Model size effects on calculated electronic and bonding properties of adsorption sites in zeolites

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Abstract

A theoretical comparative study of NO adsorption on FeO-ZSM5 zeolite catalyst models was done using a quantum chemistry parametric method for catalysis (CATIVIC) with clusters of 19, 46, 123 and 327 atoms. Results show that the cluster model size is of fundamental importance for modeling NO catalytic adsorption. There is a notable strengthening of the Fe-N bond and a significant electronic transfer from adsorption site surroundings to the Fe atom, as the cluster model size increases. Theoretical methods, such as parametric ones, permit the utilization of large models that are relevant in modeling catalytic adsorption sites, because take into account geometrical and electronic long range effects.

Key words: Adsorption site; catalysis modeling; model size effect; NO-FeO-ZSM5; parametric method; zeolite.

Efecto del tamaño del modelo sobre las propiedades electrónicas y enlazantes calculadas de los sitios de adsorción en zeolitas

Resumen

Un estudio teórico comparativo de la adsorción de NO sobre modelos de zeolita FeO-ZSM5 fue llevado a cabo usando un método paramétrico de química cuántica para catálisis (CATIVIC), con cúmulos de 19, 46, 123 y 327 átomos. Los resultados muestran que el tamaño del cúmulo modelo es de fundamental importancia para el modelaje de la adsorción catalítica de NO. Existe una notable fortaleza del enlace Fe-N y una significativa transferencia electrónica desde los alrededores del sitio de adsorción al átomo de hierro cuando el tamaño del cúmulo aumenta. Los métodos teóricos, tales como los paramétricos, permiten la utilización de modelos grandes, los cuales son relevantes en el modelaje catalítico de los sitios de adsorción, porque toman en cuenta efectos geométricos y de largo rango.

Palabras clave: Efecto del tamaño del modelo; método paramétrico; modelaje de catalizadores; NO-FeO-ZSM5; sitio de adsorción; zeolita.

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Introduction

Quantum mechanics modeling in heterogeneous catalysis is becoming to be a routine in studies of catalysts design. Cluster approach has been widely used in theoretical calculations of model catalysts because: (a) Some phenomena in catalysis may be considered localized. (b) A realistic model with hundred of atoms often leads to impractical calculations for standard theoretical quantum chemistry methods. (c) Clusters may be considered a good representation of small grains of dispersed metals on a support. (d) Nanoparticle research is a recent demanding area in electronics, catalysis, etc. Nonetheless, in applications of cluster approach, there is a compromise between the cluster size model, the properties to be evaluated, the software employed, and computational limitations.

Several experimental works (1-5) consistently report size effects for the measurement of physicochemical and structural properties of nanoparticles (actual clusters). These properties, such as: electrical conductivity, chemical reactivity, diffusion, adsorption, magnetism, optical absorption, etc. change with the size and morphology of nanoclusters. A catalyst, formed by the dispersion of relatively small metallic clusters on a support, requires a large amount of atoms to mimic the adsorbate-surface and catalyst-support interactions. The model size may be also relevant to evaluate activation barrier heights and stability of intermediates, because the electric field generated by the adsorption site surroundings affects the kinetics and, therefore, the reactivity of the catalytic system, in special, for supports that have ionic nature.

Theoretical studies of zeolites have been of great importance in recent years, particularly, for zeolites doped with transition metals. A good example is the Fe-ZSM-5 zeolite used for NOx catalytic elimination of atmospheric pollution from automobile exhaust and chemical industries (6-9). Nor-

mally, quantum chemistry modeling of zeolite reactions is performed with small systems (clusters of few atoms), such as, $Si_2AlO_4H_8$ (10, 11). This is mainly due to the fact that a sensible representation of a catalytic system presents serious restrictions in computer time.

A theoretical work at DFT-(BLYP) level for a Na-zeolite-Y using three different cluster sizes of 16, 29 and 36 atoms ($NaSiAlO_7H_6$, $NaSi_2Al_2O_{13}H_{11}$, and $NaSi_5Al_2O_{18}H_{12}$) was performed by Chatterjee and Iwasaki (12). They showed that the global softness increases and charge on Na is more dissipated, as the size of the cluster increases. The variation of charge dissipation with the cluster size has strong significance in the reactivity of the catalytic active site. Nevertheless, more realistic cluster size models are convenient because, in many cases, the reaction products may be controlled by the size of the zeolite micro cavities. Therefore, it would be important to understand the effect of a three-dimensional cavity in the properties of the active site.

In this work we study the effect of the cluster size in the adsorption of a NO molecule on a metallic catalytic site of FeO-ZSM5 zeolite. Several cluster sizes were considered to simulate a straight channel of a micropore formed by 10-rings with all adjacent 5- and 6-rings. The aim of this work is to confirm that the use of standard small clusters has considerable deficiencies in the representation of the catalytic active site and the use of parametric methods can be very useful in catalysis modeling. Calculated clusters of small, medium, and high sizes were evaluated using a quantum parametric method, CATIVIC (13). This publication is organized in the following way: (a) A brief discussion of the method used and parameters employed are presented in Section 2. (b) The analysis of results is shown in Section 3 in terms of bond distances, angles, bond orders, diatomic energies, and electronic charge changes for four different cluster si-

zes. (c) Finally, in the last Section, conclusions and comments are summarized.

Method and parameterization

All calculations and geometry optimizations were performed with a parametric method called CATIVIC (13) which has been tested with respect to the Gaussian-94 program (14) at DFT (Density Functional Theory) level using the Becke´s three-parameters hybrid functional (15) with Lee, Yang and Parr correlation functional (16) (B3LYP). The basis sets and the relativistic compact effective potentials for Fe include explicitly the $(n-1)s^2$, $(n-1)p^6$, $(n-1)d^x$ and $(n)s^y$ electrons from Stevens *et al.* (17). The all-electron 6-311G(d, p) for N and O, and the 6-31G(d, p) for Al, Si and H basis sets, both provided by Gaussian-94 package, were employed.

Parametric methods, such as CATIVIC, are based on simulation techniques (18) and parametric functionals (19-21). The total energy parametric functional (E_{pa}^{XY}) is defined in terms of parameters that are optimized with respect to accurate data obtained from experiment or theoretical *ab initio* calculations (E_{exa}^{XY}) of *XY* diatomic molecules. Notice that parametric energy functionals $\left(E_{pa}^{XY} \right)$ depend on atomic and molecular parameters ($E_{pa}^{XY} = f[\{atomic\ parameters\}, \{molecular\ parameters\}]$). The starting point of these methods is to find the set of parameters and functionals that minimize the following expression,

$$\min_{fE_{pa_J}^{XY} \in \{f^{XY}\}} \left(\sum_J \left| fE_{exa_J}^{XY} - fE_{paJ}^{XY} \right|^2 \right)^{1/2} \qquad [1]$$

where $\{f^{XY}\}$ is a family of parametric functionals for different *J* states of *XY* diatomic molecule. In the case of molecular parameters, *fEs* are evaluated as binding energies (*BE*), and in the situation of atomic parameters, as atomic excitation energies (*EE*). Here, *BE* is calculated as the energy difference between the expectation value of a XY

system in the state J ($E_{t_J}^{XY} = (\Psi_J^{XY},\ H_t^{XY},\ \Psi_J^{XY})$) and those of the corresponding separated fragments, $\left(E_t^X = \left(\Psi^X, H_t^X, \Psi^X \right) \right.$ and $E_t^Y = \left(\Psi^Y, H_t^Y, \Psi^Y \right)$, ($t = pa$, *exa*).

$$BE_{t_J}^{XY} = \left(\Psi_J^{XY}, H_t^{XY}, \Psi_J^{XY} \right) - \left(\Psi^X, H_t^X, \Psi^X \right)$$
$$- \left(\Psi^Y, H_t^Y, \Psi^Y \right) \qquad [2]$$

The *EEs* are evaluated as the energy difference between excited states of atom X represented by the wave function Ψ_J^X and the ground state, Ψ_0^X. Thus, *EE* for *J* state is calculated as,

$$EE_{t_J}^X = \left(\Psi_J^X, H_t^X \Psi_J^X \right) - \left(\Psi_0^X, H_t^X \Psi_0^X \right) \qquad [3]$$

Atomic parameters for H, O, N, and Si come from Reference (22). Fe parameters were obtained from previous work (23) and those for Al were selected from Reference (13), using a technique presented in Reference (24). Molecular parameters for O-H, H-N, O-O, N-O, and H-H bonds were taken from Reference (22). Others parameters were calculated according to expressions [1] and [2] with respect to diatomic molecules properties, as shown in Reference (13, 23).

Results and Discussion

Before to start discussion the results of different cluster sizes, a comparison between CATIVIC and B3LYP-DFT methods was performed for the smallest cluster of $Si_2AlO_4H_8$-OFe-NO, see Figure 1(A). Results of cluster geometry optimization indicate that there is a reasonable good correlation between parametric and B3LYP-DFT calculations, as shown in Table 1. However, the Fe-O interaction requires a new reparameterization in order to obtain a better concordance with DFT calculations. Therefore, novel parametric techniques (13, 24) should be applied in order to find atomic and molecular parameters to fit with DFT calculations of $Fe_xSi_yAl_zO_lN_mH_n$ molecular systems.
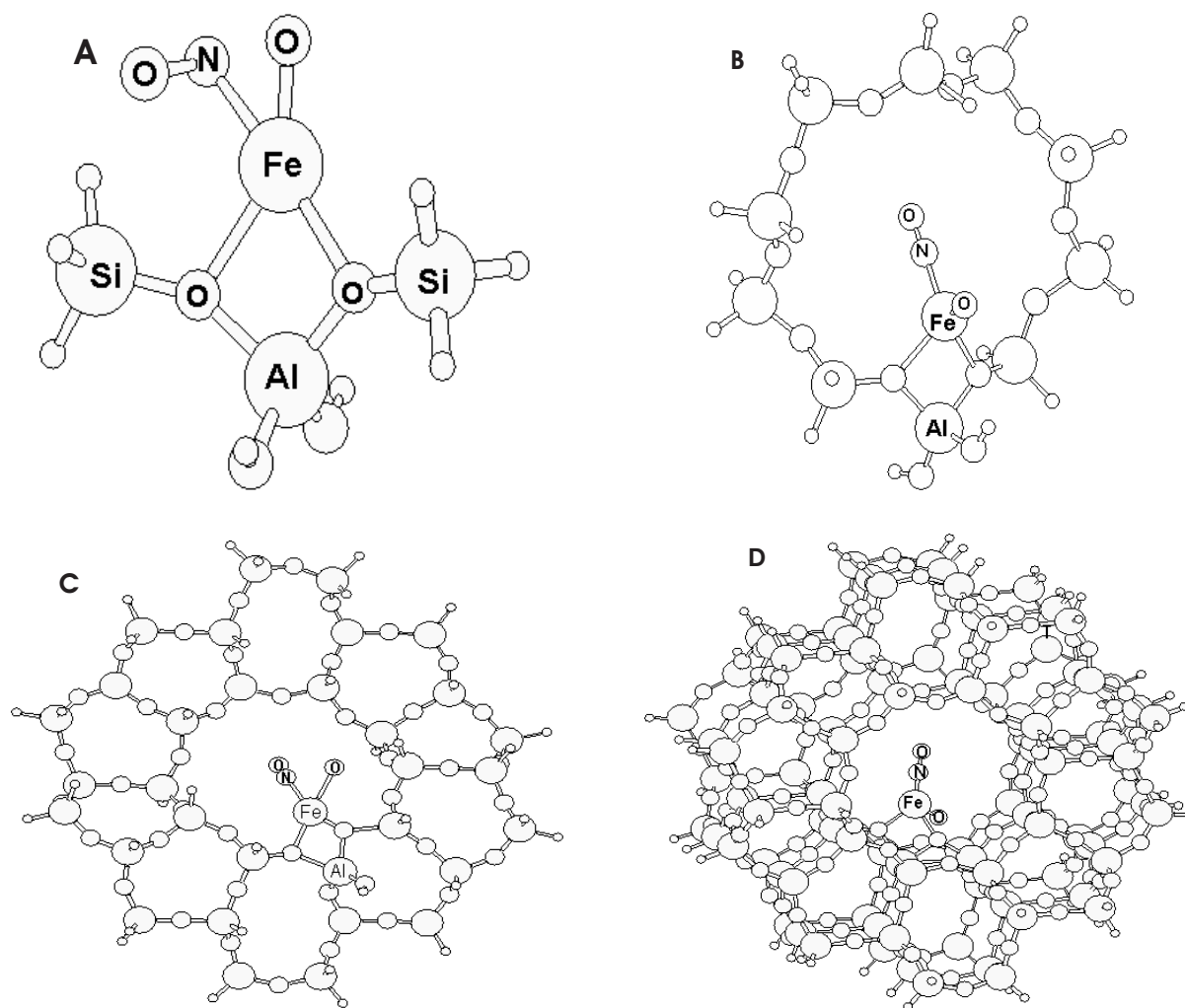
Figure 1. Model of zeolite doped with FeO with NO chemisorbed: (A) ($Si_2O_4H_8AlOFe$-NO); (B) ($Si_9O_{12}H_{20}AlOFe$-NO); and (C) ($Si_{31}O_{43}H_{44}AlOFe$-NO, (D) ($Si_{95}O_{157}H_{70}AlOFe$-NO).

In order to modeling a catalytic adsorption site on a ZSM5 zeolite, different cluster sizes were considered: $Si_2O_4H_8AlO$-Fe-NO, $Si_9O_{12}H_{20}AlOFe$-NO, $Si_{31}O_{43}H_{44}AlO$-Fe-NO, and $Si_{95}O_{157}H_{70}AlOFe$-NO of 19, 46, 123, and 327 atoms, respectively (Figure 1). The starting geometry of the substrate to build these clusters was obtained from a web site (25). The modeled adsorption site is located at a straight channel of the ZSM5 zeolite (10-ring micropore), Figures 1(B), 1(C) and 1(D). Border Si atoms were saturated with H atoms. The first step was to optimize H atoms, keeping the rest of the system fixed. Then, for the following calculations, the H atoms were maintained unchanged, in order to simulate the cluster surroundings into the zeolite bulk. A total optimization was carried out for all systems without adsorbate. Multiplicities of 1, 3, 5, 7, and 9 were evaluated for clusters without NO, being the 5 multiplicity the most stable one, very close in energy to 7 one. Then, local optimizations of Fe, all oxygen atoms bonded to Fe, and NO were performed for each system after adsorption of NO. The NO molecule

is bonded by the N atom; however, adsorption for O atom is also feasible.

Results were discussed in terms of bond distances, angles, diatomic energies (DE) (26)), Wiberg bond orders (BO) (27) and changes in the Mulliken charge population (ΔCharge) (28). Values of these properties for A, B, C, and D models (Figure 1) are displayed in Tables 2-4. Fe-O(zeo), Fe-O, Fe-N, N-O bond distances and Fe-N-O angles are presented in Table 2, for all models shown in Figure 1. Results describe different Fe-O(zeo) bond lengths because the Fe atom is bonded to two O(zeo). There is, however, a small variation of Fe-O(zeo) distances with the increase of the cluster size. On the contrary, the FeO$^{¥}$ increases from 1.67 to 2.03 Å. A non-clear effect is observed with the Fe-N bond distance; i.e., there is initially an increase of the bond distance and then the tendency to decrease. Nevertheless, a very clear trend is observed for the N-O distance; it decreases with the size of the model, although it is slightly different from free N-O. These results show a no convergence in the bond distances with the cluster size. The Fe-N-O angle shows some deviation from 180° between (179-174°) due to asymmetric bonding of Fe with O atoms.

Values of BO and DE for Fe-O(*zeo*), Fe-O, Fe-N, and N-O are presented in Table 3. Trends observed in the equilibrium bond distances of Fe-O(*zeo*) are reproduced for the bond strength; i.e, an enlargement of Fe-O bond distance produces a weakening of the corresponding bond. There is a clear increase of the total Fe-O(*zeo*) BOs (see values in parentheses) with the size of the model. A similar trend is observed in all Fe-O(*zeo*) DEs, except for the D model.

With respect to the Fe-O$^{¥}$ bond, there is a decrease of BOs and DEs, as the zeolite cluster size increases. This can be explained by Fe-O(*zeo*) and Fe-N strong interactions that weakening the Fe-O$^{¥}$ bond. In fact, there is a very strong increase in the adsorbate-surface interactions (Fe-N bond), see Table 3.

Table 1
Comparison between CATIVIC and DFT calculations for model A with and without FeO

Distance (Å)	DFT	CATIVIC
Si-O	1.685	1.690
Al-O	1.846	1.850
Al-O(OH)	1.724	1.725
Si-H	1.483	1.495
O-H	0.956	0.940
Fe-Al	2.875	2.986
Fe-O(zeo)	1.979	2.233
FeO	1.684	1.674

Note that the DE(Fe-N) value for D model is twice the value for A model. Another interesting feature is that the N-O bond on the adsorption site is slightly stronger than in the free molecule and it seems to increase with the model size. This stronger bond in the adsorbed NO is explained by analyzing the frontier orbitals of this molecule. The HOMO of NO is an antibonding orbital and a transfer of electron density from NO to the adsorption site (Fe^{+}) will strength the N-O bond, as will be showed below. A contrary effect is observed with BOs. Notice that BO only includes covalent bond contributions.

Qualitative information can be obtained from the charge changes in different atoms of the substrate and the adsorbate. The charge difference between models with NO adsorbed and the model A without NO is presented in Table 4. In all cases one can observe that the Fe atom gains electrons with the NO adsorption, and the charge change increases with the model size. These results show a significant increase of the electronic density at the adsorption site. This is in agreement with other theoretical findings in which the charge of the compensation cation is dissipated with the size of the cluster (12). The increase of the electronic charge on the Fe atom is also in correlation with the enlargement and strength decrease of the

Tabla 2

Bond distances (Å) and angles for zeolite-FeO models with NO. NO is adsorbed through the N atom.

Model	Bond Distances				
	Fe-O(zeo)§	*Fe-O*¥	*Fe-N*	*N-O*	*Angle*
A	2.221 2.260	1.668	1.875	1.178	174.3
B	2.225 2.328	1.726	2.094	1.164	175.3
C	2.181 2.337	1.840	2.014	1.154	179.1
D	2.129 2.179	2.028	1.927	1.126	173.9
NO(free)	–		–	1.16	–

§ Oxygen of zeolite,   ¥ Oxygen only bonded to Fe. *Oxygen of NO.

Table 3

Bond orders and diatomic energies (*DE*) for models with NO. Values in parentheses correspond to the sum of two *Fe-O*§ bonds.

Model	Bond Orders				DE(au)			
	Fe-O§*(zeo)*	*Fe-O*¥	*Fe-N*	*N-O*	*Fe-O*§*(zeo)*	*Fe-O*¥	*Fe-N*	*N-O*
A	0.49 0.40 (0.89)	1.60	0.62	2.03	-0.213 -0.161 (-0.374)	-0.798	-0.362	-0.998
B	0.53 0.44 (0.97)	1.50	0.59	2.02	-0.240 -0.183 (-0.423)	-0.764	-0.350	-1.033
C	0.63 0.44 (1.07)	1.25	0.72	2.02	-0.271 -0.162 (-0.433)	-0.646	-0.450	-1.018
D	0.78 0.52 (1.30)	0.64	0.84	1.97	-0.256 -0.165 (-0.421)	-0.355	-0.693	-1.077
NO (free)	–	–	–	2.05				-0.984

§Oxygen of zeolite.   ¥Oxygen only bonded to Fe. *Oxygen of NO.

Fe-O¥ bond, see Tables 2 and 3. For the zeolite oxygen atoms directly bonded to Fe, the changes are small. Similarly, the charge changes in the oxygen atom bonded to the iron (O¥) are unimportant. A different charge change (loss of electrons) is observed in the O and N atoms of NO. Adsorption of N-O produces an electronic charge withdrawing from N-O to Fe, as was anticipated above. The negative charge on the O* atoms seems to increase as the size of the substrate increases. On the other hand, the N atom losses electronic charge and the largest charge reduction occur in the D model.

Table 4

Charges changes on Fe, O, O*, N, and NO for models A, B, and C with NO. Positive values indicate that electronic density increase in the corresponding atom.

Model	ΔCharge[†] (au)					
	Fe	$O^{\S}$(zeo)	$O^{\yen}$	O*	N	N-O
A	0.24	0.06 0.01	0.01	0.26	-0.70	-0.44
B	0.28	0.06 -0.01	0.04	0.25	-0.63	-0.38
C	0.44	0.05 -0.02	0.07	0.25	-0.72	-0.47
D	1.21	-0.08 -0.14	-0.01	0.33	-0.94	-0.61

[§]Oxygen of zeolite.   [¥]Oxygen only bonded to Fe.   *Oxygen of NO.   [†]with respect to the model A without NO.

Convergence of the charge and bond strength is not observed for the clusters of 19, 46, 123, and 327 atoms. This behavior may be due to two causes:

i)   The number of atoms is not enough for obtaining convergence. In this sense, Illas et al. [29] found that the convergence in binding energy and bond distances in the fourfold site is not achieved even for clusters of ~100 atoms in the case of H adsorption at the Cu(001) surface. They also found that the cluster model approach is incapable of reproducing accurately the charge density and electrostatic potential of extended surfaces in Cu clusters. Therefore it is necessary to use clusters of larger size.

ii)   Our method does not have a good convergence at long distances. Long range interactions do not decrease rapidly to zero at long distances and the repulsion of other atoms with Fe atom increases with the augment of the cluster size. Thus, corrections of parametric functionals are necessary at long distances.

The above analysis show that a more complete study has to be carried out considering different parameterization techniques, new functionals, and bigger clusters.

One way to analyze the size effect in clusters is the study of the global softness (S = 1/(IE - EA), where IE and EA are ionization energy and electron affinity of the system) (12). Values of S are evaluated considering energies of HOMO and LUMO for IE and EA, respectively. The calculated values of S for A, B, C, and D models show a small increase with the cluster size (3.33, 3.61, 3.60, and 3.64, respectively). The trend obtained by Chatterjee and Iwasaki (12) is the same, but their S value changes are higher, may be due to the use of small clusters models.

There are experimental evidences of non-local long range interactions into the zeolite structure. For example, the acidity changes with the Si/Al relation (30). It means that Al atoms, in spite of having a long separation distances, maintain important interactions. The presence of Al into the zeolite produces influence in the electronic charge concentration at other adsorption sites. These experimental results show, without hesitation, that the size of the model has an important influence in the catalytic properties of the adsorption site. In addition, long-range interaction relevance in the computation of adsorbate-substrate interactions have been proposed in molecular dynamics simulation (31). Similar results

were reported in a previous work (13) with different clusters and smaller charged systems. In short, it is significant for quantum modeling of catalytic reactions with zeolites to use methods that allow a good representation of substrate's active sites.

Conclusions and Comments

1. The parametric method CATIVIC, based on properties in diatomic molecules and evaluation of atomic parameters for Al from atomic spectrum, gives a reasonable agreement with DFT (B3LYP) method.

2. A natural application of parametric methods is for systems that required a relative large number of atoms. Therefore, these methods are convenient for modeling catalytic systems with complex amorphous structure. Calculations are very accessible because they can be carried out on a modest PC (800 MHz and 512 Mega of RAM) in a reasonable time.

3. Qualitative results of modeled FeO-ZSM-5 indicate that the Fe-N bond strength changes drastically with the size of the model. The DE(Fe-N) in model D (327 atoms) is about the double of model A (19 atoms). There is also a noteworthy change in the electronic density at the adsorption site (Fe atom) with the size of the cluster model. These results, however, do not show a convergence in the properties with the size of the cluster.

4. Results show that it is relevant to use an aggregate of a sufficient size to model the chemisorption of NO on a FeO-ZSM-5 model catalyst. Notice that changes induced by the set of partial charges on Si, O, and Al on the adsorption site may be also of great importance in the chemical kinetics that go through charged transition states, as has been described in other works (32-34).

5. The chemical selectivity can be obviously affected by cluster-size effect. Thus, in relatively large hydrocarbons, the formation of intermediates (for example, $C_nH_m^+$) can be influenced by the micropore dimensions (cage effect [35]). This confirms, even more, the importance of the use of theoretical methods that allow calculations of realistic models for the study of adsorbate-substrate interactions.

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