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ORBITAL-CONTROLLED REACTIONS CATALYSED BY ZEOLITES: ELECTROPHILIC ALKYLATION OF AROMATICS

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The role of orbital control in product selectivity during electrophilic aromatic alkylation catalysed by zeolites was studied both theoretically and experimentally. In order to discuss this, the alkylation of toluene and *m*-xylene by methanol was carried out on a series of large-pore zeolites (HY). The changes in the *para* to *ortho* ratio observed on changing the framework Si/Al ratio of the zeolites were related to *ab initio* molecular orbital calculations of the LUMO energy of structurally alike model clusters but containing different tetrahedral cations around the active site. The observed correlation is discussed in terms of the HSAB principle by taking into account the influence of the catalyst composition on the reactivity of the electrophilic reagent.

INTRODUCTION

After the introduction of zeolites as acid catalysts in the early 1960s, it was recognized that the product selectivity for carbonium ion reactions was different on these microporous catalysts than on amorphous silica–alumina or liquid superacids. In order to explain the selectivity features of zeolites, two catalyst variables have been considered: one is the acid strength and the other is related to geometrical factors, which are responsible for the so-called zeolite shape selectivity.[1–3] However, when alkylation of aromatics is carried out on large-pore zeolites in which there are no geometrical restrictions, differences in selectivity are found that cannot be explained on the basis of differences in acid strength.[4–6] In these cases one must consider, in order to predict the position of the electrophilic attack, not only the total electron density on each potential position, but also the frontier electron population.[7] This, in turn, implies that interactions which induce the formation of covalent bonds may play an important role in some types of reactions catalysed by zeolites. This may appear surprising in the case of zeolites which, intuitively, may appear to be ionic materials. However, molecular orbital calculations reveal a strong covalent character.[8]

It appeared of interest to study the acid sites of zeolites, not only from the point of view of their acid strength, but also their softness–hardness as stated by Pearson[9] and the parameters which control these properties.[10] There is no doubt that in those reactions in which orbital control may play a significant role, the softness of the acid sites in zeolites will be the parameter responsible for selectivity changes.

In this work, the energy of the LUMO of the zeolite clusters and of the electrophile adsorbed on the zeolite was used as a measure of acid softness. This energy was obtained by means of quantum-chemical calculations, and the influence of the chemical composition of the zeolite on the softness was determined. Following this, the *para*/*ortho* ratio in the xylenes formed during the alkylation of toluene by methanol was predicted and compared with values obtained experimentally on a series of HY zeolites.

METHODOLOGY

Orbital control evaluation

Orbital control, as defined originally by Klopman[11a] and Salem,[11b] is a concept which is related to the energy released when two fragments, a donor and an acceptor, react to form a covalent bond. It has been proved that this energy is approximately equivalent to the second-

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order energy term of the perturbational expansion obtained by decomposing the Hamiltonian of the whole system into two terms, the first describing the system composed by the non-interacting reactants and the second the perturbation of each fragment under the influence of the other. By assuming the molecular orbital (MO) approach and some other improvements, such as the neglect of differential overlap between the interacting MO or assuming that the perturbation is small ($| |\beta ab | \ll E_r - E_s/2$ for any a, b, r and s),[11] the total interaction energy is expressed by the following equation:

$$\Delta E = -\sum_{ab} (q_a + q_b)\beta_{ab}S_{ab} + \sum_{k<l} \frac{Q_kQ_l}{\varepsilon_0 R_{kl}}$$

first order

$$+\left(\sum_r^{\text{occ}}\sum_s^{\text{virt}} - \sum_s^{\text{occ}}\sum_r^{\text{virt}}\right)\frac{2\Sigma C_{ra}C_{sb}\beta_{ab})^2}{E_s - E_r} \quad (1)$$

second order

where a and b refer to the atomic orbital of the acceptor (A) and donor (B) fragments respectively, k and l to the atoms of each and r and s to the molecular orbital of the same fragments but non-interacting. In equation (1), q_a represents the electron population on atomic orbital a and Q_k the total charge on atom k, R_{kl} the distance between the nuclei of atoms k and l, β_{ab} and S_{ab} the resonance and overlap integrals, respectively, between orbitals a and b, E_r the energy level of MO r and C_{ra} the component of atomic orbital a on MO r.

Whereas the first-order energy term is mainly dependent on the charge distribution along the system, that is, on the energy attributed to the Coulombic interaction among the fragments, the second accounts for the energy gain produced by the mixing of the orbital of each fragment to form the MOs of the whole system. In such cases, where the main orbital interaction (the more energetic) is the one in which the HOMO of the donor reacts with the LUMO of the acceptor, this approach runs parallel to the Fukui frontier orbital theory.[12] This feature will occur whenever the difference between the frontier orbital energies of both fragments, $E^{(A)}_{\text{LUMO}} - E^{(B)}_{\text{HOMO}}$, is the smallest of the $E_r - E_s$ values in the second-order term of equation (1). Then, provided the numerator of the corresponding term is not too small, this term dominates and the whole second-order part might be improved by the following:

$$\Delta E^{(2)} \approx \frac{2\left(\sum_{ab} C_{\text{LUMO},a}C_{\text{HOMO},b}\beta_{ab}\right)^2}{E^{(A)}_{\text{LUMO}} - E^{(B)}_{\text{HOMO}}} \quad (2)$$

where $C_{\text{LUMO},a}$ represents the component of atomic orbital a on the LUMO of the acceptor (A) and $C_{\text{HOMO},b}$ the component of b on the HOMO of fragment B.

In the classical literature on reactivity,[12] there is general agreement to attribute the *para/ortho* selectivity in electrophilic aromatic substitution to a competence among charge- and orbital-controlling effects. This implies, in terms of Klopman's language [see equation (1)], the predominance of the energy stabilization of the complex by either the first-order or the second-order terms, respectively. Then, one can expect that the more orbital-controlled the reaction is, the higher the *para/ortho* ratio will be during the alkylation of alkylaromatics by electrophiles, since the density of the frontier orbital is higher at a *para* than at an *ortho* position.

When dealing with acid zeolites as catalysts, the electrophilic agent can be considered as a complex formed by the lattice and the alkylating reactant whose reactivity is highly modified by adsorption. If this is so, zeolite framework properties such as composition, topological density and Coulombic fields should influence the type of electrophilic attack.

The effect of the zeolite framework composition can be predicted, at a semi-quantitative level, by determining the energy of the LUMO of the complexes formed by the alkylating reactant and zeolite clusters with different Si/Al ratios. Indeed, from equation (2), it can be deduced that the lower the LUMO energy of the electrophilic agent, i.e. the softer the acid, in Pearson's terminology,[9] the more orbital controlled will be the reaction and, therefore, a higher *para/ortho* is to be expected in the electrophilic alkylation of aromatics such as toluene, anisole and aniline.

Model cluster

The calculations were made with the model cluster approximation, in which the 'dangling' bonds, which should connect the chosen fragment with the bulk, are saturated by hydrogen atoms. Such a model has been used successfully to predict most of the properties of the zeolitic active sites.[13] To simulate the zeolite active centre and its next nearest neighbours, we performed the calculations using the model cluster shown in Figure 1. This system represents a reasonable range of Si/Al compositions for the active site environment. Because of the large size of the system, all calculations were performed using a fixed geometry. The distortions which are frequently produced by the use of a 'far-stable' geometry were avoided by the appropriate selection of the geometrical parameters. In this way, the parameters corresponding to the proper active site were obtained by optimizing the smaller cluster, shown in Figure 2(a).

We assume that the geometry of the neighbourhood of the centre does not influence the calculations to a large extent, provided that in each calculation the same 'shape' of the fragment was used. For this reason we

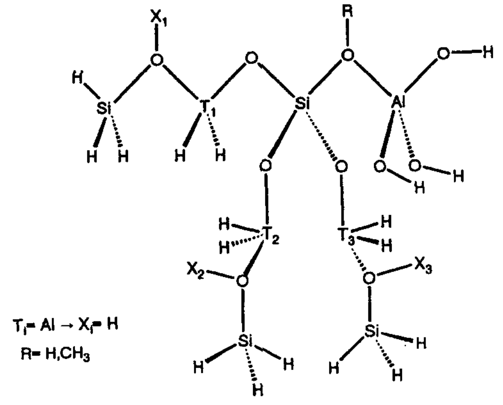


Figure 1.

Table 1. Standard geometrical parameters

SiO distance	1·62 Å
AlO distance	1·70 Å
TOT angle (T = Si, Al, H)	130·0°
OH distance	0·975 Å

fixed the geometrical parameters according to the set of standard values listed in Table 1.

Using the previous zeolite clusters, we also studied the complex methoxy-zeolite (see Figure 1). As was done before for the protonic clusters, a small model cluster of the methoxy-zeolite complex was optimized [see Figure 2(b)] to obtain the geometrical parameters of the active site. The neighbouring atoms were disposed according to the parameters listed in Table 1.

In all the calculations C_s symmetry was maintained and, for geometry optimizations, HTO angles of the border atoms were fixed at 109·47°.

Theoretical methodology

All the calculations were carried out at the *ab initio* Hartree–Fock level.[14] This method, providing a judicious choice of the atomic basis set, gives the energy eigenvalues corresponding to an electron which moves independently in the main fields of the other electrons and the nuclei. Calculations were performed by means of Gaussian 88.[15]

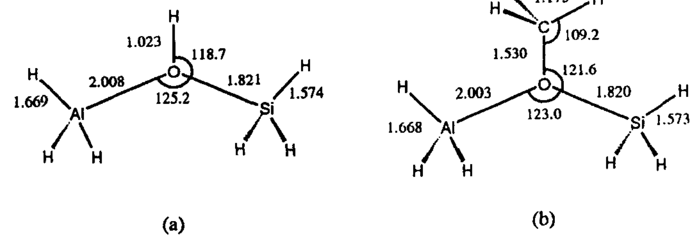
Owing to the size of the clusters studied, which contain a large number of heavy atoms, CEP (compact effective potentials), pseudo-potentials[16] were used to substitute the core electrons in order to lower the computational cost. The valence electrons were treated by using a minimal basis set CEP-4G.[16] Both pseudo-potentials and basis set are implemented in the Gaussian package.

Optimizations of geometry were carried out with the Berny method[17] when searching for the most stable conformation of the active site model cluster.

EXPERIMENTAL

Materials. A series of HY zeolites with different framework Si/Al ratios were prepared by dealumination of a NaY zeolite (SK-40) using $SiCl_4$ at temperatures in the range 573–673 K. 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 XRK and calculated by comparing the peak height of the (5,3,3) peak in the sample with that of SK-40 taken as 100%. The crystallinities of the HY samples studied were between 80 and 90%. The unit cell size of the dealuminated HY zeolites was determined by x-ray diffractometry using Cu Kα radiation and following ASTM procedure D-3942-80. The estimated standard deviation was 0·01 Å.

Reaction procedure. The alkylation of toluene by methanol was carried out in an electrically heated differential, fixed-bed, tubular glass reactor with an internal diameter of 15 mm. Toluene and methanol



(a) (b)

Figure 2.

(4 : 1 molar ratio) were fed at the top of the reactor by a positive displacement pump. Nitrogen was used as the gas carrier at a nitrogen to methanol molar ratio of 1 : 1.

Samples were taken at 10, 30, 60, 180 and 360 s and analysed by gas chromatography using a 3 m 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 obtained. The contact time was varied in order to compare selectivities at the 5% conversion level.

RESULTS AND DISCUSSION

Table 2 shows the calculated variation of LUMO energies when changing the Si/Al composition of the zeolite cluster supporting the acid site. It can be seen that the larger the Si/Al ratio of the zeolite cluster, the lower is the LUMO energy on the active site and, consequently, the softer is its acidity, assuming that the energy of the HOMO remains the same or at least the HOMO of a potential hydrocarbon molecule interacting with the cluster remains constant. The LUMO energy decreases almost linearly on removing Al and introducing Si in next nearest neighbour positions of the acid site. The energy involved per Al substituted is in the range 15–20 kcal mol^{-1} (1 kcal = 4·184 kJ).

This trend has also been observed in two recent studies. In one of them, the LUMO energies were calculated using semi-empirical molecular orbital calculations on cluster models,[18] and in the other the softness was determined by means of a semi-empirical density functional methodology using the infinite solid model.[19]

However, one has to take into account that, as stated previously, during electrophilic alkylations on zeolites what really becomes important from the orbital control point of view is not the softness of the zeolite acid site, but the softness of the alkylating agent. In the case of zeolites, and if we take for instance methanol and toluene as reactants, the true alkylating molecule is not the methanol or the protonated methanol, but a zeolite–methanol complex. This complex can be simulated, in a first approximation, by the ester formed by the acid zeolite and the methanol, that is, a methoxy-zeolite (see Figure 1), since recent experimental evidence has shown that this type of complex can be active for aromatic alkylations. We studied here the softness of methoxy-zeolite complexes (see Figure 1) as a function of the Si/Al composition of the zeolite cluster.

Table 2. LUMO energy levels on zeolites of different composition

Si/Al ratio	ΔE_{LUMO} (eV)	
	R = H[a]	R = CH_3[a]
7 : 1	0	0
6 : 2	0·92	0·87
5 : 3	1·74	1·74
4 : 4	2·53	2·48

[a] See Figure 1.

In a first step, we investigated the variation of the LUMO energy with the Si/Al ratio on methoxy-zeolite clusters, the geometry of which remains close to the most stable configurations (see Table 2).

The results in Table 2 show that the LUMO energy of the system is not much altered by removal of the acidic proton and its replacement by an alkyl group. Consequently, if one assumes that this complex is the possible alkylating agent, one would expect that, since the orbital control appears to have a significant influence on the selectivity of the electrophilic aromatic substitution,[12] the softness (or hardness) in large-pore zeolites will yield *para/ortho* ratios of the same order as other equivalent electrophiles. From this point of view, and considering the above results, the higher the framework Si/Al ratio of the zeolite, the higher should be the selectivity for alkylation in the *para* position during the electrophilic methylation of toluene by methanol.

However, one must consider that, when the donor and the acceptor fragments do interact to form a covalent bond, they will not stay in the most stable configuration but become geometrically distorted, in order to favour the electronic transfer among the fragments and consequently to favour the chemical reaction. This activation should produce changes in the chemical properties of the reactants with respect to the most stable configuration, and this may be determinant for the reaction selectivity.

In recent works, Kazansky[22] stressed that carbenium ions adsorbed on acid zeolites, which have been traditionally assumed to be intermediate species in the heterogeneous catalytic cracking of hydrocarbons, may correspond to an alkoxy-zeolite compound remaining in a thermally activated form. This activation would correspond to elongation of the CO distance between the alkyl group and the zeolite active centre. It was shown that the charge density and also the geometry of such activated alkoxy-zeolite species not only appear more feasible than those of a free carbenium ion, but in addition become energetically stabilized by the framework of the catalyst.

Therefore, by taking this into account we would expect that, if the methoxy-zeolite is taken as the alkylating agent for toluene methylation, it will not react as an effective electrophile when it is in its most stable form, but it should be in an activated configuration in which the charge-deficient character of the methyl carbon atom is increased with respect to the stablest form in order to react efficiently with the

Table 3. Lumo energy levels and atomic orbital components for several O—C distances

O—C distance (Å)	ΔE_{LUMO} (eV)	LUMO components							
		$2s_{\mathrm{O}}$	$2p_{\mathrm{O}}$	$2s_{\mathrm{C}}$	$2p_{\mathrm{C}}$	$3s_{\mathrm{Si}}$	$3p_{\mathrm{Si}}$	$3s_{\mathrm{Al}}$	$3p_{\mathrm{Al}}$
1·53[a]	0	0·791	0·267 (119)[b]	−0·018	−0·303 (10)[b]	−0·356	0·783 (120)[b]	−0·189	0·397 (−112)[b]
1·70	−0·65	0·776	0·261 (51)[b]	−0·165	0·576 (3)[b]	−0·299	0·620 (108)[b]	−0·143	0·340 (−105)[b]
1·85	−1·77	0·612	0·429 (40)[b]	−0·256	0·780 (1)[b]	−0·197	0·407 (97)[b]	−0·076	0·181 (−95)[b]
2·0	−3·02	0·463	0·501 (12)[b]	−0·252	0·856 (1)[b]	−0·124	0·271 (90)[b]	−0·034	0·111 (−82)[b]

[a] Equilibrium distance.

[b] The numbers in parentheses indicates the angle (in degrees) of the p orbital with respect to the direction of the C—O bond.

nucleophile. We therefore studied how the softness of the alkylating agent changes when it is activated by elongation of the CO bond.

A series of calculations were carried out on the model cluster given in Figure 2(b), by fixing the CO distance at different discrete values in the region of 2·0 Å, and the equilibrium distance. In each situation the remainder of the most important geometrical parameters were always optimized.

In Table 3, the LUMO energy and its main atomic orbital components are listed for the methoxy-zeolite complex at each CO distance. It can be seen that the energy of the LUMO decreases dramatically when the complex becomes activated, which implies that the hardness of the alkylating agent should decrease in the same way. This is not surprising since it was stated previously[23] that destabilization of the chemical systems leads to a decrease in hardness. Zhou and Parr[23] introduced the concept of activation hardness, which gives the relationship between variations in hardness and activation energy for a chemical process.

It should also be stressed that a decrease in the energy of the LUMO means that the specific weight of the second-order term in equation (1) will become more important the closer the system is to the transition state. Thus, our results explain that, despite the fact that LUMO energies on the acid zeolite and on the stablest methoxy-zeolite configuration are too high to expect the reaction to be orbital controlled, when the reactants adopt a geometry near the transition state this becomes more easy and the orientation induced by the frontier density on the toluene ring can be effective in producing a selective alkylation.

From equation (2), it is possible to see that in addition to the energy of the LUMO, another factor which has an influence on the amount of the energy related to the mixing of the HOMO and LUMO orbitals of the reactants orbitals is the frontier density (C_{ar}) on each fragment. When mixing frontier orbitals in an orbital-controlled reaction, it would be expected that a large frontier density would exist in the spatial region where the interaction of both fragments occurs.

In the case of the methoxy-zeolite complex, one expects a large LUMO component to be found on the carbon atom of the methyl group, especially on the 2p atomic orbital which is oriented parallel to the CO bond. The spatial direction of the carbon 2p component of the LUMO indicates the facility of the methyl transfer via an $S_{\mathrm{N}}2$-type reaction.

The LUMO components listed in Table 3 show that the frontier density changes significantly when the methoxy-zeolite complex becomes activated. The general trend observed is that the LUMO density on the methyl carbon atom increases on increasing the elongation of the CO bond. Moreover, the variation of the LUMO during the activation is very complex. In Figure 3 the LUMO of the methoxy-zeolite complex at the equilibrium geometry and at a CO distance of 2·0 Å is presented in order to show qualitatively the changes in the frontier density when the complex becomes activated. One can see that at the equilibrium distance, the character of the LUMO is mainly that of an antibonding σ^*_{SiO} MO. The components on the carbon and aluminium atoms are clearly smaller than those on silicon and oxygen atoms. Moreover, when the complex is activated the character of the LUMO approaches the antibonding σ^*_{CO} MO, because the contribution of carbon atomic orbitals increases at the same time as the contribution of silicon atomic orbitals decreases. Simultaneously, the sp orbital of the oxygen rotates just to be in a direction near to that of the CO bond. The large LUMO component on the 2p orbital of the carbon in the CO direction should make the interaction with the π system of the toluene easier than when dealing with the stable complex. This implies that a more effective electron transfer should occur. On the other hand the σ^*_{CO} character of the LUMO of the activated complex strongly suggests that the mixing of frontier orbitals of both fragments leads to cleavage of the CO bond, and simultaneously to the formation of a C—C bond between the methyl group and the toluene.

Finally, we stress that, despite the fact that the activation of the alkylating complex increases the localization of the LUMO on the CO bond, the fact that even at relatively long CO distances such as 2·0 Å the frontier density at Si and Al atoms remains important

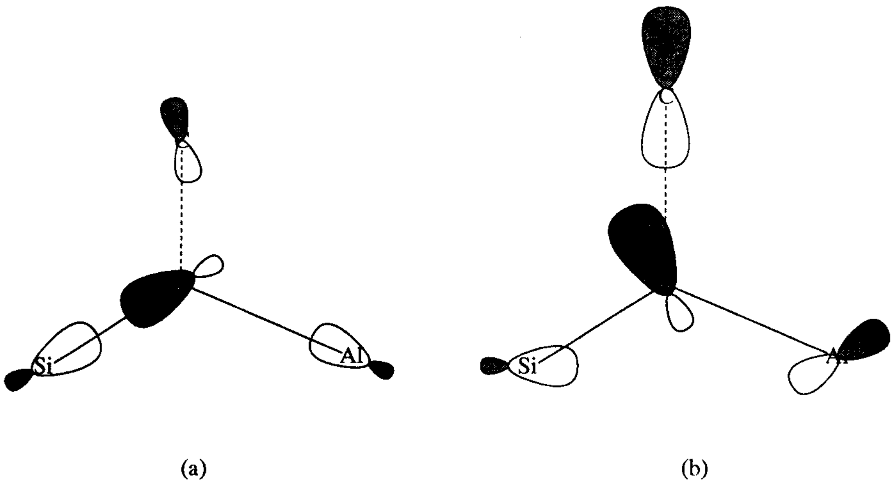


Figure 3.

indicates that partial delocalization of the orbital into the bulk occurs and thus the influence of the zeolite composition continues to be substantial, even though transfer of the methyl group is taking place.

We conclude that the chemical hardness of zeolites as acid catalysts seems to be an important factor in controlling the position in which alkylation of substituted aromatics will occur.

The same trend of hardness for the zeolite in its acid form is observed with the methoxy-zeolite complex, which may be the origin of the alkylating agent. Finally, activation of this complex by elongation of the CO bond increases its electrophilicity and its softness, both by decreasing the LUMO energy and by increasing the LUMO density on the methyl group. This would explain the relative importance of the orbital control on the alkylation of toluene by methanol on zeolites, and in general on the alkylation of alkylaromatics by electrophiles on zeolite catalysts.

Catalytic results

While theoretical calculations are very powerful in visualizing reaction mechanisms, the simplification one

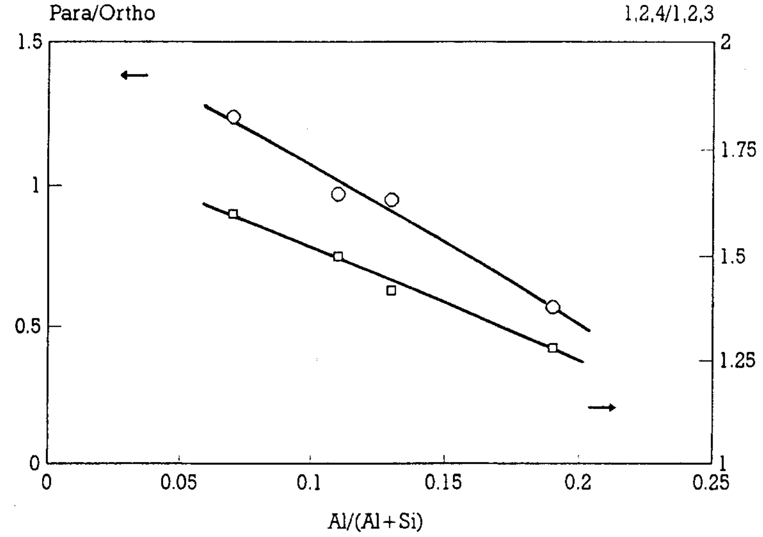


Figure 4.

has to introduce when carrying out such calculations for solid–gas interactions makes experimental confirmation of the conclusions desirable. In order to do so, we have carried out the alkylation of toluene and *m*-xylene by methanol, using a series of USY zeolites with different framework Si/Al ratios. We have predicted that in this series of zeolite samples, the softness of the acid sites and the softness of the methoxy-zeolite complex should increase on increasing the framework Si/Al ratio. On the other hand, if this were so, one would expect the contribution of the orbital control to be higher the larger is the framework Si/Al ratio of the zeolite. Thus, the higher the orbital contribution, the higher should be the selectivity for alkylation at the aromatic ring positions at which the density of the frontier orbital is higher, i.e. *para* in toluene and C-4 in xylene. In other words, the *para*/*ortho* and 1,2,4/1,2,3 ratios should change on increasing the framework Si/Al ratio of the zeolite.

The results in Figure 4, clearly show that the *para*- to *ortho*-xylene and the 1,2,4- to 1,2,3-trimethylbenzene ratios increase on increasing the framework Si/Al ratio in the range studied here.

These results support the hypothesis that in electrophilic alkylation of aromatics on zeolite catalysts, orbital control plays an important role, and therefore for the reactions not only is the acid strength of the catalyst important but also the softness–hardness, i.e. the covalent component, should be taken into account. Moreover, it is possible to change the softness–hardness of the zeolite by changing the framework composition. Finally, the importance of orbital control in these type of reactions is higher than one would expect *a priori*, considering that during the activation of the electrophile–zeolite complex the energy of the LUMO decreases and its density at the reaction site increase at the same time, producing a softer alkylating agent.

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