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Role of outer surface/inner bulk Brønsted acidic sites in the adsorption of a large basic molecule (simazine) on H-Y zeolite

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Abstract

The simple means adopted for investigating H-Y zeolite acidity in water is the pH-dependence of the amount adsorbed of a basic molecule under isochoric conditions, a technique capable of yielding, under equilibrium conditions, an estimate of the pK_a of involved acidic centres: the behaviour with temperature of adsorbed amounts yields instead some information on the thermodynamics. Simazine (Sim, 2 chloro-4,6 bis(ethylamino)-s-triazine) was chosen as adsorbate because the transverse dimension (7.5 Å) is close to the opening of the supercage in the faujasite structure of H-Y (7.4 Å).

In short term measurements, Sim adsorption at 25 °C occurs only at the outer surface of H-Y particles. Two types of mildly acidic centres occur (with pK_a ca. 7 and ca. 8, respectively) and no strong one. Previous adsorption of ammonia from the gas phase discriminates between the two. The former survives, and shows features common with the silanols of amorphous silica. The other is suppressed: because of this and other features distinguishing this site from silanol species (e.g. formation of dimeric Sim_2H^+ species, favoured by coverage and unfavoured by temperatures of adsorption higher than ambient) a candidate is an Al based site. We propose a Lewis centre coordinating a water molecule, exhibiting acidic properties. This acidic water molecule can be replaced by the stronger base ammonia, also depleting inner strong Brønsted sites. A mechanism for the generation of the two sites from surface Brønsted species is proposed.

Long term adsorption measurements at 25°C already show the onset of the interaction with inner strongly acidic Brønsted sites: because of its size, activation is required for Sim to pass the supercage openings and reach inner acidic sites. When adsorption is run at 40-50 °C, uptake is much larger and increases with temperature. Isochoric measurements suggest a pK_a value ca. 3 compatible with their marked acidic nature, although attainment of equilibrium conditions is questionable. Measurements at 60 °C (both isochors and DRIFT) show the onset of changes at the outer surface brought about by the presence of hot water. Control experiments run with USY (Ultra

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Stabilized zeolite Y), featuring wormholes and cavities rendering accessible internal sites, show the

extensive involvement of internal Brønsted sites already at 25° C.

1. Introduction

Adsorption on acidic solids is a means for the remediation of water polluted by the agrochemical molecule Simazine (2 chloro-4,6 bis(ethylamino)-s-triazine, hereafter Sim, Scheme 1).[1-4] The study of such process at different pH values, besides giving information on the feasibility of practical application, showed that Sim can yield remarkable knowledge on the Brønsted acidity of the solid, so acting as a probe molecule.[1,5] This concept is common in gas-solid interactions (e.g. for CO, ammonia, pyridine, etc.), whereas it is unknown for liquid-solid systems.

Adsorption on amorphous silica illustrates the case.[1,5] Two types of species are formed, one irreversibly held at 25°C, the other partially reversible. Adsorption takes place in a narrow pH interval around 5.5 and involves proton transfer from acidic SiOH species to N atoms at ethylamino chains, those at the ring being not basic. Species arise from a two step process, described by eqns. (1) and (2) below: that mono-protonated is formed first ($SimH^+$), onto which a second molecule may anchor so forming a dimer (Sim_2H^+), held together by both sharing of the positive charge and possibly hydrophobic interactions (Scheme 2):

$$Si\text{-}OH + Sim(aq) \rightarrow Si\text{-}O^{\cdots}SimH^+ \tag{1}$$

$$Si\text{-}O^{\cdots}SimH^+ + Sim(aq) \leftrightarrow Si\text{-}O^{\cdots}Sim_2H^+ \tag{2}$$

A way to investigate such processes is to vary the pH of the system at constant: i) volumes of the solid and the liquid phases; ii) total amount of Sim; iii) temperature and iv) pressure, circumstances hereafter referred to as isochoric conditions. The partition of the adsorbate between the two phases as a function of pH yields a sort of "pH resolved" adsorption isochore, usually featuring a maximum, examples of which are given below.

A simple model for adsorption involving proton transfer from the solid to Sim[5] relates the pH value at which uptake is maximum (pH*) to the pK_a of both the H-donor species and the protonated entity given rise:

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$$pH^* = [pK_a(1) + pK_a(2)]/2 \qquad\qquad (3)$$

Eqn. (3), which accounts for the use of Sim (or analogous molecules) as probes for acidity, is no surprise, as it coincides with the result of a formally equivalent problem, the isoelectric point of aminoacids in solution.

In the case of amorphous silica, the use of eqn. (3) allows to infer that adsorbed Sim is more basic than the molecule in solution by ca. 2 units in pK_a. Also, the pK_a of the silanol species involved is probably not ca. 4, as recently proposed,[6,7] but more likely ca. 7, in agreement with old views.[8,9]

The present paper deals with the adsorption of Sim, under the same circumstances, on a similar, though structurally different, acidic solid, the zeolite H-Y, obtained via ionic exchange from the commercial Na form.[10] Interest in such adsorbent stems from the presence of strong acidic sites within the crystalline structure, present in principle also at the outer surfaces, and the fact that Sim has dimensions close to the openings between the zeolite nano-cavities (Scheme 3):[11,12] the questions so arise whether internal cavities are accessible to Sim and whether strongly acidic sites are available at the external surface.

For comparison, data concerning amorphous silica (Aerosil) are reported. Materials also considered for comparison were H-Y zeolite after saturation in gaseous ammonia, where Brønsted acidic sites are absent, having been converted into ammonium species, and commercial USY, where internal Brønsted acidic sites are accessible because of the cavernous nature of the solid.

2. Experimental

2.1. Materials

Amorphous silica was commercial Aerosil 250 Degussa; Na-Y (from Sigma-Aldrich reagent grade, SiO_2/Al_2O_3 (mol/mol) = 1.24), and USY (from Tosoh USA, Inc, product name 360HUA, SiO_2/Al_2O_3 (mol/mol) = 15).

To prepare H-Y zeolite, Na-Y zeolite was repeatedly exchanged in ammonium aqueous solution (t = 2 h, 0.1 M NH_4NO_3, solid/liquid ratio = 1/100, room temperature), then subjected to a 3 h treatment at 550 °C.[13]

An aliquot of the H-Y sample was contacted at room temperature with 20 torr NH_3 in static conditions, then evacuated. This sample is referred to as H-Y-amm.

2.2 Characterization of samples

The residual Na^+ content was 0.05 atomic fraction.[14, 15] XRD patterns of the original Na-Y zeolite and H-Y zeolite (not reported) show that, as expected,[13] thermal treatments did not damage its crystalline structure. Literature evidence also indicates that under the circumstances adopted for preparation, no dealumination occurs.[13] Opposite is the case of the procedure for obtaining USY zeolite, also utilized in the present paper, in which hydrothermal treatment causes extensive dealumination, with formation of the so called extra-framework Al, then removed by washing with acidic solution. It appears very likely that the dealumination of USY is practically complete over its external surface, which is more exposed to such hydrothermal treatments and, thus, is more prone to undergo its effects.

 Attention was paid to the evaluation of the extent of both external and internal areas, which was carried out by N_2 adsorption at 77 K on samples previously outgassed at 523 K, to remove atmospheric water and other atmospheric contaminants (Quantachrome Autosorb 1). Specific surface area (SSA) values were calculated according to both the BET (Brunauer-Emmett-Teller) and the Langmuir method; total pore volumes were determined from adsorbed amounts at $P/P^0 =$ 0.98; both micropore volume and external surface area were calculated according to the t-plot method.

For DRIFTS measurements, an amount of simazine corresponding to the maximum sorption value as obtained from the pseudo-isotherm was added to each adsorbent at the optimal sorption pH. After incubation, the samples were centrifuged and the precipitates washed twice with H_2O, then dehydrated by lyophilisation. Finally, 2.0 mg sample were mixed with 200 mg KBr (FTIR grade, Aldrich, Chemical, Co., Milwaukee, WI, USA). The mixture was finely ground in an agate mortar and transferred to a sample holder. Its surface was smoothed with a microscope glass slide, and DRIFT spectra were recorded (on a Perkin Elmer Spectrum One FT-IR Spectrometer at a resolution of 1 cm^{-1}).

2.3 Adsorption/desorption experiments

A stock solution of Sim was prepared by dissolving 2 mg simazine weighted with M2P Sartorius Electronic Microbalance featuring a resolution (minimum limit) of 1 μg in 500 mL doubly distilled water. The obtained concentration, 20 μmol L^{-1}, is close to saturation at 25°C (*ca.* 25 μmol L^{-1}). Solubility increases with temperature, reaching e.g. 84.30 μmol L^{-1} at 50°C.[16]

Although in principle isochoric measurements consist in altering the pH of a system otherwise closed, for practical reasons measurements were all done with replicas of the same system, prepared afresh, run in parallel.

Many sorption experiments were carried out by adding 0.3 mg sorbent, weighted with M2P Sartorius Electronic Microbalance featuring a resolution (minimum limit) of 1 μg, to 3.0 mL Sim solution (corresponding to 10 μmol L^{-1} total Sim amount) in glass vials with Teflon caps at the desired temperature. Two other values of Sim total amounts, 5 and 7 μmol L^{-1}, were considered.

In isochoric experiments, the pH value was changed between 3.0 and 7.0, in steps of 0.5, by adding the proper amount of 0.01 mmol L^{-1} HCl or NaOH solution, at a constant temperature, 25, 40 and 50 °C, respectively.

After 24 hours contact, the samples were centrifuged at 7000 rpm for 20 min, and the concentration in the supernatant solution, C, determined as detailed below. The amount of adsorbed Sim was calculated as the difference between the initial amount and that at the steady state. During adsorption, a slight increase was observed in pH, discussed in a previous paper,[1] which was adjusted by the addition of 0.01 mM HCl solution.

In a second type of experiments, to determine adsorption isotherms, different volumes of solution (20 μmol L^{-1}) were added to the silica sample at the chosen temperatures keeping constant the pH at the respective value pH*. To check the reversibility of the processes, desorption runs were also carried out by contacting samples loaded with Sim with different volumes of pure water, and measuring the amount of released Sim.

When adsorption only concerned the external surface (Aerosil and H-Y at 25°C), results are normalized to this. When also internal surfaces appear to be involved, results are given per unit mass of the solid.

2.4   Simazine evaluation

Sim content was measured by means of an Agilent 1200 Series HPLC apparatus (Wilmington U.S.A.), equipped with a DAD array and a ChemStation Agilent Software, using a Macharey-Nagel Nucleosil 100-5 C18 column (stainless steel 250 x 4 mm). The mobile phase, comprising a binary system of 65 : 35 acetonitrile: water, was pumped at 1 mL·min^{-1} flow in an isocratic mode. The detector was set at 220 nm and the injection volume was 20 μL. Quantitative determination was done on the basis of a calibration curve in the concentration range between 0.15-20 μmol L^{-1}.

2.5 Analysis of the data

All the experiments were repeated three times and average values were considered. The standard deviation was found to be lower than 4% and the values of correlation coefficient were in the range 0.98-0.99.

3. Results and Discussion

3.1 Measurements at 25 °C.

Figure 1 describes the isochoric experiments run with H-Y at three different total amounts of Sim, obtained by the use of different concentrations: 5 μmol L^{-1} (circles); 7 μmol L^{-1} (triangles);10 μmol L^{-1} (squares).

Curve obtained with 5 μmol L^{-1} only shows one rather narrow peak at pH* = 6.0, whereas an additional component at pH* = 5.5 is observed when concentration is 7 μmol L^{-1}. The curve corresponding to 10 μmol L^{-1} (squares) shows two components, that at pH* = 5.5, and a further one at pH* = 6.5.

Interpretation of data in Figure 1 is possible taking into account Figure 2, which compares data concerning H-Y, Aerosil and H-Y-amm for a Sim concentration of 10 μmol L^{-1}. With the latter zeolite, only the component at pH* = 5.5 survives: this, on the other hand, is observed to coincide with what observed with Aerosil, the surface of which only features silanols. It is therefore straightforward to ascribe the presence of the component at pH* = 5.5 to silanols species also in the case of both H-Y-amm and H-Y.

Because, as shown in the following, in adsorption measurements run at 25 °C only the external area of samples is involved, data in Figure 2 are normalized to such area. Taking this point into consideration, the population of acidic centres in H-Y-amm and Aerosil appears also similar. This provides further support to the similar nature for the acidic sites.

We ascribe the component at pH* = 6.0, only observed with H-Y at 5 μmol L^{-1}, to an acidic species (labelled for the moment generically X-OH) not involving silanols, more prone than these to form monomeric protonated species, so observed at lower Sim loadings. At higher loadings the X-OH species forms dimeric protonated species, similar to those depicted in Scheme 2, originating the component at pH* = 6.5.

Both species SiOH and X-OH appear, as a whole, weakly acidic. Because the related pH* values are 5.5 and 6.0, application of eqn. (3) suggest that acidity of SiOH and X-OH differs by ca. 1 unit pK_a. The main conclusion is that strong Brønsted sites are absent at the external surface, in agreement with the literature: the evolution of surface strong Brønsted sites yields a possible interpretation of the presence of the sites Si-OH and Al-OH, as reported by Hughes and White.[17]

A classical scheme for the creation of Lewis sites in thermally treated zeolites starts with the commonly accepted structure of the strong Brønsted site (scheme 4, structure *a*) and envisages a rearrangement implying the cleavage of the O ⋯Al bond.[18,19] This yields a silanol species and an exposed Al atom, which is the Lewis centre (structure *b*). If this is the process taking place at the surface of H-Y nanocrystals during preparation, when in contact with water the newly formed Al centre will coordinate one water molecule (structure *c*). Both experimental[20] and theoretical modelling[21] show that such centre has mild acidic properties. We propose that structure *c* for the acidic centre referred to so far as X-OH. We note that structure *c* provides a simple way to account for the disappearance of acidity after treatment with gaseous ammonia, which displaces the water molecule and depletes acidic properties (structure *d*).

Another piece of evidence in favour of the similarity (if not identity) of the two silanol sites on Aerosil and HY-amm comes from Figure 3, which reports adsorption isotherms at 25 °C on these two samples, which indeed appear rather similar.

The results reported so far may be instructively compared with the same results concerning the zeolite USY, which, because of the post synthesis hydrothermal treatment it suffers, features a cavernous structure exposing both outer and inner sites. Related results are reported in Figure 4: the trend of the isochore indicates clearly the accessibility of inner sites, as adsorption copiously takes place at pH values ca. 4.5, together with weaker sites revealing themselves at higher pH values. Moreover the far higher entity of Sim adsorption on USY than on zeolite H-Y may be also related to the fact that the former zeolite exhibits a decidedly more hydrophobic character than the latter.

Finally, in a separate experiment, Sim has been let in contact with the H-Y powder at a concentration of 10 μmol L^{-1} for three days at a pH = 3.5, a value able to ensure reaction of Sim with stronger inner sites, as demonstrated later on. The result is represented as bar in both Figure 1 and Figure 5 below: some adsorption is observed, i.e. interaction between Sim and strong inner sites, which indicates that the process of entering the inner cavities of H-Y zeolite is possible but activated .

3.2 Adsorption at higher temperatures

The basic conclusion is that on H-Y at 25°C adsorption only involves the external surface in relatively short experiments, because of the activated nature of the transport from outer to inner regions of the zeolite. Sim molecules should instead be facilitated in entering the zeolite cavities at higher temperatures. Figure 5 compares Sim adsorption on H-Y at 25, 40, 50 °C, data being reported this time as normalized to unit weight. The curve at 25 °C is the same as in Figure 1. At T = 40°C the curve is much wider, extending from ca. 4 to 7.5 and definitely larger adsorbed amounts are also observed. This does indeed correspond to an easier migration from the surface into the bulk (or subsurface), and to the involvement of strong acidic sites. The same features are observed even more markedly for the experiments run at 50°C.

A temperature increase affects, besides kinetics, the thermodynamics of occurring processes. We believe those occurring at the surface to be not too strictly kinetically controlled (some evidence is given below), and that they may provide some thermodynamic information. For instance, the disappearance with temperature of the component at pH* = 6.5, assigned to dimeric protonated species involving the Al acidic centre, seems to indicate an exothermic nature for its formation. Instead, the population of the species corresponding to the component at ca. pH* = 5.5, a monomeric species involving the surface silanols, is observed to grow with temperature, because its formation is endothermic.

Such process, however, is spontaneous, and so appears to be entropy-driven. Prediction of entropy changes is not readily made *a priori*, as it is often the case with species in solution: in the present case, the increase in order due to the localization of a second molecule is probably overbalanced by the disorder brought about by freeing water molecules coordinated to simazine.

The portion of the curves corresponding to inner sites has a remarkable width, and extends from ca. 3.0 to ca. 5.5 pH units. This is probably evidence of the heterogeneity of the Brønsted acidic centres.

Both curves at 40 and that at 50 °C have a maximum at pH* = 3.5. Application of eqn. 3 indicates that Brønsted sites have a Ka value about 6 orders of magnitude greater than silanol species, in fair agreement with their marked acidity. A precise evaluation of the actual value of the pKa requires the knowledge of pK_a for the Sim molecule. That for Sim molecules in water is 1.79: previous work, however, concerning Aerosil has shown that a value ca. 4 is more feasible. It is likely that a similar circumstance is also encountered here. Indeed, basicity of a molecule is known to depend on the surroundings (e.g. solvent) so that it is not surprising that a simazine molecule interacting on one side with a highly hydroxylated surface, and on the other side with water may display acid/base properties somewhat different from the sister molecules in water environment. If a value equal to 4 is assumed for $pK_a(SimH^+)$, then pKa for Brønsted sites is ca. 2, that for silanol 7 and that for the Al site 8.

Reversibility of the adsorption process has been checked by desorption runs, carried out at both 25 and 50 °C, reported in Figure 6. At ambient temperature, desorption takes place of molecules adsorbed at the outer surfaces, and no (or little) amount is released from the interior. This is instead observed at 50 °C, although full reversibility is not observed under the adopted experimental circumstances.

Finally, it has been observed that adsorption at higher temperatures (60 °C) starts modifying the surface. Figure 7 reports a comparison between the isochoric data at 50 and 60 °C, together with the room temperature DRIFT spectra of the samples after drying. These latter clearly show an

increment in the hydroxyl population because of heating in water, to which corresponds an increment in the amount adsorbed at pH values between 5 and 7. The rest of the isochor is instead unchanged.

Conclusions

The use of a relatively simple and basic technique has allowed to gain interesting information on the surface properties of a most studied system, H-Y, one of the ten or so zeolites widely used in industry, at least in the USY form. The comparison with related systems (Aerosil, USY, and ammonia-treated H-Y) has proven vital.

In short term measurements, Sim adsorption at 25 °C occurs only at the outer surface of H-Y particles. Two types of mildly acidic centres occur (with pK_a ca. 7 and ca. 8, respectively) and no strong one. Previous adsorption of ammonia from the gas phase discriminates between the two. The former survives, and shows features similar to those of silanols of amorphous silica. The other is suppressed: because of this and other features distinguishing this site from silanol species (e.g. formation of dimeric Sim_2H^+ species, favoured by coverage and unfavoured by temperatures of adsorption higher than ambient) a candidate is an Al based site, i.e. a Lewis centre coordinating a water molecule, exhibiting acidic properties. This water molecule can be displaced by the stronger base ammonia which does not, however, exhibit in the present circumstances any H-donor properties. A mechanism for the generation of the two sites from surface Brønsted species is proposed, which appears to account for all features observed.

Long term adsorption measurements at 25°C already show the onset of the interaction with inner strongly acidic Brønsted sites: because of the closeness of its size to the opening of the supercage, activation is required for Sim to pass those latter and reach inner acidic sites. When adsorption is run at 40-50 °C, uptake is much larger and increases with temperature. Isochoric measurements suggest a pK_a value ca. 3.5 compatible with their marked acidic nature, although attainment of equilibrium conditions is questionable. Measurements at 60 °C (both isochors and

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DRIFT) show the onset of changes at the outer surface brought about by the presence of hot water.

Control experiments run with USY, featuring wormholes and cavities rendering accessible internal

sites, show the extensive involvement of internal Brønsted sites already at 25° C.

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REFERENCES

(1) S. Esposito, F. Sannino, M. Pansini, B. Bonelli, E. Garrone, *J. Phys. Chem. C* 2013, **117**, 11203.

(2) B. Paul, D. Yang, X. Yang, X. Ke, R. Frost, H. Zhu, *Appl. Clay Sci.* 2010, **49**, 80.

(3) S. Wang, Y. Peng, *Chem. Eng. J.* 2010, **156**, 11.

(4) J. B. Weber, *Residue Rev.* 1970b**, 33***,* 93-129.

(5) S. Esposito, F. Sannino, M. Armandi, B. Bonelli, E. Garrone, *J. Phys. Chem. C* 2013, **117**, 27047.

(6) S. Ong, X. Zhao, K. B. Eisenthal, *Chem. Phys. Lett*. 1992, *191*, 327.

(7) K. Leung, I.M.B. Nielsen, L.J. Criscenti, *J. Am. Chem. Soc*. 2009, **131**, 18358.

(8) R. K. Iler, The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry. *Wiley-Interscience publication New York*, 1979, 659.

(9) A. Rimola, D. Costa, M. Sodupe, J.F. Lambert, P. Ugliengo, *Chem. Rev*. 2013, **113**, 4216.

(10) F. Sannino, S. Ruocco, A. Marocco, S. Esposito, M. Pansini, *Journal of Hazardous Materials* 2012 , **229– 230**, 354.

(11) B. Van der Bruggen, J. Schaep, W. Maes, D. Wilms, C. Vandecasteele, *Desalination* 1998, **117**, 139.

(12) S. S. Chen, J. S Taylor, L. A. Mulford, C. D. V. Norris, *Desalination* 2004, **160**, 103.

(13) D.W. Breck, Zeolite Molecular Sieves: Structure, Chemistry and Use, Wiley, New York, 1974.

(14) A. Langella, M. Pansini, G. Cerri, P. Cappelletti, M. de Gennaro, *Clay Clay Miner.* 2003, **51**, 625.

(15) C. Ferone, S. Esposito, G. Dell'Agli, M. Pansini, *Solid State Sci.* 2005, **7**, 1406.

(16) M. S. S. Curren, J. W. King, *Anal. Chem* 2001, **73**, 740.

(17) T. R. Hughes, H. M. A. White, *J. Phys. Chem*, 1967, **71**, 2192.

(18) V.B. Kazansky, *Catal. Today* 1988, **3**, 367.

(19) A. Zecchina, C.O. Arean, *Chem. Soc. Rev*. 1996, 187.

(20) F. Di Renzo, B. Chiche, F. Fajula, S. Viale, E. Garrone, in: J.W. Hightower, W.N. Delgass, E. Iglesia (Eds.), 11th International Congress on Catalysis - 40th Anniversary, *Studies in Surface Science and Catalysis, Part B* 1996, **101**, 851. Elsevier, Amsterdam.

(21) E. Garrone, B. Onida, B. Bonelli, C. Busco, P. Ugliengo, *J. Phys. Chem. B*, 2006, **110**, 19087.

Table 1

External and total surface area of samples examined as determined by adsorption/desorption

isotherms of N_2 at 77 K.

Sample	BET SSA (m^2/g)	Langmuir SSA (m^2/g)	Total pore volume (cm^3/g)	Micropores Volume (cm^3/g) [a]	External Surface Area (m^2/g) [a]
H-Y zeolite	820	900	0.38	0.32	82
USY*	550	/	/	/	550
Aerosil*	250	/	/	/	250

[a]As obtained according to the t-plot method

*Commercial data

Caption to Figures and Schemes

Scheme 1. Structure of Sim [2-chloro-4,6-bis(ethylamino)-1,3,5-triazine].

Scheme 2. Possible configurations for the adsorbed molecule: (a) protonated monomer; (b) the same with a second molecule interacting via sharing of the proton and possibly hydrophobic interactions.

Scheme 3. Comparison of the molecular dimensions of Sim and the size of Y zeolite openings.

Scheme 4. Generation of acidic Lewis sites from Brønsted sites at the zeolite surface.

Figure 1. Sim uptake by H-Y as a function of the solution pH at 25°C under isochoric conditions at different concentrations of simazine solution. Circles: 5 μmol/L; Triangles: 7 μmol/L; Squares: 10 μmol/L. The vertical bar at pH = 3.5 measures the amount adsorbed in a long term measurement (3 days) at 25 °C.

Figure 2. Sim uptake as a function of the solution pH at 25°C under isochoric conditions per unit outer surface area. Circles: H-Y; Triangles: Aerosil; Squares: H-Y-amm.

Figure 3. Adsorption isotherms of Sim at 25 °C. Circles: Aerosil; Squares: H-Y-amm.

Figure 4. Sim uptake by USY as a function of the solution pH at 25°C under isochoric conditions.

Figure 5. Sim uptake by H-Y as a function of the solution pH under isochoric conditions at different temperatures. Triangles: H-Y at 25 °C; Circles: H-Y at 40 °C; ; Stars: H-Y at 50 °C. The

vertical bar at pH = 3.5 measures the amount adsorbed in a long term measurement (3 days) at 25 °C.

Figure 6. Reversibility of Sim uptake at 50 °C per unit mass of H-Y as a function of the equilibrium concentration in the liquid. Full circles: adsorption (data obtained by increasing the starting solute concentration). Empty circles: desorption at 50 °C (data obtained by contacting the solid after adsorption at 50 °C) with pure water; empty squares: desorption at low temperature (data obtained after adsorption at 50 °C by contacting at 25 °C the solid with pure water).

Figure 7. Sim uptake by H-Y as a function of the solution pH at 50 °C (squares) and 60 °C (stars) under isochoric conditions. The inset shows DRIFT spectra in the 4000-2000 cm^{-1} range of simazine-loaded samples at different temperatures after drying. H-Y at 25 °C (curve a); H-Y at 60°C (curve b).

Scheme 1
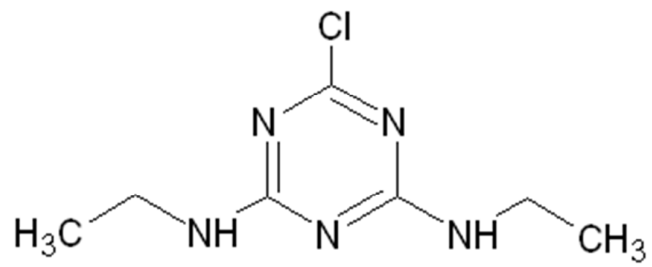
Scheme 2
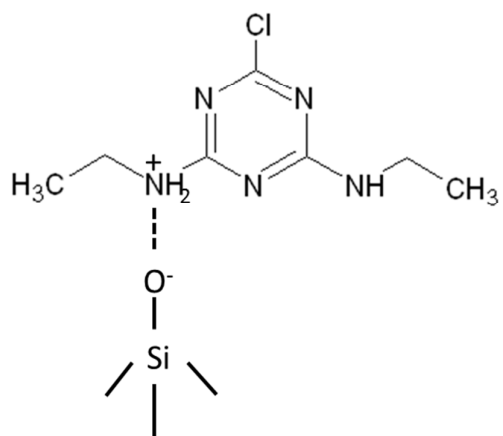
Scheme 2a
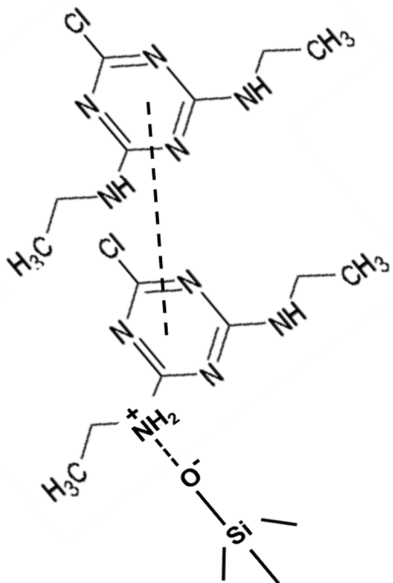
Scheme 2b

Scheme 3
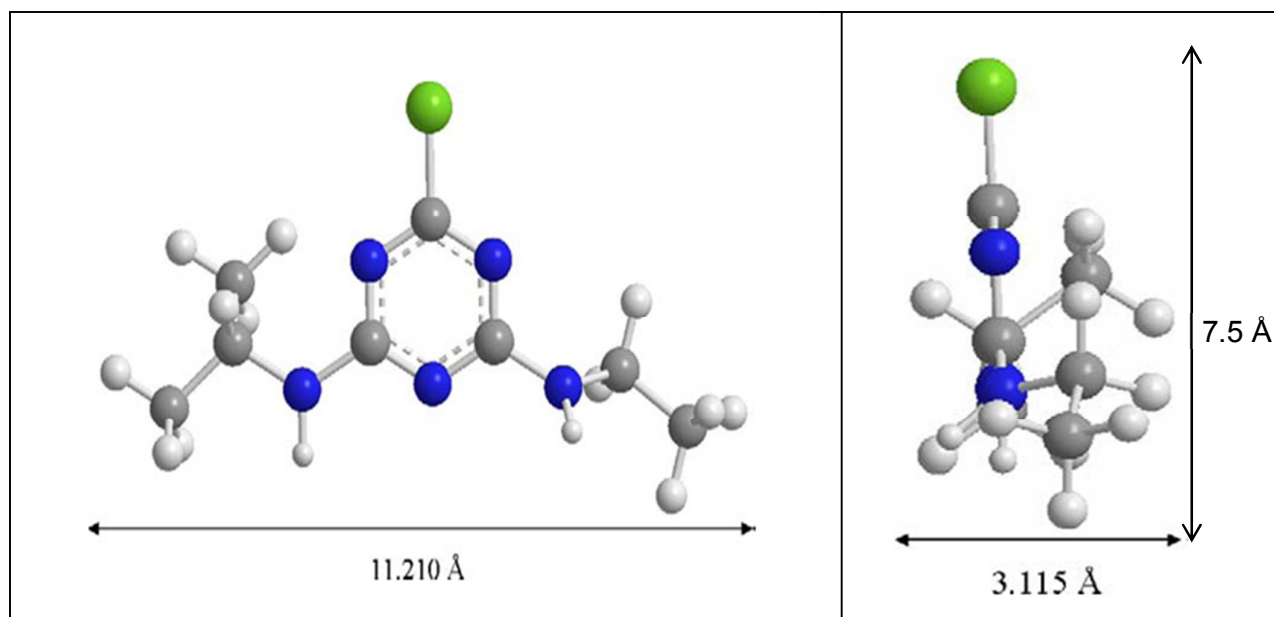
Simazine Size
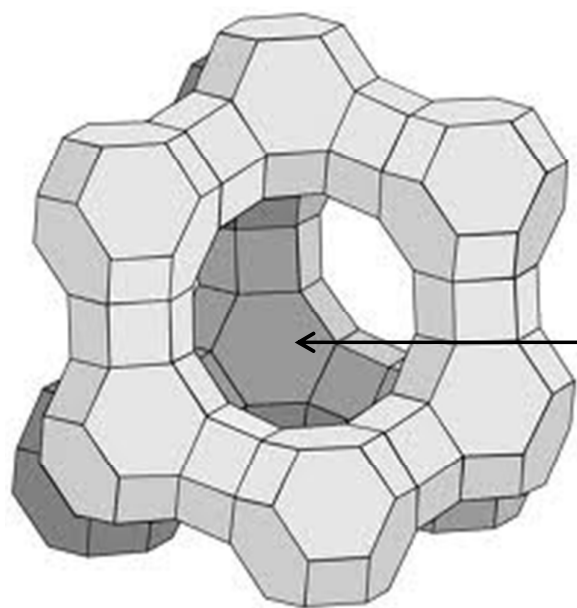
Faujasite supercage 7.4 Å

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Scheme 4
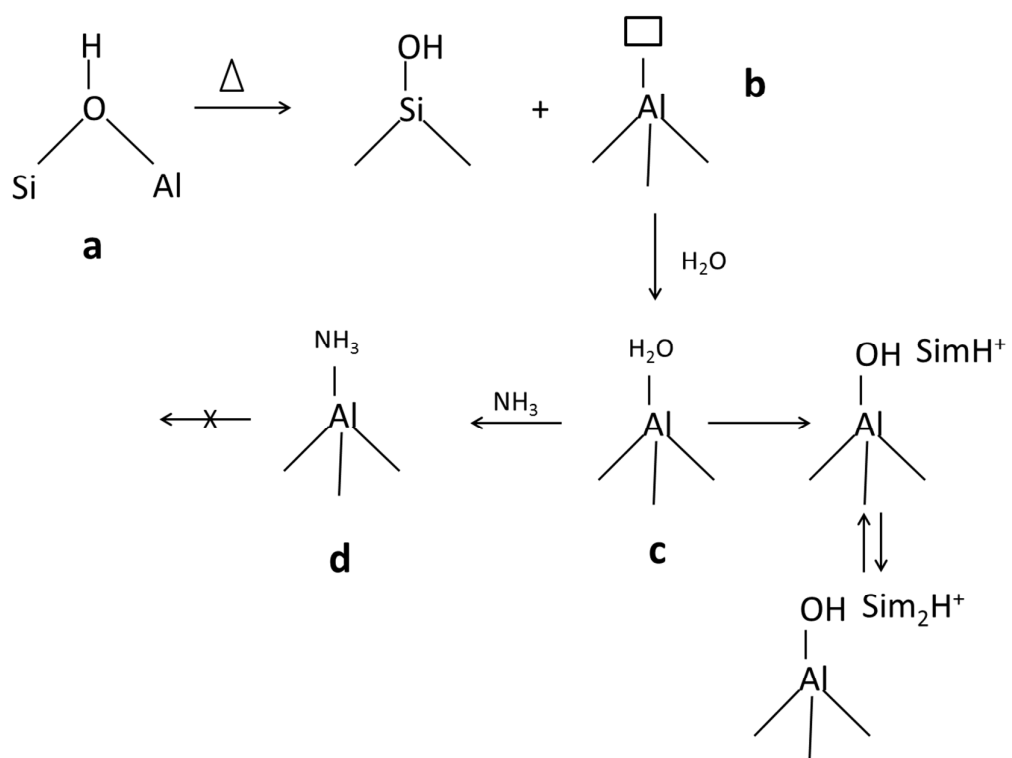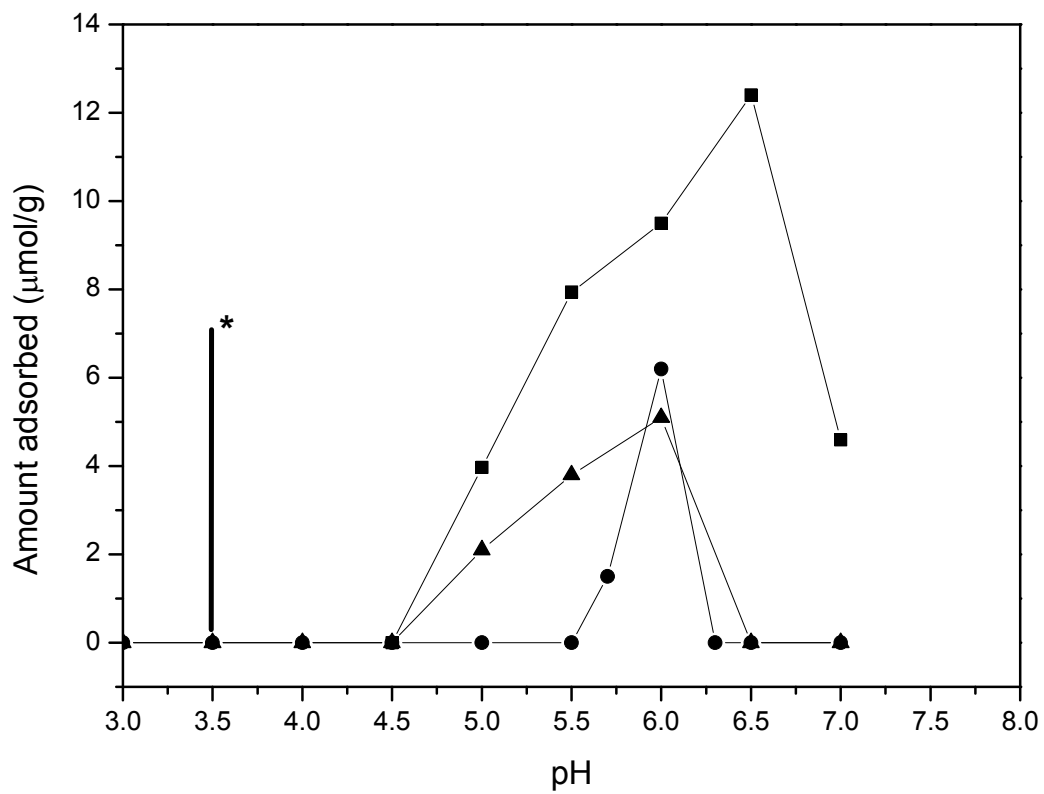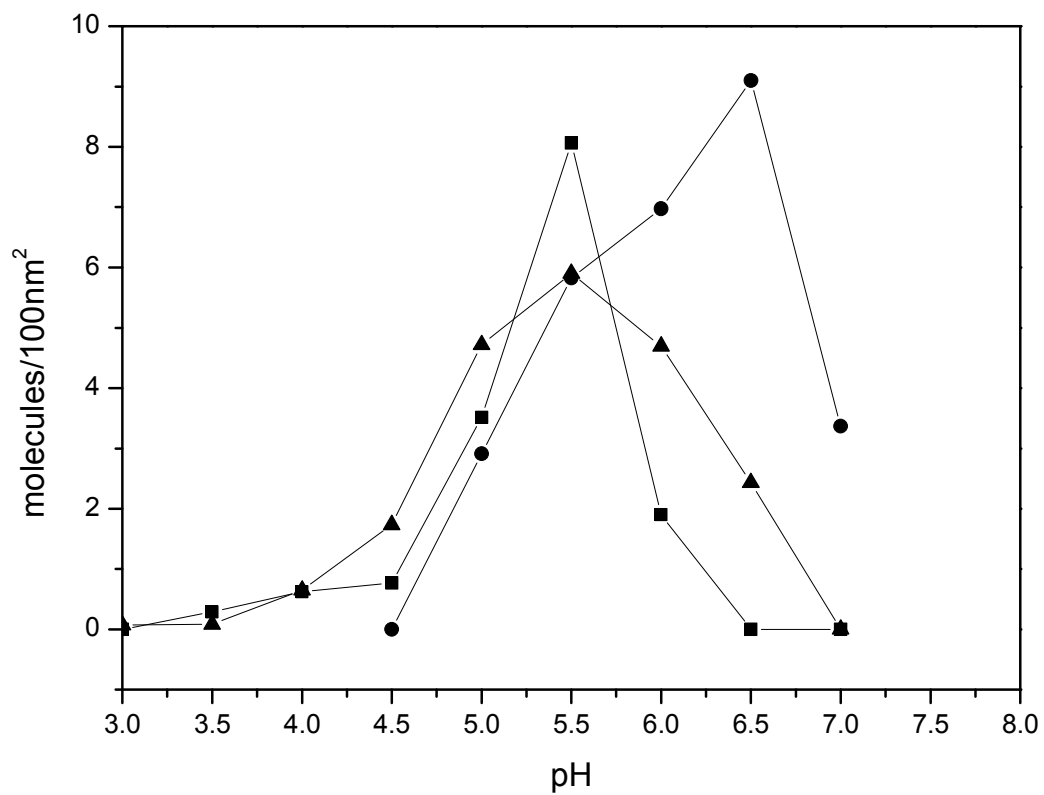
Figure 1

Figure 2
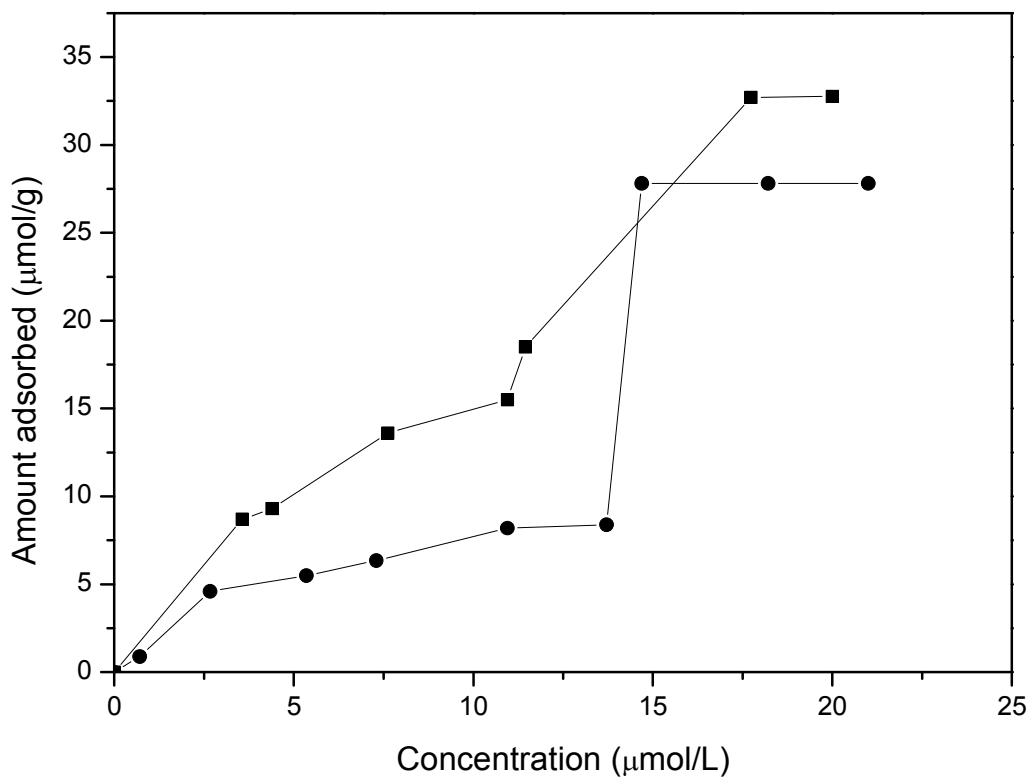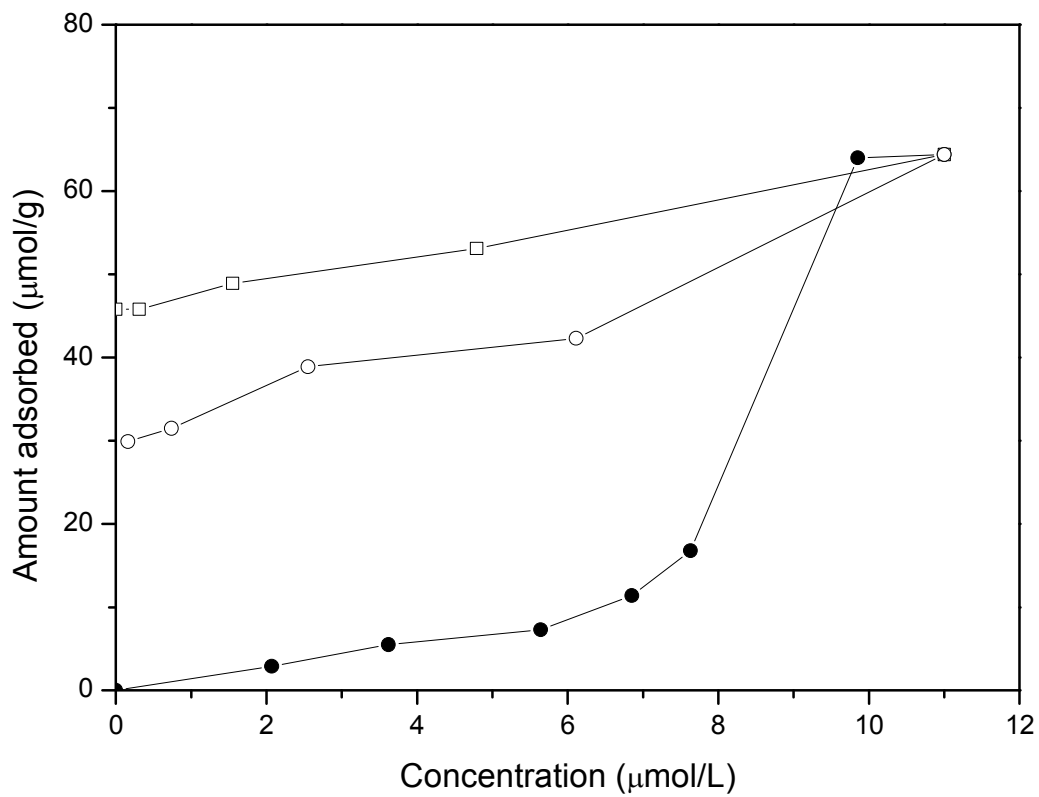
Figure 3
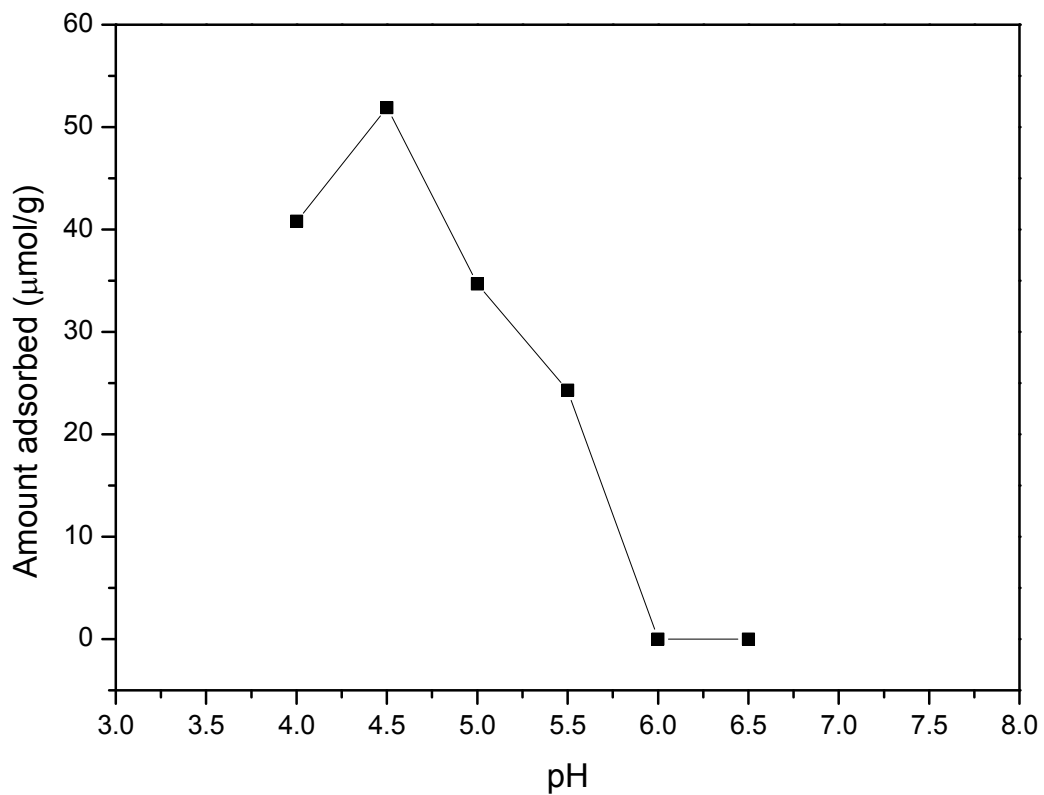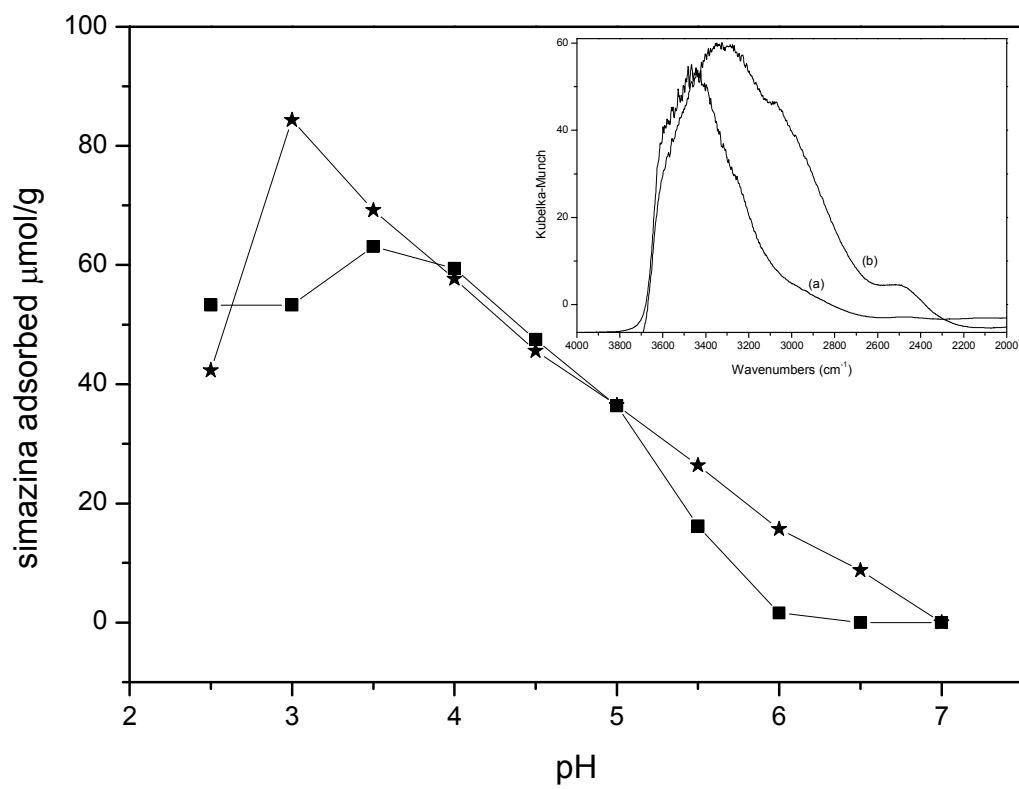
Figure 4
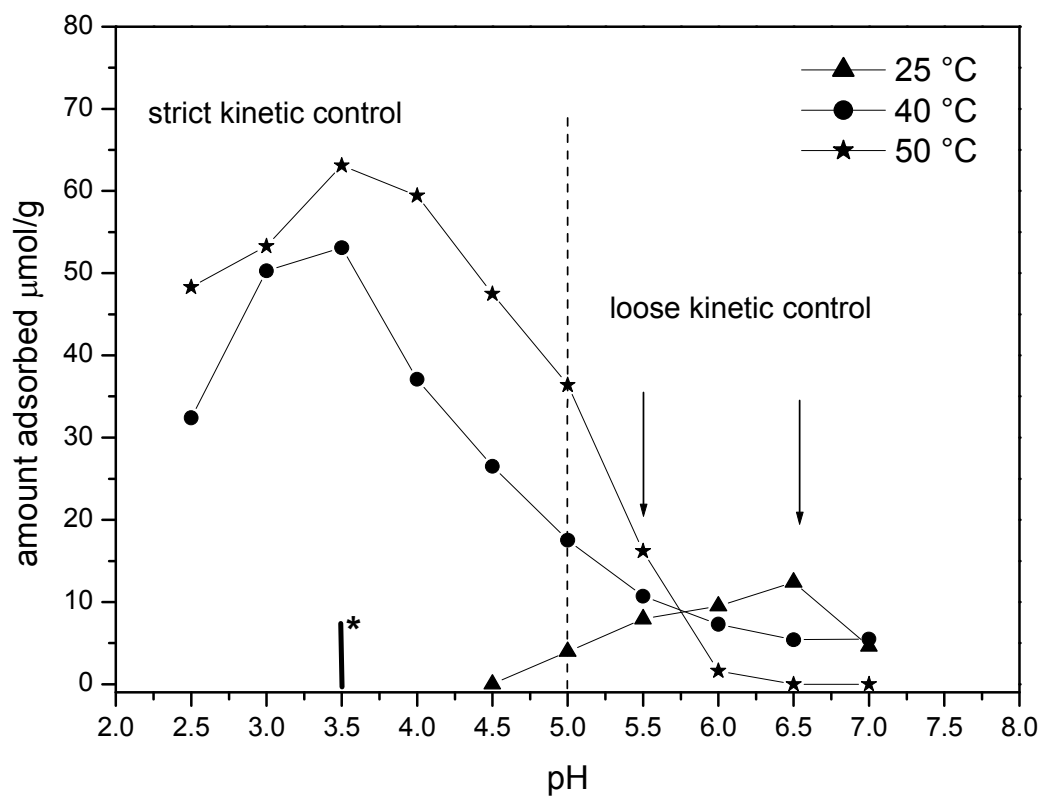
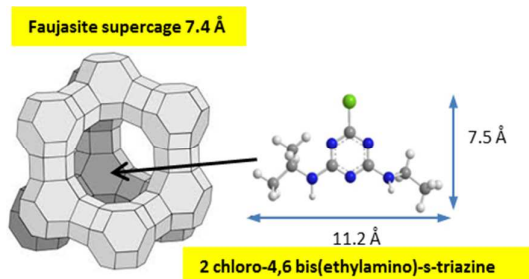**Figure 5**

Figure 6

Fig. 7

Graphical Abstract

Interesting information on the surface properties of a most studied system, zeolite H-Y, are derived

from the adsorption of simazine in a liquid/solid system.