features of dispersive forces interactions (confinement effects), H-bonding interactions with surface silanols and specific interactions with Lewis and Brønsted acidic sites. The adsorption of the molecular probes with model clusters mimicking surface silanols, Lewis and Brønsted sites has been simulated at *ab-initio* level. The combined use of the two different approaches allowed to discriminate among the different processes contributing to the measured $(-\Delta_{ads}H)$. Whereas CO and N_2 single out contributions from Lewis and Brønsted acidic sites, Ar is only sensitive to *confinement effects*. For H_2O, CH_3CN and NH_3 the adsorption on Brønsted sites is competitive with the adsorption on Lewis sites. The energy of interaction of H_2O with all considered zeolites is surprisingly higher than expected on the basis of $-\Delta_{ads}H$ *vs* PA correlation.

Keywords: *ab initio* calculations, adsorption, Brønsted acidity, Lewis acidity, microcalorimetry, zeolites

1. Introduction

Very recently it has been suggested that silica-rich surfaces of zeolites and feldspars might be responsible for the generation of replicating biopolymers thanks to the presence of acidic sites and/or hydroxylated species localized in molecular-sized cavities (Smith *et al.*, 1998; Parson *et al.*, 1998). Indeed, a prebiotic synthesis of purine and pyrimidine derivatives from formamide has been recently reported to be facilitated in presence of a variety of inorganic oxides like silica, alumina and Y-zeolite (Saladino *et al.*, 2001). This fact is expected, in that proton-exchanged zeolites have a widespread use as catalysts in many industrial reactions that require Brønsted acidity (Corma, 1995). The catalytic activity of Al-containing zeolites is due to the presence of charge-balancing protons in the form of Brønsted acidic species ($\equiv Si(OH)^+Al^-\equiv$), as shown in Figure 1, in which the different kind of potential acidic sites present in shape-selective microporous systems are depicted. The population of Brønsted acidic sites depends upon the Si/Al ratio, whereas the acidic strength of the sites seems to depend on the structure of the three-dimensional network (Hölderich *et al.*, 1988). Much less deeply characterized is

a different kind of sites present in some materials (β-zeolites are a well known case) showing Lewis acidic properties. These sites, involving coordinatively unsaturated (*cus*) Al^{III} species likely resulting from complex rearrangements of the Brønsted sites (Figure 1), play a major role in catalytic processes in which the ability to engage charge transfer processes with molecules is needed (i.e. Friedel-Craft reactions). Conversely, no charge-balancing protons are needed in Al-free zeolites which are expected to be hydrophobic, and for which confinement effects due to plain dispersive forces are dominant. The real Silicalite systems are however much more hydrophylic than expected in that framework defects due to Si atoms vacancies are healed by silanol (SiOH) groups originating the so called 'hydroxyl nest' (Figure 1), characterized by mild acidic properties (Bolis *et al*., 2002). At the external surface of zeolites isolated SiOH groups, which presence is ubiquitous at the surface of all silica-based materials (Sauer *et al*., 1994), terminate the crystals (Figure 1) and exhibit extremely weak acidic features. In order to characterize the different kinds of acidic sites (Brønsted, Lewis, and silanols) operating in the zeolite nanocavities together with dispersive forces due to the walls of the pores (*confinement effect*), the interaction of molecules of increasing proton affinity (Ar, CO, N_2, H_2O, CH_3CN and NH_3) with zeolites of different structure and Si/Al ratio has been studied by adsorption microcalorimetry. *Ab-initio* calculations have been run on molecular clusters modeling Lewis and Brønsted sites as well as SiOH groups. H-β zeolite has been chosen because it exhibits a population of Lewis acidic sites much more abundant than H-ZSM-5, which in turn is expected to sport almost only Brønsted acidic sites. H-ZSM-5, in virtue of its smaller pores size (5.6 Å) with respect to H-β (7.6 Å), does show the largest effect of molecules confinement. Al-free defective Silicalite has been studied in order to assess the acidic strength of SiOH nests, and to energetically quantify the confinement effects.

2. Methods

2.1. MATERIALS

H-β zeolite (BEA, Si/Al = 9.8, Al/uc = 5.9), H-ZSM-5 (MFI, Si/Al = 15, Al/uc = 6.0) and Al-free Silicalite (MFI Si/Al $\rightarrow \infty$) have been kindly supplied by Polimeri Europa, Novara, Italy. Samples have been vacuum activated at T = 673K (H-ZSM-5, Silicalite) or T = 873K (H-β), in order to achieve the maximum dehydration of the surface compatible with the stability of the structure.
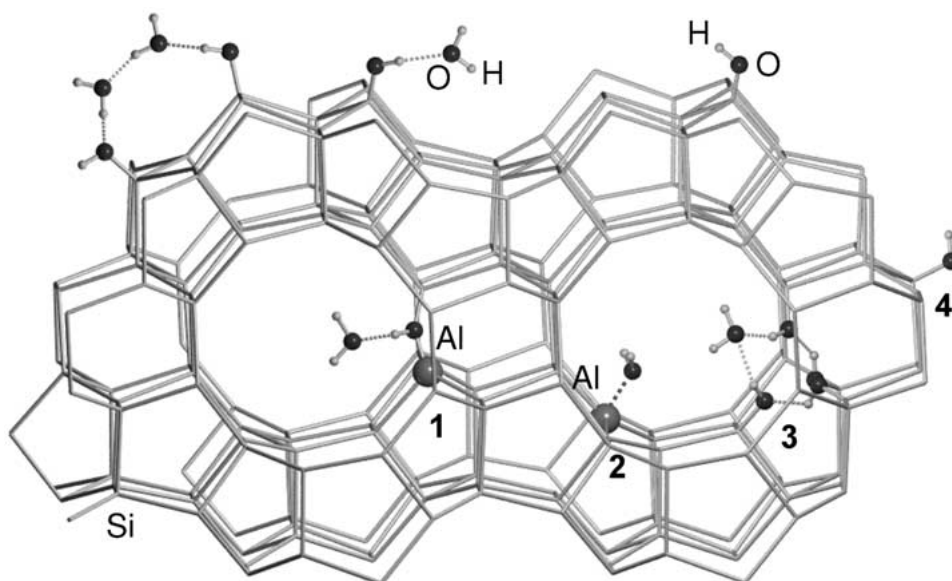
Figure 1. MFI framework (grey sticks) showing all possible active sites (stick & balls): Brønsted site (1), Lewis site (2), hydroxyls nest (3) and isolated surface silanol (4). Adsorbed H_2O allows to show the structural features of the surface complexes.

2.2. METHODS

2.2.1. *Adsorption microcalorimetry*

The heats of adsorption have been measured at 303K by a heat-flow microcalorimeter (Calvet C80, Setaram) in order to evaluate the enthalpy changes ($q = -\Delta_{ads}H$) related to the adsorption as a function of increasing coverage. A well-established stepwise procedure was followed (Bolis *et al.*, 2002).

2.2.2. *Molecular modeling*

All calculations have been run at *ab-initio* level using the B3-LYP functional on selected molecular clusters modelling the different sites. For Lewis sites the different geometrical strains around the *cus* Al^{III} species likely present in the real material, has been modeled with two different clusters (LSC and LLC of Figure 2); for the Brønsted site (BRO cluster of Figure 2), one Si atom has been replaced by Al in a cluster cut out from the faujasite zeolite (chosen because of its geometrical rigidity), whereas silanol group has been modelled by a silica cage cluster envisaging one SiOH group (SIL model of Figure 2). Geometries have been optimized at ONIOM[B3-LYP/6-31+G(d,p):MNDO] for Lewis cluster models and at ONIOM[B3-LYP/SVP:AM1] for BRO and SIL clusters, either free or interacting with the probes. Final basis set superposition error corrected binding energy computed at B3-LYP/6-31+G(d,p) on the ONIOM geometries.
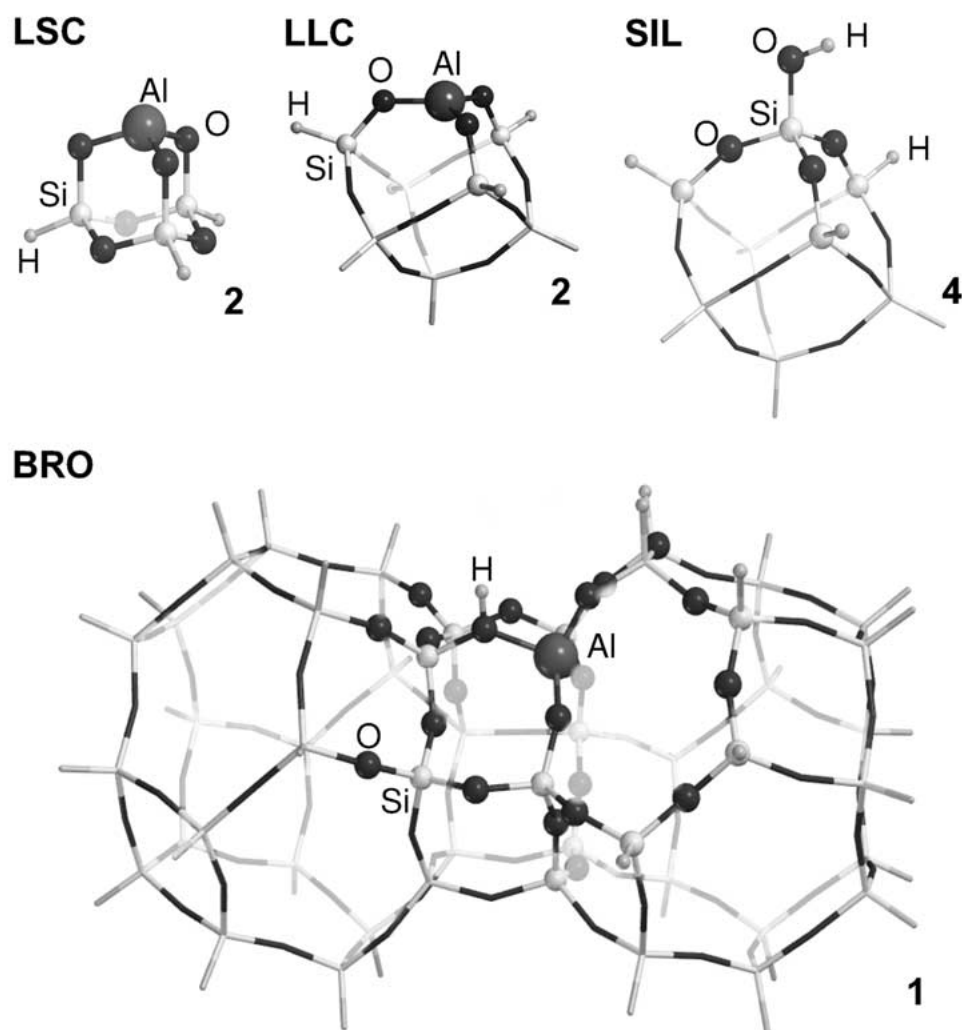
Figure 2. Cluster models used in the *ab initio* modeling: LSC, LLC for the Lewis site, BRO for Brönsted site and SIL for the isolated silanol. Atoms shown as balls belong to the ONIOM model region and have been computed with higher accuracy.

3. Results and Discussion

3.1. COMPUTATIONAL RESULTS

Figure 2 shows the model clusters adopted for modeling the different kind of acidic sites potentially present in microporous materials, whereas Figure 3 gathers the optimized structures for the complexes formed with the molecular probes considered. The B3-LYP/6-31+G(d,p) binding energy (BE, kJ/mol) are also shown. The structures of the adducts formed on the LSC Lewis model have not been reported in

that they are equivalent to the LLC ones. BE values for LSC structures (data in parentheses, Figure 3) are however much higher than for LLC ones, indicating that the Lewis acidic strength of the sites depends on the local environment of the *cus* Al^{III} species. Indeed, LSC model is more strained than LLC one, as witnessed by the Si-O-Al angle which is $\approx 105°$ for the former and $\approx 130°$ for the latter. This indication must be considered in interpreting experimental data for real materials, as thermal treatments are known to create Al defects of variable geometrical strain. The geometry of the adducts formed at the Brønsted site (BRO cluster in Figure 3) are all typical of H-bonding interactions between $\equiv Si(OH)^+Al^- \equiv$ species and the molecular probes. For H_2O and NH_3 a secondary interaction between the H atoms (of the probe) and the O atoms (of the cluster in the closeness of the Brønsted site) originates an extra stabilization of the adducts. For NH_3 the structure of the formed species suggests that the acidic proton is transferred to the molecular probe, creating a $ZeO^-NH_4^+$ ion pair. It is worth noting that BE calculated for Brønsted sites adducts are by far lower than BE computed for Lewis acid-base complexes. The weakest acidic sites (among the different species investigated) are silanols, which exhibit structural features of classical H-bonding interactions with all molecular probes (see SIL cluster in Figure 3). BE are very small in this latter case, particularly for weak bases such as CO and N_2, and no evidence of proton transfer for NH_3 has been given.

3.2. MICROCALORIMETRIC RESULTS

In Figure 4a, the enthalpy of adsorption ($-\Delta_{ads}H$) measured at very low coverage for the various zeolites investigated has been contrasted with the proton affinity (PA) of the probes. In the case of Al-free Silicalite, for molecular probes with low polarizability ($\alpha \approx 2 \times 10^{-40}$ C^2 m^2 J) such as Ar, CO and N_2, the energy released is quite low (< 25 kJ/mol) and very close to each other, because the interaction is dominated by dispersive forces. By contrast, for molecular probes of medium-high basic strength, such as H_2O, CH_3CN and NH_3, the energy of interaction increases with PA. In particular, the adsorption enthalpy for H_2O (≈ 120 kJ/mol) is surprisingly high with respect to ≈ 50 kJ/mol, the value expected on the basis of the linear trend found for the other probes. Conversely, for the acidic zeolites $-\Delta_{ads}H$ values (much higher than for Silicalite) increase linearly with their PA for all molecular probes, according to the presence of specific Brønsted and Lewis sites in the micropores. Again H_2O behaves peculiarly, $-\Delta_{ads}H$ being much higher than expected on the basis of the correlation with PA (> 150 instead of ≈ 120 kJ/mol). This result must be stressed in that it indicates that H_2O is able: i) to open strained SiOSi bridges in Silicalite (Pascale *et al.*, 2002); ii) to strongly interact with hydroxyl nests via H-bonds; iii) to self-aggregate (even at very low coverage) in proximity of H_2O adsorbed on Brønsted (or Lewis) sites.

In general, Brønsted, Lewis, H-bonding and confinement effects contributions to the measured $-\Delta_{ads}H$ are inextricably intermingled. In Figure 4b, an attempt has
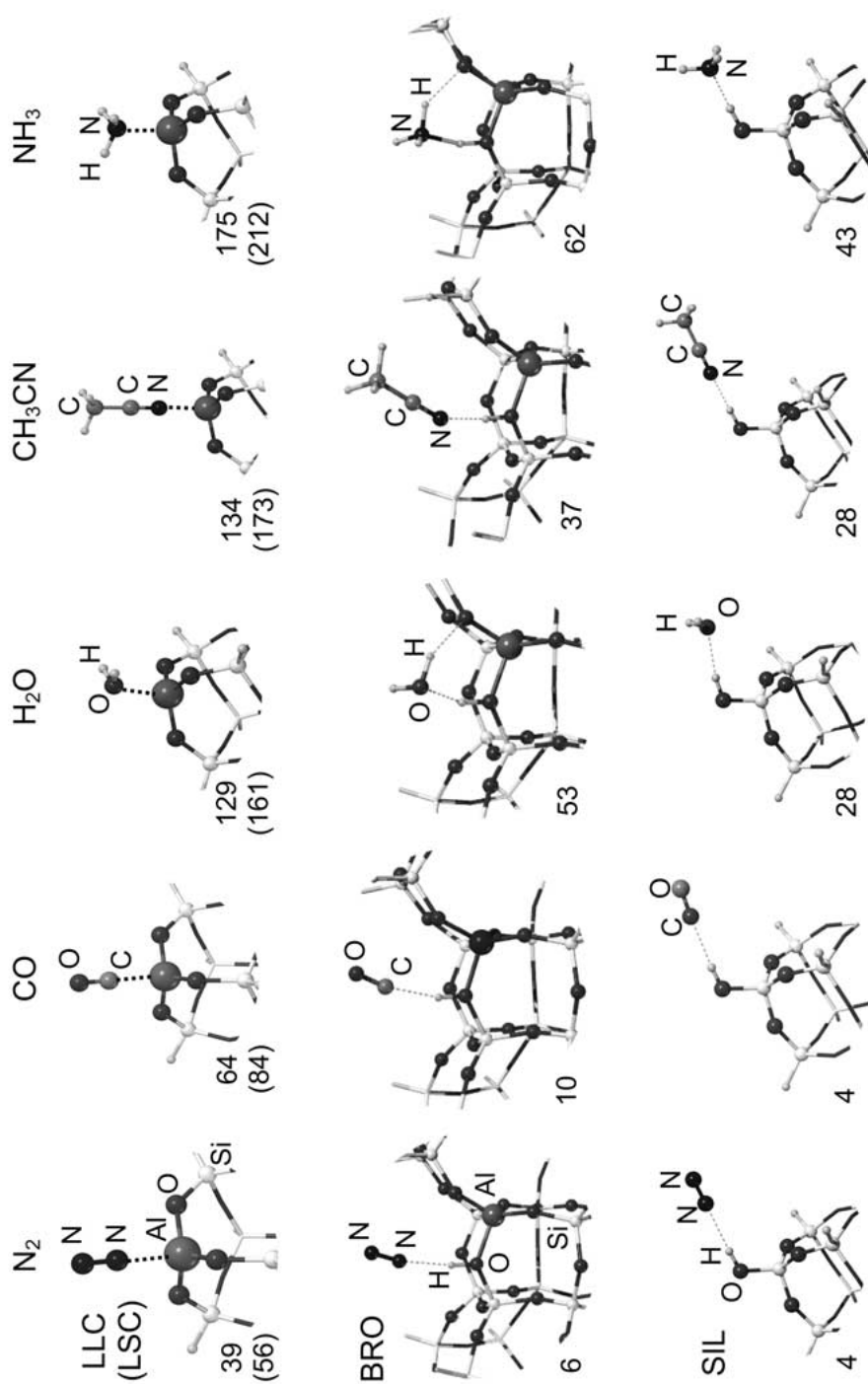
Figure 3. Structures and B3-LYP/6-31+G(d,p) binding energy values for the surface complexes with the Lewis site (LLC cluster), Brönsted site (BRO cluster) and silanol group (SIL cluster). Reported binding energy (kJ/mol) are corrected for basis set superposition error computed as a single point energy calculation. Data for LSC in parentheses.
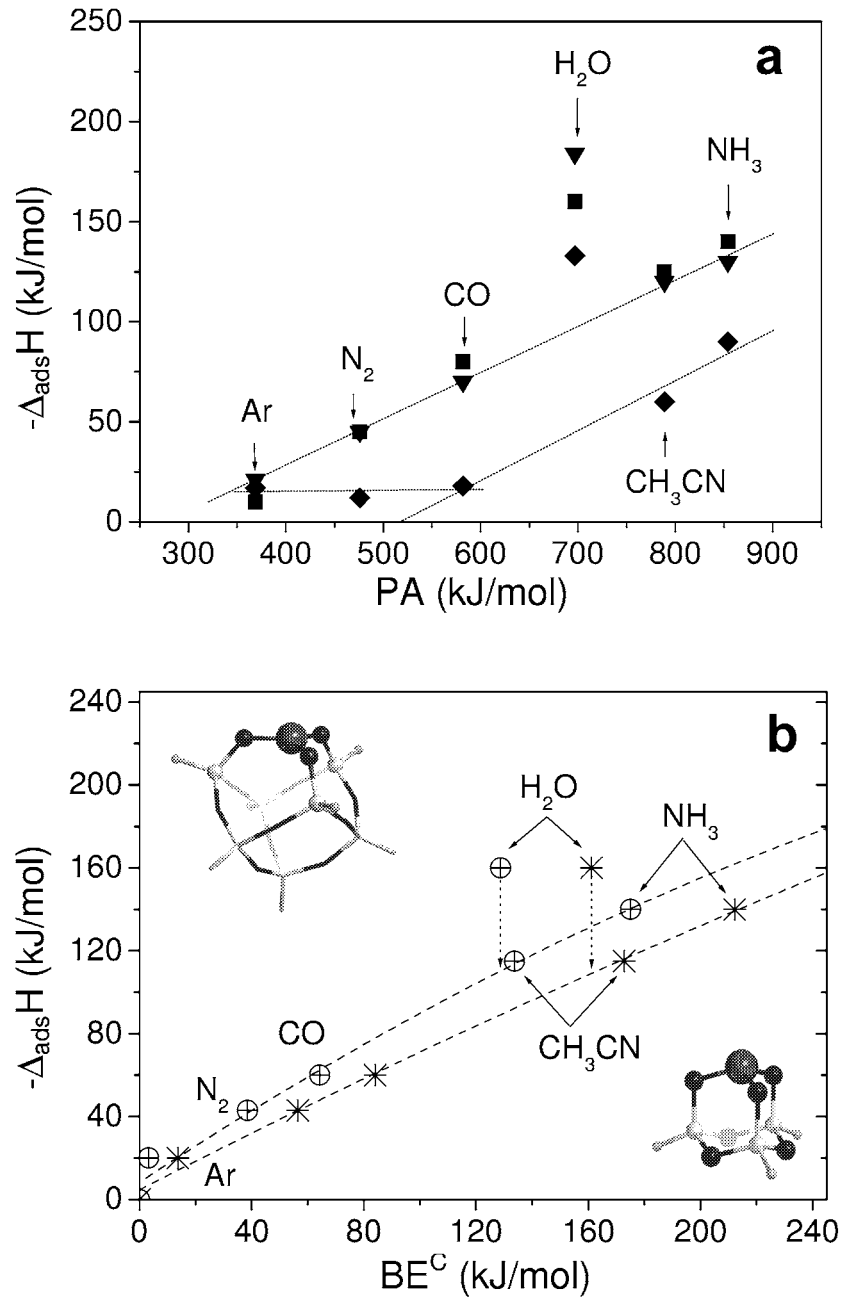
Figure 4. Section a): proton affinity PA of the molecular probe *vs* measured heat of adsorption, $\Delta_{ads}H$ for silicalite (diamond symbols), H-ZSM-5 (triangle symbols) and H-β (square symbols). Section b): *ab initio* binding energy BE^C *vs* measured heat of adsorption, $\Delta_{ads}H$. Computed data for the LSC (star symbols) and LLC (crossed circle symbols) clusters, models of the Lewis site.

been made to single out the various components, by comparing the low coverage experimental value with the highest values arising from *ab initio* calculations, i.e., the ones for LSC and LLC Lewis models. Experimental and calculated data for N_2 and CO correlate well, showing that the largest contribution to the experimental $-\Delta_{ads}H$ is due to the Lewis interaction, as clearly indicated by the large gap between the *ab initio* BE for LLC and BRO models (Figure 3). By contrast, the experimental values for the polar probes (H_2O, CH_3CN and NH_3) are lower than the computed ones (still for the Lewis sites) showing that a sizable fraction of the energy is due to the interaction with Brønsted sites, which are in general less strong than the Lewis ones. This result is confirmed by the *ab initio* BE on BRO sites which values are not so distant from the BE for LLC sites as in the case of N_2 and CO, for which the Brønsted interaction contribution is negligible. Thus, in the real systems the energy of interaction of H_2O, CH_3CN and NH_3 does involve a significant contribution from the Brønsted sites, being the adsorption favoured on both kind of sites.

4. Conclusions

The interaction of organic molecules with inorganic surfaces has long been considered a process relevant to the origin of life (Bernal, 1951). Among inorganic solids, zeolites have been suggested as one of the preferential candidates for the generation of replicating biopolymers (Smith *et al.*, 1998; Parson *et al.*, 1998). The present paper shed further light into the physico-chemical features of the variety of adsorption sites (of acidic nature) present at the internal and external surfaces of three different zeolites (silicalite, H-ZSM5 and H-β). Simple molecules have been used, i.e. Ar, N_2, CO, H_2O, CH_3CN and NH_3 in order to selectively probe sites of different acidic strength. Two different techniques have been used, i.e. adsorption microcalorimetry and molecular modeling to understand the energetic features of the interaction with Brønsted and Lewis acidic sites, with silanols and with the cavity walls of microporous materials. Even if the adopted probes are simpler than the molecules relevant for the abiotic synthesis of biogen molecules the present results will serve as a base for understanding the role of the different components of the interaction energy in the catalytic processes of biogen molecules. In particular, the relevance of the dispersive forces between adsorbates and the inorganic walls (*confinement effects*) has been singled out by the adsorption of Ar. Lewis and Brønsted acidic sites are selectively engaged by using N_2 and CO, whereas polar molecules such as H_2O, CH_3CN and NH_3 are preferentially adsorbed on Brønsted sites than on Lewis ones, in virtue of their ability to form H-bonds with the basic O atoms of the zeolite framework. The peculiar behaviour of H_2O has also been shown and explained in terms of its self-aggregating capability in the proximity of the active sites. On the base of the present study it is also expected that single aminoacids and nucleotides, in virtue of their highly polar character,

will be preferentially adsorbed on silanols (either at the external surface or at the hydroxyls nests) via moderately strong hydrogen bonds. Once captured, diffusion processes will move them in proximity of the acidic Brønsted sites, where proton transfer may indeed occur giving rise to the first steps of catalytic reactions.

Acknowledgements

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