

Adsorption of Small Molecules in Zeolites: A Local Hard–Soft Acid–Base Approach

Ramesh Ch. Deka,^{*,†} D. Ajitha,[‡] and Kimihiko Hirao[‡]

Department of Chemical Sciences, Tezpur University, Napaam, Tezpur 784 028, India, and
Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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The interaction of small probe molecules with clusters chosen to represent Brønsted acid sites in zeolites has been investigated using a local hard–soft acid–base approach. Condensed Fukui functions and local softness values of all the atoms of the probe molecules, namely, CH₄, CO, and NH₃, have been calculated, and these values are compared with that of the acidic hydrogen atoms of zeolite clusters to find out the most favorable adsorption sites. We calculated the interaction energy of the molecules using local HSAB principle, and the interaction energy values are in good agreement with the experimental results. Density functional and Hartree–Fock methods are used for the calculation of reactivity descriptors. We observed that the intermolecular interaction takes place via the atoms comparable softness values rather than via atoms of equal Fukui functions.

1. Introduction

The chemical reactivity of a system is inherently a local phenomenon and thus the apt choice and definition of local descriptors is crucial. The use of Fukui function and local softness to understand the local reactivity of the chemical systems is an emerging approach.^{1–5} The local hard–soft acid–base (HSAB) principle proposed by Gasquez and Mendez⁶ predicts the reactivity of two chemical systems on the basis of the local softness values. Geerlings and co-workers¹ rationalized the regioselectivity of Diels–Alder reactions within the framework of HSAB principle and stated that “the interaction between two molecules A and B will not necessarily occur through the softest atoms but through those whose Fukui functions are approximately equal.” In the case of systems with nearly equal global softness values, this also implies nearly equal local softness values of the reacting sites of the two systems. The feasibility of local HSAB principle has been studied by Pal and co-workers⁷ and Nguyen and co-workers.^{8,9} It has been shown that the local softness values and their ratio are very efficient tools in predicting the relative electrophilicity and relative nucleophilicity, and in general the local softness values is a better descriptor than the local charges.¹⁰ On the basis of the principle of maximum hardness and chemical potential equalization principle, Mendez and Gazquez¹¹ derived a relationship between the reactivity descriptors and the interaction energy of molecules. The aim of the present study is to use the DFT-based descriptors to investigate the acidity of zeolites and to determine the adsorption sites of small molecules in zeolites.

The catalytic activity of the zeolite framework essentially hinges from the breakup of the charge neutrality of the all silicious lattice when the silicon is substituted by aluminum atom. The negative charge thus created in the local tetrahedron environment can attract the positive cations. Brønsted acid sites in the zeolite framework are generated when the negative charges are compensated with protons. Understanding the local structure of the Brønsted acid sites, their modification upon

adsorption and reactivity are considered important aids in the area of catalyst research and development. Hence, the acidity and reactivity of zeolites need to be defined in a more significant way. While the influence of zeolite composition and structure on acidity has been studied by several theoretical calculations,^{12–16} only a very few of these studies have used the local hardness and softness principle.^{17,18} Local softness values have been found very significant in defining acidity and basicity of zeolites compared to atomic charges of the active atoms.^{10,18} In this paper we analyze adsorption sites through the local version of the hard–soft acid–base (HSAB) principle by studying both weak and strong interaction with the acidic hydrogen atoms. We choose small probe molecules such as CH₄, CO, and NH₃ for studying their interaction with the acidic sites. The interaction of CH₄ and CO molecules with the acid sites is weak, whereas there is a strong interaction between NH₃ and acidic zeolite. Here, we investigate the adsorption of these small molecules in the zeolite framework using reactivity descriptors.

We organize the paper as follows: in section 2, we give brief description of DFT-based reactivity descriptors. Section 3 deals with computational details, and in section 4 we present results and discussion. Finally, in the section 5 we present the conclusions of our study.

2. DFT-Based Reactivity Descriptors

In the present work, we use the local descriptors. In density functional theory, global hardness (η) and global softness (S) are related to the first-order change in the chemical potential (μ) with the change in the number of electron (N) and thus can be evaluated from the second order change in the energy of the system at constant external potential $v(r)$.¹⁹ The global softness is defines as the inverse of the global hardness with a factor $1/2$. The equation describing the global parameters are

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)} = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{v(r)} \quad (1)$$

$$S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial \mu} \right)_{v(r)} \quad (2)$$

* Corresponding author.

[†] Tezpur University.

[‡] The University of Tokyo.

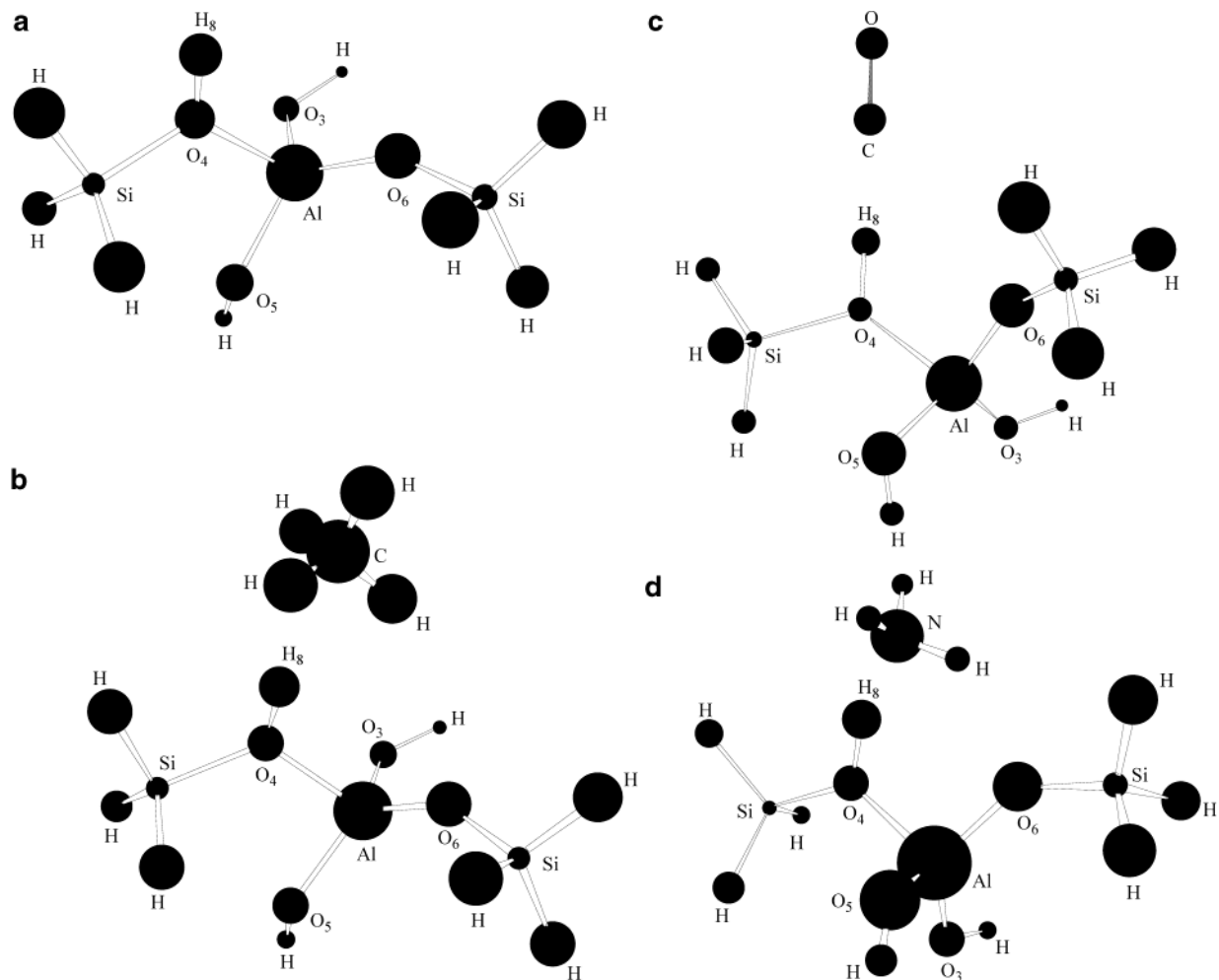


Figure 1. Optimized structure of (a) trimer cluster of zeolite with the Brønsted acid site, (b) methane adsorbed on acid site, (c) carbon monoxide adsorbed on acid site, and (d) ammonia adsorbed on acid site.

Using the finite difference approximation for the small change in the number of the particles, we can approximate the η and S as

$$\eta = \frac{IP - EA}{2}, \quad S = \frac{1}{IP - EA} \quad (3)$$

The condensed Fukui function, f , and local softness, s , in this finite difference approximation for the k th atom in a molecule are defined as^{20,21}

$$s_k^+ = f_k^+ S = [\rho_k(N_0 + 1) - \rho_k(N_0)]S \quad (\text{for nucleophilic attack on the system}) \quad (4)$$

$$s_k^- = f_k^- S = [\rho_k(N_0) - \rho_k(N_0 - 1)]S \quad (\text{for electrophilic attack on the system}) \quad (5)$$

$$s_k^0 = f_k^0 = \frac{1}{2}[\rho_k(N_0 + 1) - \rho_k(N_0 - 1)]S \quad (\text{for radical attack on the system}) \quad (6)$$

where $\rho_k(N_0)$, $\rho_k(N_0 + 1)$, and $\rho_k(N_0 - 1)$ are electronic population on atom k for N_0 , $N_0 + 1$, and $N_0 - 1$ electron systems, respectively.

From a local point of view, if the interaction between two chemical systems A and B occurs through the k th atom of A, one can express the interaction energy as²

$$(\Delta E_{\text{int}})_{Ak} \approx -\frac{1}{2} \left(\frac{(\mu_A - \mu_B)^2}{S_A f_{Ak} + S_B} \right) (S_A f_{Ak} S_B) - \frac{1}{2} \left(\frac{\lambda}{S_A f_{Ak} + S_B} \right) \quad (7)$$

where f_{Ak} is the Fukui function of the atom k of the system A. The first term on the right-hand side corresponds to the charge transfer process between A and B arising from the chemical potential equalization principle at constant external potential, and the second term corresponds to a reshuffling of the charge distribution, and it is basically a manifestation of the maximum hardness principle and takes place at constant chemical potential. The λ is defined as

$$\lambda = q_{Ak}^{\text{eq}} - q_{Ak}^0 \quad (8)$$

where q_{Ak}^{eq} and q_{Ak}^0 are the charges of the k th atom of the system A in the complex AB and in the isolated system A, respectively.

3. Computational Details

We have used a trimer cluster to model the acid site of zeolite, and the cluster is shown in Figure 1. A large cluster is necessary when properties of various zeolites are compared and while studying the reaction mechanism of zeolite-catalyzed reactions. However, for calculating acidity or basicity and interaction of small molecule, a trimer cluster has been used as a good model.^{10,12} We studied the interaction of CH₄, CO, and NH₃ at acidic site of the zeolite cluster and adsorption complexes are

TABLE 1: Selected Geometrical Parameters of T3 Cluster, CH₄-T3, CO-T3, and NH₃-T3 Adsorbed Models Calculated Using HF and DFT Methods^a

	T3	CH ₄ -T3	CO-T3	NH ₃ -T3
Bond Lengths (Å)				
O ₄ -H ₈	0.945 (0.973)	0.946 (0.976)	0.949 (0.985)	0.987 (1.075)
Si-O ₄	1.726 (1.745)	1.724 (1.743)	1.719 (1.736)	1.698 (1.702)
Al-O ₄	1.935 (1.976)	1.932 (1.974)	1.930 (1.967)	1.906 (1.933)
Al-O ₃	1.708 (1.739)	1.708 (1.754)	1.709 (1.740)	1.722 (1.749)
Al-O ₅	1.727 (1.756)	1.736 (1.739)	1.723 (1.752)	1.733 (1.744)
Al-O ₆	1.709 (1.738)	1.712 (1.742)	1.718 (1.748)	1.715 (1.778)
H ₈ -X		2.723 (2.506)	2.301 (2.093)	1.726 (1.527)
(X = C, N)				
Bond Angles (deg)				
Si-O ₄ -Al	131 (122)	120 (122)	121 (123)	124 (127)
Si-O ₄ -H ₈	122 (117)	118 (117)	117 (117)	119 (120)
Al-O ₄ -H ₈	107 (121)	122 (119)	96 (116)	112 (112)

^a The geometrical parameters derived from DFT calculations are given inside the parenthesis.

TABLE 2: Global Properties of Zeolite Cluster and Molecules (in Atomic Units)

system	chemical potential		global softness	
	HF/6-31G**	DFT/blyp/dnp	HF/6-31G**	DFT/blyp/dnp
T3 cluster	-0.13291	-0.14523	2.20954	3.79867
CH ₄	-0.12128	-0.19241	1.34749	1.51398
CO	-0.17402	-0.22229	1.58639	1.56999
NH ₃	-0.06253	-0.14476	1.78867	1.95014

shown in Figure 1b-d. The geometry optimizations of the cluster as well as the adsorption complexes were performed by both Hartree-Fock and DFT methods. The HF calculations were performed using 6-31G** basis sets with the program GAMESS²², and DFT calculations were carried out with DMol²³ programs using dnp basis sets and blyp functionals.

4. Results and Discussion

Geometries. The optimized geometries of T3 cluster, CH₄-T3, CO-T3, and NH₃-T3 are shown in Figure 1, and selected geometrical parameters evaluated at HF/6-31G** level are given in Table 1. Comparing the O₄-H₈ bond of the free T3 cluster with the adsorption complexes, the O₄-H₈ bond found to increase by 0.001 Å in CH₄-T3 to 0.042 Å in NH₃-T3 complexes. The Si-O₄ and Al-O₄ distances decrease in the adsorption complexes in the order compared to the free T3 cluster. The deviation of Si-O₄ and Al-O₄ bond lengths from T3 cluster is maximum in the case of NH₄-T3 complex and minimum in the case of CH₄-T3 cluster. The most significant difference is observed in the H₈-X (X = C, N) distance. Due to this large difference in the H₈-X distance for CH₄, CO and NH₃ adsorption complexes, their charge distribution and interaction energy will be different. The interaction energy values of the molecules are calculated using eq 7. The λ values required to calculate the interaction energy are derived from the change in electron density of H₈ atom in T3 cluster and in the adsorption complexes.

Interaction Energy. In our earlier work we have extensively used the local HSAB principle to determine the order of acidity and basicity of zeolites, more specifically to study the intramolecular reactivity.^{10,18} Here we extend the reactivity descriptors to describe the intermolecular reactivity.

Table 2 contains the chemical potential and global softness of T3 cluster and the interacting molecules calculated at HF/6-31G** and DFT/blyp/dnp levels. The global softness values calculated by HF and DFT methods increases from CH₄ to NH₃ via CO. Hence, the interaction energy between NH₃

TABLE 3: Condensed Fukui Function and Local Softness Values of Selected Atoms of Zeolite Cluster and Isolated Molecules

system	Fukui function		local softness	
	HF/6-31G**	DFT/blyp/dnp	HF/6-31G**	DFT/blyp/dnp
T3 Cluster				
H ₈	0.09498	0.22905	0.20987	0.86971
Al	0.02971	-0.02699	0.06565	-0.10254
O ₃	-0.00017	-0.01299	-0.00037	-0.04937
O ₄	-0.11570	-0.09800	-0.25565	-0.37219
O ₅	-0.03095	-0.03000	-0.06840	-0.11394
O ₆	-0.01248	-0.03998	-0.02757	-0.15191
CH ₄				
C	0.32810	0.26100	0.44212	0.39515
H	0.14551	0.18500	0.19607	0.28009
CO				
C	0.72324	0.65799	1.14734	1.03305
O	0.27676	0.34200	0.43905	0.53694
NH ₃				
N	0.52720	0.50099	0.94298	0.97702
H	0.15758	0.16600	0.28186	0.32372

and zeolite cluster is expected to be maximum due to soft-soft interaction. Since the global softness values of CO and CH₄ molecules lie far away from zeolite cluster, their interaction (soft-hard) will be weaker than NH₃. The global hardness, inversely related to global softness, for zeolite cluster is 0.132, and that of CH₄, CO, and NH₃ are 0.330, 0.318, and 0.256, respectively. The detailed calculation for the stability of two interacting species, A and B, was given by Gazquez,²⁵ and he proved that the interaction energy becomes maximum (ΔE becomes more negative) when A and B have similar hardness. Since the hardness value of NH₃ and the zeolite cluster are close to each other compared to CH₄ and CO molecules, the energy will be maximum for the NH₃ molecule. Due to the large difference in the global hardness values between CH₄ and T3 cluster, their interaction energy would be minimum.

The Fukui function and local softness values for the acidic hydrogen as well as for O and Al atoms around the acid sites are given in Table 3. From these values it is seen that the Fukui function is maximum for the bridging hydrogen atom and it is the softest atom. In NH₃ the Fukui function as well as local softness values are higher for the N atom than the H atoms. The carbon atom is the softest atom in CH₄ and CO molecules. Since the local softness values of N in NH₃ and that of C atoms of CH₄ and CO are comparable to that of H atom of zeolite, NH₃ will interact the acidic hydrogen of zeolite via nitrogen, and CH₄ and CO will interact via their carbon. Although it is quite evident from experimental and theoretical results that nitrogen of NH₃ and carbon of CH₄ are the reactive atoms, the problems arises in the case of CO. Theoretical calculations suggest that either carbon or the oxygen atom of CO may act as a nucleophile and estimates the interaction energy of CO via either carbon or oxygen with simple models of Brønsted or Lewis acid sites show that, although interaction via carbon is energetically preferred, the interaction energy associated with linkage via oxygen is not insignificant.¹⁶ The Fukui function and local softness values of carbon and oxygen atoms of CO molecule clearly indicate that the carbon atom is softer than the oxygen atom and the reactive center is located near to it.

The interaction energies of the adsorbed molecules are calculated using eq 7. According to eq 7, among various sites in A, each one characterized by its own value of f_{Ak} , when S_B is large, there is a greater stabilization and the interaction occurs at the site with greater value of f_{Ak} . Moreover, the interaction energy largely depends on the λ value that demands a quantita-

TABLE 4: Mulliken Charge on Acidic Hydrogen of Zeolite (H₈) in Free Cluster and in Adsorption Complexes, λ Values, and Interaction Energy Values of the Molecules Calculated Using HSAB Principle

system	Mulliken charge		HF/6-31G**	DFT/blyp/dnp	interaction energy kcal/mol	
	HF/6-31G**	DFT/blyp/dnp			HF/6-31G**	DFT/blyp/dnp
free zeolite cluster	0.395	0.305				
complex with CH ₄	0.405	0.310	0.010	0.005	-2.021	-1.043
complex with CO	0.411	0.319	0.016	0.014	-2.893	-2.843
complex with NH ₃	0.489	0.443	0.094	0.138	-15.049	-15.353

tive definition of λ . Gazquez and Mendez² as well as Geerlings and co-workers²⁴ arbitrarily choose λ values to be 0.5 and 1.0 to describe the reactivity of enolate ions and 1,3-cyclo addition reactions of benzonitrile oxide with an alkene, respectively. Recently, Pal and Chandrakumar⁵ defined λ values for weakly adsorbed molecules in zeolites. In this study we show that the λ value calculated from the difference in changes of isolated molecule and the adsorption complex could be used for both weak and strong interaction when the interacting molecules are small.

While calculating the λ , it can be explicitly assumed that when A and B molecules interact via the k th atom of molecule A and l th atom of molecule B, only these two atoms participate in the reshuffling process of charge distribution. Hence, the changes in the electron population on other atoms can be neglected. In Table 4, the Mulliken charges of acidic hydrogen atom in the free cluster and in the adsorption complexes are given. The λ values are calculated from the differences of the charges and are also presently in Table 4. It is seen from Table 4 that the λ values are positive and decrease in the order NH₃ > CO > CH₄ for the adsorption complexes. These λ values are used to calculate the interaction energy of the molecules and they are given in Table 4.

Considering the case of CO, the interaction of CO molecule with acidic hydrogen atom of zeolite cluster is a weak interaction, which is evidenced by theoretical²⁶ as well as experimental²⁷ values of the interaction energy that is around -2.25 to -3.25 kcal/mol. The interaction energy obtained from the HSAB principle is -2.893 kcal/mol at HF/6-31G** level, and the agreement between the theory and the experiment is satisfactory.

The interaction energy values of NH₃ and CH₄ molecules^{28,29} are found around -16.73 kcal/mol and -1.25 kcal/mol, respectively, and they are in agreement with interaction energy calculated using the local HSAB principle.

5. Conclusions

In this study, we have investigated the active sites of zeolites as well as adsorbed molecules using local reactivity descriptors. Due to large softness values for nitrogen and carbon atoms in NH₃, CH₄, and CO molecules, the interactions take place between acidic hydrogen of zeolite and nitrogen atom of NH₃ and with carbon atoms in cases of CH₄ and CO. Hence, it could be concluded that the interaction between zeolite cluster and interacting molecules takes place via the atoms of comparable softness values rather than those atoms of nearly equal Fukui function. Moreover, the softness values calculated using DFT at blyp/dnp level for the interacting atoms are comparable. Fukui function and local softness values are calculated using both HF and DFT methods. The local softness values derived from DFT calculations are found to be more reliable in determining the

interacting sites. The interaction energy of the molecules can be calculated by evaluating λ values from the charge transfers at the active site. This scheme results interaction energy of molecules that are in good agreement with experimental and other theoretical results.

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