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Acid Softness and Hardness in Large-Pore Zeolites as a Determinant Parameter to Control Selectivity in Orbital-Controlled Reactions

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Abstract: It has been found by means of quantum chemical calculations that by modifying the framework composition, i.e., changing the Si/Al ratio, and substitution of Al by other trivalent atoms such as Ga and B, in a given zeolite, the energy of the frontier orbitals of the zeolite changes and therefore the softness of the acid site changes. The acidity softness increases when increasing the Si/Al ratio and also when going from B to Ga and to Al in the framework. Since the acid softness can play a determinant role specially in orbital-controlled reactions, the catalytic implications of the changes in the acidity softness–hardness of zeolites have been shown by carrying out the alkylation of toluene by methanol and looking into the para–ortho selectivity changes obtained when using HY zeolites with different framework Si/Al ratios and H–β zeolites with Al, Al + Ga, Ga, and B as trivalent framework elements.

Introduction

After the introduction of medium-pore zeolites as catalysts, and with them the concept of shape selectivity, it has been a general tendency to explain the selectivity features of zeolites on the bases of geometrical factors. While these factors can be dominant in a situation where the traveling of molecules through the channels can be strongly influenced by diffusion, and also when the size of the activated complex is close to the size of the cavities, they become much less important when the size of the reactant molecules, the products formed, and the activated complex are sensibly smaller than the dimensions of channels and cavities. Under these circumstances, and for acid-catalyzed reactions, the only parameter which is normally considered to explain zeolite catalyst behavior is the acid strength. In this way, it has been shown that the density of positive charge on the potential acid hydrogen, and therefore its acid strength, increases when decreasing the number of Al atoms in the second coordination sphere of a given Al.[1–3] Then, by changing the framework Si/Al ratio of the zeolite, one should expect to change not only the total number of acid sites but also the strength of the remaining ones. It is therefore understandable that when acid-catalyzed competitive reactions occur, if their selectivity changes when changing the zeolite framework Si/Al ratio, the first approach to explain this is to try to correlate selectivity with acid strength. However, when data from the literature are analyzed, it is found, for instance, that, during the methylation of toluene on a large-pore zeolite such as faujasite, the ratio of *p*- to *o*-xylene increases in the order NaY < $Ca_{0.5}Y$ < $Ca_{0.3}Na_{0.4}Y$ < $H_{0.3}Na_{0.7}Y$ < $H_{0.7}Na_{0.3}Y$ < HY(Si/Al = 17).[4]

In the case of zeolite substituted by mono-, di-, or trivalent cations, the para to ortho ratio in the xylenes formed increases in the order mono- < di- < trivalent.[5] Moreover, if the zeolite parameter modified is the level of Na^+ exchanged by NH_4^+, the para to ortho ratio increases with increasing level of exchange.[6] On the bases of these results it has been supposed that the higher the acid strength of the sites the higher is the para selectivity for electrophilic alkylations at toluene. Nevertheless, this explanation can be questioned when one analyzes the total electron population on the different positions of the toluene molecule. Indeed, the total electron population is slightly higher in the ortho than in the para position, and therefore the Coulombic interactions should direct preferentially to ortho when increasing the acid strength of the zeolite. However, in large-pore zeolites and for those reactions in which no geometrical constraints exist, either for the transition state or for product diffusion, one must consider not only the total electron density on each potential position but also the frontier electron population in order to predict the position for electrophilic attack. In this way, in the case of toluene, the frontier electron population is larger on the para than on the ortho position. This in turn means that the Coulombic component will preferentially direct alkylation to the ortho position, while the interaction of the frontier orbitals will direct to the para position. In other words, in reactions occurring on zeolites where the Coulombic component is not the absolutely predominant one, besides the concept of acid strength one should also consider the concept of hard and soft acidity and basicity (HSAB) as introduced by Pearson.[7] This is especially important when discussing reactions where orbital control may exist.

Several calculations of the acid strength properties of zeolite sites have been made in the past years.[8] Structural[8a–c] and compositional[8b–e] effects were related with observations that can

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be associated with the Brönsted or Lewis acidity. However, theoretical studies on the hardness of the acid sites in zeolites are limited. Recently, one study[8f] has been performed on the variation of the Fukui function with changing electronegativity in the neighborhood of the zeolite acid site. Fukui's function is related, by means of the density functional theory,[9] to the frontier orbital density[10] and can be interpreted as a local softness.

In this work we have attacked the problem of zeolite softness and hardness and the catalytic implications, both theoretically and experimentally. By using quantum chemical calculations the variation of the energy of the LUMO has been determined when changing Si/Al zeolite composition, as well as when changing the nature of the framework atoms, i.e., Si, Al, Ga, and B. Ab initio and semiempirical SCF calculations were performed over model clusters, allowing us to determine the influence of the atoms near the acid site with a minimum cost.

To carry out the experimental work, two large-pore zeolites for which no geometrical constraints exist during the alkylation of toluene by methanol, i.e., Y and β zeolites, have been chosen as catalysts. They have been obtained with different framework Si/Al ratios and also, in the case of Beta, with different atoms in the framework. The alkylation of toluene by methanol has been studied on these catalysts, and the evolution of the para–ortho selectivity with chemical composition has been compared with the order predicted on the bases of the calculated softness–hardness of the corresponding acid sites and the methanol–zeolite alkylating complex.

Theoretical Approaches to the HSAB Principle

There are two theoretical approaches to explain Pearson's HSAB principle. The first was developed by Klopman and Salem.[11] By using a second-order perturbational approximation to the molecular orbital theory, this approach relates the HSAB principle to the frontier molecular orbital theory of Fukui et al.[12] If one considers a system composed of two reactants, A and B, during the formation of a covalent bond, one can decompose the Hamiltonian of the system into two terms, the first describing the system composed of the noninteracting reactants and the second describing the perturbation of each fragment by the influence of the other. Developing this in second-order perturbation theory and performing some approximations, Klopman obtained the expression of the change of energy during the reaction

$$\Delta E = -\sum_{ab}(q_a + q_b)\beta_{ab}S_{ab} + \sum_{k<l}\frac{Q_kQ_l}{\epsilon_0 R_{kl}} + \left(\sum_{r}^{occ}\sum_{s}^{virt} - \sum_{s}^{occ}\sum_{r}^{virt}\right)\frac{2(\sum_{ab} C_{ra}C_{sb}\beta_{ab})^2}{E_r - E_s} \quad (1)$$

where the indexes a and b refer to the atomic orbitals of fragments A and B, k and l to the atoms of each fragment, and r and s to the molecular orbital of each fragment without interaction.

The first and second terms correspond to the first-order approximation and represent respectively the closed-shell repulsion term between the occupied orbitals of each fragment and the Coulombic interaction between the atoms of each fragment considering them as point charges Q_i. Both terms are related to the charge distribution in the system.

The third term is a second-order approximation and depends mainly on the energy differences between the occupied molecular orbitals of one fragment and the virtual orbitals of the other. The chemical meaning of this term refers to the energy related to the formation of a covalent bond and, for instance, might be associated with the hardness of the reactants.

Applying the frontier orbital theory, which says that the terms other than those with the smallest difference ($E_r - E_s$)—that is, ($E^A{}_{LUMO} - E^B{}_{HOMO}$)—can be neglected, the energy related to the second order might be approximated by

$$\Delta E^{(2)} \approx \frac{2(\sum_{ab} C_{ra}C_{sb}\beta_{ab})^2}{E_r - E_s} \quad (2)$$

where r is the HOMO of fragment B (donor) and s is the LUMO of fragment A (acceptor). This depends only on the energy difference ($E_r - E_s$), the resonance integral β_{ab}, and the coefficients C_{ra} that correspond to the HOMO and LUMO, i.e., to the frontier orbital density.

In this approach a reaction would be "orbital controlled" (i.e., soft acid–soft base) if the energy difference between the HOMO of the donor and the LUMO of the acceptor is small. In addition, a reaction would be "charge controlled" (i.e., hard–hard) if the energy difference HOMO – LUMO is large. This implies that soft acids are related to those that have low LUMO energy and soft bases are related to the ones with high HOMO energy.

On the other hand, one must consider that, because of the numerator in eq. 2, the orbitals which can mix to form a covalent bond must be localized in the zone where the AOs of both fragments overlap.[12b] This implies that the named HOMO and LUMO in eq. 2 cannot be strictly the frontier orbitals but the ones with high and low energy levels, respectively, that have an important component at the site of the reaction.

This theory stands on two different types of approaches which should be discussed in order to evaluate the range of validity. First of all, the perturbation theory up to second order is only valid when the perturbation is weak. This in turn means that it can predict the chemical behavior of a given system only at the very beginning of the reaction.[13] Nevertheless, in some cases such as the electrophilic aromatic substitutions, this control can be determinant to explain the reaction selectivity.[12] In addition, the theory considers the evaluation of eq 2 as a sufficient improvement to the second-order term. While this is not true in most of the cases, it still gives a semiquantitative idea and is better when the second-order term is larger. It should be realized that the $E^{(A)}{}_{LUMO} - E^{(B)}{}_{HOMO}$ becomes the lower limit of the $E_r - E_s$ difference, r being the virtual orbital of the electrophile and s the occupied one of the nucleophile; and for instance the term which contains this would be, if not the most important, at least an effective representative of the whole term.

The second simplification which should be considered is that the theory is based on an independent particle model, considering only a mean electron–electron repulsion. It is well-known that the exact solution of this model (Hartree–Fock theory) does not require the exact determination of the virtual orbitals, and for instance, these ones may have, sometimes, an unclear meaning.[14] It should be pointed out from a more basic point of view than that of the molecular orbital theory that if the energy required to ionize atom B (I_B) is provided by the energy gained by giving an electron to atom A (A_A), a very effective electron transfer will occur and thus a covalent bond between A and B will be established. In other words, the smaller the difference between the ionization potential of B and the electron affinity of A ($I_B - A_A$), the more probable will be the formation of a covalent bond between A and B. This difference may be improved by using Koopman's theorem. Within the Molecular Orbital Theory, LUMO and HOMO energies are approximations to the electron

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affinity ($-A$) and ionization potential ($-I$) with opposite sign, respectively. Thus it is correct to say, in a first approximation

$$I_B - A_A \approx E_{\mathrm{LUMO,A}} - E_{\mathrm{HOMO,B}} \tag{3}$$

Then, despite the fact that the value of the virtual orbital energy strongly depends on the basis set used, we can assume that its variations preserve, at least, the same tendency regardless of the basis set used when very similar compounds are compared.

There is a more recent theoretical approach to the HSAB principle made by Parr and Pearson,[15] which is a general approach based on the density functional theory.[9] The hardness is related there to a magnitude named "absolute hardness" of a fragment S (η_S) and defined as

$$\eta_S = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_z \tag{4}$$

where z is the total number of charges in the system and N is the number of electrons in the fragment (not necessarily a whole number). On the other hand, using the finite difference approximation, the absolute hardness is defined as

$$\eta_S = \frac{1}{2}(I_S - A_S) \tag{5}$$

where I_S is the ionization potential of a fragment S, and A_S is the corresponding electron affinity. This approach is more general than the first one because it does not depend on any approximation to the exact solution of the Schrödinger equation. However, it should be realized that one is dealing in each case with a different language which is not always equivalent. Whereas the concept of "orbital- controlled" reactions stands for the *relative* tendency of the donor to give an electron to the acceptor ($I_B - A_A$), *absolute* hardness is a measure of each noninteracting fragment. In fact the denominator of eq 2 in terms of HSAB language should be written as

$$E^{(A)}_{\mathrm{LUMO}} - E^{(B)}_{\mathrm{HOMO}} \approx I_B - A_A \approx {}^1/_2(\eta_A + \eta_B) - (\mu_B - \mu_A) \tag{6}$$

which means that not only hardness controls the magnitude of electron transfer but also the electronegativity difference of the systems should be taken into account. This is in agreement with the original interpretation of the HSAB principle performed by Parr and Pearson[15] and indicates that both points of view, if not the same, are at least complementary.

Theoretical Methodology and Model Cluster

In our work, we have chosen the energy of the LUMO as a parameter to evaluate the "hardness acidity" of the zeolites. As we have seen in the previous section, with this parameter we can study the tendency on the influence of the "orbital control" term, provided that other factors such as orbital components and the HOMO energy of the donor remain constant. We assume in this work that these factors have a less relevant variation when changing the zeolite composition, and therefore the variations in the energy of the LUMO of the electrophilic moiety can give us the trend for the covalent bond formation.

All calculations were performed using the model cluster approximation, since it has been used successfully to explain a large number of zeolite properties.[16] This success might be justified by the fact that small clusters are, in general, strainlessly embedded within the extended system,[16,17] and it describes very well the local properties in molecular crystals such as zeolites.[17]

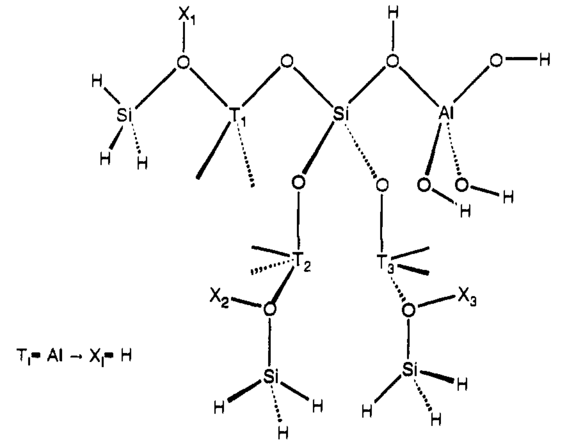

Figure 1. Model to simulate different Si/Al ratio acid zeolites. The tetrahedral atoms T_i can be Si or Al. Four different models were constructed by varying T_i: Si/Al = 7, all T_i atoms are silicon atoms; Si/Al = 3, T_1 = Al (x_1 = 4) and T_2, T_3 = Si; Si/Al = 1.67, T_1 = Si and T_2, T_3 = Al (x_2, x_3 = 4); and, finally, Si/Al = 1, all T_i atoms are aluminum atoms (x_i = H).

Ab initio calculations were performed using both GAUSSIAN 88[18] and MONSTERGAUSS[19] packages of programs. When modeling large clusters, the core electrons were substituted by pseudopotentials in order to reduce the computational cost of the calculations. In this case CEP pseudopotentials with a double-ζ basis set CEP-31G and a minimal basis set CEP-4G were used.[20] Both are implemented in the GAUSSIAN 88 program. Semiempirical SCF calculations were performed by using MNDO,[21] AM1,[22] and PM3[23] methods implemented in the MOPAC 6.0[24] package. When studying systems with only three tetrahedral ions, a split valence 3–21G basis set was utilized with the MONSTERGAUSS program. Optimizations of geometry were carried out using both the Berny method[25] in the first case and the optimally conditioned method[26] in the second one.

Figure 1 shows the basic model cluster with the acidic group of the zeolite and its next nearest neighbors. This model allows modification of the cluster composition in the range Si/Al = 7/1 to 4/4, which is sufficient to simulate the variations of the framework Si/Al ratio in a real zeolite system (see details in figure).

Figure 2 shows the scheme of a larger cluster where bond lengths and angles correspond to those of the HY zeolite.[27] This cluster accounts for an acid center and its environment up to the 5th coordination sphere. The cluster has been terminated by OH groups in order to preserve the electroneutrality of the model. The bridging hydroxyl was situated on the most stable position following the geometry recommended by Sauer et al.[8h] T_i represents tetrahedral cations which can be either Si(IV) or Al(III). The negative charge produced when introducing Al(III) in tetrahedral positions has been compensated by protons. In our cluster, added hydrogens have been generally bonded to the terminating oxygens. However, for two cases (T_8 and T_3 = Al), calculations were also made with the hydrogen atom bonded to

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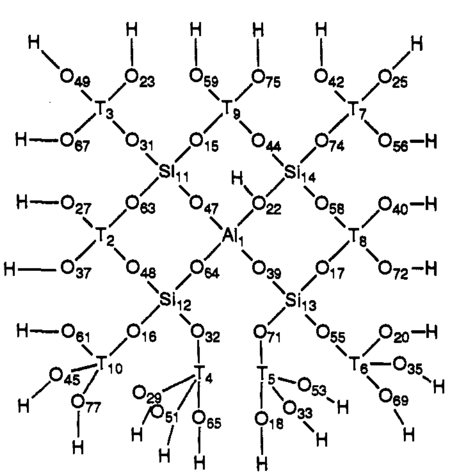

Figure 2. Figure 2. Cluster that represents a fragment of the FAU structure in which an acid center and the atoms up to the fifth coordination sphere are included.

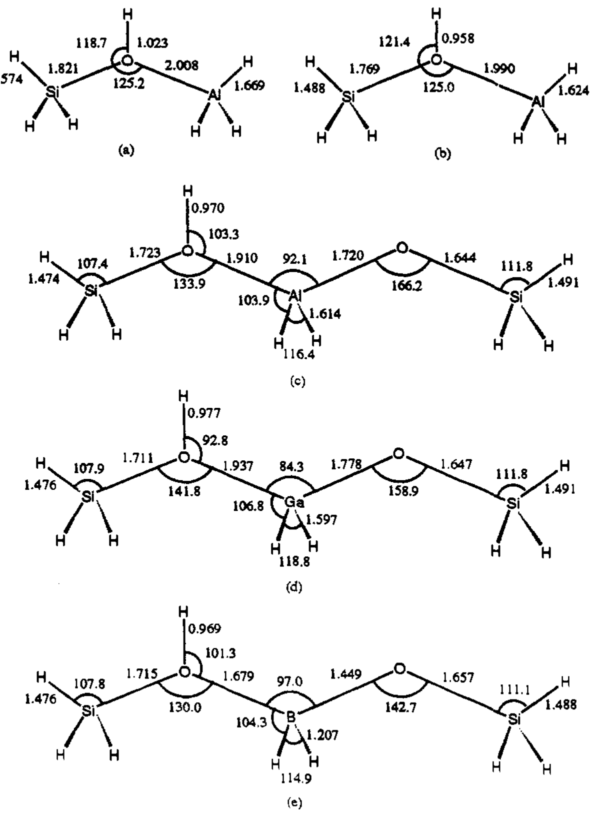

Figure 3. Figure 3. Optimized parameters for the different models used to simulate the active site, (a) using the CEP-4G, (b) CEP-31G, and (c, d, and e) 3–21G basis sets.

a bridging O (O_{17} and O_{31}, respectively) (see Figure 2). In all cases the hydrogens were located maintaining the following geometrical parameters: $d_{O-H} = 0.96$ Å and AlOH = 110°.

To model the clusters in which the nature of the trivalent atoms is changed, we have considered not only the bridge hydroxyl group as the active center but also the basic O-bridging coplanar adjacent to the trivalent cation (B^{3+}, Al^{3+}, Ga^{3+}) (Figure 3c,d,e). Three different models were performed which allowed us to study the hardness when changing the nature of the trivalent framework cations.

In all the models being utilized, the "dangling" bonds which connect the chosen fragment with the bulk of the catalyst are saturated by hydrogen atoms. This technique has been shown to be effective in modeling the active site in several previous works.[16]

Table I. Characteristics of the HY Zeolite Samples

sample	unit cell (Å)	Al/u.c.	crystallinity (%)
HYD-1	24.56	36.9	90
HYD-2	24.43	22.1	85
HYD-3	24.36	14.2	90

Table II. Characteristics of the β Zeolites

sample	T framework atoms	Al/ u.c.	Ga/ u.c.	B/ u.c.	T^{+4}/T^{+3} ratio	cryst (%)	d (μm)
β-1	Si–Al	4.40			13.4	100	0.70
β-2	Si–Al	4.50			13.1	95	0.17
β-3	Si–Al–Ga	1.76	2.19		15.2	95	0.19
β-4	Si–Ga		2.06		30.1	90	0.17
β-5	Si–B			4.92	12.0	90	0.17

In all the geometry optimizations the C_s symmetry was fixed.

Catalytic Experiments

Materials. A series of HY zeolites with different framework Si/Al ratios were prepared by dealumination of a NaY zeolite (SK-40) using $SiCl_4$ and following the procedure given by Corma et al.[28] The samples were then thoroughly washed, exchanged with NH_4^+, and calcined at 773 K. This exchange–calcination procedure was carried out three times in order to bring the sodium content of the final zeolite below 0.20 wt %. The crystallinity of the resultant samples was measured by XRD and calculated by comparing the peak height of the (5.3.3) peak in the sample with that in the NaY SK-40 taken as 100% crystalline.

The unit cell size of the dealuminated HY zeolites was determined by XRD using Cu Kα radiation and following ASTM procedure D-3942-80. The estimated standard deviation was ±0.01 Å. The framework Si/Al ratio was obtained from the unit cell size values and the Fichtner-Schmittler equation.[29] The final characteristics of the catalyst samples are given in Table I.

β zeolite and its isomorphous Ga- and B-substituted forms were prepared by direct synthesis following the procedures previously reported.[30] After synthesis, the samples were NH_4^+ exchanged at 353 K, and after the samples were dried, they were calcined at 773 K. The exchange–calcination was repeated twice, and the characteristics of the resultant samples are given in Tables I and II.

Reaction Procedure. The alkylation of toluene with methanol was carried out in an electrically heated, differential, fixed-bed, glass tubular reactor with an internal diameter of 15 mm. Toluene and methanol (4/1 molar ratio) were fed at the top of the reactor by a positive displacement pump. N_2 was used as a gas carrier in a N_2 to methanol molar ratio of 1/1.

Prior to the addition of the reactants, the catalyst was heated in the reactor at 723 K in a flow of N_2 (60 $cm^3 \cdot min^{-1}$). Samples were taken at 10, 30, 60, 180, and 360 s and analyzed by GC using a 3 m long column, packed with 16% DC-200 Me and 3% Bentone-34 on chromosorb W. From the results obtained at different times on stream, the conversion and yields at zero time on stream were always obtained.

In previous experiments it was found that for total flows in the range used here (≥0.142 $mol \cdot h^{-1}$), and catalyst particle sizes in the diameter range from 0.30 to 0.50 mm no control by external or internal diffusion occurs. Within these limits, the contact time was varied in order to compare selectivities at the 5% conversion level.

Theoretical Results and Discussion

Influence of the Si/Al Ratio. The effect of chemical composition on the LUMO energy of a given acid site of the zeolite has been studied by calculating the compositions of the four different clusters presented in Figure 1. Due to the considerable size of the systems to be studied, the calculations were made assuming a fixed geometry. The geometrical parameters of the atoms

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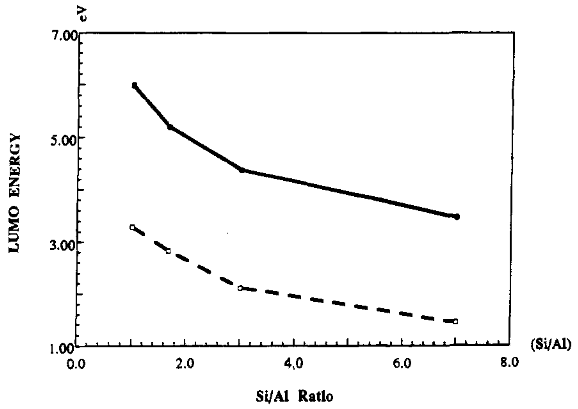

Figure 4. Figure 4. LUMO energy vs Si/Al ratio: solid line, calculations made with the CEP-4G basis set; dashed line, calculations made using the CEP-31G basis set.

located out of the active site were fixed to standard values, while the geometry of the group of atoms giving rise to the active site was fixed on the basis of the parameters obtained optimizing a smaller "model cluster" (Figure 3a,b). This model has been successfully used in the literature.[8a-h] The optimized parameters are detailed in the figure. The standard values used in the neighborhood of the acid site were SiO = 1.62 Å; AlO = 1.7 Å; TOT = 130.0°; T = Si, Al, H; OH = 0.975 Å; and the TH distance in the cluster termination was the same as that obtained in the smaller optimized cluster.

Two atomic basis sets (ABS), CEP-4G and CEP-31G, with pseudopotentials to simulate the core electron potential were used to study the influence of the basis set on the LUMO energy calculated.

Figure 4 shows the variation of this parameter with the Si/Al ratio calculated with each ABS.

As seen there, two different sets of values are obtained, but nevertheless they follow the same tendency with the chemical composition (Si/Al ratio), regardless of the ABS used. This agrees with our previous assumption that the impact of the ABS on the differences between the energies of the LUMO, while being important to the energy of the orbitals, is very minor and describes tendencies on similar compounds. Then it can be seen that, on the CEP-4G basis set, the energy of the LUMO increases in an amount of 15–20 kcal mol^{-1} when a framework Si is substituted by an Al. When the CEP-31G basis was used, the increment was 10–15 kcal mol^{-1} per Si exchanged, but nevertheless the general tendency was the same as before. In a previous work[26] the same tendency was observed when using PM3-MNDO semiempirical calculations to evaluate the LUMO energy although the differences of energy calculated there were significantly smaller than those obtained by ab initio calculations.

In order to see if the oversimplified model used here, which corresponds to a very small cluster terminated by H atoms, represents a much larger zeolite framework, regardless of the exact framework geometry, calculations were also carried out on a larger cluster of a zeolite HY (Figure 2). In this larger cluster the actual bond lengths and angles from crystallographic data have been taken, and three semi empirical parametrizations have been used to calculate the LUMO energies and the orbital components, as well as the Mulliken population analysis. The results obtained are given in Table III. There are listed the LUMO energy for each model (E_i) and also the increment in the LUMO energy (ΔE_i) taking as a reference the value corresponding to the acid center surrounded by only Si(IV) cations (T_1 in Table III).

One can observe that the three parametrizations used (AM1, PM3, MNDO) lead to similar trends on the LUMO energy increment (ΔE_i) when substituting a Si atom by an Al. AM1 and MNDO show equivalent behavior whereas PM3 shows some deviations probably because these parametrizations are optimized to reproduce heats of formation of compounds instead of orbital energies that are used here. Nevertheless, some interesting observations can be pointed out from these results.

From Table III one can see that the increase of the LUMO energy varies with the position where the Si atom is substituted by Al. It should be noticed that the distance of the substituting Al atom to the acidic OH seems to have some importance on determining the hardness of the acid center. In most of the cases the closer to the OH is the substituted Al, the higher is the LUMO energy of the acid center and, therefore, the harder its acidity. This is not surprising, since, when an acid proton remains bonded to an oxygen to form an OH bridging, then the tetrahedral centers on the next near neighbors will become not equivalent with respect to the acid center and they should influence differently the acidic properties.

The influence of the location of the charge-compensating proton on the LUMO energy of the acid site when an Al(III) substitutes a Si(IV) in the framework was also studied. For substitution on the T_3 and T_8 positions, we have also calculated with the AM1 parametrization the LUMO energy of the acid center when the charge compensating proton was located both in the farthest and, in the closest position to the acidic OH (see Table III and Figure 2). One can observe that location in the closest position contributes negatively to the increase of the LUMO energy of the acid center, producing an inversion of the effect when the influence of the Al(III) cation is small, as occurs in the case of the substitution on T_3.

By using AM1 parametrization we have also studied the effect of increasing the Al content of the zeolite on the LUMO energy of the acid site and, consequently, on its hardness (Table III). There it can be seen that the increase in the LUMO energy, calculated for models with two or more cations substituted (see Si/Al > 3.67 in Table III), is in all the cases practically equal to the sum of the increases produced by each substituted cation (third row in Table III). From this, one can deduce that the influence of the neighboring Al(III) cations on the hardness of the acid center seems to be additive, which is in agreement with the results obtained when using ab initio calculations on the smaller cluster presented above.

The information obtained by this series of calculations suggests that the exchange of tetrahedral cations in the neighborhood of the acid site influences the hardness in a way that depends on the charge of the environment. The negative charge produced when an Al(III) replaces a Si(IV) in the framework would lead to an increase of the LUMO energy of the acid site and, consequently, to an increase of its hardness. The fact that the effect depends on the distance to the substituted position and also the fact that the effect is additive lead us to postulate that the increase in the LUMO energy of the acid site when Si is replaced by Al would be principally produced by an electrostatic influence of the framework of the zeolite on the acidic OH group. In order to establish the effect of the compensating proton, it should be taken into account that the closer position is statistically one in four.

On the other hand we have studied the influence of the Si/Al composition on the LUMO component of the 1s orbital of the acidic H atom. This value is indicative of the LUMO extent on the reactive site and together with the LUMO energy determines the importance of the orbital control (see eq 1).

Thus, in Table III, one can see that the LUMO component on the acidic proton shows no trend when increasing the Al content of the zeolite, contrary to what has been observed with the LUMO energy. As a consequence, from these calculations one should conclude that the variation in the hardness when changing the Si/Al ratio of zeolites should mainly be attributed to the changes in the LUMO energy produced when changing the framework chemical composition.

In conclusion, our calculations indicate that the higher the framework Si/Al ratio of the zeolite, the softer should be the acid

Table III. LUMO Energies and Component on the Acidic Hydrogen Calculated for a Cluster with Faujasite Geometry[a]

	AM1				PM3		MNDO	
substituted centers[a]	E_i (eV)	$\Delta E_i = (E_i - E_1)$ (eV)	$\Sigma\Delta E_i$ (eV)	^{c}LUMO,H	E_i (eV)	ΔE_i (eV)	E_i (eV)	ΔE_i (eV)
(Si/Al = 13.0)								
T_1	−0.621	0.0		0.216	1.517	0.0	−0.954	0.0
(Si/Al = 6.0)								
T_1, T_2	−0.405	0.216		0.211	1.581	0.064	−0.729	0.225
T_1, T_3 (OH on 23)[a]	−0.538	0.083		0.208	1.454	−0.063	−0.899	0.055
T_1, T_3 (OH on 31)[a]	−0.834	−0.213		0.220				
T_1, T_6	−0.545	0.076		0.210	1.433	−0.084	−0.905	0.049
T_1, T_7	−0.098	0.523		0.239	1.971	0.454	−0.235	0.719
T_1, T_8 (OH on 40)[a]	−0.059	0.562		0.197	1.686	0.169	−0.132	0.822
T_1, T_8 (OH on 17)[a]	−0.248	0.373		0.226				
T_1, T_9	−0.272	0.349		0.216	1.615	0.098	−0.530	0.424
T_1, T_{10}	−0.493	0.128		0.213	1.558	0.041	−0.849	0.105
(Si/Al = 3.67)								
T_1, T_2, T_3	−0.327	0.294	0.299	0.204				
T_1, T_2, T_7	0.116	0.737	0.739	0.233				
T_1, T_7, T_9	0.228	0.849	0.872	0.240				
(Si/Al = 2.5)								
T_1, T_2, T_3, T_6	−0.256	0.365	0.375	0.197				
T_1, T_2, T_3, T_7	0.207	0.828	0.822	0.230				
T_1, T_7, T_8, T_9	0.832	1.453	1.434	0.227				
T_1, T_2, T_7, T_9	0.456	1.077	1.088	0.232				

[a] See Figure 2.

sites. This is in agreement with EEM semiempirical calculations[32a] of different zeolites using density functional theory, which shows the same trend for the softness.[32b] Since the orbital control appears to have a sensible influence on the para selectivity for the alkylation of toluene by methanol, we must then expect that the absolute hardness in large-pore zeolites and, thus, in the possible alkylating agent must be on the same order as those of other effective electrophiles for aromatic substitutions. Then, from this point of view one may expect that the higher the framework Si/Al ratio of a given zeolite catalyst, the higher should be the selectivity to alkylation in the para position during the electrophilic alkylation of toluene by methanol.

Influence of the nature of the framework atoms. When the nature of the trivalent atom was changed, the analysis of each composition model was performed on the most stable geometry in order to avoid spurious effects produced by artificial geometry distortion. It is known that the acidic properties of active sites are strongly dependent on geometrical parameters such as TOT angles and TO distance.[8a,33] Besides, we were interested here in modeling the behavior of large-pore zeolites, and in those solids, the flexibility of the framework may allow the active site to adopt a geometry close to that reached without lattice restrictions. Optimized parameters are shown in Figure 2c,d,e. In general, no large differences in geometry are observed between different composition models.

Due to the possible role of the base O-bridging on zeolite activity,[29] we must consider not only the hardness of the acid site but also that of the base site when studying the behavior of different composition models in an orbital-controlled reaction. Therefore, both LUMO and HOMO energies of the active center will be considered here.

Frontier orbital energies are listed in Table IV. Evidently, as it was pointed out above, frontier orbitals do not mean, here, the true lowest unoccupied and highest occupied orbitals of all the model system, but the ones which have their mean components on the active site and not on the hydrogen boundary atoms. Following this criterion, LUMO majority components correspond to the acid site atomic orbitals and HOMO components to the base site ones.

Table IV. Frontier Orbital Energies of Different Trivalent Cation Models

	$H_3Si(OH)$-$BOSiH_3$	$H_3Si(OH)$-$GaOSiH_3$	$H_3Si(OH)$-$AlOSiH_3$
E_{HOMO} (au)	−0.425	−0.420	−0.419
E_{LUMO} (au)	0.122	0.109	0.105
$\eta \simeq \dfrac{E_{LUMO} - E_{HOMO}}{2}$ (eV)	7.44	7.20	7.13

We can see that the difference between LUMO and HOMO energies (η, see Table II), and therefore hardness, increases in the order Al < Ga ≪ B when substituting the trivalent cations in the framework. The same trend is observed when only the LUMO energies of the acid site are considered.

A relatively small increase in hardness is observed when substituting Al by Ga. On the other hand substitution of Al by B produces a meaningful increment of that property. Then, it is expected that the para/ortho (P/O) ratios in the alkylation of toluene by methanol must show the inverse trend of hardness, i.e. P/O, Al > Ga ≫ B.

At the same time we have studied the effect of the substitution of the trivalent cation on the hardness not only of the acid site but also of the possible alkylating agent in the methylation of toluene by zeolites. It has been proposed[34] that alkylating species on acid zeolites ought to be alkoxy–zeolite type compounds which would take some carbenium behavior by thermal activation.[35] This activation would be produced when the C–O distance increases from its equilibrium position.

In the case of methylation of toluene the proposed alkylating agent has been modeled in this work by replacing on the cluster in Figure 2c and e the acidic proton by a methyl group. The C–O distance was fixed at 1.8 Å to simulate the activation of the complex, and the remaining variables have been optimized to an energy minimum.

In Table V the Mulliken charges on the methoxy group are listed. One can see that, whereas ionicity, which is a reliable measurement of the acidity,[8d] decreases when replacing Al by B, as it is expected, the charge on the methyl group does not follow the same tendency. Indeed, one can see that the negative charge on the oxygen atom is the main factor responsible for the ionicity of the complex, i.e., the absolute value of $q_O q_{CH_3}$ (Table V), since

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(32) (a) Van Genechten, K. A.; Mortier, W. J.; Geerlings, P. *J. Chem. Phys.* **1987**, *86*, 5063. (b) Baekelandt, B. G.; Mortier, W. J.; Schoonheydt, R. A. In *Modelling of Structure and Reactivity in Zeolites*; Catlow, R. A., Ed.; Plenum Press: New York and London, 1992; p 157. Baekelandt, B. G.; Mortier, W. J.; Lievenes, J. L.; Schoonheydt, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 6730.

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Table V. Hardness and Mulliken Charges for the Possible Alkylating Agent Using Different Trivalent Cations

trivalent cation	Q_C	Q_{CH_3}[a]	Q_O	$\lvert Q_{CH_3}Q_O\rvert$	η (eV)
Al	−0.373	0.465	−0.902	0.419	6.97
B	−0.360	0.474	−0.829	0.393	7.24

[a] Group charges obtained by addition of atomic charges in the group.

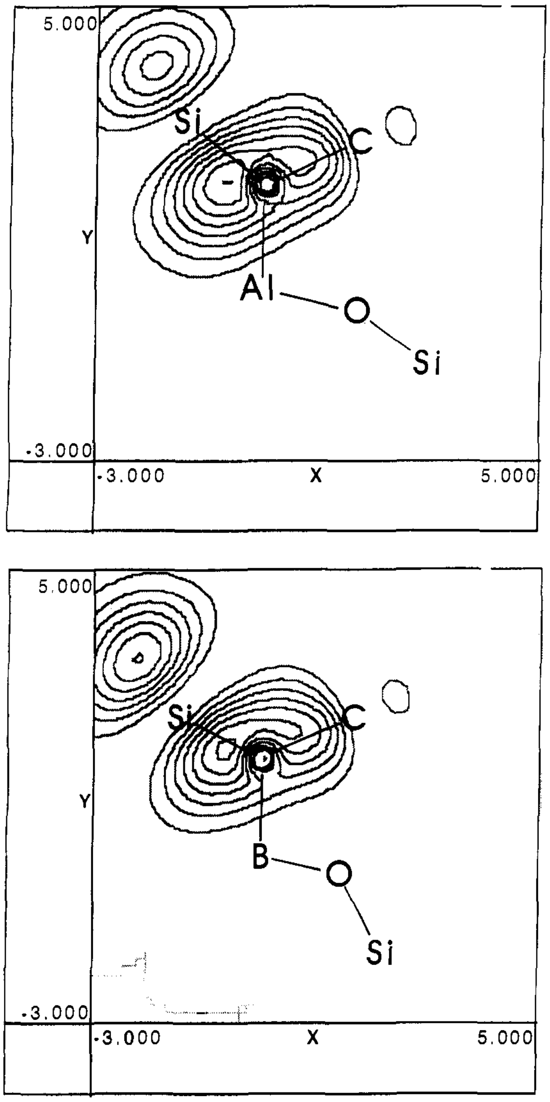

Figure 5. Figure 5. Representation of the LUMO density on the x–y plane for the activated methoxy–zeolite complex when the trivalent atom is both Al (top) and B (bottom). Levels are depicted by 0.2 density units, and the light line represents the 0th level.

the total charge of the methyl group varies only slightly. On the other hand, one can see in Table V that the hardness ($\eta = E_{LUMO} - E_{HOMO}/2$) shows the same trend on the methoxy complex as on the free acid site, i.e., η increases when changing Al by B in the cluster.

When the complex is being activated, the influence of the chemical composition of the zeolite remains significant to determine the hardness of the active centers because of the delocalization of the LUMO through the neighboring atoms. This makes the role of the trivalent cation on the stabilization of the LUMO important even in the activated complex. This can be seen in Figure 5, where the LUMO density is depicted for B- and Al-containing clusters. Nevertheless, the charge on the methyl is not affected to a large extent by the substitution of the tetrahedral cation. It is clear that, the more elongated the C–O distance is, the more charged will be the methyl group, but at the same time, the lesser will be the influence of the composition on the charge of methyl group.

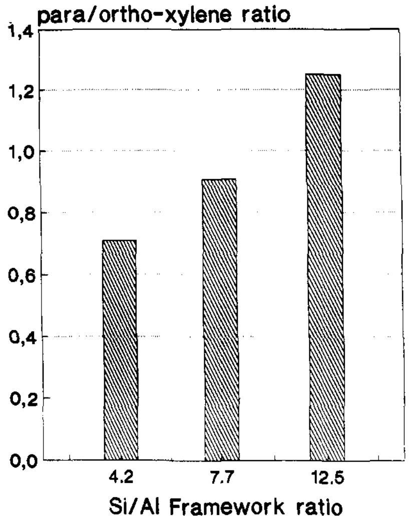

Figure 6. Figure 6. para/ ortho ratio when increasing the framework Si/Al ratio of the zeolite Y at 498 K.

Then, the differences in selectivity for the alkylation of toluene should not be attributed to changes in acid strength, but it seems to be related with the hardness of the complex, which shows significant differences when changing the zeolite composition.

Finally, one can notice from Figure 5 that LUMO extent has no greater variation when changing trivalent cations, which, as it was pointed above, indicates that it is the LUMO energy and not the LUMO extent which can determine the orbital control in the alkylation of toluene by zeolites.

Catalytic Results

During alkylation of toluene by methanol on Y zeolites with framework Si/Al ratios from 4 to 15, the main products formed are para and ortho xylenes, while a smaller amount of *m*-xylene is found. The latter comes from isomerization of the para and ortho forms. Notice that, in order to minimize secondary reactions, a differential reactor has been used here, and all zeolite catalysts are compared at a very close level of conversion (~5%).

Results from Figure 6 clearly show that the para/ortho ratio during the alkylation of toluene by methanol increases, when increasing the framework Si/Al ratio of the zeolite Y. In order to avoid variations in the para/ortho ratio due to the different rates of isomerization of the para and ortho xylenes to give the meta isomer, the amounts of para and ortho xylene transformed to the meta isomer by isomerization have been calculated on the basis of the kinetics of these two isomerization processes,[36] and the corrected ratios are given in Figure 7. The same tendency as shown in Figure 6 was observed.

In the case of faujasite zeolites with cavities of ~12 Å connected by windows of 7.4 Å, one cannot expect the product distribution during alkylation of toluene by methanol to be controlled by diffusion through the pores. Then, chemical factors must be responsible for selectivity changes. It has been demonstrated that the acid strength of faujasite increases up to a framework Si/Al ratio of 6 and then remains constant.[2] Therefore, if changes in the acid strength would be responsible for the observed selectivity variations, changes in the para/ortho ratio may occur until a framework Si/Al ratio of 6 is achieved. Above this value, and since the acid strength remains constant, no variations in the selectivities to the different isomers should be observed.

However, results from Figures 6 and 7 show that the para/ortho ratio keeps increasing when increasing the framework Si/Al ratio of the zeolite above 6.

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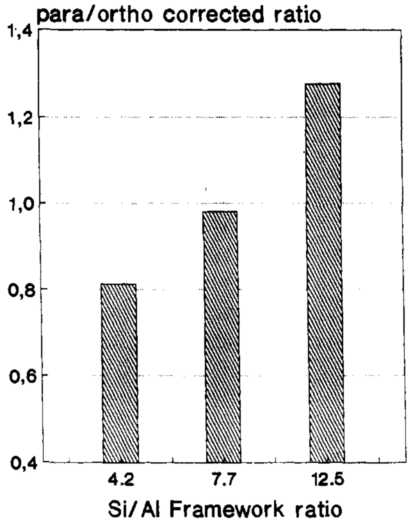

Figure 7. Figure 7. para/ortho ratio corrected for elimination of the para and ortho xylenes to give the meta isomer, when increasing the framework Si/Al ratio of the zeolite Y at 498 K.

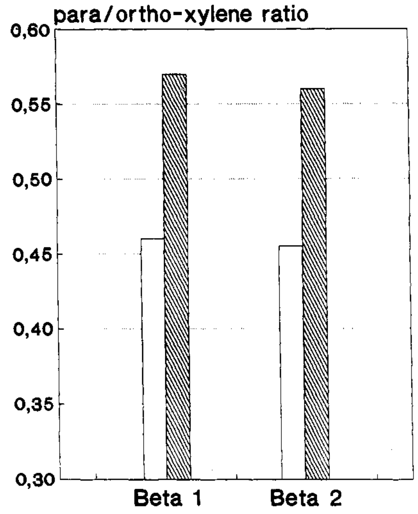

Figure 8. Influence of the crystallite size on the para/ortho ratio in β zeolites at 498 K (blank bar) and 573 K (dashed bar).

It was said above that the density of the frontier orbital of toluene will direct to the para isomer. On the other hand, it appears clear from our molecular orbital calculations that the higher the framework Si/Al ratio of the zeolite, the higher will be the contribution of orbital control, the softer the resulting acid sites, and therefore the more para directing should be the catalyst. This is indeed corroborated by the experimental results from Figures 6 and 7.

However, there is another way of changing the acid characteristics of a zeolite, and this is done by changing Al by other trivalent atoms.

Up to now, it is not possible to do this efficiently in the case of Y zeolite, but it has been shown in our laboratories that it can be done by synthesis, in another large-pore twelve-member ring zeolite such as β.[30] In this way, different samples have been prepared in which the framework Al has been substituted by Ga and B. However, β zeolite is formed by channels of 5.6–7.3 Å, which are smaller than the windows of a Y zeolite, and therefore the possible influence of the diffusion of products through the channels on the para/ortho selectivity has to be studied. To do this, two β zeolites with the same framework Si/Al ratio but with different crystallite sizes, i.e., 0.17 and 0.70 μm, were synthesized, and the alkylation of toluene by methanol was carried out on these two samples. Results from Figure 8 clearly show that a very close para/ortho ratio was found on the two samples regardless of the zeolite crystallite size, indicating that in β zeolite the alkylation selectivity results are not disguised by diffusional problems. This observation is in agreement with the work of Ratnasamy et al.[37] which found no shape selectivity in the xylenes fraction during the methylation of toluene. Then, the selectivities for para and ortho xylenes were calculated for Al-, Ga-, and B-containing β zeolites, as was done for the faujasite zeolite, and the results are given in Figure 9. It can be seen there that the para/ortho ratio decreases in the order SiAl > SiAlGa > SiGa > SiB.

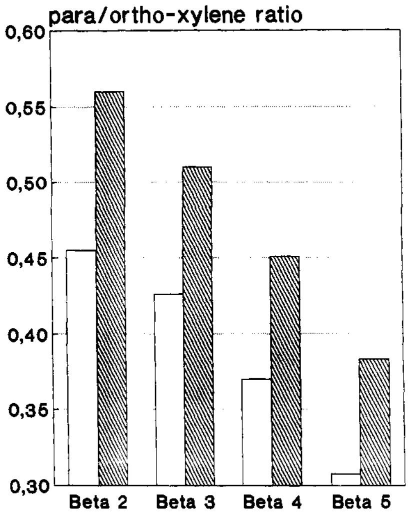

Figure 9. Figure 9. Influence of the Al-, Ga-, and B-containing β zeolites on the para to ortho xylene ratio at 498 K (blank bar) 573 K (dashed bar).

This order is in full agreement with the softness of the acid sites calculated for the different clusters and again shows that a correspondence exists between zeolite catalyst composition, HSAB, and selectivity for reactions in which the contribution of orbital control is significant.

There is another interesting observation, and this is that the para/ortho ratio is higher for a Y zeolite than for a β zeolite, both with the same framework Si/Al ratios (see Figures 6 and 8). Since in this case one can assume, as a first approximation, that the influence of the chemical composition of the zeolite should be very similar on the two samples, it becomes necessary to discuss another factor which can be important to determine the acidic properties of zeolites, which is the T–O–T angle. To do this, molecular orbital calculations were performed to study the influence of the TOT angle of the bridging OH on the LUMO energy of the acid site. Using the model cluster shown in Figure 3c, the SiOAl angle of the acid site was fixed in several values within the 124–159° range and the other variables were optimized. The variation of LUMO energies as a function of the SiOAl angle is shown in Figure 10. The maximum variation of the LUMO energy within the range is on the order of $\approx$5 kcal/mol, and this is not big enough to explain by itself the differences in the para/ortho ratio observed among the β and Y zeolites. Moreover, it should be stressed that, whereas the TOT angle in the latter varies approximately between 132 and 146°,[38] in the former the variation is between higher values such 137–165°.[38] Because the Beta zeolite has larger TOT angles than the Y one, it can be expected, regarding the calculations presented here, that this feature might contribute to the observed differences in selectivity. However, another factor such as the topological density may have a more important contribution in order to explain the observed para/ortho difference between Y and β zeolites.

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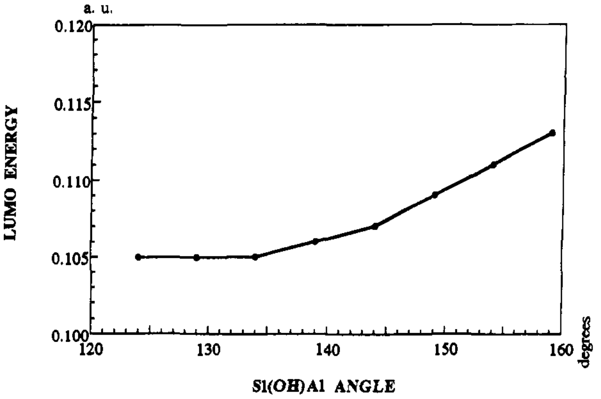

Figure 10. Figure 10. Dependence of the LUMO on the OH bridging angle.

In conclusion, it has been shown here that in order to explain selectivity behavior in reactions catalyzed by zeolites, besides geometric factors and acid strength, another characteristic such as HSAB properties has to be considered. This can be determinant in orbital-controlled reactions.

It has been demonstrated that, by modifying the framework chemical composition of a given zeolite, i.e., Si/Al ratio, and substitution of Al by other trivalent atoms, the energy of the frontier orbitals of the zeolite changes and therefore the softness of the acid sites changes. Moreover, two zeolites with the same chemical composition but with different structures can show different HSAB properties since the T–O–T angles and topological densities are different, and the smaller the angle the softer the acidity. Finally, the implications of these factors have been seen experimentally when zeolites were used to catalyze the alkylation of toluene by methanol, a reaction in which Coulombic factors favor the ortho alkylation, while the orbital factors favor alkylation in the para position.

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