J. Phys. Chem. A **1997,** *101,* 7253−7257

The Local Hard−Soft Acid−Base Principle: A Critical Study

Sailaja Krishnamurty,[†] Ram Kinkar Roy,[†] Rajappan Vetrivel,[†] Suehiro Iwata,[‡] and Sourav Pal*,[†,‡]

*Physical Chemistry Division, National Chemical Laboratory, Pune 411 008, India,
and Institute for Molecular Sciences, Myodaiji, Okazaki 444, Japan*

Received: February 4, 1997; In Final Form: July 14, 1997[⊗]

The recently proposed local hard−soft acid−base principle characterizes the reactive centers of two systems on the basis of equal Fukui functions or/and equal local softnesses. We make a quantum chemical study of this principle using ab initio and density functional calculations in cases where the global softnesses of the reacting systems are different. We consider reactions of a dimer cluster model of faujasite X-type zeolite with the probe molecules CO, NH_3, and H_2O.

1. Introduction

The concepts of hardness and softness have been of recent interest. The hard−soft acid−base (HSAB) principle classifies interaction between acids and bases in terms of global softness. It states that hard likes hard and soft likes soft. This global HSAB principle was proposed by Pearson,[1] who, along with Parr, gave a quantitative definition of global hardness and its inverse softness.[2] The global hardness was defined as the second derivative of energy with respect to the number of electrons at constant temperature and external potential, which includes the nuclear field. The global softness is the inverse of this. Pearson also suggested a principle of maximum hardness[3] (PMH), which states that for a constant external potential, the system with the maximum global hardness is the most stable. Parr and Chattaraj gave a proof of the PMH[4] as well as the global HSAB principle.[5] The PMH, in particular, was numerically tested by several groups.[6−8] Subsequently, the PMH was subjected to more severe investigations. It was shown that the PMH was not as general as originally realized,[9] and the conditions of the PMH were more satisfactorily found in the recent years.[10]

Parallel to the above developments, the concepts of local softness and hardness have emerged. The local quantities describe atoms in molecule viewpoint. Several definitions of the local quantities have been proposed. While the definition of local hardness is ambiguous, the local softness has been defined clearly.[11] The definition assumes a density functional theory (DFT) approach. The local softness has been related to the Fukui function, which has been associated with the reactivity of the local sites.[12,13] Reactivity of different sites of a molecule toward electrophilic and nucleophilic attacks has also been defined through the corresponding electrophilic and nucleophilic definitions of local softness. In particular, the condensed definitions based on finite difference approximation of obtaining the derivatives have been conveniently used. In general, it has been shown that for any individual molecule the most reactive site is located at the atom with the largest value of local softness of Fukui function.[12,13] However, recently Gazquez and Méndez[14] have shown that the interaction between two molecules will occur not necessarily through their softest atoms but rather through those atoms whose Fukui functions are the same. This version of the local HSAB principle was proved by the minimization of the grand canonical potential. Assuming the global softnesses of the molecules to be similar, the local HSAB principle states that the local softnesses of the interacting atoms are same. It is interesting to investigate if the equality of local softnesses of the interacting atoms is a more general principle, i.e., whether this holds even when the global softnesses of the two molecules have different values.

In this article we study some of the above points and present a numerical test of the local HSAB principle at the ab initio and density functional theory (DFT) levels. We have taken, as examples, the interaction of molecules such as CO, NH_3, and H_2O with faujasite X-type zeolite represented by a dimeric cluster model $(OH)_3Si{-}OH{-}Al(OH)_3$. We will use the known quantum chemical studies as benchmark results. The dimer cluster model is commonly used as a model for zeolites for theoretical studies. Our impetus to choose this interaction for the present study stems from our future objective of using the local HSAB principle to study the modes of interactions of CO, NH_3, and H_2O molecules with different types of zeolites. In section 2, we define the softness indices and describe the local HSAB principle, and we use this section to introduce the necessary notations as well. In section 3, we describe the methodology and computational procedure. In this section we also discuss the example systems studied in more detail. In the section 4, we record the results of our investigation along with a critical analysis of the results. Finally, in the section 5 the conclusions of our study are presented.

2. The Local HSAB Principle

The definitions of global softness and global hardness were given in Pearson and Parr.[2] Finite difference approximations to these quantities were also derived by them. By using the concept of electron density $\rho(r)$, one can define a descriptor of local softness.[12,13] The local softness at an orbital r is given by

$$s(r) = f(r)S \tag{1}$$

where $f(r)$ is known as the Fukui function and is defined to be $[\delta\rho(r)/\delta N]_{\upsilon(r)}$. Thus $f(r)$ describes the sensitivity of chemical potential to local change in external potential and is considered as the measure of reactivity at a local point. Using left and right derivatives with respect to the number of particles, electrophilic and nucleophilic Fukui functions and local softnesses can be defined. Thus, for an atom k, the nucleophilic

---

* Author for correspondence.

[†] National Chemical Laboratory.

[‡] Institute for Molecular Science.

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1997.

S1089-5639(97)00431-3 CCC: $14.00

condensed local softness $s_k^+ \equiv s^+(r_k)$, where r_k is the position of atom k in a molecule. It can be defined as

$$s_k^+ = f_k^+ S \tag{2}$$

where the condensed nucleophilic Fukui function f_k^+ may be defined as

$$f_k^+ = f^+(r_k) = \rho_{N+1}(r_k) - \rho_N(r_k) \tag{3}$$

f_k^+ was approximated by Parr and Yang[13] as $\rho_{\mathrm{LUMO}}(r_k)$. This can be obtained by using the N-electron orbitals to describe the $N + 1$ electron state. Similarly electrophilic condensed local softness $s_k^- \equiv s^-(r_k)$ can be defined as

$$s_k^- = f_k^- S \tag{4}$$

where

$$f_k^- = \rho_N(r_k) - \rho_{N-1}(r_k) \tag{5}$$

This may be approximated as $\rho_{\mathrm{HOMO}}(r)$.

According to Parr and Yang,[12,13] the softest atoms are the most reactive atoms to electrophilic or nucleophilic attack. This general statement was verified by several groups.[15-17] Later, Gazquez and Méndez showed that the energy of stabilization between the two reacting systems A and B is greater if the Fukui functions of the reacting atoms in A and in B are greater.[14] This is in line with the observations made by Parr and Yang.[13] However they also showed that the interaction between A and B does not necessarily occur through the softest atoms of A and B, but through those atoms (for example, atom k in A and atom l in B) whose Fukui functions ($f_{\mathrm{A}k}$ and $f_{\mathrm{B}l}$) are approximately close to each other, i.e., $f_{\mathrm{A}k} \approx f_{\mathrm{B}l}$. In deriving the equality of the Fukui functions, the global HSAB principle was assumed, i.e., the global softness of A (S_{A}) was assumed to be equal to that of B (S_{B}). Under these conditions, the local softness of atom k in A is also equal to that of atom l in B, i.e. $s_{\mathrm{A}k} \approx s_{\mathrm{B}l}$. This principle was applied to rationalize the regioselectivity in Diels–Alder reactions between terminally monosubstituted 1,3-butadienes and monosubstituted ethenes by Damoun et al.[18]

Gazquez and Méndez made remarks that the general statement of equal local softnesses of the atoms participating in a reaction may be obtained directly by minimization of the grand canonical potential and without assuming $S_{\mathrm{A}} = S_{\mathrm{B}}$. This is a more general statement of their earlier definition of the local HSAB principle to determine the atoms through which the reaction between A and B takes place. The principle may also be viewed as a generalization of the global HSAB principle.

3. Computational Details

We describe here the details of the systems studied and the methodology followed to calculate the relevant reactivity indices. The structure of one of the participating systems $(OH)_3$ Si–(OH)–Al$(OH)_3$ is generated from the experimental crystal structure of faujasite X-type zeolite.[19] Here the bridging oxygen atom is protonated at a distance of 1.08 Å keeping the H–O_b–Si (O_b is bridging oxygen atom between Si and Al) and H–O_b–Al bond angles at 104.6 and 103.4°, respectively. The adjacent silicon and aluminum atoms occurring in the faujasite lattice are replaced by hydrogens in order to preserve the electroneutrality of the model as shown in Figure 1. The terminal hydrogens are maintained at a distance of 1.66 Å (i.e., terminal O–H bond distances are 1.66 Å). This model structure has been used for a more realistic picture for faujasite X-type zeolite crystals (though it is limited by the fact that the model dimer cluster is not a good approximation of the actual crystal). In several other theoretical studies[20-22] the structure of the cluster model is generated by geometry optimization at some level of sophistication. So those structures neither belong to any particular type of zeolite nor do they reflect the actual experimental situation (or environment). The calculations on the reacting molecules CO, NH_3, and H_2O have been performed at the experimental geometry.

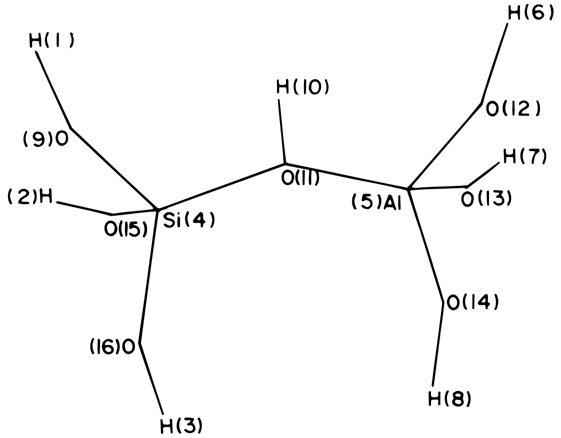

Figure 1. Dimer cluster model of faujasite zeolite. The numbering of atoms is given in parentheses.

The calculations have been performed at the ab initio Hartree–Fock and DFT with B3LYP functional levels. The ionization potential and electron affinity have been evaluated using a ΔSCF procedure. (i.e., as the difference of separate SCF energies of neutral and monopositive or mononegative ions, as the case may be). Since all the neutral systems considered in this study are closed shells, restricted Hartree–Fock (RHF) has been used for these. For the ab initio calculations, the restricted open shell Hartree–Fock (ROHF) doublet wave function has been used for monopositive and mononegative ions. The ab initio calculations have been performed using a double-ζ basis for the valence (DZV) and GAMESS system of programs.[23] In addition to ab initio calculations, DFT calculations have been reported, since it is well-known that the DFT with the B3LYP functional can describe the interaction of the chosen probe molecules with the zeolite cluster adequately. For DFT calculations, we have used a more extensive basis set 6-31 G** and the calculations have been done with the help of the Gaussian 94 program system.[24] For monopositive and mononegative ions, the unrestricted B3LYP functional has been used.

The global softness (S) values have been evaluated using finite difference approximation. The condensed local softness and Fukui functions are obtained by calculating the electronic density in two ways, (a) by Mülliken population and (b) by Löwdin population analysis in the ab initio case. However, for the DFT level, these have been computed using only Mülliken atomic charges. As the validity of the local HSAB principle warrants the satisfaction of the condition $S_{\mathrm{A}k} = S_{\mathrm{B}l}$, we have to evaluate the local softness (or better, condensed local softness) values of all atoms in cluster models as well as probe molecules. Our strategy will be to compare the local softness values of the atoms of the cluster with those of the atoms in the probe molecules. The atoms for which these values will be closer will be considered as the most probable sites of interaction. The H atom of the bridging O–H group acts as electrophilic center in the interaction with CO, NH_3, and H_2O, which will donate electrons to the zeolite cluster model. Hence we will be interested in the s_k^+ values (from eq 2) of all atoms of the cluster model.

TABLE 1: Global Softness Values for Different Molecules

molecule	global softness ab initio[a]	 DFT[b]
zeolite cluster model	2.687	2.903
carbon monoxide	1.682	1.589
water molecule	1.463	1.837
ammonia	1.846	1.346

[a] Basis set used is DZV. [b] Basis set used is 6-31G**.

TABLE 2: Condensed Local Softness and Fukui Function Values for the Zeolite Cluster Model from Mülliken and Löwdin Population Analysis

	Mülliken (ab initio)		Löwdin (ab initio)		Mülliken (DFT)	
atom[a]	f_k^+	s_k^+	f_k^+	s_k^+	f_k^+	s_k^+
1 (hydrogen)	0.036	0.097	0.025	0.067	0.038	0.109
2 (hydrogen)	0.062	0.165	0.040	0.108	0.052	0.151
3 (hydrogen)	0.030	0.080	0.019	0.051	0.038	0.110
4 (silicon)	0.009	0.024	0.033	0.089	0.154	0.447
5 (aluminum)	0.015	0.041	0.049	0.132	0.196	0.568
6 (hydrogen)	0.049	0.131	0.034	0.091	0.117	0.340
7 (hydrogen)	0.061	0.163	0.043	0.115	0.128	0.371
8 (hydrogen)	0.047	0.126	0.034	0.092	0.103	0.300
9 (oxygen)	−0.054	−0.144	0.193	0.519	0.062	0.018
10 (hydrogen)	0.747	2.008	0.464	1.247	0.303	0.879
11 (oxygen)	0.010	0.027	0.013	0.035	0.013	0.037
12 (oxygen)	0.004	0.011	0.017	0.045	−0.025	−0.073
13 (oxygen)	0.017	0.044	0.018	0.047	0.003	0.010
14 (oxygen)	0.019	0.051	0.026	0.069	−0.005	−0.013
15 (oxygen)	−0.036	−0.095	−0.010	−0.028	−0.013	−0.037
16 (oxygen)	−0.016	−0.043	0.003	0.007	−0.039	−0.114

[a] The numbering of the atoms is given in Figure 1. Atom number 10 is the bridging hydrogen (Brönsted acid site) attached to the bridging oxygen (atom no. 11).

TABLE 3: Condensed Local Softness and Fukui Functions for Carbon Monoxide from Mülliken and Löwdin Population Analysis

	Mülliken (ab initio)		Löwdin (ab initio)		Mülliken (DFT)	
atom	f_k^-	s_k^-	f_k^-	s_k^-	f_k^-	s_k^-
carbon	0.666	1.125	0.653	1.100	0.711	1.684
oxygen	0.334	0.558	0.347	0.583	0.289	0.459

Similarly we will be interested in the s_k^- values (from eq 4) of all atoms in the probe molecules as they act as nucleophiles at the time of interaction. However, in addition, we have also evaluated the f_k^+ (eq 3) values of all atoms of the cluster model and the f_k^- values (eq 5) of all atoms in the probe molecules. This will help us to compare which of the two parameters (f or s) is more appropriate in the general statement of the local HSAB principle as discussed in section 2.

4. Results and Discussion

Table 1 contains the global softness values of the zeolite cluster model as well as probe molecules at both ab initio and DFT levels of theory. The values of the nucleophilic condensed local softness (s_k^+) and condensed Fukui function (f_k^+) of the individual atoms of the cluster model obtained through both Mülliken and Löwdin population analysis schemes at the ab initio level and through the Mülliken population scheme at the DFT level are presented in Table 2. Similarly the electrophilic condensed local values for the probe molecules (s_k^- and f_k^-) are given in Table 3 (CO), Table 4 (NH_3), and Table 5 (H_2O). It is clear from the Table 1 that the global softness values of the zeolite cluster model differ widely from those of the three probe molecules. So in testing the local HSAB principle, it becomes important to check whether the Fukui functions or the condensed local softness values will be more reliable parameters.

TABLE 4: Condensed Local Softness and Fukui Function Values for Ammonia from Mülliken and Löwdin Population Analysis

	Mülliken (ab initio)		Löwdin (ab initio)		Mülliken (DFT)	
atom	f_k^-	s_k^-	f_k^-	s_k^-	f_k^-	s_k^-
nitrogen	0.577	1.065	0.725	1.339	0.512	0.949
hydrogen[a]	0.141	0.260	0.092	0.169	0.160	0.293

[a] As all the three hydrogen atoms are identical their f_k^- and s_k^- *values are also same.*

We discuss the interaction of the zeolite cluster model with each of the three probe molecules below.

(a) Interaction of the Cluster Model with CO. It is known that the interaction of CO with the Brönsted acid sites of a zeolite lattice is a weak interaction. This is evidenced by the experimental[25,26] as well as theoretical[27,28] values of the interaction energy, which is below 5 kcal/mol. The lengthening of the bridging O−H bond (decreasing of vibrational frequency) and the shortening of the CO bond distance (according to Gutmann's second rule[29]) shows that the interaction takes place between the C atom of carbon monoxide and the H atom of the bridging OH group of the cluster. The fact that the C atom of CO acts as the electron donor can also be justified by the positive dipole moment in the C ← O direction.

Table 3 shows that both s_k^- and f_k^- values obtained from Mülliken analysis at the ab initio (1.125 and 0.666, respectively) and DFT levels (1.684 and 0.711) are higher for the C atom, indicating that the carbon atom is a preferable nucleophilic site.

Although there are some differences in numerical values of ab initio and DFT calculations, it is gratifying to note the similar trends of ab initio and DFT results. From the consideration of the local HSAB principle and the s_k^+ and f_k^+ values presented in the Table 2, one expects that the H atom of the bridging O−H group of the zeolite cluster should behave as a preferable electrophilic site. The corresponding values evaluated through Löwdin population analysis using the ab initio level of calculation also obey the same trend. If we match the s_k^- and f_k^- values of the CO molecule with s_k^+ and f_k^+ values of the zeolite cluster, one finds clearly that the s_k^- as well as f_k^- values of the C atom of the CO molecule match better with the s_k^+ and f_k^+ values of the H atom of the bridging O−H group. Thus the local HSAB principle also predicts the interaction in accordance with the experimentally proved evidence. That these two participating atoms are also the softest atoms of the respective molecules is extremely gratifying.

However, if we want to check which of the parameters, local softness or Fukui functions, manifest the local HSAB principle better, we have to compare the corresponding numerical values. Results obtained by ab initio Mülliken population analysis show that the difference of the condensed local softness of the two reacting atoms is substantially higher than the difference of the corresponding Fukui functions. However, it is interesting to note that the results of the Löwdin population show an opposite trend, i.e., the condensed local softnesses of the reacting atoms are much closer than the corresponding Fukui functions. In case of the DFT results, the relative difference of the Fukui function and the condensed local softness of the participating atoms is similar. Nevertheless, the interaction sites are clearly identifiable from the values of both local softness and Fukui functions.

(b) Interaction of the Cluster Model with NH_3. Previous theoretical studies show that there are possibilities of interaction of the NH_3 molecule, with the Brönsted acid site in two different ways. The first one is called the covalent interaction,[30,31] and the second one is known as the ionic interaction[32] (see Figure

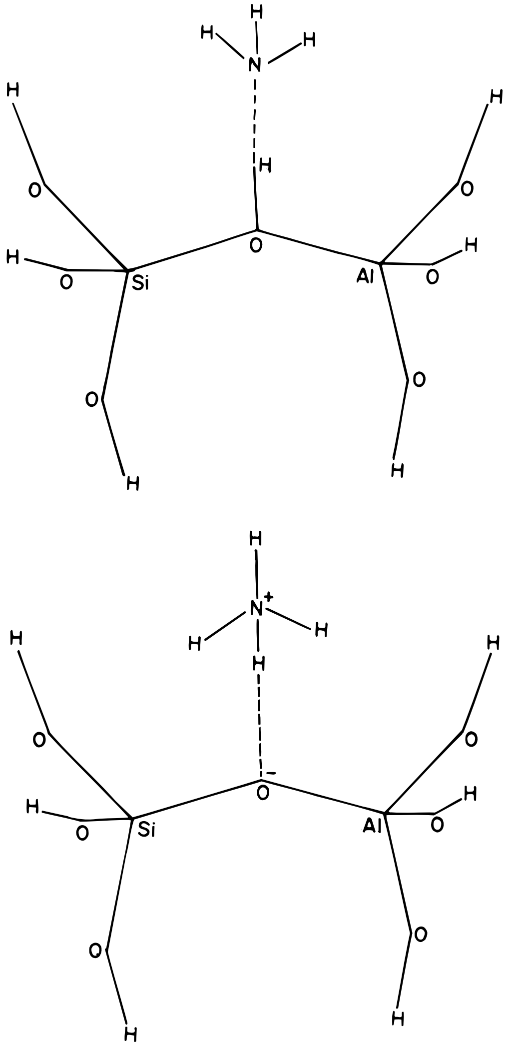

Figure 2. (a) Covalent interaction of ammonia with the zeolite dimer cluster model. (b) Ionic interaction of the zeolite cluster model with NH_4^+.

2a,b). The experimental heats of adsorption,[26,33,34] however, favor the ionic interaction to be the prominent one. Our explanation based on the local HSAB principle will, however, predict the preferable site of attack at the initial stages of the interaction process. As the interaction proposed by the ionic model becomes operative in the next stage, we are not considering that in our study.

The local condensed electrophilic softness and Fukui functions for the ammonia molecule are presented in Table 4. Nitrogen atom has the largest s_k^- and f_k^- values. If we compare the s_k^- and f_k^- values of the nitrogen atom with the s_k^+ and f_k^+ of the zeolite cluster model, we find that they match best with the acidic H atom. Ab initio results obtained by Mülliken analysis show that the f_k values match better than the s_k values. For Löwdin analysis, however, the opposite is true. The s_k values of the participating atoms match better than the f_k values. This is similar to what we observed in case a. For the DFT study, we see that the local softness values of the participating atoms match better than the Fukui functions. Despite this difference, the local HSAB principle convincingly predicts that the preferable interaction takes place between the N atom of ammonia and the acidic hydrogen atom of the zeolite cluster model in accordance with the known experimental and theoretical results.

(c) Interaction of the Cluster Model with H_2O. The energy of adsorption of H_2O molecule in the Brönsted acid site of the zeolite model crystal is in the range of 7−9 kcal/mol.[35] So the strength of interaction is in between those of the interaction of CO and NH_3. Table 5 presents the electrophilic local softnesses and Fukui functions of the H_2O molecule. From the values presented, the oxygen atom in H_2O molecule can be considered as the strongest nucleophilic center. For both Mülliken and Löwdin population analysis, the s_k^- and f_k^- values of the oxygen atom are the highest in the H_2O molecule. Now, when we compare with the values in Table 2 we easily see that the favorable interaction takes place between the oxygen atom of H_2O and the hydrogen atom of the bridging OH group of the zeolite cluster model, which is also established by previous theoretical studies.[36,37] A relative comparison of the f_k^- and s_k^- values of the oxygen atom of H_2O and f_k^+ and s_k^+ values of the acidic H atom of the zeolite cluster model again show that in ab initio Mülliken population case the Fukui functions match better, while the local softness values match better when computed by the ab initio Löwdin or DFT case.

TABLE 5: Condensed Local Softness and Fukui Function Values for Water from Mülliken and Löwdin Population Analysis

	Mülliken (ab initio)		Löwdin (ab initio)		Mülliken (DFT)	
atom	f_k^-	s_k^-	f_k^-	s_k^-	f_k^-	s_k^-
oxygen	0.714	1.044	0.787	1.151	0.680	0.915
hydrogen[a]	0.143	0.210	0.107	0.156	0.160	0.216

[a] As the two hydrogen atoms are identical their f_k^- and s_k^- values are also same.

5. Conclusion

In this study we have considered the possible sites of reactivity of a dimer cluster model of faujasite X-type zeolite with CO, NH_3, and H_2O at the ab initio RHF/ROHF level and DFT using B3LYP functional to test the local HSAB principle. These interacting systems have different global softness. In all these cases we find that the local HSAB principle is satisfied. In such cases, as discussed before, the equality of Fukui functions of the atoms participating in a reaction is not the same as equality of local softness. Our results cannot convincingly show which of the parameters, local softnesses or Fukui functions, should be used in implementing the local HSAB principle in the case of the reaction between systems with different global softness. This aspect of the results is sensitive to the method of calculation of electronic density. We also observe that the interacting atoms are the softest (electrophilic/nucleophilic as the case may be) in the molecules. Perhaps a more critical study will be a case (if there is any) where the local HSAB principle (either through equal softness or equal Fukui functions) predicts interaction between two atoms that are not the softest in the parent molecules. Apart from this slightly different aspect of the local HSAB principle, our preliminary case study shows that the local HSAB principle is satisfied. By appropriate extension of the cluster model, we hope to use the above principle to predict site selectivity for host−guest interactions in the zeolites.

Acknowledgment. The authors thank the Indo-French Center for the Promotion of Advanced Research, New Delhi, for the research grant (No. 1206-1) in partial support of this work. One of us (R.K.R.) acknowledges the Council of Scientific and Industrial Research, New Delhi, for granting a Research Associateship.

References and Notes

(1) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.
(2) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512.

(3) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561.

(4) Parr, R. G.; Chattaraj, P. K. *J. Am. Chem. Soc.* **1991**, *113*, 1854.

(5) Parr, R. G.; Chattaraj, P. K. *J. Am. Chem. Soc.* **1991**, *113*, 1856.

(6) Pearson, R. G.; Palke, W. E. *J. Phys. Chem.* **1992**, *96*, 3283.

(7) Gazquez, J. L.; Martinez, A.; Méndez, F. *J. Phys. Chem.* **1993**, *97*, 4059.

(8) Pal, S.; Vaval, N.; Roy, R. K. *J. Phys. Chem.* **1993**, *97*, 4404.

(9) Sebastain, K. L. *Chem. Phys. Lett.* **1994**, *231*, 40.

(10) Chattaraj, P. K.; Liu, G. H.; Parr, R. G. *Chem. Phys. Lett.* **1995**, *237*, 171.

(11) Ghosh, S.; Berkowitz, M. *J. Chem. Phys.* **1985**, *83*, 2976.

(12) Yang, W.; Parr, R. G. *Proc. Natl. Acad. Sci.* **1985**, *82*, 6723.

(13) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049.

(14) Gazquez, J. L.; Méndez, F. *J. Phys. Chem.* **1994**, *98*, 4591.

(15) (a) Langenaeker, W.; Coussement, N.; De Proft, F.; Geerlings, P. J. *J. Phys. Chem.* **1994**, *98*, 3010. (b) Damoun, S.; Langeneaker, W.; Van de Woude.; Geerlings, P. *J. Phys. Chem.* **1995**, *99*, 12151.

(16) Corma, A.; Lopis, F. L.; Viruela, P.; Wilson, C. Z. *J. Am. Chem. Soc.* **1994**, *116*, 134.

(17) Baekelandt, B. G.; Mortier, W. J.; Livens, J. L.; Schoonheydt, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 6730.

(18) Damoun, S.; Van de Woude, G.; Méndez, F.; Geerlings, P. *J. Phys. Chem. A* **1997**, *101*, 886.

(19) Olson, D. H. *J. Phys. Chem.* **1970**, *74*, 2758.

(20) van Santen, R. A.; Kramer, G. J. *Chem. Rev.* **1995**, *95*, 637.

(21) Sauer, J. *Chem. Rev.* **1989**, *89*, 199.

(22) Zygmut, S. A.; Curtiss, L. A.; Iton, L. E.; Erhardt, M. K. *J. Phys. Chem.* **1996**, *100*, 6663.

(23) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(24) Firsch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petesson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision D.1; Gaussian Inc.: Pittsburgh, PA, 1995.

(25) Zecchina, A.; Bordiga, S.; Spoto, G.; Scarano, D.; Pertrini, G.; Leofanti, G.; Pardovan, M. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2959.

(26) Buzzoni, R.; Bordiga, S.; Spoto, G.; Scarano, D.; Ricchiardi, G.; Lamberti, C.; Zecchina, A. *Stud. Surf. Sci. Catal.* **1995**, *98*, 104.

(27) Bates, S.; Dwyer, J. *J. Phys. Chem.* **1993**, *97*, 5897.

(28) Farnworth, K. J.; O'Malley, P. J. *J. Phys. Chem.* **1996**, *100*, 1814.

(29) Gutmann V. *The Donor-Acceptor Approach to Molecular Interaction*; Plenum Press: New York, 1978.

(30) (a) Teunissen, E.; van Duijneveldt, F. M.; van Santen, R. A. *J. Phys. Chem.* **1992**, *96*, 266. (b) Geerlings, P.; Tariel, N.; Botrel, A.; Lissillour, R.; Mortier, W. J. *J. Phys. Chem.* **1984**, *88*, 5752.

(31) Kassab, E.; Fouquet, J.; Allavena, M.; Evleth, E. M. *J. Phys. Chem.* **1993**, *97*, 9034.

(32) Teunissen, E.; van Santen, R. A.; Jansen, A. P.; van Duijneveldt, F. M. *J. Phys. Chem.* **1993**, *97*, 1993.

(33) Dima, E.; Rees, L. V. C. *Zeolites* **1990**, *10*, 8.

(34) Medin, A. S.; Borovkov, V. Y.; Kazanasky, V. B.; Pelmenschikov, A. G.; Zhidomirov, G. M. *Zeolites* **1990**, *10*, 668.

(35) Parker, L. M.; Bibby, D. M.; Burns, G. R. *Zeolites* **1993**, *13*, 107.

(36) Sauer, J.; Zahradník, R. *Int. J. Quantum Chem.* **1984**, *26*, 793.

(37) Sauer, J.; Kölmel, C. M.; Hill, J. R.; Ahlrich, R. A. *Chem. Phys. Lett.* **1989**, *164*, 193.