

A philicity based analysis of adsorption of small molecules in zeolites

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Abstract. Adsorption of small molecules like CH₄, CO and NH₃ into the acid sites of zeolites is analysed as an interaction between an electrophile and a nucleophile. Global reactivity descriptors like softness and electrophilicity, and local reactivity descriptors like the Fukui function, local softness and local philicity are calculated within density functional as well as Hartree–Fock frameworks using both Mulliken and Hirshfeld population analysis schemes. The HSAB principle and the best electrophile–nucleophile combination suggest that the reaction between the NH₃ and Brønsted acid site of the zeolite is the strongest. Interaction between the zeolite and a small probe molecule takes place through the most electrophilic atom of one with the most nucleophilic atom of the other. This result is in conformity with those provided by the frontier orbital theory and the local HSAB principle.

Keywords. Density functional theory; Hartree–Fock calculations; Global and local reactivity descriptors; HSAB principle; electrophile; nucleophile.

1. Introduction

There has been an upsurge of interest in recent years in understanding the catalysis phenomenon using zeolites. Most of these studies^{1–8} highlight the creation of Brønsted acid sites owing to the substitution of silicon by aluminum in the tetrahedral units of the zeolite framework. It is important to know the variation of reactivity and selectivity in those acid sites when small molecules like CH₄, CO and NH₃ get adsorbed there, in order to have a better understanding of the associated catalytic activity. Recently, Deka *et al.*⁸ have studied this aspect using local softness.

Density functional theory^{9,10} (DFT) has been found to be quite successful in analysing chemical reactivity and selectivity. While global quantities like electronegativity^{11,12} (*c*), hardness^{13–15} (*h*), and electrophilicity index¹⁶ (*w*) take care of the reactivity, the selectivity of each atomic site in a molecule is characterized by local quantities like the Fukui function^{17,18} (*f*(**r**)), local softness¹⁹ (*s*(**r**)) and philicity²⁰ (*w*(**r**)).

Various electronic structure principles involving the global reactivity descriptors exist. The important one for the present study is the hard-soft acid-

base^{13,21} (HSAB) principle which states that “hard acids like to coordinate with hard bases and soft acids with soft bases for both their kinetic and thermodynamic properties”. A local version of this principle is also available²² through the matching of local softness values. An electrophile–nucleophile interaction can become favorable between two molecules with high and low electrophilicity indices respectively so that the former is a better electrophile and the latter may be considered as a better nucleophile.¹⁶ Corresponding philicities²⁰ may be used in analysing the specific site-site interactions.

In the present work, we study the nature of adsorption of small molecules like CH₄, CO and NH₃ inside the zeolite framework especially into the Brønsted acidic hydrogen atomic sites. We use the global electrophilicity and local philicity for this purpose. Theoretical background is provided in §2 and in §3 we present the computational details. Results are discussed in §4 and §5 contains some concluding remarks.

2. Theoretical background

Electronegativity¹¹ (*c*), and hardness¹³ (*h*), for an *N*-electron system with total energy *E*, are defined as follows:

*For correspondence

$$\mathbf{c} = -\mathbf{m} = -(\partial E/\partial N)_{v(\mathbf{r})}, \quad (1)$$

$$\mathbf{h} = (1/2)(\partial^2 E/\partial N^2)_{v(\mathbf{r})} = (1/2)(\partial \mathbf{m}/\partial N)_{v(\mathbf{r})} \quad (2)$$

where \mathbf{m} and $v(\mathbf{r})$ are chemical and external potentials, respectively. The global softness (S) is the following inverse of hardness,⁹

$$S = 1/2\mathbf{h} = (\partial N/\partial \mathbf{m})_{v(\mathbf{r})}. \quad (3)$$

The electrophilicity index (\mathbf{w}) is introduced by Parr *et al*¹⁶ as follows:

$$\mathbf{w} = \mathbf{m}^2/2\mathbf{h}. \quad (4)$$

Local quantities are important in gaining insights into the reactivity and selectivity of a specific site in a molecule.

The Fukui function¹⁷ or the frontier function captures the essence of Fukui's frontier orbital theory²³ and is defined as

$$f(\mathbf{r}) = (\partial \mathbf{r}(\mathbf{r})/\partial N)_{v(\mathbf{r})} = (\mathbf{d}\mathbf{m}/\mathbf{d}v(\mathbf{r}))_N. \quad (5)$$

Owing to the discontinuities in the plot of $\mathbf{r}(\mathbf{r})$ versus N there exist three different types of Fukui functions,¹⁷ namely,

$$f^+(\mathbf{r}) = \mathbf{r}_{N+1}(\mathbf{r}) - \mathbf{r}_N(\mathbf{r}), \quad \text{for nucleophilic attack,} \quad (6a)$$

$$f^-(\mathbf{r}) = \mathbf{r}_N(\mathbf{r}) - \mathbf{r}_{N-1}(\mathbf{r}), \quad \text{for electrophilic attack,} \quad (6b)$$

$$f^0(\mathbf{r}) = \mathbf{r}_{N+1}(\mathbf{r}) - \mathbf{r}_{N-1}(\mathbf{r})/2, \quad \text{for radical attack,} \quad (6c)$$

where $f_N(\mathbf{r})$ is the electron density of the N -electron ($N \equiv N - 1, N, N + 1$) species. Substituting these electron densities by respective electron populations (q_k) on the atomic site k of the molecule one can define the corresponding condensed-to-atom variants as,

$$f_k^{\mathbf{a}}; \mathbf{a} = +, -, \text{ and } 0 \quad (7)$$

where $\mathbf{a} = +, -, \text{ and } 0$ represent nucleophilic, electrophilic, and radical attacks respectively.

The local softness is given by⁹

$$s(\mathbf{r}) = (\partial \mathbf{r}(\mathbf{r})/\partial \mathbf{m})_{v(\mathbf{r})} = (\partial \mathbf{r}(\mathbf{r})/\partial N)_{v(\mathbf{r})}$$

$$(\partial N/\partial \mathbf{m})_{v(\mathbf{r})} = f(\mathbf{r})S, \quad (8a)$$

$$s^{\mathbf{a}}(\mathbf{r}) = f^{\mathbf{a}}(\mathbf{r})S, \quad (8b)$$

$$s_k^{\mathbf{a}} = f_k^{\mathbf{a}}S. \quad (8c)$$

The philicity is defined as²⁰

$$\mathbf{w}(\mathbf{r}) = \mathbf{w}f(\mathbf{r}), \quad (9a)$$

and hence

$$\mathbf{w}^{\mathbf{a}}(\mathbf{r}) = \mathbf{w}f^{\mathbf{a}}(\mathbf{r}) \quad (9b)$$

and

$$\mathbf{w}_k^{\mathbf{a}} = \mathbf{w}f_k^{\mathbf{a}}. \quad (9c)$$

Since these quantities are products of one local and one global reactivity descriptors, they are supposed to explain the intermolecular interactions as well.

Recently Roy and coworkers^{24,25} have tried to check the reliability of the philicity index along with its global counterpart (claimed to be the negative of chemical potential). He has shown²⁴ that the philicity properly explains the intermolecular reactivity in most cases for a series of carbonyl compounds although the global electrophilicity fails in many cases. He claims that the relative electrophilicity, originally introduced to avoid negative values of condensed softness,²⁶ is the most reliable intramolecular reactivity index. His claim is based on the results on the same set of molecules considered in their old paper.²⁷ Recently relative electrophilicity has been criticized by several authors²⁸ including the manipulation mentioned by Roy himself.²⁹ Moreover, counter to the claim of Roy *et al*²⁵, in the Ref. 11 of his paper²⁴ and in many other papers by Contreras, Perez, Fuentealba, Chatterjee, Toro-Labbe and others³⁰⁻³³ it has been pointed out that the relative electrophilicity^{24,27} is less universal than the local electrophilicity and also unlike the latter, the former does not provide the proper normalization apart from the fact that it is not trustworthy in interpreting intermolecular interactions. Obviously philicity (like local softness) cannot provide more reliable intramolecular reactivity (when only one molecule is considered) than that is obtainable from the Fukui function but for the cases where the

molecule is undergoing an intramolecular process like vibration, rotation, rearrangement and/or interaction with a solvent or an external field where both the local and the global descriptors change during the physico-chemical process. The constancy of the external potential is generally tacitly assumed in all such cases. The philicity is, however, not less reliable than the Fukui function and the local softness. In addition philicity and local softness contain information about global electrophilicity and global softness respectively. As shown rather trivially their relative electro(nucleo)philicity^{24,27} is also identical with the corresponding relative Fukui function for the same molecule even for the various intramolecular physico-chemical processes described above and hence does not warrant any additional significance when intramolecular reactivity is analyzed.³⁴

His analytical proof based on his (15), does not contain any extra information than the (13) (see also the lines surrounding it) of the original paper of Chattaraj *et al.*²⁰ and his confusion is the result of the improper perusal of that paper (see the point 5 towards the end of ref. 20). The relative electro(nucleo)philicity treats the anions and the cations at par but the anions are known to require a more sophisticated technique than the cations to produce the same quality wavefunctions. The argument²⁵ of its being less sensitive to basis set and correlation effects is handwaving. Also the analysis of the radical reactions using these descriptors is not straightforward. Philicity and local softness respectively would be better intermolecular reactivity indices (since a product of a global and a local indices) than the Fukui function to analyze electrophile–nucleophile interactions and hard–soft interactions. It may be noted that the numerical results should be taken with care because, as it is well known to the experts in the field of chemical reactivity, the calculation of the Fukui function involves the inherent inadequacies associated with different population analysis schemes/frozen core approximation/finite difference approximation, etc. and the approximations involved in the calculation of the global quantities like relaxation/symmetry/basis set/Koopmans' theorem etc. to provide wrong trends in both intramolecular and intermolecular reactivity studies not necessarily originating from the improper definitions of the various global and local reactivity parameters. Incidentally their claim^{24,35} of guaranty of non-negative Fukui functions from Hirshfeld population analysis scheme has been provided with a counterexample recently.³⁶ Moreover, a given reac-

tivity descriptor may provide better result in comparison to other for a specific set of molecules and may give worse result for the other set. Incidentally the types of molecules on which the relative electro(nucleo)philicity are calculated so far (see refs 24, 25, 27, 29, 35 and other related references) are very limited and are by no means representative of the wide variety of organic molecules and hence it is premature to claim their descriptor to be the most reliable.²⁴ Since philicity and local softness are defined through a decomposition of the corresponding global quantities, local descriptors will definitely reflect the corresponding global reactivity, as opposed to the conclusion drawn by Roy,²⁴ if one takes care of all the atomic sites. Of course the major contribution will come from the most reactive site(s). Similar analysis on the connection between local and global properties has been carried out by Legon,³⁷ as discussed in ref. [30] in the context of electrophilicity, supporting our argument. During an electrophile–nucleophile interaction process, when two reactants approach each other from a large distance they see each other's global electrophilicities without any idea about their local counterparts. One with the larger electrophilicity will behave as an electrophile and the other as a nucleophile. The most electrophilic site of the electrophile will prefer to interact with the most nucleophilic site of the nucleophile. It may be noted that the atom with the maximum value of the local electrophilicity in the electrophile may not necessarily have larger local electrophilicity value than that of the most electrophilic atom in the nucleophile. A similar situation will arise during hard–soft interaction and will show that the local HSAB principle may not be always in conformity with its global counterpart. If two molecules with different electronegativities (first order effect) approach each other there will be electron transfer between them even if their hardness (second order effect) values are far removed and it is not a violation of the HSAB principle. The Fukui function and all other related descriptors like local softness and philicity may not provide reasonable trends for the hard–hard reactions where charge based descriptors are known to be more appropriate.³⁸ Counter to what is claimed by Roy,²⁴ philicity has been shown³⁹ to be a reliable descriptor of intramolecular reactivity as well. Meneses *et al.*³⁹ have shown that the philicity model is better than the Li-Evans⁴⁰ model and is as reliable as the newly proposed empirical local hardness³⁹ in explaining the orientation of the electrophilic aromatic substitution,

addition reaction, alkylation and acylation of lithium enolates. The reliability of philicity and related descriptors *vis-à-vis* that of relative electrophilicity has been analyzed in some more recent papers^{21,30,32,41,42} where the superiority of the former has been highlighted.

In order to avoid misconceptions^{24,25} the relative electro(nucleo)philicity is compared⁴³ with philicity for all the molecules considered in references 24 and 25 using same population analysis schemes, same global and local reactivity descriptors, by grouping the molecules as they did, and by analysing in the same line as they did to show that philicity is better than relative electro(nucleo)philicity when the intermolecular reactivity trends are considered and there is hardly any preference of one above the other as far as the intramolecular reactivities are concerned. On the contrary philicity concept has got some advantages over the other concept.⁴³

3 Computational details

Zeolite is modeled as a trimer cluster (3T) which has been shown^{1,8,44} to be sufficient in representing the Brønsted acid sites of the zeolites and the adsorption of small probe molecules therein. The geometries of the cluster as well as CH₄, CO and NH₃ are optimized using DFT method with Becke,⁴⁵ Lee–Yang–Parr (BLYP)⁴⁶ functional and a double- ζ numerical polarized (DNP) basis set⁴⁷ from DMol³ computer program coupled in the Accelrys package.⁴⁸ The population analysis is performed under the Hirshfeld⁴⁹ scheme.

Using finite difference approximation for the small change in the number of the particles, we can approximate the \mathbf{m} , \mathbf{h} , S and \mathbf{w} as

$$\mathbf{m} = -((IP + EA)/2), \quad (10)$$

$$\mathbf{h} = (IP - EA)/2, \quad (11)$$

$$S = 1/(IP - EA), \quad (12)$$

$$\mathbf{w} = \mathbf{m}^2/2\mathbf{h}. \quad (13)$$

Equations (6a)–(6c) have been condensed to an atom-in-molecule (AIM) resolution by Yang and Mortier.⁵⁰

$$f^+ = Q_{N^0} - Q_{N^0+1} \quad (14a)$$

$$f^- = Q_{N^0-1} - Q_{N^0} \quad (14b)$$

$$f^0 = (Q_{N^0-1} - Q_{N^0+1})/2, \quad (14c)$$

where Q is the atomic charge in the molecule. But in our case instead of ± 1 electron, ± 0.1 electron was used by the DMol³ program.⁴⁸ Equations (8c) and (9c) for the local softness and local philicity can be approximated using this scheme and employing (14a)–(14c). Then, we can write

$$s^+ = f^+S, \quad (15a)$$

$$s^- = f^-S, \quad (15b)$$

$$s^0 = f^0S, \quad (15c)$$

and

$$\mathbf{w}^+ = \mathbf{w}f^+, \quad (16a)$$

$$\mathbf{w}^- = \mathbf{w}f^-, \quad (16b)$$

$$\mathbf{w}^0 = \mathbf{w}f^0. \quad (16c)$$

For completeness, the supporting information includes results obtained at the Hartree–Fock level using the 6-31G** basis set within the Gaussian 98 program.⁵¹

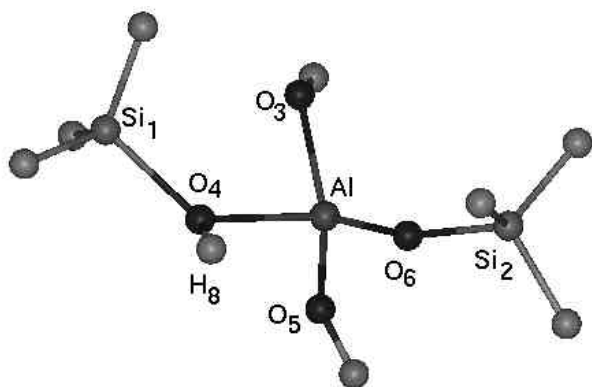
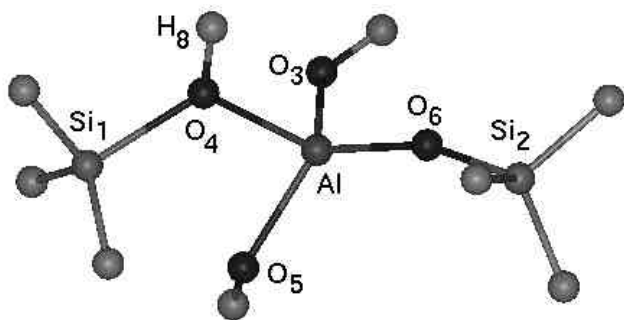
4. Results and discussion

Two different minimum energy structures are obtained for the 3T cluster at BLYP/DNP level of theory as shown in the figures 1 and 2. Pertinent geometrical parameters of these clusters are provided in table 1. Bond lengths and bond angles of one of them compare very well with those reported by Deka *et al.*⁸

Table 2 contains the global reactivity parameters; chemical potential, global softness and global electrophilicity for 3T clusters, CH₄, CO and NH₃. The strongest interaction is between the zeolite and NH₃ according to the HSAB principle since they are the two softest species considered here as per their global softness values. It is important to note that the zeolite is a better electrophile and NH₃ is a better nucleophile (poorer electrophile) and hence will have strong interaction. Since CO is a better electrophile than the zeolite its nucleophilic character may not be properly ascertained during its reaction with the zeolite as hinted by others.⁵

Table 1. Pertinent geometrical parameters of 3T cluster calculated using DFT method at BLYP/DNP level of theory.

Parameter	3T cluster-1(*)	3T cluster2 (*)	3T (**)
<i>Bond lengths (Å)</i>			
O ₄ -H ₈	0.975	0.973	0.973
Si-O ₄	1.740	1.746	1.745
Al-O ₄	1.990	1.979	1.976
Al-O ₃	1.738	1.739	1.739
Al-O ₅	1.750	1.756	1.756
Al-O ₆	1.744	1.738	1.738
<i>Bond angles (deg)</i>			
Si-O ₄ -Al	122.7	121.2	122
Si-O ₄ -H ₈	116.8	117.3	117
Al-O ₄ -H ₈	113.8	121.2	121

*Present work; **From Deka *et al*⁸**Figure 1.** 3T H-ZSM-5 cluster model (3T cluster-1) used to simulate the active site of the H-ZSM-5 zeolite. It contains three tetrahedral units.**Figure 2.** 3T cluster model (3T cluster-2) used to simulate the active site of the zeolite. It contains three tetrahedral units. Bond lengths and bond angles compare well with that reported by Deka *et al*.⁸

Various local quantities like the Fukui function, local softness and local philicity are presented in table 3. Apart from the silicon-1 site, the acidic hydrogen (H₈) site in the zeolite is the most reactive, the soft-

Table 2. Global reactivity descriptors for the zeolite cluster and molecules (in atomic units), using finite difference approximation for the small change in the number of particles (± 0.1 electron), at BLYP/DNP level of theory.

System	Chemical potential	Global softness	Global electrophilicity
3T cluster-1	-0.14759	4.99226	0.10874
3T cluster-2	-0.14855	4.96396	0.10954
CH ₄	-0.15472	2.43032	0.05818
CO	-0.19570	3.30739	0.12667
NH ₃	-0.11594	3.89747	0.05239

est and the most apt for nucleophilic attack. The philicity values of N in NH₃ and of C in CH₄ and CO are the largest and these sites are preferable for adsorption into the H₈-site of the zeolite, through favorable electrophile-nucleophile interactions, complementing a local HSAB result²² reported by Deka *et al*⁸ who have shown through the calculations of interaction energy that the local HSAB principle should be realized via a softness-matching criterion rather than a Fukui function matching criterion as the confusion was there before.⁵ It is important to note that the Fukui function and local softness provide different trends⁸ as will be the case with philicity.²⁰ Respective criteria are based on three different chemical theories of reactivity and selectivity, viz., preferred interactions are through maximum Fukui function sites (frontier electron theory), hard-hard or soft-soft sites (local HSAB principle) and maximum electrophilic site of the electrophile-maximum nucleophilic site of the nucleophile (best electrophile-nucleophile interactions). Philicity based study is somewhat better in the sense that it can account for most of the cases studied here as opposed to several

Table 3. Condensed Fukui function, local softness and local philicity values for the zeolite cluster and molecules (in atomic units). The quantities are calculated by means of a finite-difference approximation (± 0.1 electron) calculated using DFT method (BLYP/DNP) and Hirshfeld population scheme.

System	Fukui function	Local softness	Local philicity
<i>3T cluster-1</i>	f^+	s^+	w^+
H ₈	0.14500	0.72388	0.01577
Al	0.06800	0.33947	0.00739
O ₃	0.01400	0.06989	0.00152
O ₄	0.07700	0.38440	0.00837
O ₅	0.02400	0.11981	0.00261
O ₆	0.00400	0.01997	0.00043
Si ₁	0.30300	1.51265	0.03295
Si ₂	0.04100	0.20468	0.00446
<i>3T cluster-2</i>	f^+	s^+	w^+
H ₈	0.16900	0.83891	0.01851
Al	0.07800	0.38719	0.00854
O ₃	0.02400	0.11914	0.00263
O ₄	0.07700	0.38222	0.00843
O ₅	0.02000	0.09928	0.00219
O ₆	0.00400	0.01986	0.00044
Si ₁	0.27500	1.36509	0.03012
Si ₂	0.03700	0.18367	0.00405
<i>CH₄</i>	f^-	s^-	w^-
C	0.30800	0.74854	0.01792
H	0.17300	0.42045	0.01007
<i>CO</i>	f^-	s^-	w^-
C	0.69700	2.30525	0.08829
O	0.30300	1.00214	0.03838
<i>NH₃</i>	f^-	s^-	w^-
N	0.52500	2.04617	0.02750
H	0.15800	0.61580	0.00828

violations in the proper softness matching (on local HSAB) criterion as seen in the present work as well as that of Deka *et al.*⁸ Philicity results are in conformity with frontier orbital theory since the interactions between sites of maximum Fukui function values (hence the most reactive) are most favorable according to their philicity values also although with different w values, but counter to that claimed by Deka *et al.*⁸ regarding the Fukui function. Similar analysis on adsorption of CO, NH₃ and H₂O in faujasite x -type zeolite was made by Krishnamurty *et al.*⁵ using local HSAB principle which provided similar quantitative results on a qualitative basis. Before the related work by Deka *et al.*⁸ a quantitative extension of that study⁵ to calculate interaction energies between zeolite and N₂, CO₂ and CO was also reported⁶. These results are interesting although the minimization of a local grand potential²² and use of an adjustable parameter made this analysis weak⁵².

The quantities calculated with the HF/6-31G**//BLYP/DNP procedure by using both finite-difference and Koopmans' approximations with Mulliken as well as Hirshfeld charges are provided as supporting information. In most of the cases the active sites of the zeolite (H₈), CH₄ (C), CO (C) and NH₃ (N) are properly accounted for. In the present work, mainly Hirshfeld population is used because Mulliken population provides negative values for the local quantities like the Fukui function, local softness and local philicity in many cases as in ref. [8].

5. Concluding remarks

Different global and local density functional theory based descriptors are calculated for understanding the nature of interaction, reactivity and selectivity associated with the adsorption of small molecules such as CH₄, CO and NH₃ to the Brønsted acidic

sites of zeolites. Interaction between the zeolite and NH_3 is the strongest because it results from the combination of two softest species as well as between the best electrophile and the nucleophile. The N atom in NH_3 and the C atoms in CH_4 and CO are most active towards adsorption to the acid sites of the zeolite. Philicity concept, frontier orbital theory and local HSAB principle provide identical inferences based on local philicities, Fukui functions and local softnesses.

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Supporting information (Tables S4–S6) is available on the Journal website: www.ias.ac.in/chemsci