JOURNAL OF CATALYSIS **136,** 521–530 (1992)

Molecular Orbital Calculation of the Soft–Hard Acidity of Zeolites and Its Catalytic Implications

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Received December 6, 1991; revised March 2, 1992

The relative hardness of different compositions of model clusters of acid zeolites and the same clusters containing a metoxy group as alkylating agent were evaluated using the energy of the lowest unoccupied molecular orbital as the index. Different basis sets and pseudopotentials were used in ab initio calculations. Semiempirical MNDO-PM3 calculations were also performed. The results show that the hardness of the zeolite increases when the Si/Al ratio decreases. On the basis of Pearson's HSAB principle, the selectivity obtained during the alkylation of toluene with methanol catalyzed by acid zeolites was interpreted. © 1992 Academic Press, Inc.

INTRODUCTION

The concept of hard and soft acids and bases (HSAB) was introduced by Pearson (*1*) to explain affinities between acids and bases that do not depend on electronegativities or other related macroscopic properties. He established two simple rules: soft acids prefers to react with soft bases, and hard acids prefer to react with hard bases. Soft bases are defined as those electron donors whose valence electrons are easily polarizable and hard bases as those whose valence electrons are not. Otherwise hard acids are recognized as small-sized, highly positively charged, and not easily polarizable, while soft ones are defined as those possessing the reverse properties (*1*).

The HSAB principle has been proposed as a determinant for the paraselectivity of zeolite-catalyzed methylation of toluene with methanol (*2*). In a further work Corma (*3*) related the change in Si/Al composition on zeolite with the hardness of acid sites and the paraselectivity in the formation of xylene. This relation could not be demonstrated because of the difficulty of the experimental evaluation of hardness. In this case, quantum chemical calculations can give a semiquantitative approximation of the problem.

Several calculations of the acidic properties of the active zeolite sites have been made in the past years (*4*). Structural (*4a–4c*) and composition (*4b–4g*) effects were related with observations that can be associated with the Brønsted or Lewis acidity. However, no theoretical studies on the hardness of the acid sites were made. Recently, Langemaeker *et al.* (*4f*) have performed a study on the variation of the Fukui function with changing electronegativity in the neighborhood of the zeolite acid site. Fukui function is related, density functional theory (*5*), to Fukui's frontier density (*6*) and can be interpreted as a local softness (*6b*). This function can give information on the spatial distribution of the reactivity but not on the hardness or softness, which are global properties of the molecule.

In this work we present a semiquantitative quantum chemical study of the variation of hard acidity with changing Si/Al zeolite composition. Ab initio RHF and semiempir-

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0021-9517/92 $5.00
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ical PM3 calculations were performed over model clusters, allowing us to determine the influence of the atoms near the acid site with a minimum computational cost.

THEORETICAL APPROACHES TO THE HSAB PRINCIPLE

There are two theoretical approaches useful in explaining the HSAB principle. The first was developed by Klopman and Salem (*7*). 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.* (*8*). 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 in two terms, the first describing the system composed by the noninteracting reactant and the second describing the perturbation of each fragment by the influence of the other. Developing this in second-order perturbation theory, Klopman obtained the expression of the change of energy during the reaction

$$\Delta E = -\sum_{ab}(q_a + q_b)\,\beta_{ab}S_{ab} + \sum_{k<l}\frac{Q_kQ_l}{\varepsilon_0 R_{kl}} + \left(\sum_r^{\text{occ}}\sum_s^{\text{virt}} - \sum_s^{\text{occ}}\sum_r^{\text{virt}}\right)\frac{2\left(\sum_{ab} c_{ra}c_{sb}\beta_{ab}\right)^2}{E_r - E_s}, \quad (1)$$

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 punctual charges Q_i. Both terms are related to the charge distribution on the system, which can be correlated with the electronegativity difference between the fragments.

The third term is second order 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, can 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, $(E_{\text{LUMO}} - E_{\text{HOMO}})$—can be neglected, the energy related to the second order can be approximated by

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

where r is HOMO of fragment A (donor) and s is LUMO of fragment B (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 contribution of each atomic orbital 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 that can mix to form a covalent bond must be localized in the zone where the AOs of both fragment overlap (*8b*). This implies that the named HOMO or LUMO in Eq. (2) can not be strictly the frontier orbitals but the ones with high or low energy level, respectively, that have an important component at the site of the reaction.

This theory can explain the chemical behavior of several compounds, but it is not of general application. First, it is based on the molecular orbital approach which considers the model of independent particle, neglecting the electronic correlation effects and assigning an important role to the virtual orbital energy that has no clear physical meaning (*9*). Moreover, Klopman's theory uses the second-order perturbation theory which is valid only when the perturbation is weak, i.e., when there are little changes in the molecules during the interaction process. Therefore, this approximation can be used efficiently in reactions where the transition state is "early" (*10*). Finally, neglecting all the terms in the second-order contribution to the energy other than that of smaller energy differences on the denominator ($E_{\text{LUMO}} - E_{\text{HOMO}}$) can be difficult to justify sometimes (*10*).

The second and more recent theoretical approach to the HSAB principle has been made by Parr and Pearson (*11*). This is a more general approach based on the density functional theory (*5*). The hardness is related to a magnitude named "absolute hardness" of a fragment S (η_S) and defined as

$$\eta_s = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_z, \qquad (3)$$

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 can be defined as

$$\eta_s = \frac{1}{2}(I_s - A_s), \qquad (4)$$

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, following this approach the calculation of the hardness becomes problematic, even in the simplest finite difference form, due to the difficulty of accurately determining the ionization potentials and electronic affinities. Moreover, there are additional problems when the anion is metastable (*12, 5f*).

METHODOLOGY AND MODEL CLUSTER

In our work, we have chosen the energy of the LUMO as a parameter with which to evaluate the "hard acidity" of the zeolites. Despite the objections to Klopman's theory discussed before, we adduce the following reasons for choosing the above parameter:

(a) Because of the size of the systems to be studied and the computational time needed, for our calculations we use the molecular orbital (MO) approximation with the particle independent model (Hartree Fock).

(b) Even though a second-order perturbational treatment in the MO approximation does not give a detailed description of any chemical interaction, it does give an adequate qualitative interpretation of a large number of reactions. This is especially true in acid–base reactions that do not involve large changes in the electronic structures of reactants and products. In a second-order perturbational treatment, the virtual orbitals acquire physical meaning since these determine the magnitude of the perturbational term, related to the formation of a covalent bond.

(c) If it is true that the energy of the virtual orbital and, more specifically, the energy of the LUMO depend on the atomic basis set used, it can be assumed that this effect will be similar in systems of similar electronic structure. This implies that, even though the discrete orbital energy values are going to depend on the atomic basis set, the changes caused in these energies due to relatively small changes in the system produced when substituting Si by Al will keep the same tendency for any basis set chosen.

(d) Despite the fact that it is not possible to neglect, in the second-order term of Eq. (1), the interactions between orbitals other than the HOMO of the donator and the LUMO of the acceptor, the $E_{\text{LUMO}} - E_{\text{HOMO}}$

becomes the lower limit of the $E_r - E_s$ difference, r being the virtual orbital of the electrophile and s the occupied orbital of the nucleophile. In other words, when $E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}} \leq E_r - E_s$, this difference will always give a semiquantitative idea of the importance of the second order, or the equivalent will give a semiquantitative idea of the extension of the orbital control in the reaction.

Ab initio calculations were carried out with the GAUSSIAN-88 program (*13*). Because the size of the system studied, calculations were performed using pseudopotentials instead of core electrons (*14*). A minimal basis set VSTO-3G with Coreless H-F pseudopotentials (*14a*), a minimal CEP-4G, and a double-Z CEP-31G with CEP pseudopotentials (*14b*) were utilized.

To find the geometry with the minimum energy, Berny's method (*15*) with analytic gradients has been used. The basis set, pseudopotentials, and the optimization method are implemented in the GAUSSIAN-88 program.

Semiempirical calculations were performed with the MOPAC-6.0 program (*16*) using the PM3 method (*17*). Optimizations to a minimum in semiempirical calculations were made using the BFGS method (*18*).

All the ab initio calculations were made with an IBM-3090 computer, while the semiempirical calculations were made with a VAX-4000-200.

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).

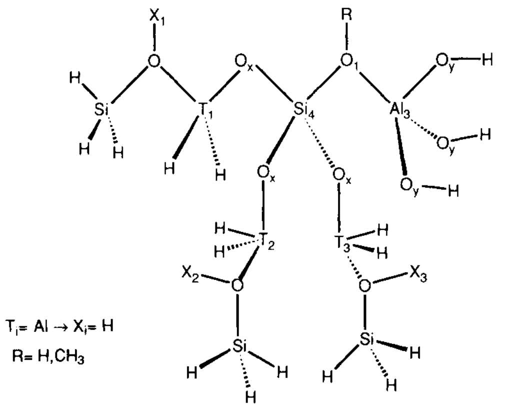


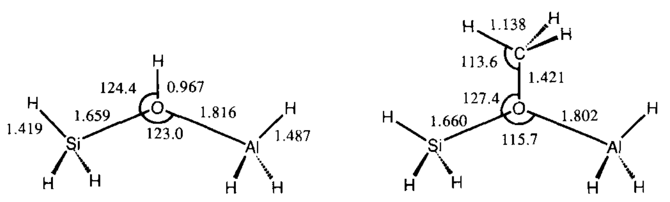
FIG. 1. Model cluster of an acid zeolite (R = H) or methyl zeolite (R = CH_3). The tetrahedral atoms T_i can be Si or Al. Using this model we constructed four different composition clusters that keep the C_s symmetry: in the 7/1 cluster all T_i were Si; in the 6/2 cluster T_1 = Al (X_1 = H) and T_2, T_3 = Si; in the 5/3 cluster T_1 = Si and T_2, T_3 = Al (X_2, X_3 = H); and finally in the 4/4 cluster all T_i = Al (X_i = H).

RESULTS AND DISCUSSION

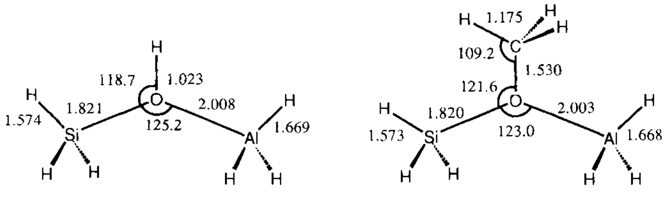
Ab Initio Calculations

(*1*) *Geometry of the active site.* The effect of chemical composition on the hardness of a given acid site of the zeolite has been studied by calculating the compositions of the four different clusters presented in Fig. 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 parts located away from the active site were fixed to the 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." This model has been successfully used in the literature (*4a–4h*). The optimized parameters are detailed in Fig. 2. The standard values used 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.

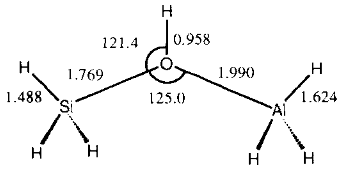
All the parameters in the active site model cluster (Fig. 2) were optimized except for the tetrahedral angles of Si and Al, which were kept at their standard value of 109.47°. This choice was based on the fact that in optimizing the HAlO angle, the AlH_3 group tends to be planar, decreasing the electron acceptor effect of the Al atom. This favors the polarization of the OH group in the zeolite (*4a*) and the softness of the acid site.



optimized parameters VSTO-3G



optimized parameters CEP-4G



optimized parameters CEP-31G

FIG. 2. Optimized parameters of the active site model cluster for three different basis sets and pseudopotentials.

Indeed, the LUMO energy decreases in ≈16 kcal/mol when one constrains the HAlO angle to 109.47°. Because of the acidic properties of zeolites, one can expect the framework rigidity to play an important role in maintaining a pyramidal structure on the Al atom, and we have conserved the regular tetrahedral form in our calculations to approach it. In all the optimizations the C_s symmetry was also maintained.

The more relevant population analysis values obtained using the three atomic basis sets (ABS) are listed in Table 1. On the other hand, LUMO energies as a function of the Si/Al ratio for the same ABSs are showed in Figs. 3 and 4. One can see that the VSTO-3G basis set with Coreless H-F pseudopotentials leads to an acceptable equilibrium geometry, except for the OCH angle that appears rather distorted. However, the Mulliken population analysis shows very little charge separation and a too high LUMO energy (Fig. 3). Furthermore, the CEP-4G basis set tends to overestimate equilibrium distances but produces correct angles, more charge separation, and low LUMO energy. The CEP-4G basis set with four gaussians is more diffuse and therefore favors the charge separation. Moreover, because the LUMO energy is an approximation to the electron affinity (Koopman's theorem), a more diffuse basis set should favor a negative charge, decreasing the LUMO energy.

As expected, the CEP-31G basis set corrects in part the geometry distortion of CEP-4G and leads to a much better population analysis and a better value of LUMO energy.

(2) *Influence of the atomic basis set on the LUMO energy.* As seen in Fig. 3, the

TABLE 1

Total Atomic Charges (q_R) and Bond Order (P_{OR}) Obtained for the Clusters Using the PM3 Method and the Various ABS

Si/Al ratio:	7/1		6/2		5/3		4/4	
R:	H	CH_3[a]	H	CH_3[a]	H	CH_3[a]	H	CH_3[a]
				PM3 Calculations				
q_R	0.227	0.188	0.218	0.167	0.216	0.178	0.209	0.160
q_O	−0.334	−0.298	−0.336	−0.297	−0.332	−0.300	−0.325	−0.289
$\lvert q_O \cdot q_R \rvert$	0.0758	0.0560	0.0732	0.0496	0.0717	0.0534	0.0679	0.0462
				VSTO-3G Basis set				
q_R	0.198	0.258	0.187	0.243	0.181	0.237	0.170	0.221
q_O	−0.336	−0.385	−0.339	−0.388	−0.344	−0.394	−0.347	−0.396
$\lvert q_O \cdot q_R \rvert$	0.066	0.099	0.063	0.094	0.062	0.093	0.059	0.088
P_{OR}	0.341	0.313	0.341	0.316	0.340	0.316	0.340	0.318
				CEP-4G Basis set				
q_R	0.402	0.266	0.389	0.245	0.383	0.236	0.370	0.215
q_O	−0.817	−0.690	−0.820	−0.691	−0.823	−0.694	−0.825	−0.693
$\lvert q_O \cdot q_R \rvert$	0.328	0.184	0.319	0.169	0.315	0.164	0.305	0.149
P_{OR}	0.301	0.235	0.302	0.240	0.301	0.240	0.302	0.243
				CEP-311G Basis set				
q_R	0.525		0.514		0.512		0.501	
q_O	−1.033		−1.036		−1.047		−1.047	
$\lvert q_O \cdot q_R \rvert$	0.542		0.533		0.536		0.525	
P_{OR}	0.271		0.272		0.272		0.273	

[a] The total charge over the CH_3 is the sum of the total charges over the group atoms.

different sets of values obtained for the LUMO energies 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, while being important to the energy of the orbitals, is very minor on the differences between the energies of the LUMO for similar compounds. Then it can be seen that on both minimal basis sets, i.e., VSTO-3G and CEP-4G, the energy of the LUMO increases linearly with the increasing Si/Al ratio, the increment being 15–20 kcal · mol^{-1} per Si exchanged. 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.

Semiempirical PM3 Calculations

Semiempirical PM3 calculations on the same clusters were also carried out. In this case both distances and angles included in the second coordination sphere were optimized. From the results given in Table 2, it can be seen that only small changes in the optimized parameters are produced when the chemical composition is changed.

The population analysis values of the active site are listed in Table 1 and the energies of the LUMO for different compositions are shown in Fig. 3. Exactly the same tendencies are observed when ab initio calculations are used, but the increments of energy per Si exchanged are somewhat smaller when PM3 is used.

Acid Strength versus Hardness

It should be noted that acid hardness is a property fundamentally different from acid strength and a direct correlation between them should not exist.

Analysis of the Mulliken population of the

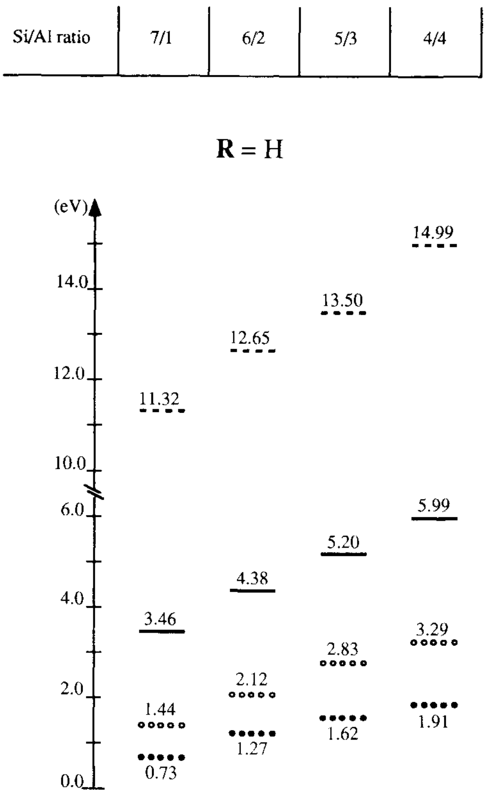


FIG. 3. LUMO energy of the acid zeolite in function of the Si/Al ratio. (---) VSTO-3G basis set, Coreless H-F pseudopot; (—) CEP-4G basis set, CEP pseudopot; (∘∘∘) CEP-31G basis set, CEP pseudopot; (•••) PM3 calculations.

OR group (Table 2) and the LUMO energy (Figs. 3 and 4) allows us to evaluate the relation between the acid strength of the Brønsted acid site in a given cluster and the "acidity hardness" of that zeolitic cluster.

Then, if one uses the ionicity of the OH bond, i.e., $|q_O \cdot q_H|$, as the index of acid strength (*19*), one can see that the evolution of this index with the Si/Al ratio does not follow a linear correlation with the energy of the LUMO. This indicates that factors other than composition are important for determining the acid strength. For instance, the spatial distribution of the other acid sites in the vicinity of the reference site has a much larger influence on the acid strength of the Brønsted site than on its "hardness."

Indeed, the hardness, i.e., the energy of LUMO, in cluster 5/3 in which both neighboring acid sites are out of the symmetry plane, increases with respect to 7/1 to almost twice to the observed value in the cluster 6/2 in which the neighboring acid site is found on the same plane as the active site. This seems to indicate that the increment of hardness is relatively independent of the spatial distribution of the adjacent centers surrounding the active center. On the other hand, if the two neighboring acid sites are out of the plane (cluster 5/3), the ionicity is much less than twice that in the case where only one is on the plane (cluster 6/2).

The influence of the location of the neighboring acid sites could be explained by considering that when both sites are in the same

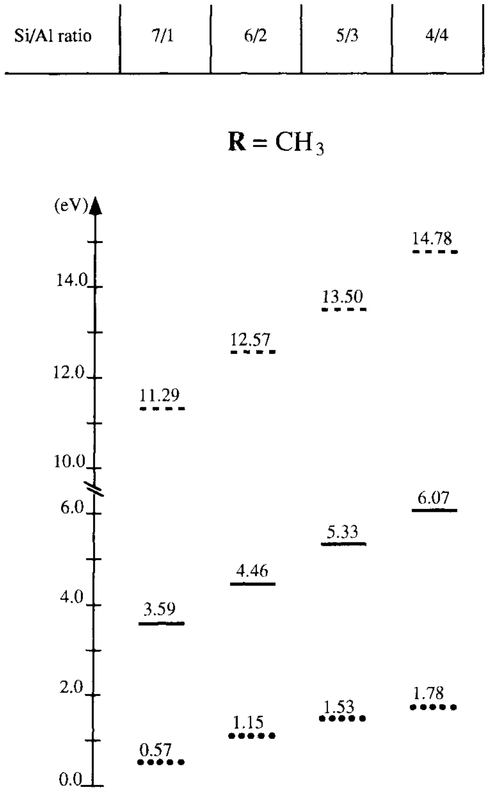


FIG. 4. LUMO energy of the methyl zeolite in function of the Si/Al ratio. (---) VSTO-3G basis set, Coreless H-F pseudopot; (—) CEP-4G basis set, CEP pseudopot; (•••) PM3 calculations.

TABLE 2

PM3-Optimized Geometries (Distances in Angstoms, Angles in Degrees)

Si/Al ratio: *R*:	7/1		6/2		5/3		4/4	
	H	CH_3	H	CH_3	H	CH_3	H	CH_3
r(O − R)	0.963	1.415	0.964	1.411	0.964	1.413	0.964	1.409
r(4 − 1)	1.734	1.745	1.76	1.781	1.761	1.795	1.798	1.814
r(3 − 1)	1.914	1.900	1.095	1.893	1.893	1.887	1.886	1.888
$r(O_x - 4)$	1.653	1.656	1.660	1.663	1.662	1.664	1.665	1.668
$r(T - O_x, T = \text{Si})$	1.677	1.677	1.680	1.681	1.681	1.684	—	—
$r(T - O_x, \text{T} = \text{Al})$	—	—	1.792	1.796	1.784	1.791	1.761	1.794
$r(O_y - 3)$	1.751	1.756	1.755	1.759	1.759	1.764	1.761	1.766
a(3, 1, 4)	149.2	149.2	151.2	151.2	150.9	150.9	152.0	152.0
a(4, 1, R)	105.8	111.4	105.3	113.6	105.6	113.8	105.0	114.7
$a(O_x, 4, 1)$	108.2	108.6	100.7	102.0	98.2	98.8	96.4	97.4
$a(O_y, 3, 1)$	98.2	102.3	99.8	103.5	101.8	106.4	102.6	107.0
a(H, C, 1)[a]	—	110.7	—	111.1	—	109.1	—	109.1
d(H, C, 1, 4)[a,b]	—	60.5	—	60.0	—	120.0	—	120.0

[a] H and C correspond to the methyl group.

[b] Dihedral angle.

plane, the inductive effect of one site on the other can be favored by a larger delocalization on the plane of the electrons from both sites.

Zeolite Composition, Acid Hardness, and Catalytic Implications

From either the ab initio or the semiempirical calculations, it can be seen that the hardness of the acid zeolite increases with decreasing Si/Al ratio, or equivalently, the more silicon that reaches a zeolite the softer is the acid catalyst. Then, when there exist in a given molecule two reactive points with the same electron density but with a different frontier orbital energy, i.e., with a different softness, and the attack of each can drive the reaction to a different product, it should be possible to change the selectivity by changing the softness of the zeolite. This is the case, for instance, during alkylation of alkylaromatics by carbocations catalyzed by acids.

In the case of toluene, the *para*-position is softer than the *ortho*-position due to a larger contribution in the HOMO of the atomic orbital p_z of the carbon in the former position. Then, from the HSAB theory (*3*) it should be expected that the greater the softness of the alkylating agent, the higher the amount of the *para*-isomer.

However, it should be taken into account that the alkylating agent is not a "free" carbocation, but is adsorbed on the zeolite. From this point of view, the softness of the zeolite can determine the softness of the alkylating agent. Indeed, we have modeled a series of zeolite clusters with different framework compositions, including all of the metoxy group as a potential alkylating agent (Fig. 1). The results presented in Fig. 4 indicate that, as with the parent zeolites, the higher the Si/Al ratio of the complex, the softer is the alkylating agent, and therefore the more para-directing the alkylation should be. It is interesting to note that the atomic orbital of the methyl C atom, which largely contributes to the LUMO, is a 2*p* orbital in almost the same direction as the CO bond. This suggests that the interaction with the HOMO of a nucleophile, being a good alkylating agent, could produce an SN_2 type reaction (see Figs. 5 and 6).

All the observations presented here could explain a whole series of experimental re-

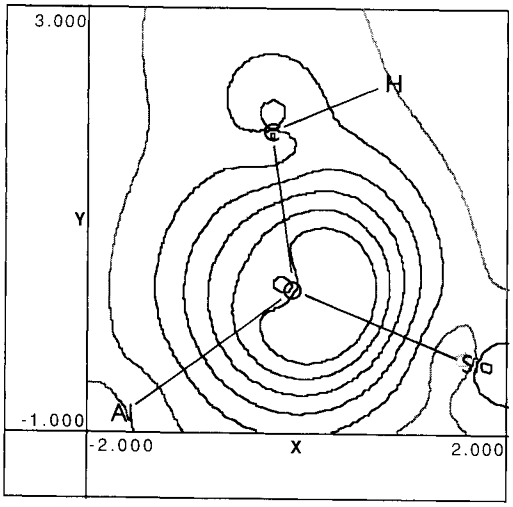


FIG. 5. Cut through the X–Y plane of the methylzeolite LUMO function (CEP-4G basis set) in the neighborhood of the active center (distance in Å).

sults (*20–24*) that were not able to be explained on the basis of zeolite acid strength. Then the concept of soft and hard applied to zeolites (*2*) and their quantification through the frontier orbital, i.e., HOMO and LUMO, energies (*3*) can be very useful in better understanding the catalytic properties of these materials.

CONCLUSIONS

In this work, the energy of the LUMO has been used as an index of the hardness of the zeolite acidity, and the influence of the framework composition on the softness and hardness has been quantified. In this way, it has been found that the softness of a given acid site increases with increases in the framework Si/Al ratio of the zeolite.

Different basis sets in ab initio and semiempirical PM3 calculations show the same tendency for the LUMO energy with the composition, which implies that it is possible to study the relative hardness in larger systems with little computational cost.

The hardness and the acid strength (ionicity of the OH) have been compared and it has been found that, while the acid strength depends on both chemical composition and spatial distribution of the atoms surrounding the active site, the hardness is mainly dependent on the chemical composition. This clearly indicates that it should be possible to independently control both acid strength

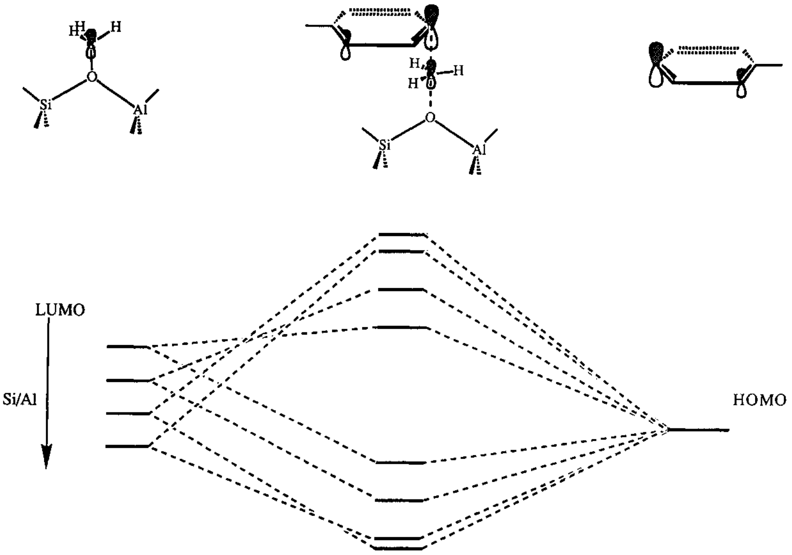


FIG. 6. Qualitative HOMO and LUMO of the complex of alkylating and nucleophile, related to the MOs of the nucleophile and the alkylating agent formed on zeolites of differents Si/Al.

and acid hardness to optimize catalyst activity and selectivity.

Finally, the influence of the zeolite chemical composition on the softness–hardness of a potential alkylating agent has been obtained and therefore the preferential alkylating position could be predicted.

ACKNOWLEDGMENTS

The authors thank the CIUV (Centro de Informática de la Universitat de València) for the use of their computing facilities. They thank the Secretaría de Estado de Universidad e Investigatión (Project OP90-0042), CICYT (Project MAT 91-1152), and Consellería de Cultura, Educación y Ciencia del la Generalitat Valenciana for financial support. C.Z. thanks the ITQ for scholarship.

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