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Reactivity Index Scale for Interaction of Heteroatomic Molecules with Zeolite Framework

Abhijit Chatterjee,* Takashi Iwasaki, and Takeo Ebina

Inorganic Material Section, Tohoku National Industrial Research Institute, 4-2-1 Nigatake,
Miyagino-ku, Sendai 983-8551, Japan

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The activity of different interacting heteroatomic molecules such as CO_2, CO, CH_4, NO, NO_2, NH_3, and H_2O along with the zeolite framework is investigated using a range of reactive indexes using density functional theory (DFT). From the values of the local softness and the charge on the hydrogen atom of the bridging hydroxyl, used as the first approximation to the local hardness, it is concluded that the acidities of the zeolite-type model systems, used in the calculations, are dependent on several characteristics which are of importance within the framework of the hard and soft acids and bases (HSAB) principle. We investigated the local softness of the interacting species, namely, CO_2, CO, CH_4, NO, NO_2, NH_3, and H_2O, to compare their affinity with the zeolite framework cluster models. The recently proposed local hard−soft acid−base principle characterizes the reactive centers of two systems on the basis of equal local softness. We validate the proposition by considering the interaction between systems with different global softness, which further paves the way for proposing a novel qualitative scale "reactivity index" in comparing the activity of reactant species interacting with the zeolite framework. The results were compared with interaction energy calculations using DFT to validate the proposition. The result shows good agreement with the reactivity index scale for heterotomic molecules where the interaction is through the most nucleophilic atoms for CH_4, CO_2, CO, NH_3, and H_2O and the results differ for multisite interaction observed in the case of NO_2 and NO. The proposed order of activity in terms of both methodologies is $CH_4 < CO_2 < NH_3 < H_2O < CO$.

Introduction

Currently global warming has become a serious problem. This is due to the increasing concentration of carbon dioxide, carbon monoxide, methane, nitrous oxide, nitrogen dioxide, chlorofluorocarbons, etc. in the atmosphere. Technologies are developing in the current decade to overcome these problems, especially removal of carbon dioxide and nitrous oxide to give a cleaner environment for the next generation.[1,2] Although direct separation processes are effective to remove carbon dioxide and NO_x from the exhaust gases released from stationary sources such as thermal power plants or fossil fuel combustion in large factories,[3,4] materials of high thermal and chemical resistance are needed for such facilities because the temperatures of the exhaust gases are very high. Zeolite is one of the potential candidates. So far, there are many experimental and theoretical studies to monitor the interaction of heteroatomic gases with zeolite framework, but there is no study to correlate the activity of the heteroatomic gas molecules in terms of interaction with zeolite framework. This will rationalize the choice of zeolite framework for removal of a particular gas from the environment or reaction mixture depending on its activity. Now, the hard−soft acid−base (HSAB) principles classify the interaction between acids and bases in terms of global softness. Pearson[5] proposed the global HSAB principle. 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 (PMH),[6] which states that, for a constant external potential, the system with the maximum global hardness is most stable. Many groups have numerically tested both HSAB and PMH.[7−10] In recent days, density functional theory (DFT) has gained widespread use in quantum chemistry. Indeed many useful and important chemical concepts such as electronegativity[11] and hardness and softness[12] appear naturally within DFT.[13] Some DFT-based local properties, e.g., Fukui functions and local softness,[14] have already been used for the reliable predictions in various types of electyrophilic and nucleophilic reactions.[15−18] The subject of reactivity index is a subject of current interest. There are many recent studies which reveal that DFT-based reactivity descriptors can reproduce the experimenatlly observed protonation sites,[19] 1,3-dipolar cycloaddition,[20−22] reactivity of intermediates of the aromatic nucleophilic substitution,[23] and reactivity sequences of carbonyl compounds toward nucleophilic attack on them.[24] But there are very few studies in the area of heteroatomic interaction with zeolites, for proposing new material of interest. Moreover, Gazquez and Mendez[25] proposed that when two molecules A and B of equal softness interact, thereby implicitly assuming one of the species is acting as a nucleophile and the other as an electrophile, then a novel bond would likely form between an atom A and an atom B whose Fukui function values are close to each other. They also propose that local softness may play the same role as Fukui functions when the softness of two interacting molecules is different. This can be considered as a local version of the HSAB principle.[26] The determination of the specific sites of interaction between two chemical species is of fundamental importance to determine the products of a given reaction without actual calculations of the corresponding potential energy surface. The aim of the present communication is to use DFT-based local reactivity descriptors such as condensed Fukui functions or local

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* Corresponding author. E-mail: chatt@tniri.go.jp. Fax: +81-22-236-6839. Phone: +81-22-237-5211.

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softness or reactivity index to explain the activity of several reacting species interacting with zeolite framework. The activity of zeolite framework clusters was also monitored. The reactivity indexes of electrophilic and nucleophilic sites were compared. The results were compared with the interaction energy calculations for each molecule with zeolite framework using DFT. The interaction site of the molecule while interacting with the zeolite framework plays a crucial role as observed in this study. Finally, a novel qualitative scale is proposed in terms of the activity of the heteroatomic molecules as obtained from their localized properties in terms of explaining their nature of interaction with zeolite framework.

Theory

Let us first recall the definitions of various quantities employed. The Fukui function, $f(r)$ is defined by[14]

$$f(r) = [\delta\mu/\delta\upsilon(r)]N = [\delta\rho(r)/\delta N]\upsilon \tag{1}$$

The function 'f' is thus a local quantity, which has different values at different points in the species, and N is the total number of electrons. Since $\rho(r)$ as a function of N has slope discontinuities, eq 1 provides the following three reaction indices:[14]

$$f^{-}(r) = [\delta\rho(r)/\mathrm{d}N]\upsilon \text{ (governing electrophilic attack)}$$

$$f^{+}(r) = [\delta\rho(r)/\mathrm{d}N]\upsilon \text{ (governing nucleophilic attack)}$$

$$f^{0}(r) = 1/2[f^{+}(r) + f^{-}(r)] \text{ (for radical attack)}$$

In a finite difference approximation, the condensed Fukui function[27] of an atom, say x, in a molecule with N electrons are defined as:

$$f_x^{\,+} = [q_{\mathrm{x}}(N+1) - q_{\mathrm{x}}(N)] \text{ (for nucleophilic attack)} \tag{2}$$

$$f_x^{\,-} = [q_{\mathrm{x}}(N) - q_{\mathrm{x}}(N-1)] \text{ (for electrophilic attack)}$$

$$f_x^{\,0} = [q_{\mathrm{x}}(N+1) - q_{\mathrm{x}}(N-1)]/2 \text{ (for radical attack)}$$

Where q_{x} is the electronic population of atom x in a molecule. In density functional theory, hardness (η) is defined as[28]

$$\eta = 1/2(\delta^2 E/\delta N^2)\upsilon(r) = 1/2(\delta\mu/\delta N)\upsilon$$

The global softness, S, is defined as the inverse of the global hardness, η.

$$S = 1/2\eta = (\delta N/\delta\mu)\upsilon$$

The local softness $s(r)$ can be defined as

$$S(r) = (\delta\rho(r)/\delta\mu)\upsilon \tag{3}$$

Equation 3 can also be written as

$$S(r) = [\mathrm{d}\rho(r)/\delta N]\upsilon[\delta N/\delta\mu]\upsilon = f(r)S \tag{4}$$

Thus, local softness contains the same information as the Fukui function $f(r)$ plus additional information about the total molecular softness, which is related to the global reactivity with respect to a reaction partner, as stated in the HSAB principle. Using the finite difference approximation, S can be approximated as

$$S = 1/(\mathrm{IE} - \mathrm{EA}) \tag{5}$$

where IE and EA are the first ionization energy and electron affinity of the molecule, respectively. Atomic softness values can easily be calculated by using eq 4, namely,

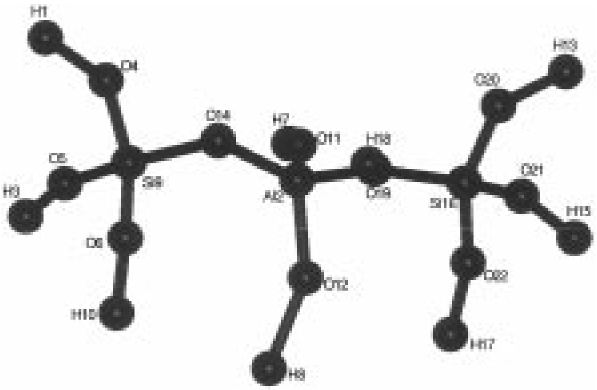

Figure 1. Zeolite framework trimer cluster model with labeled atoms.

$$s_{\mathrm{x}}^{\,+} = [q_{\mathrm{x}}(N+1) - q_{\mathrm{x}}(N)]S \tag{6}$$

$$s_{\mathrm{x}}^{\,-} = [q_{\mathrm{x}}(N) - q_{\mathrm{x}}(N-1)]S$$

$$s_{\mathrm{x}}^{\,0} = S[q_{\mathrm{x}}(N+1) - q_{\mathrm{x}}(N-1)]/2$$

Computational Methodology and Model

In the present study, all calculations have been carried out with density functional theory[29] using DMOL code of MSI Inc. BLYP[30,31] exchange correlation functional and DNP basis set[32] was used throughout the calculation. BLYP has already shown its credibility for explaining weak hydrogen bond type interactions in comparison to MP2 level calculations.[33,34] It is also useful in describing the interaction of the probe molecule with the zeolite framework cluster.[18] Basis set superposition error (BSSE) was also calculated for the current basis set in nonlocal density approximation (NLDA) using the Boys−Bernardi method.[35] Geometries of all the interacting molecules CO_2, CO, CH_4, NO, NO_2, NH_3, and H_2O along with the zeolite framework cluster chosen were fully optimized for calculating the reactivity index. Single-point calculations of the cation and anion of each molecule at the optimized geometry of the neutral molecule (demanded for constant $\upsilon(r)$) were also carried out to evaluate Fukui functions and global and local softness. The condensed Fukui functions and atomic softnesses are evaluated using eqs 2 and 6, respectively. The gross atomic charges are evaluated by Mulliken population analysis as well as using the technique of electrostatic potential (ESP) driven charges. It is well-known that Mulliken charges are highly basis set dependent, whereas ESP driven charges show less basis set dependence[36,37] and are better descriptors of the molecular electronic density distribution. Calculations have been performed on trimer clusters of the formula $[(OH)_3{-}Si{-}O{-}Al{-}(OH)_2{-}OH{-}Si{-}(OH)_3]$. Here, the bridging oxygen is protonated at a distance of 1.08 Å. The adjacent silicon and aluminum atoms occurring in the zeolite lattice are replaced by hydrogens in order to preserve the electroneutrality of the model as shown in Figure 1. The terminal hydrogens are kept at a distance of 1.66 Å (i.e., terminal O−H distances are 1.66 Å). The trimer cluster model is a rational choice between cluster size, realistic picture for the zeolite crystals, and CPU time. The trimer cluster also reproduces the electronic environment of the zeolite cluster better than the smaller cluster models. The interacting molecules CO_2, CO, CH_4, NO, NO_2, NH_3, and H_2O were fully optimized with a fixed cluster for the evaluation of interaction energy. As the validity of HSAB principle demands the satisfaction of the condition of equal local softness between two different interacting species,

TABLE 1: Global Softness Values (in au) for Zeolite Cluster along with Different Heteroatomic Molecules

molecule	global softness (S)
zeolite trimer cluster model	2.9069
carbon dioxide	1.7663
carbon monoxide	1.6163
methane	1.5909
ammonia	2.0124
nitrogen dioxide	2.7416
nitrous oxide	2.7046
water	1.6474

TABLE 2: Condensed Local Softness and Fukui Function Values for the Zeolite Cluster Model from Mulliken Population Analysis and ESP Technique

atoms of trimer cluster	Mulliken population		ESP technique	
	f_x^+	s_x^+	f_x^+	s_x^+
H1	0.129	0.375	0.116	0.337
Al2	0.179	0.520	0.162	0.470
H3	0.109	0.317	0.092	0.267
O4	0.059	0.171	0.048	0.139
O5	0.059	0.171	0.049	0.142
O6	0.079	0.229	0.067	0.195
H7	0.089	0.259	0.078	0.227
H8	0.049	0.142	0.039	0.113
Si9	0.139	0.404	0.130	0.378
H10	0.109	0.317	0.089	0.259
O11	0.019	0.055	0.011	0.032
O12	0.039	0.113	0.029	0.084
H13	0.039	0.113	0.028	0.081
O14	0.019	0.055	0.012	0.035
H15	0.009	0.026	0.003	0.010
Si16	0.239	0.694	0.229	0.665
H17	0.079	0.229	0.071	0.206
H18	0.309	0.898	0.295	0.857
O19	0.010	0.029	0.008	0.023
O20	0.049	0.142	0.039	0.113
O21	0.059	0.171	0.053	0.154
O22	0.049	0.142	0.041	0.119

our aim is to compare the local softness values of the atoms of the interacting molecules along with the zeolite framework cluster. The atoms for which those values will be closer will be considered as the most probable sites of interaction. For the electrophilic center, we need to calculate s_x^+ values, and for the nucleophilic center, we need to calculate the s_x^- values. However, in addition we have also evaluated f_x^+ and f_x^- values for all the atoms in electrophilic and nucleophilic sites, respectively. This will help us to compare the suitability of one of the parameters between f and s in the general statement of HSAB principle as mentioned in earlier paragraphs.

Results and Discussion

The global softness values of the zeolite cluster models as well as interacting molecules calculated using DFT are presented in Table 1. The values of nucleophilic condensed local softness (s_x^+) and condensed Fukui function (f_x^+) of the individual atoms of the cluster model obtained through Mulliken population analysis and ESP technique at the DFT level are shown in Table 2. The electrophilic condensed local softness (s_x^-) and condensed Fukui function (f_x^-) have been calculated for all the interacting molecules using both the methodologies as stated above and presented in Table 3. It is observed from Table 1 that the global softness values for the zeolite cluster models are higher than that of the interacting molecular species. So, to test the local HSAB principle, it seems to be important to analyze whether the local softness values, Fukui functions, or reactive indices for the constituent atoms of the cluster models and interacting molecular species will be more reliable parameters. First, the interaction of the zeolite cluster model with each of the seven probe molecules is calculated using local softness values and an activity order is proposed. This is followed by the interaction energy of the individual molecule with the zeolite framework to justify the proposed order. The trends observed in these two sets of results were compared, and a scale has been proposed.

TABLE 3: Condensed Local Softness and Fukui Functions for All the Hetroatomic Molecules Studied As Obtained from Mulliken Population Analysis at the DFT Level

atom of interacting molecule	Mulliken population		ESP technique	
	f_x^-	s_x^-	f_x^-	s_x^-
C in CO_2	0.2833	0.5004	0.2809	0.4961
O in CO_2	0.3585	0.6332	0.3547	0.6265
C in CO	0.6808	1.1004	0.6769	1.0941
O in CO	0.3192	0.5159	0.3148	0.5088
C in CH_4	0.1641	0.2610	0.1612	0.2564
H in CH_4	0.2090	0.3325	0.2043	0.3250
N of NO	0.5524	1.4940	0.5489	1.4845
O of NO	0.4476	1.2105	0.4423	1.1962
N of NO_2	0.3246	0.8899	0.3215	0.8814
O of NO_2	0.3378	0.9261	0.3338	0.9151
N in NH_3	0.3852	0.7751	0.3816	0.7679
H in NH_3	0.2049	0.4123	0.2011	0.4047
H in H_2O	0.1841	0.3032	0.1808	0.2978
O in H_2O	0.6317	1.0407	0.6288	1.0358

The potential problem of the different heteroatomic gases present, their use, the use of zeolite in this field, previous experimental and theoretical results relevant to the model, and the way to choose a right zeolite for a particular system is discussed in the following.

a. Interaction of the Zeolite Cluster Model with Carbon Dioxide. The most serious problem for the global scale environment is the climate change due to warming gases, such as carbon dioxide, carbon monoxide, methane, etc. Zeolite is one of the materials of interest. The interaction of CO_2 with the zeolite framework is not very well studied. There is some experimental work related to zeolite as a support material for noble metal used for the adsorption of CO_2. There is no quantum chemical calculation whatsoever on interaction of CO_2 with zeolite framework. There are a few molecular dynamics[38] and Monte Carlo simulations on the distribution[39] of CO_2 in zeolite lattice. The results show that for NaZSM-5 the CO_2 molecules adsorbed on cation sites. Therefore, it seems that CO_2 will have an interaction with zeolite framework. Table 3 shows that both the s_x^- and f_x^- value obtained at the DFT level are higher for oxygen atom, indicating that the oxygen atom is a preferable nucleophilic site. Now, from s_x^+ and f_x^+ values for the atoms of the zeolite cluster as presented in Table 2, it is observed that the hydrogen atom of the bridging O−H group of the cluster behaves as a preferable electrophilic site. Now, if we match the s_x^- and f_x^- values of the carbon dioxide molecule with s_x^+ and f_x^+ values of the zeolite cluster, it can be clearly seen that s_x^- as well as f_x^- values of the oxygen atom of carbon dioxide matches well with the s_x^+ and f_x^+ values of the hydrogen atom of the bridging O−H group. Thus, local HSAB principle predicts the interaction to be tested by real experiment. The interaction sites are clearly identifiable from the values of both local softness and Fukui functions.

b. Interaction of the Zeolite Cluster Model with Carbon Monoxide. Carbon monoxide is known to have an interaction with the Bronsted acid site of zeolite lattice and it is a weak interaction as observed by theoretical[40,41] and experimental[42,43] studies. One of the vibrational frequency calculations[44] shows that the interaction of carbon monoxide takes place through the carbon atom of the molecule and the hydrogen atom of the bridging O−H of the zeolite lattice. The positive dipole moment in the C ← O direction justifies the electron donor property of the carbon atom of the carbon monoxide molecule. Table 3 shows that both the s_x^- and f_x^- values obtained at the DFT levels for both the methodologies are higher for the carbon atom, indicating that the carbon atom is a preferable nucleophilic site. These values match well with the s_x^+ and f_x^+ of the H atom of the O−H bridge present in the zeolite cluster.

c. Interaction of the Zeolite Cluster Model with Methane. Selective C−H activation of saturated alkanes by various catalytic systems is an important step in the transformation of these relatively inert compounds to more useful products. Among other systems, cation-exchanged zeolites are also a suitable matrix. Recently, van Santen and co-workers have published a series of papers where they have presented the results of calculations using an ab initio density functional approach for methane activation on extended models of Bronsted zeolite active centers.[45] In the case of hydrogen exchange, the reaction coordinate represents the symmetrical transfer of the proton of the zeolite to the methane molecule and the return of the hydrogen atom from the methane to zeolite. In this process, two oxygen atoms of the zeolite are involved, one as a proton acceptor (basic) and the other as a proton donor (acidic). This shows that interaction takes place between the hydrogen atom of methane and the hydrogen atom of the bridging O−H group of the zeolite cluster. This fact also has been supported by another recent study of Broclawik et al.[46] Table 3 shows that both s_x^- and f_x^- values obtained in DFT are higher for the hydrogen atom, indicating that the hydrogen atom is a preferable nucleophilic site. As mentioned earlier, the hydrogen of the bridging O−H of a zeolite cluster behaves as the electrophilic site; the values of s_x^+ and f_x^+ match very well with the s_x^- and f_x^- of the hydrogen atom of methane. This shows the accountability of this softness values in predicting the experimental trend as well as it is also possible to locate the interaction site of the interacting species correctly.

d. Interaction of the Zeolite Cluster Model with Nitrous Oxide and Nitrogen Dioxide (NO_x). The environmental pollution caused by nitric oxides (NO_x) contained in exhaust gases from diesel or lean-burn engines of mobile sources is a serious problem of global significance that urgently needs to be solved.[47] Cation exchanged zeolites play a key role in this process.[48−50] Yamadaya et al.[51] has performed a systematic study on NO adsorption on cation exchanged zeolites. They observe that the NO molecule interacts with zeolite framework through the nitrogen atom of the NO molecule. Now, the s_x^- and f_x^- values obtained in the DFT level presented in Table 3 show a higher value for the nitrogen atom. This shows that the N of NO is the most nucleophilic site. These values, though a bit higher, match the s_x^+ and f_x^+ values of the electrophilic site, i.e., of H of the bridging O−H group of the zeolite cluster, although the values for oxygen atom are not far off compared to those for other systems.

Now, in case of NO_2 it has been predicted theoretically for a cation exchanged zeolite that NO_2 remains at the spin center of the system where the metal reached a stable tetracoordinated state.[51] NO_2 shows more activation than the NO molecule. The s_x^- and f_x^- values for the O atom are higher than those of the N atom of the NO_2 molecule. The values match with the corresponding s_x^+ and f_x^+ values of the bridging proton. In both cases (NO and NO_2), the difference of s_x^- and f_x^- between the constituent atoms is not so much in comparison to other atoms of the molecules. As in the case of other molecules we can conclusively say that the most nucleophilic is the interacting site with zeolite, in the case of NO and NO_2 we may propose a multisite interaction of these molecules with zeolite framework which will be later tested.

TABLE 4: Comparison of Condensed Local Softness and Fukui Functions of the Most Nucleophilic Atom of the Interacting Molecules from ESP Technique at DFT Level

atom of interacting molecule	f_x^-	s_x^-
H of CH_4	0.2043	0.3250
C of CO	0.6769	1.0941
O of CO_2	0.3547	0.6265
N of NO	0.5489	1.4845
O of NO_2	0.3338	0.9151
N of NH_3	0.3816	0.7679
O of H_2O	0.6288	1.0358

e. Interaction of the Zeolite Cluster Model with Ammonia. Earlier theoretical studies show that the Bronsted proton may interact with the ammonia molecule in two possible ways. One is a covalent interaction,[52−54] and the second one is an ionic interaction[55] which results from the abstraction of proton. In the present case, we assume the covalent interaction or the primary interaction, as the ionic model is operative in the next stage. The local condensed softness and Fukui functions for the ammonia molecule are presented in Table 3. It shows that the s_x^- and f_x^- values for N atom are higher than the values for H of the NH_3 molecule. The values best match that of the acidic H atom of the zeolite cluster.

f. Interaction of the Zeolite Cluster Model with Water. The interaction of a water molecule with the acidic hydrogen of the zeolite framework is through the oxygen atom of the water molecule.[56] Table 3 presents the condensed local softness and Fukui function of the water molecule. It is observed from the values that the oxygen atom of the water molecule can be considered as the strongest nucleophilic center. These values are in excellent match with the s_x^+ and f_x^+ values of the hydrogen atom of the bridging O−H group.

We observed, for all the heteroatomic molecules, that the local softness and Fukui functions of the most nucleophilic atom match those values of the most electrophilic site present as a proton in the zeolite cluster. For NO and NO_2, we observed that the other constituent atoms present in these atoms have comparable nuclephilicity, which shows that probably they will have multisite interaction with the zeolite framework.

g. Reactivity Index Scale. The aim of the current study is to rationalize an understanding of the interaction of hetroatomic molecules with zeolite framework and to propose a scale in terms of reactivity index. It is observed from Table 1 that the zeolite framework has a higher value for global softness in comparison to interacting molecules. The order of the global softness in comparison to the framework cluster is $CH_4 < CO < H_2O < CO_2 < NH_3 < NO < NO_2$. Now, we present the results of condensed local softness and Fukui functions of the most nucleophilic atom of the interacting molecules from Mulliken population analysis and ESP technique at DFT level in Table 4. The results show that in terms of Fukui functions the interacting molecules can be arranged in the order $CH_4 < NO_2 < CO_2 < NH_3 < NO < H_2O < CO$ while in terms of condensed local softness the order is $CH_4 < CO_2 < NH_3 < NO_2 < H_2O < CO < NO$. Now, as we proposed while analyzing the individual f_x^- and s_x^- values for the constituent atoms of interacting molecules, we mentioned that both for NO and NO_2 the difference between the respective values of their constituents is not much in comparison to other molecules. As in the rest of the molecules, it is assumed that there is a one-site interaction

TABLE 5: BLYP and MP2 Binding Energy Results for H_2O-H_2O and H_2O-HF Using a Similar Basis Set [6-31++G(d,p) for MP2; DNP for BLYP)[a]

	MP2		BLYP	
system	BE (kcal/mol)	BE (BSSE) (kcal/mol)	BE (kcal/mol)	BE (BSSE) (kcal/mol)
H2O−H2O[b]	−5.24	−4.47	−5.01	−4.54
H2O−HF[c]	−10.15	−8.13	−9.98	−8.76

[a] BE = binding energy, BE (BSSE) = BSSE corrected binding energy. [b] Results in ref 34. [c] Results in ref 57.

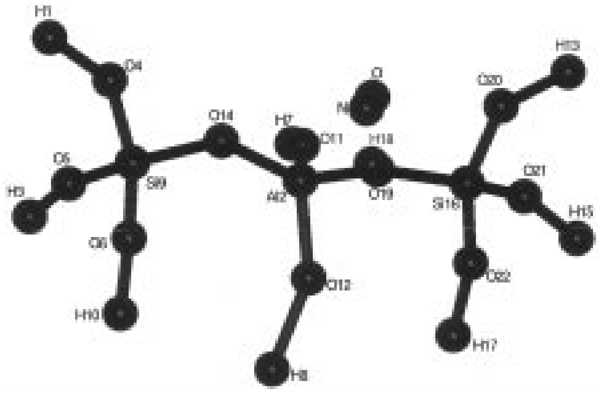

Figure 2. Optimized stucture of NO molecule during interaction with zeolite framework trimer cluster model.

with the framework, i.e., the most nucleophilic site of the molecule interacts with the most electrophilic site of the zeolite framework cluster. It may be that in the case of NO and NO_2 there exists a multisite interaction, i.e., through both of the constituent atoms of these two molecules, with the framework. So, if we drop these two molecules from the proposed order obtained both from the Fukui function and condensed local softness, we better say in terms of reactivity index we observe the order as $CH_4 < CO_2 < NH_3 < H_2O < CO$. Now, to verify our proposal in terms of site of interaction, we need to perform the interaction energy calculation using DFT.

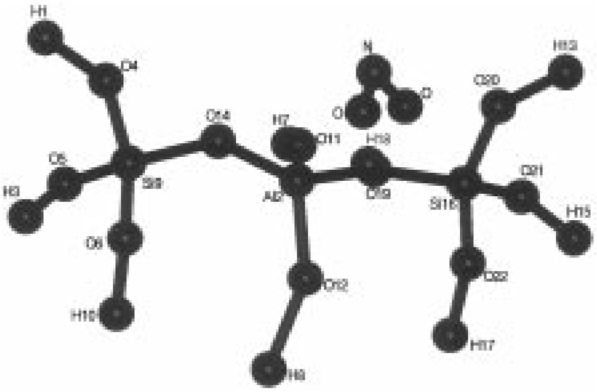

Figure 3. Optimized stucture of NO_2 molecule during interaction with zeolite framework trimer cluster model.

TABLE 6: Total Energy of the Framework and Interacting Molecules along with Interaction Energy for Each of the Individual Molecules with Zeolite Framework at Their Optimized Configuration

molecule	total energy (au)	interaction energy (kcal/mol) BSSE corrected
framework cluster (FW)	−1571.435	
CO_2	−187.263	
CO	−113.337	
CH_4	−40.490	
NO	−129.912	
NO_2	−205.135	
NH_3	−56.551	
H_2O	−76.419	
FW + CO_2	−1758.707	−3.72
FW + CO	−1684.789	−8.74
FW + CH_4	−1611.933	−3.10
FW + NO	−1701.360	−6.23
FW + NO_2	−1776.576	−1.84
FW + NH_3	−1627.997	−4.98
FW + H_2O	−1647.869	−7.49

h. Interaction Energy Calculation. The interaction energy calculation was performed using DFT with the BLYP functional. The validity of current methodology in predicting the interaction energy is tested with a small model calculation with H_2O-H_2O and H_2O-HF systems. The results are compared with existing results using MP2 level calculations.[34,57] The results are tabulated in Table 5. It shows that our current methodology can reproduce the binding energy of the smaller models with an error of ±0.01 kcal/mol. The trimer cluster is fixed throughout the calculation, and the configurations of the interacting molecules were optimized. For each case, the most nucleophilic atom (as observed from the reactive index values) of the interacting molecules was placed at a distance of 2 Å from the acidic proton of the zeolite framework. In the optimized geometry of the heteroatomic molecules with the zeolite framework, we identified two different groups of molecules depending on the nature of the interaction. The first group is with all six molecules except NO and NO_2, where they interact with the zeolite acidic proton through the most nucleophilic atom, whereas the second group is with NO and NO_2; they have multisite interaction with the framework proton as shown in Figures 2 and 3, respectively. The results of the total energy of the framework cluster and the individual interacting molecules along with the adsorption complex and interaction energy (BSSE corrected) of the individual molecules are shown in Table 6. The interaction energy values fall in the range of 1.84 kcal/mol to 8.74 kcal/mol. We will not emphasize the numbers; rather, we will analyze the trend. The values show a nice match with available experimental results for a few of the molecules. The results justify our earlier comment that in the case of NO and NO_2 there exists a multisite interaction. For the case of NO, the acidic proton of the zeolite framework interacts with both N and O of the molecule and the molecule lies perpendicular to the direction of the acidic proton. In the case of NO_2, the acidic proton of zeolite framework interacts with both the oxygens along with nitrogen as the molecule comes closer to the framework and lies at a position where N is just on top of H of bridging O−H and the two oxygens are pointing in the z direction. The interaction energy values show the order as $NO_2 < CH_4 < CO_2 < NH_3 < NO < H_2O < CO$. Now, if we drop both NO and NO_2 from this, we get the same order as we predict from the reactivity index, which is $CH_4 < CO_2 < NH_3 < H_2O < CO$. This suggests that the reactivity index is good until the point where there is a unit site interaction with the zeolite framework; this seems to be rational, as the reactivity index compares the most nucleophilic atom with most electrophilic atom. As in the case of NO and NO_2 there is not much difference in terms of nucleophilicity between the constituent atoms with which it behaves differently. So from the DFT-based local parameter descriptor, one can conclusively locate the active site in the interacting molecular species as well as by comparing with the parametric value for zeolites, can choose the best candidate for a particular reaction.

Conclusion

This is the first study to rationalize an understanding between the interaction of heteroatomic molecules with zeolite framework in terms of reactivity index. We propose here a scale of activity in terms of reactivity index which is further verified by the interaction energy calculation. This paves a novel qualitative way of estimating the activity of interacting molecules to choose a matrix for their separation, which is a prime need for the global environment. We also categorically show that the reactivity index scale is good for unit site interaction, as it compares the most nucleophilic and electrophilic site of interaction. It deviates for multisite interaction or for cases where the difference of nucleophilicity between constituent atoms is narrow. We want to explore this field with other practical examples. We also want to use a larger cluster model to predict site selectivity for host−guest interactions in zeolite catalysis.

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