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Critical Study of Local Reactivity Descriptors for Weak Interactions: Qualitative and Quantitative Analysis of Adsorption of Molecules in the Zeolite Lattice

Sourav Pal* and K. R. S. Chandrakumar

Contribution from the Physical Chemistry Division, National Chemical Laboratory, Pune 411 008, India

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Abstract: In the work described in this paper we have studied the adsorption of gaseous molecules inside the zeolite lattice using recently developed different reactivity descriptors. In particular, we have used Fukui function-based descriptors and local hard−soft acid−base (HSAB) principle for a quantitative and qualitative analysis. This represents the first case in which local HSAB principle has been used for quantitative description of weak adsorption cases.

I. Introduction

The interaction between the molecules or between the molecule and any metal surface is the major factor governing reactions occurring at the interface.[1,2] There can be several reaction sites, and it is important to develop simple descriptors to probe the reactivity of the different sites of a system. In recent years, density functional theory (DFT) has emerged as a powerful tool through which chemical concepts such as reactivity, selectivity, and reaction path of a system have been studied.[3−7] The chemical concepts of chemical potential (μ), electronegativity ($-\mu$), and hardness (η),[8−10] collectively known as chemical reactivity descriptors, have systematized the study in this area. The principle of maximum hardness (PMH),[11] relating the stability of a system to a larger value of hardness, has been tested using semiempirical as well as ab initio quantum chemical techniques.[12] Further, local descriptors such as the Fukui function (FF) and local softness, relating changes in electron density to the number of electrons and the chemical potential, respectively, have been used to determine the site reactivity of a system.[13] Electrophilic and nucleophilic FFs have been used as indications of reactivity to nucleophilic and electrophilic reagents, respectively.[14] However, in a recent study, Roy et al.[15,16] proposed that relative electrophilicity and relative nucleophilicity based on the ratio of electrophilic and nucleophilic local softnesses and its inverse are more reliable descriptors to locate the preferable sites for nucleophilic and electrophilic attack respectively within a molecule. A local version of the hard−soft acid−base (HSAB) principle, proposed by Gazquez and Mendez,[17] is an alternative description of reactivity using local descriptors. However, it involves the descriptors of both of the reacting systems for prediction of reactive sites. In general, the local HSAB principle[17] states that the interaction between any two molecules will occur not necessarily through their softest atoms, but rather through those atoms of the two systems whose FFs are the same. The local version of this principle was proved by minimization of the grand canonical potential. 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. However, for systems with different global softness values, the criterion of application of the local HSAB principle is still an issue. This issue and the feasibility of the local HSAB principle have been studied in part by Pal and co-workers,[18] Geerlings and co-workers,[19] and Ngyuen and co-workers.[6,20,21]

So far, attempts have been made to study the interaction between molecules by employing the local reactivity descriptors at the qualitative level only. The cases studied are cases of

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* Author for correspondence. E-mail: pal@ems.ncl.res.in.

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medium and strong chemical interactions.[22,23] However, there are very few reports of studies of weak interactions using local reactivity descriptors. It would be interesting to assess the performance of the reactivity descriptors for the cases of weak interactions. For such cases, it is important to obtain a quantitative description by the use of descriptors. Local HSAB principle allows the possibility of such a quantitative study. This paper will represent the first such study of weak interactions in the literature. A similar quantitative study of the local HSAB principle has been done only sparingly by Gazquez and Mendez[23] and Mendez et al.[22] for the case of stronger interactions than those described in this paper. The theoretical basis for the quantitative analysis of the local HSAB principle was proposed by Gazquez and Mendez. The formulas of interaction energy derived by Gazquez and Mendez consist of two parts.[17] The first term, ΔE_v,[17] corresponds to the energy change due to chemical potential equalization process at constant external potential, and the second term, ΔE_μ.[24] corresponds to reshuffling of the charge distribution at constant chemical potential μ, which is actually a manifestation of the principle of maximum hardness. The second term, ΔE_μ, involves a constant λ. It has been physically related to the effective number of valence electrons involved in the interaction between the molecules.[23] The term λ bears information on the stability of the system. In an earlier study by Gazquez and Mendez,[23] the reactivity of enolate anions and pyridine derivatives was studied using an arbitrary value of $\lambda = 0.5$. Mendez et al.[22] have studied the reactivity of benzonitrile oxides using the value of $\lambda = 1.0$. They could relate the reactivity of various sites of the given molecule with the energy that is involved in the interaction only at the qualitative level. However, the term λ, representing the dynamical behavior of an electron cloud during a chemical reaction, may become dominant in the case of weak interactions. Hence, an arbitrary definition of λ or complete neglect of that term may lead to erroneous results even at the qualitative level. Consequently, there is a high demand for an intuitive and correct theoretical approach to investigate the problem of obtaining a reliable value of λ for the study of interaction energy and more so for weak cases.

To study the above factors for weak interactions, in the present work we have taken weak adsorption of gaseous molecules at different cationic sites of zeolites as an example problem. There has been a lot of interest[25−27] in studying the reactivity of various sites and the effect of exchange of various metal cations in the zeolite framework using a cluster model from the point of view of adsorption and catalysis. However, experimentally it is difficult to access or observe the effect of interactions of the molecules at different cationic sites due to the complex framework nature of zeolites. Hence, a theoretical study to explore the effects of zeolite framework structure and the cations present inside the zeolite cavity on the interaction of molecules is a pertinent exercise. This study will constitute an important calibration and application of the local HSAB principle to the area of weak interactions and will, at the same time, greatly help us to understand zeolite−molecular interactions. Specifically, we would like to focus our attention on the following issues: (i) prediction of the preferable adsorption reactive site among the various cationic adsorption sites in the zeolite lattice surface and the energy involved at the each reactive site. (ii) the importance of the parameter λ in the case of various molecular interaction processes and the ability to distinguish the interaction process of N_2, CO_2, and CO toward the various cationic sites (Li, Na, and K). and (iii) the reliability of our calculation with the experimental adsorption energy values and trends of the adsorption patterns over different cations.

Our paper is organized as follows: In section II, we give a brief theoretical background of the local HSAB principle and the reactivity descriptors. Section III deals with the interaction energy expression using the local HSAB principle and the definition of the factor λ, and in section IV the methodology and computation details are given. In section V, we present the results of our study and discuss the implications of our results. While discussing the absolute site reactivity of the zeolite and the energy associated with each cationic site, the focus has been kept on a systematic study of the parameter λ and its effect on the adsorption energy.

II. Theoretical Background

II.1. The Local HSAB Principle. In density functional theory, the ground-state energy of an atom or a molecule in terms of its electron density ρ(r) is written as[28]

$$E[\rho] = F[\rho] + \int \mathrm{d}r v(r)\rho(r) \tag{1}$$

where $v(r)$ is the external potential that includes the nuclear potential also, and $F[\rho]$ is the universal Hohenberg−Kohn functional composed of the electronic kinetic energy and the electron−electron interaction energy. The first and second partial derivatives of $E[\rho]$ with respect to the number of electron N under the constant external potential $v(r)$ are defined as the chemical potential μ and the global hardness η of the system, respectively.[8,10]

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(r)} \tag{2}$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} \tag{3}$$

The inverse of the hardness is expressed as

$$S = 1/2\eta \tag{4}$$

The global descriptor of hardness has been an indicator of the overall stability of the system. A rigorous principle of maximum hardness (PMH) relating hardness to stability at constant chemical potential has been proposed by Pearson[29] and proved by Parr and Chattaraj.[11] It has been customary to use a finite difference approximation for μ and η.[5] Using the energies of N, $(N + 1)$, and $(N - 1)$ electron systems, we get the operational

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definition of μ and η as

$$\mu \approx -(\mathrm{IP} + \mathrm{EA})/2 \tag{5}$$

$$\eta \approx (\mathrm{IP} - \mathrm{EA})/2 \tag{6}$$

where IP and EA are the first vertical ionization energy and electron affinity of the chemical species, respectively.

II.2. Local Quantities. The site selectivity of a chemical system cannot, however, be studied using the global descriptors of reactivity. For this, appropriate local descriptors need be defined. An appropriate definition of local softness $s(r)$ is given by

$$s(r) = \left(\frac{\partial \rho(r)}{\partial \mu}\right)_{v(r)} \tag{7}$$

such that

$$\int s(r)\,\mathrm{d}r = S \tag{8}$$

Combining eqs 8 and 4, we can write

$$s(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)}\left(\frac{\partial N}{\partial \mu}\right)_{v(r)} = \left(\frac{\partial \mu}{\partial v(r)}\right)_{N} S = f(r)S \tag{9}$$

where $f(r)$ is defined as the FF.[13] It is obvious that the local softness contains the same information as the FF (i.e., the sensitivity of the chemical potential of a system to a local external potential)[30] as well as additional information about the molecular softness. Using left and right derivatives with respect to the number of electrons, electrophilic and nucleophilic FF and local softness can be defined. To describe the site selectivity or site reactivity of an atom in a molecule, it is necessary to condense the values of $f(r)$ and $s(r)$ around each atomic site into a single value that characterizes the atomic contribution in a molecule. This can be achieved by electronic population analysis. Thus, for an atom x in a molecule, depending upon the type of electron transfer, we have three different types of condensed FF of the atom x:[14]

$$f_{x+} = [q_x(N+1) - q_x(N)] \qquad \text{for nucleophilic attack} \tag{10a}$$

$$f_{x-} = [q_x(N) - q_x(N-1)] \qquad \text{for electrophilic attack} \tag{10b}$$

$$f_{x0} = [q_x(N+1) - q_x(N-1)]/2 \qquad \text{for radical attack} \tag{10c}$$

where q_x is the gross electronic population of atom x in the molecule. The corresponding condensed local softnesses s_{x+}, s_{x-}, and s_{x0} can be defined. Parr and Yang proposed that larger values of FF indicate more reactivity.[13] Hence, the greater the value of the condensed FF, the more reactive is the particular atomic center in the molecule. Subsequently, Gazquez and Mendez proposed a local version of the HSAB principle[17] which states that the interaction between any two chemical species will occur through the centers with nearly equal condensed FFs. This can determine the behavior of different reactive sites with respect to the hard and soft reagents.

III. Local HSAB Principle: Expression for the Interaction Energy and the Definition of λ

Considering the interaction between the stable systems A and B with the number of electrons N_A and N_B, respectively, the interaction energy between these two chemical species can be written within the framework of DFT[5,23] as

$$\Delta E_{\mathrm{int}} = E[\rho_{AB}] - E[\rho_A] - E[\rho_B] \tag{11}$$

where ρ_{AB}, ρ_A, and ρ_B are the electron densities of the systems AB at equilibrium and of the isolated systems A and B, respectively. It has been shown by Gazquez that the interaction between A and B is assumed to take place in two steps.[9,24] In the first step, the interaction will take place at constant external potential through the equalization of chemical potential. In the second step, A and B evolve toward the equilibrium state through changes in the electron density of the global system produced by making changes in the external potential at constant chemical potential. This step is actually a manifestation of the principle of maximum hardness.[24] Hence, the total interaction energy between A and B can be given as

$$\Delta E_{\mathrm{int}} = \Delta E_{\mathrm{v}} + \Delta E_{\mu} \tag{12}$$

Following Gazquez et al,[9,23] the expressions for each term in eq 12 can be written:

$$\Delta E_v \approx -\frac{1}{2}\left(\frac{(\mu_A - \mu_B)^2}{\eta_A + \eta_B}\right) \tag{13}$$

and

$$\Delta E_\mu \approx -\frac{1}{2}N^2(\eta_{AB} - \eta^*_{AB}) \tag{14}$$

In eq 14, η_{AB} is the hardness of the system AB at equilibrium and η^*_{AB} is the hardness of the system when the constituents of the system are far away from each other.

Equation 13 can be written in terms of softnesses as

$$\Delta E_v \approx -\frac{1}{2}\left(\frac{(\mu_A - \mu_B)^2}{S_A + S_B}\right)(S_A S_B) \tag{15}$$

However, the corresponding changes for eq 14 are not so simple, as they involve the total hardness of the system. One has to relate the total hardness of the system AB in terms of the softnesses of the individual systems. In general, the total softness of the system AB at equilibrium can be written as[9]

$$S_{AB} = k(S_A + S_B) \tag{16}$$

where k is the proportionality constant, and S_A and S_B are the softnesses of the isolated systems A and B. It has been shown by Yang et al.[31] that the molecular softness of a system at equilibrium can be replaced by the average of the softness of each constituent of the molecular system. In the limit of separation or dissociation of the molecule into its constituents, the proportionality constant can be approximated as 1, and in the interacting limit, the total softness decreases (conforming to the principle of maximum hardness) and thus k attains a value less than 1. The lower the value of k, the more stable the system is expected to be. In that sense, the proportionality constant k contains information about the stability of the system AB. It can be related to the extent of overlap between the isolated atomic species in the molecule. As the total molecular softness is insensitive to the number of electrons, the difference in the

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softness ($S_{AB} - S*_{AB}$) can be approximated by

$$\Delta S = k'(S_A + S_B) \tag{17}$$

where k' is another proportionality constant. By applying eq 17 in eq 14,

$$\Delta E_\mu \approx -\frac{1}{2}N_{AB}^2 K\left(\frac{1}{(S_A + S_B)}\right) \tag{18}$$

where N_{AB} is the total number of electrons of the system AB. The product of the terms N^2 and K, known as λ,[23] can be related physically to the effective number of valence electrons that have participated in the interaction between A and B. We define the parameter λ as the change in the electron densities of the systems before and after the interaction process. This change will give the effective number of valence electrons participating in the interaction process. Thus, an expression for the term λ can be written as the difference of electron densities of the system A before and after the interaction:

$$\lambda_A = \sum_{i=1}^{M}\rho_{Ai}^{eq} - \sum_{i=1}^{M}\rho_{Ai}^{0} \tag{19}$$

Alternatively, the term λ can be defined as the difference of electron densities for the system B,

$$\lambda_B = \sum_{j=1}^{N}\rho_{Bj}^{eq} - \sum_{j=1}^{N}\rho_{Bj}^{0} \tag{20}$$

where the first terms of the right-hand side of eqs 19 and 20 refer to the sum of the electron densities of each atom in A and B in the molecule AB at equilibrium, respectively, and the second terms in eqs 19 and 20 refer to the electron densities of each atom in the isolated systems A and B, respectively. The number of electrons that are donated effectively to another system will be equal to the number of electrons that have been accepted by the other system. Hence, in principle, the change in electron density of the system A, λ_A in isolated system A, and in the system AB should be equal to the corresponding change in electron density of the system B, λ_B, but with the opposite sign.

From a local point of view, if the interaction between two chemical systems A and B occurs through the kth atom of A, one can express the interaction at the kth atom by replacing the global softness of A with the local softness of the site k in A as

$$(\Delta E_{int})_{Ak} \approx -\frac{1}{2}\left(\frac{(\mu_A - \mu_B)^2}{S_A f_{Ak} + S_B}\right)(S_{Ak} f_{Ak} S_B) - \frac{1}{2}\left(\frac{\lambda}{S_A f_{Ak} + S_B}\right) \tag{21}$$

where f_{Ak} is the Fukui function value of the site k of the system A. According to eq 21, in the case where S_B is large, there is a greater stabilization when the interaction occurs at the site with the greater value of f_{Ak} and vice versa. If the change in the electron density of system A is only at the site of interaction k of A, then the factor λ can be conveniently given as the change in electron density at the site k,

$$\lambda_{Ak} = q_{Ak}^{eq} - q_{Ak}^{o} \tag{22}$$

where q_{AK}^{eq} and q_{Ak}^{o} are the densities of the kth atom of the system A in the complex AB and in the isolated system A, respectively.

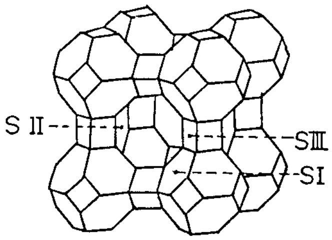

Figure 1. Unit cell of A-type zeolite. The reactive sites SI, SII, and SIII are located at the 6-m, 8-m, and 4-m rings.

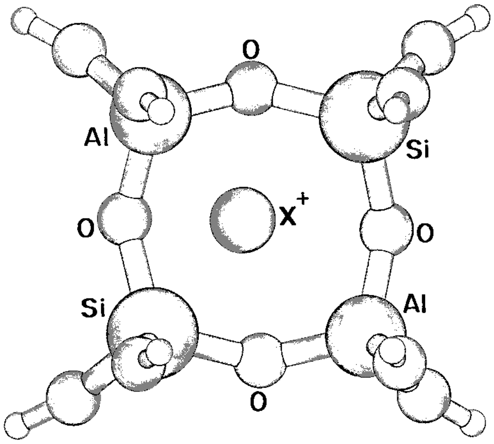

Figure 2. Cationic (X^+) position at the four-membered ring, site SIII. The nearest oxygen−cation distances are 2.59 and 2.95 Å for Na and K, respectively. All Si and Al atoms are terminated by OH groups.

IV. Methodology and Computational Details

The unit cell of Li−A, Na−A, and K−A zeolite was generated from the crystal structure as reported in the literature, where the Si/Al ratio is 1.[32] Three distinct cationic sites were located. To study the nature of the reactivity of sites SI and SIII toward the incoming molecules, we have considered a dimer cluster model. The dimer cluster for each site SI and SIII has been cut from the six-membered (6-m) ring and the four-membered (4-m) ring, respectively, and the Si−O and Al−O dangling bonds of the cluster are saturated with hydrogen atoms. The O−H bond distance of the terminal OH bond is kept fixed at 0.96 Å, and the H atoms are aligned in the direction of the T−O−T (T = Si, Al) bond axis. The zeolite cluster and the complexes of molecules studied are shown in Figures 1−4. All the calculations using this model were performed at the level of the ab initio Hartree−Fock (HF) method using 3-21G(d,p) and a more extensive 6-31G(d,p) basis set. Since in the case of potassium the 6-31G(d) basis set is not available in the GAMESS ab initio program,[33] the basis set is given externally.[34] To examine the effect of cluster size, we have also considered a trimer cluster model (Figure 5) and studied the interaction of the molecules for the site SI using 3-21G(d,p) and 6-31G(d,p) basis sets. Since the trimer model cluster cannot be generated from a 4-m ring (site SIII), we have considered only the site SI, and it has been generated from a 6-m ring, as in the case of the dimer cluster model of site SI. The restricted HF method has been used for the energy calculation of neutral

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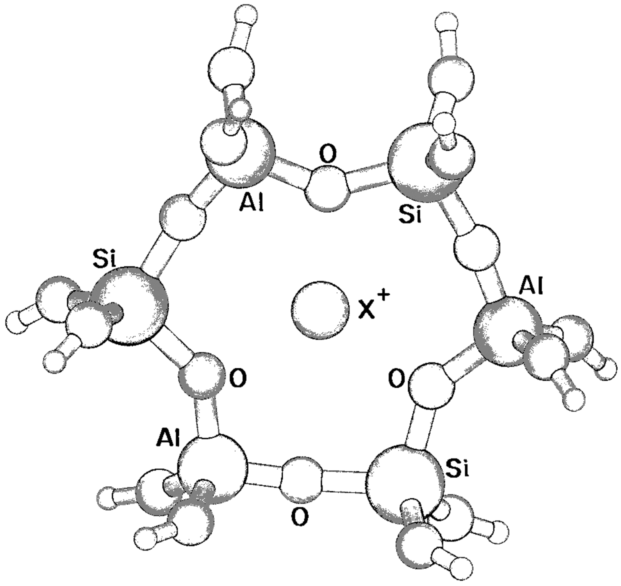

Figure 3. Cationic (X^+) position at the six-membered ring, site SI. The nearest oxygen−cation distances are 1.88, 2.32, and 2.60 Å for Li, Na, and K, respectively.

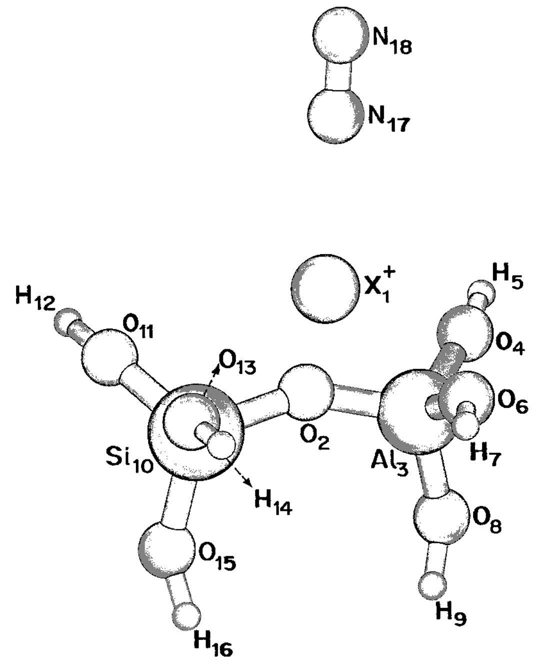

Figure 4. Dimer model cluster with N_2 molecule for X^+ cations (Li, Na, and K) used for the interaction energy calculation.

species, and for the corresponding anionic and cationic systems the ROHF method has been performed.

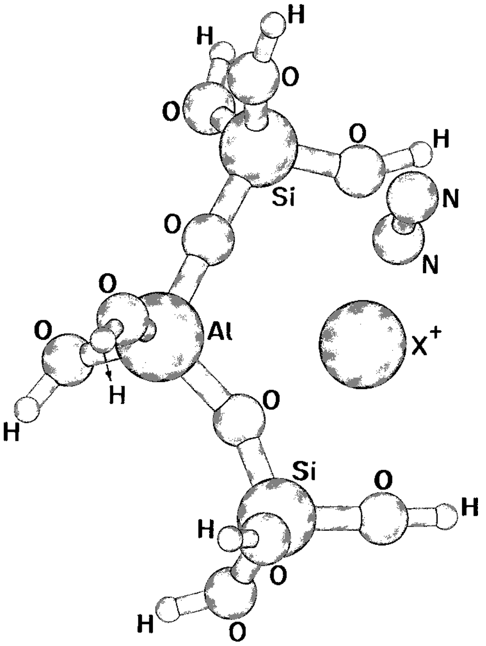

Figure 5. Trimer model cluster with N_2 molecule for X^+ cations (Li, Na, and K) of site SI, used for the interaction energy calculation.

Condensed FF and local softness for each cationic cluster were calculated via eq 10a using Mulliken[35] and Löwdin[36] population analysis (MPA and LPA). MPA and LPA are based on the partition of the electrons into net atomic populations in the atomic basis functions ψ_n. In MPA, population on an atom is defined to be sum over the diagonal elements centered on that atom of the (**PS**) matrix, where **P** is the density matrix over the atomic orbital basis and **S** is the overlap matrix of atomic orbitals. On the other hand, LPA atomic population is the sum of the corresponding diagonal elements of ($\mathbf{S}^{1/2}\,\mathbf{P}\,\mathbf{S}^{1/2}$). Thus, in LPA, the total number of electrons is the trace of the density matrix in terms of a symmetrically orthogonal basis. The ab initio calculations were performed using the GAMESS[33] system of programs on an IRIX-6.2 Silicon Graphics workstation. Since the extraframework cations are the usual adsorption sites in zeolites that are electrophilic in nature, the condensed local reactivity descriptors s_x^+ and f_x^+ (x = Li, Na, and K) for the cations at different reactive sites of the zeolite were calculated. Along with these local descriptors, we have also used the recently proposed new descriptor, namely, relative electrophicity (s_x^+/s_x^-), defined as the ratio of s_x^+ and s_x^-, to obtain the site reactivity of the various cationic sites. In a recent study by Roy et al.[15,16] the "relative electrophilicity" and its inverse "relative nucleophilicity" have been considered as reliable parameters to locate the intramolecular reactive sites. When there are two reactive sites, the reactant molecule or the incoming molecule will prefer to bind where the relative electrophilicity or relative nucleophilicity is high for a nucleophilic or an electrophilic kind of reaction, respectively. This ratio of s_x^+ and s_x^- has also been shown to be less sensitive to the basis set and correlation effects.

Only the bond between the cation and the molecule in the complex is optimized. The molecules are allowed to interact perpendicularly with the cationic site, and the angle between the cation−molecule is kept at 180°. Throughout our calculations, the interaction site for the zeolite model is the cation, and for the molecule, the end part of it has been considered; i.e., N atom in N_2, O in CO_2, and C in CO are considered as the interacting part. As the geometry of molecules is less affected in the presence of the zeolite lattice, we have fixed the experimental geometry for the above molecules and hence only the the cation−molecule distance is varied.

V. Results and Discussions

V.1. Site Reactivity Order in Various Cation-Exchanged Zeolite−A: A Qualitative Analysis. The zeolites are aluminosilicate materials,[37] and most of the zeolites will show the varying catalytic properties that are related to several factors,[38] namely (i) the Al content in the framework, Si/Al ratio, (ii) the shape and pore size of the cavity, and (iii) the presence and nature of the cations at various positions. For example, the cations can be found at the big cavities or small rings like the six-membered (6-m) or four-membered (4-m) rings, depending upon the framework structure of zeolite, and thus it offers different types of reactive sites for the interaction of the

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Table 1. Global Property Values for the Zeolite-A Model Cluster and Molecules (in Atomic Units)

system		chemical potential		global softness	
		3-21G(d,p)	6-31G(d,p)	3-21G(d,p)	6-31G(d,p)
Li	SI	−0.134	−0.142	7.280	6.719
Na	SI	−0.143	−0.151	8.411	8.070
	SIII	−0.137	−0.148	8.330	7.764
K	SI	−0.136	−0.144	8.303	7.855
	SIII	−0.135	−0.145	8.325	7.697
N_2		−0.216	−0.227	2.758	2.788
CO_2		−0.183	−0.192	3.351	3.364
CO		−0.176	−0.175	3.147	3.137

molecule.[39] At all sites the interactions of molecules with the cations are critical in determining the catalytic transformation of the molecules[40] or in the molecular gas separation processes.[41] In A-type zeolites, three different types of cations are distributed which are located at the 6-, 8-, and 4-m rings in the zeolite lattice,[37] and we will hereafter refer to these as SI, SII, and SIII, respectively, as shown in the Figure 1. The extraframework cations are the actual adsorption sites for the interaction of any incoming molecule, and the adsorption or any kind of catalytic transformation of molecules will normally take place at the cages of the zeolites. Since the cationic site SII is located at an 8-m ring, i.e., at the entrance of the zeolite α cage (see Figure 1), it hinders the incoming molecule entering inside the cages, and hence the site SII is of least importance. Thus, we have not considered the site SII for the present study. We have not optimized any cluster fully as the complete relaxation of the cluster leads to structures that do not resemble experimental geometry. Especially for our calculations, we would like to address the reactivity of the available sites that depends on the structural geometry of the local sites, and therefore we have not optimized any of the clusters. The difficulty of geometry optimization of a cluster model was pointed out in a study by Hill et al.[27] This fact has also been realized in a recent study by Deka et al.[42] and Brand et al.,[43] and it has been shown that the full relaxation of the cluster does not lead to the experimental acidity sequence of various metal-exchanged zeolite clusters. Table 1 contains the chemical potential and the global softness values of the zeolite model cluster as well as the interacting molecules at both 3-21G(d,p) and 6-31G(d,p) basis sets. The global softness values of the zeolite and the adsorbed molecules differ significantly, and hence the mapping of reactivity of adsorbed molecules with the cationic zeolite model clusters becomes difficult on the basis of the softness values.

We now consider the reactivity of site SI. The values of condensed FF, local softness, and relative electrophilicity, obtained through Mulliken and Löwdin population schemes, are tabulated in Table 2. The FF values of the site SI cations calculated through the Mulliken population analysis (MPA) in the 3-21G(d,p) and 6-31G(d,p) basis sets are in the increasing order of Li > K > Na and K > Li > Na, respectively. The trend of FF values obtained from the Löwdin population analysis (LPA) is in the order of K > Na > Li. On the other hand, the local softness parameter follows the reactivity order as K > Na > Li. The reactivity order obtained by the relative electrophilicity values increases as Li > K > Na, and it is important to note that the reactivity order derived from the relative electrophilicity parameter follows the same order irrespective of the basis set and the electron population analysis.

We now turn to the reactivity of site SIII. The SIII cations are generally found in the α cage of the zeolite, in front of the 4-m ring. The Li ion-exchanged zeolite is normally synthesized with a sodium cation.[32] Li ions are located at sites SI and SII, but at site SIII sodium cations are occupied. Hence, the SIII reactivities of only Na− and K−A zeolites are described here. Based on the FF and local softness values, one can infer from Table 3 that the reactivity order of SIII in K−A should be greater than that of the Na−A zeolite model cluster. The relative electrophilicity values for both of the cationic sites indicate that the reactivity order of SIII in Na−A should be greater than that in K−A, which is contradictory with the reactivity order derived from the FF and condensed local softness values. From the above arguments, a definite conclusion about the site reactivity order for the different cations from the reactivity parameters such as FF, local softness values, and relative ratio term is not so obvious. Despite this apparent conflict in the conclusions on the reactivity order drawn from the reactivity parameters, we believe that the relative electrophilicity term is a good parameter to locate the reactive site, as the values give a consistent trend irrespective of the basis set and electron population analysis. From the various systematic studies such as the acidity order for the various metal-exchanged zeolites[42] and the electrophilic or nucleophilic attack of the molecules at the various sites of the aromatic and aliphatic carbonyl compounds,[15,16] we have confirmed that the relative ratio term gives a better description of the intramolecular site reactivity than other reactive parameters.

Although the ambiguity arises in the prediction of the reactivity order in the above systems, one can observe in all cases that the site SIII is more reactive than SI on the basis of FF and the relative ratio terms. In the case of Na−A, the difference between the FF values for the sites SI and SIII is less compared to that of the relative electrophilicity terms. Both the FF and relative electrophilicity values in cases of K−A zeolite for the sites SI and SIII differ marginally. The reason for the greater reactivity of SIII is clearly indicated by the spatial extra stability of SI cations, as they are coordinated to more oxygen atoms, in contrast to the naked site SIII cations (Figures 2 and 3). Hence, the reactivity of the site SIII cation is expected to be more than that of the partially shielded SI cationic site. The local reactivity descriptors nicely interpret the trend on the reactivity of the cationic sites. The recent study carried out by our group[44] on the determination of electric field exerted by the zeolite lattice ions shows that the electric field strength is greater at the site SIII than at the other cationic sites SI and SII. Moreover, the experimental studies based on infrared[45] and molecular dynamics studies[46] reveal that the interaction of methane and nitrogen molecules takes place at the site SIII of the Na−A zeolite. It should be mentioned here that, despite

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Table 2. Condensed Local Softness and Fukui Function Values for the Zeolite-A Model Cluster from Mulliken and Löwdin Population Analysis for the Cationic Sites Li, Na, and K at Site SI (in Atomic Units)

		Fukui function f_x^+		local softness s_x^+		relative electrophilicity (s_x^+/s_x^-)	
system		3-21G(d,p)	6-31G(d,p)	3-21G(d,p)	6-31G(d,p)	3-21G(d,p)	6-31G(d,p)
Li	Mulliken	0.955	0.948	6.951	6.368	52.058	44.452
	Löwdin	0.880	0.852	6.404	5.727	30.873	39.833
Na	Mulliken	0.920	0.924	7.736	7.452	18.629	23.893
	Löwdin	0.923	0.922	7.767	7.440	19.395	27.025
K	Mulliken	0.949	0.975	7.880	7.663	25.789	45.560
	Löwdin	0.953	0.905	7.911	7.106	23.800	38.197

Table 3. Condensed Local Softness and Fukui Function Values for the Zeolite-A Model Cluster from Mulliken and Löwdin Population Analysis for the Cationic Sites Na and K at Site SIII (in Atomic Units)

		Fukui function f_x^+		local softness s_x^+		relative electrophilicity (s_x^+/s_x^-)	
system		3-21G(d,p)	6-31G(d,p)	3-21G(d,p)	6-31G(d,p)	3-21G(d,p)	6-31G(d,p)
Na	Mulliken	0.921	0.937	7.672	7.273	39.940	46.590
	Löwdin	0.913	0.909	7.605	7.060	27.198	41.033
K	Mulliken	0.947	0.978	7.886	7.531	26.187	41.438
	Löwdin	0.951	0.960	7.916	7.387	24.214	43.165

the small size of the model cluster considered in our calculations, we could retain the structural reactivity of each site consistent with the experimental studies and other theoretical studies.

V.2. Interaction of N_2, CO_2, and CO Molecules with the Cluster Model: A Quantitative Analysis. The quantitative energy analysis through the local HSAB principle is expected to solve the ambiguity raised in the interpretation of the site reactivity order obtained from the reactivity descriptors as discussed in section V.1. Local HSAB principle can give a quantitative estimate of this using only local quantities. However, this demands the definition of the parameter λ empirically as we discussed in section III. Gazquez and Mendez as well as Geerlings and co-workers have used arbitrary values of 0.5 and 1.0 for λ to describe the reactivity of enolate ions and 1,3-cycloaddition reactions of benzonitrile oxide with an alkene, respectively.[23,22] This was adequate to describe the above reaction. However, the bonding involved in that case is quite different from the ones we would like to study. Our study involves weak interaction for which no λ value exists in the literature. In the course of our study as detailed in what follows, we establish the value of this quantity for the weak interaction of gaseous molecules N_2, CO_2, and CO with the zeolite extraframework cations Li, Na, and K. We conclude that the value of λ is substantially different than those in the cases of stronger interactions.

Considering the case of nitrogen, the interaction of a nitrogen molecule with the cationic sites of the zeolite lattice is a weak interaction that is evidenced by the experiment[47] as well as theoretical[48] values of the interaction energy below 20 kJ/mol. As shown in Table 5, the ΔE_v value for sites SI and SIII of Li, Na, and K in dimer cluster models ranges from 14.163 to17.887 kJ/mol. These quantities cannot be regarded as large compared to the ordinary covalent or ionic bond energy. At the same time, the calculation of ΔE_μ becomes difficult, as the value of the parameter λ is not defined, and it is also observed that the nature of binding changes with the value of λ. For example, for the value of λ from 0.0 to 0.5, the corresponding ΔE_{int} is calculated. The linear relationship between λ and ΔE_{int} is plotted in Figure 6 for all molecules. It can be seen from the plot of λ vs ΔE_{int} that the stability of nitrogen complexes increases with increasing value of λ. The results show the need for an accurate λ value. As we know from chemical intuition that the binding nature of N_2 with Na cation is a weak interaction, it is expected that the effective electron transfer should be much less. To obtain this, the zeolite model cluster with Na cation and the N_2 molecule are allowed to interact in a linear fashion, and the optimization of the cluster cation−molecule is carried out. MPA gives a better description of the reactive sites in a molecule through the descriptors, and hence the factor λ has been calculated through MPA. MPA usually results in larger charge separation between the atoms. This may be a probable reason why it performs well in ionic systems as zeolites.

Table 4. Mulliken Electron Population on Each Atom[a] in the Nitrogen-Adsorbed Complex of Na−A Zeolite Model Cluster at Site SIII

	complex far from equilibrium		complex at equilibrium	
atom	3-21G(d,p)	6-31G(d,p)	3-21G(d,p)	6-31G(d,p)
Na1	10.543	10.346	10.644	10.380
O2	8.803	8.866	8.803	8.867
Al3	11.823	11.591	11.820	11.587
O4	8.657	8.850	8.657	8.850
H5	0.752	0.678	0.753	0.678
O6	8.677	8.849	8.678	8.849
H7	0.778	0.696	0.779	0.697
O8	8.720	8.873	8.720	8.873
H9	0.751	0.675	0.753	0.676
Si10	12.445	12.514	12.442	12.510
O11	8.650	8.741	8.650	8.742
H12	0.687	0.627	0.687	0.627
O13	8.683	8.730	8.683	8.731
H14	0.678	0.618	0.680	0.619
O15	8.652	8.714	8.653	8.715
H16	0.701	0.634	0.702	0.634
N17	7.000	7.000	7.006	7.008
N18	7.000	7.000	6.892	6.958

[a] The numbering of the atoms is given in Figure 4.

In the determination of λ, it can implicitly be assumed that when A and B are interacting weakly through the *k*th atom of molecule A and *l*th atom of molecule B, only those two atoms participate in the reshuffling process of charge distribution. Hence, the changes in the electron population on all other atoms

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Table 5. Interaction Energy of N_2 with Li, Na, and K−Zeolite-A Dimer Model Cluster (Energy Values in kJ/mol and λ Value in Atomic Units; ΔE_{TE} Is the Available Theoretical and Experimental Interaction Energy)

cation		λ		ΔE_v		ΔE_μ		ΔE_{tot}		
		3-21G(d,p)	6-31G(d,p)	3-21G(d,p)	6-31G(d,p)	3-21G(d,p)	6-31G(d,p)	3-21G(d,p)	6-31G(d,p)	$\Delta E_{TE}{}^a$
Li	SI	0.121	0.047	−17.692	−18.156	−16.398	−6.774	−34.090	−24.930	−27.2
Na	SI	0.099	0.034	−14.163	−15.248	−12.393	−4.317	−26.557	−19.565	−20.0
	SIII	0.102	0.034	−16.692	−16.496	−12.830	−4.472	−29.522	−20.969	
K	SI	0.088	0.021	−17.183	−18.172	−10.804	−3.431	−27.988	−20.820	
	SIII	0.094	0.028	−17.874	−17.792	−11.600	−3.676	−29.475	−21.376	

[a] References 47 and 48.

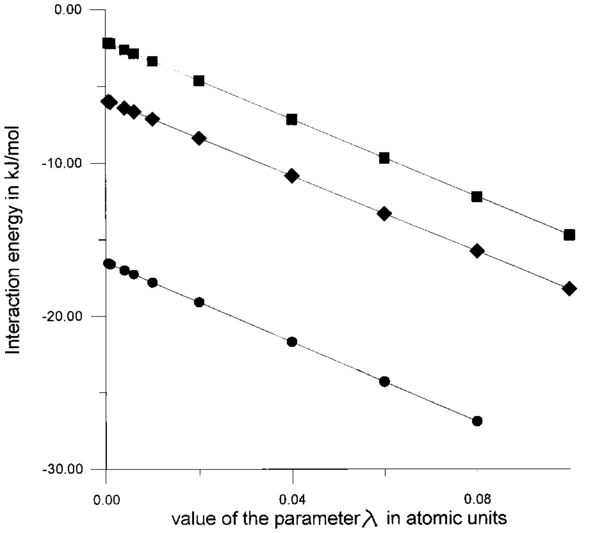

Figure 6. Variation of interaction energy ΔE_{int} with the parameter λ. Only the data for the cationic site SIII of sodium at the 6-31G(d,p) basis set level are given. (●, N_2; ◆, CO_2; ■, CO).

can be neglected. Although this may be an approximation, it can be reasonably assumed that the greatest change in the population will occur at the atomic sites that participate directly in the interaction. In Table 4, the electron population on each atom in the Na−A zeolite model clusters for the cationic site SIII is explicitly given. Evidently, it can be seen from Table 4 that the most significant change in the electron population has occurred only at the cationic site of the zeolite model cluster. Using eq 22, the λ values for the Li, Na, and K zeolite cluster complexes of N_2 are calculated. It can be seen that the λ values listed in Table 5 are all positive and small. This λ value is used to calculate the interaction energy arising out of reshuffling. In the case of the interaction of the nitrogen molecule with the cations, the energy term ΔE_v calculated with 6-31G(d,p) contributes to a larger extent rather than the reshuffling of the charge distribution. However, the energy terms ΔE_v and ΔE_μ calculated with 3-21G(d,p) indicate that both are contributing equally. It may be due to the overestimation of the electron population on the reactive sites by the use of the 3-21G(d,p) basis set. To verify the efficiency of this method, some available experimental data are also shown in Table 5 for comparison with our computed adsorption energy. It can be seen that the overestimation in the order of a few kilojoules per mole is present in all the complexes listed here, probably because of the limited accuracy in the calculation of structural parameters and the cluster termination. Nevertheless, such overestimation is systematic and consistent, and there is an excellent linear relationship between the computed and the experimental adsorption energies. The computed ΔE_{int} of N_2 with the cationic sites at SIII is significantly greater than that of the site SI, which unambiguously supports our earlier discussion on the greater site reactivity of SIII as explained by the relative electrophilicity term and the FF.

The adsorption mechanism of N_2 with cations is well established and it is essentially electrostatic in nature, and the interaction arises due to the quadrupolar interaction of the nitrogen molecule with the electric field generated by the cation. The quadrupole moment of the N_2 molecule is −1.093 atomic units.[49] The charges of the molecule are less affected by the presence of cations, which clearly indicates that the interaction of N_2 is influenced by the larger quadrupolar moment of the N_2 and the field generated by the cation. When we exchange the Na cation by Li and K, the interaction behavior is affected significantly due to the variation in the electric field that is exerted by the cations.

The interaction of CO_2 follows the same trend as in the case of N_2 interaction: the dipole moment of CO_2 is zero, and the interaction with cations arises partially due to the electrostatic interaction as well as by the notable charge-transfer process. The interaction energy for CO_2 with cations is expected to be higher than that in the nitrogen case. It should be noted that the mean polarity of the C−O bond in CO_2 is greater than that of N_2. Hence, the contribution of the interaction energy due to the charge transfer will be more than that in the nitrogen case. In other words, the value of the factor λ should be considerably higher than the value of λ in the case of nitrogen interaction. The inspection of the energy values in Table 6 indicates that ΔE_v is lower and ΔE_μ is higher than that of the nitrogen case that can be easily analyzed by looking at the values of the quadrupole moment of N_2 and CO_2. Since the quadrupole moment of N_2 is higher than that of CO_2, the contribution of interaction energy due to the ΔE_v term will be small, but the contribution of ΔE_μ is high due to the increase in the cation−dipole interaction. The energy value that is calculated using the basis set 6-31G(d,p) for the case of CO_2 is lower than the experimental value. However, it essentially follows the trend expected from the experimental studies.[50,51] The use of basis set 3-21G(d,p) gives better interaction energy values, which are comparable to the experimental energy values.

Finally, in the case of the CO molecule, the most significant aspect is that the maximum part of the interaction energy comes from the ΔE_μ term and the parameter λ has a vital role in determining the interaction energy, as results presented in Table 7 show. The agreement between the interaction energy calculated using local HSAB principle and the experimental values[47] is quite satisfactory. The recent DFT[52,53] study on the CO

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Table 6. Interaction Energy of CO_2 with Li, Na, and K−Zeolite-A Dimer Model Cluster (Energy Values in kJ/mol and λ Value in Atomic Units; ΔE_{TE} Is the Available Theoretical and Experimental Interaction Energy)

cation		λ		ΔE_v		ΔE_μ		ΔE_{tot}		
		3-21G(d,p)	6-31G(d,p)	3-21G(d,p)	6-31G(d,p)	3-21G(d,p)	6-31G(d,p)	3-21G(d,p)	6-31G(d,p)	ΔE_{TE}[a]
Li	SI	0.124	0.051	−7.320	−7.161	−15.858	−6.922	−23.178	−14.083	−54.4
Na	SI	0.110	0.037	−4.884	−5.112	−13.068	−4.474	−17.952	−9.586	−48.2
	SIII	0.105	0.039	−6.539	−5.923	−12.488	−4.483	−19.027	−10.756	
K	SI	0.101	0.024	−6.844	−6.958	−11.786	−2.915	−18.630	−9.873	−46.9
	SIII	0.114	0.030	−7.314	−6.727	−13.348	−3.584	−20.662	−10.311	

[a] References 50 and 51.

Table 7. Interaction Energy of CO with Li, Na, and K−Zeolite-A Dimer Model Cluster (Energy Values in kJ/mol and λ Value in Atomic Units; ΔE_{TE} Is the Available Theoretical and Experimental Interaction Energy)

cation		λ		ΔE_v		$\Delta E\mu$		ΔE_{tot}		
		3-21G(d,p)	6-31G(d,p)	3-21G(d,p)	6-31G(d,p)	3-21G(d,p)	6-31G(d,p)	3-21G(d,p)	6-31G(d,p)	ΔE_{TE}[a]
Li	SI	0.111	0.146	−5.230	−2.941	14.417	−20.155	−19.648	−23.096	−19.7
Na	SI	0.086	0.088	−3.220	−1.650	−10.397	−10.921	−13.617	−12.571	−15.07
	SIII	0.088	0.091	−4.556	−2.122	−10.666	−11.500	−15.222	−13.621	
K	SI	0.063	0.063	−4.798	−2.716	−7.481	−7.818	−12.278	−10.382	−8.79
	SIII	0.082	0.073	−5.184	−2.584	−9.716	−9.002	−14.900	−11.586	

[a] Reference 53.

Table 8. Interaction Energy of N_2, CO_2, and CO with Li, Na, and K at Site SI−Zeolite-A Using Trimer Model Cluster (Energy Values in kJ/mol and λ Value in Atomic Units)

cation at site SI		λ		ΔE_v		$\Delta E\mu$		ΔE_{tot}	
		3-21G(d,p)	6-31G(d,p)	3-21G(d,p)	6-31G(d,p)	3-21G(d,p)	6-31G(d,p)	3-21G(d,p)	6-31G(d,p)
N_2	Li	0.115	0.034	−19.720	−20.807	−15.585	−5.011	−35.305	−25.818
	Na	0.099	0.031	−18.584	−19.546	−12.631	−4.097	−31.215	−23.646
	K	0.062	0.013	−20.292	−21.143	−7.553	−7.553	−27.845	−22.760
CO_2	Li	0.109	0.039	−8.747	−9.023	−13.902	−5.417	−22.649	−14.441
	Na	0.096	0.034	−7.849	−7.949	−11.605	−4.247	−19.454	−12.196
	K	0.065	0.013	−8.990	−8.957	−7.537	−1.528	−16.528	−10.485
CO	Li	0.095	0.118	−6.421	−4.417	−12.453	−16.703	−18.874	−20.870
	Na	0.088	0.080	−5.639	−3.364	−10.809	−10.120	−16.449	−13.484
	K	0.058	0.042	−6.569	−3.397	−6.764	−4.898	−13.333	−8.956

molecular interaction with the alkali metal cation-exchanged zeolite cluster also predicts the interaction energies as 19.7, 15.0, and 8.8 kJ/mol for the cations Li, Na, and K, respectively, which is very close to our results.

To check the effect of cluster size, the interaction energies of the above molecules with the cations in a trimer model cluster of zeolite have been reported in Table 8, and it can be seen that the interaction energy follows essentially the experimental order, Li > Na > K in all cases. On comparing these interaction energy values with those obtained using the dimer model cluster, one can see that the variation is only marginal and the change in the interaction energy values is in the order of ±2−3 kJ/mol. Thus, we can conclude that the interaction energies obtained through the local HSAB principle and using the reactivity descriptors are quite stable with respect to the dimension of the cluster model of zeolites.

Conclusions

We have critically analyzed the site reactivity and the effect of zeolite framework on the adsorption of the molecules using the local reactivity descriptors. We observed that all the reactivity descriptors suggest the site SIII to be the most reactive site in zeolite-A irrespective of the cation present in the sites. We have studied adsorption of N_2, CO, and CO_2 molecules in the zeolite lattice. The condensed FF reproduces the reactivity order in most of the cases, only when it is evaluated using Mulliken population. Local softness fails to produce the correct reactivity order for each case. However, the relative electrophilicity furnishes the correct site reactivity order most reliably independent of the population scheme or the basis set. We have also used local HSAB principle to obtain a quantitative estimate of the adsorption energy using only variables of the reacting molecules. The estimate of the interaction energy was done by evaluating the value of the parameter λ as charge transfer at the reactive site. This scheme results in the interaction energies, which are in good agreement with experimental and other theoretical interaction energy values. This suggests the efficacy of local HSAB principle in describing the weak intermolecular interaction and the validity of our quantitative definition of the parameter λ. Our work suggests the possible use of local HSAB principle in describing weak interactions, and the simplicity and flexibility of this approach allow one to consider easily a wide range of model geometries, thus facilitating the systematic investigation of structural and energetic trends.

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