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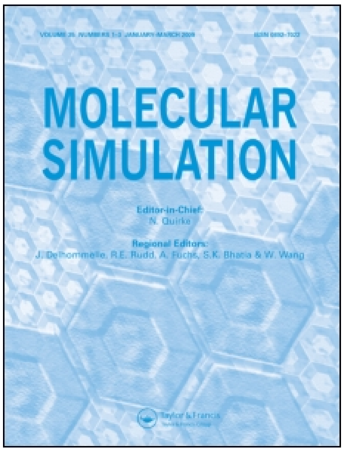

Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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P. Mondal[a][b]; K. K. Hazarika[a]; A. Deka[a]; R. C. Deka[a]
[a] Department of Chemical Sciences, Tezpur University, Tezpur, Assam, India [b] Department of Chemistry, Assam University, Silchar, Assam, India

To cite this Article Mondal, P. , Hazarika, K. K. , Deka, A. and Deka, R. C.(2008) 'Density functional studies on Lewis acidity of alkaline earth metal exchanged faujasite zeolite', Molecular Simulation, 34: 10, 1121 — 1128

To link to this Article: DOI: 10.1080/08927020802073032

URL: http://dx.doi.org/10.1080/08927020802073032

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Molecular Simulation
Vol. 34, Nos. 10–15, September–December 2008, 1121–1128

Density functional studies on Lewis acidity of alkaline earth metal exchanged faujasite zeolite

P. Mondal[ab], K.K. Hazarika[a], A. Deka[a] and R.C. Deka[a]*

[a]*Department of Chemical Sciences, Tezpur University, Napaam, Tezpur 784 028, Assam, India;* [b]*Department of Chemistry, Assam University, Dargakona, Silchar 788 011, Assam, India*

(Received 20 December 2007; final version received 12 March 2008)

Lewis acidity of alkaline earth metal exchanged faujasite zeolite is investigated using density functional based reactivity descriptors with a 6T ring cluster which represents active site of the zeolite. We calculated global reactivity descriptors such as chemical hardness, chemical softness, electrophilicity index of the optimised cluster and local reactivity descriptors namely fukui function and relative electrophilicity of the exchanged cations at PWC/DNP (Double numerical with polarisation) and VWN-BP/DNP levels of theory. The electrophilicity index of the modelled clusters and relative electrophilicity values of the exchanged cations show that Lewis acidity of alkaline earth metal cation-exchanged zeolites decreases in the order: $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$, which is in agreement with the available experimental results.

Keywords: Lewis acidity; faujasite zeolite; hardness; electrophilicity

1. Introduction

Cation-exchanged faujasite zeolites are widely applied as selective adsorbents for gas separation and purification as well as catalysts and supports for catalysts. The ion-exchange capacity of faujasite zeolite leads to important industrial applications like removal of ammonia and heavy metals from municipal, industrial and drinking water and absorbing Cs and Sr from nuclear wastes [1]. Cation-exchanged zeolites are used in separation of *p*-xylene from C_8 aromatics [2,3], separation of carbon dioxide from methane, nitrogen from oxygen [4], etc. In cation-exchanged zeolites, the exchanged cations behave as Lewis acid sites and the framework oxygen atoms bearing partial negative charges act as Lewis base. The simultaneous presence of both acidic and basic sites in these zeolites has been found to catalyse several organic reactions of industrial importance. Recently, it has been found that the alkali and alkaline earth exchanged faujasite zeolite promotes selective oxidation of hydrocarbon with molecular oxygen via either thermal or photochemical activation [5,6]. Alkali and alkaline earth cations in zeolites do not show any redox properties and cannot dissociate either hydrocarbon or oxygen molecules. Thus, the activation of hydrocarbon and oxygen molecules in cation-exchanged zeolites is different from conventional processes.

The Lewis acid strength of the exchanged cations plays an important role in directing the guest molecules both for gas separation and for their chemical activation. It has been shown by Pidko and van Santen [7] that in case of photo-oxidation process the main role of the cations is to prearrange the reactants in the zeolite cavity via adsorption so that they can be activated in the subsequent reaction steps. Obviously, depending on the Lewis acid strength of the exchanged cations and adsorption fashion of guest molecule within zeolite cavities, the property and reactivity of the adsorbed molecules vary significantly. Hence, it is important to predict the influence of different cations on structure as well as activity of cations for catalytic reactions. The structure–property relationships of proton-exchanged zeolites have been extensively studied using various experimental and theoretical methods [8,9]. However, little attention has been paid to the Lewis acidity of alkaline earth cation-exchanged zeolites.

Cohen De Lara and co-workers [10,11] had employed probe molecules such as N_2, H_2, CH_4, etc. to evaluate the strength of local electric fields of cation sites in zeolites. The acid–base properties of cation-exchanged zeolites have been investigated by means of FTIR and TPD-MS techniques using ammonia as a probe molecule [12]. Larsen and co-workers [13] have studied a series of alkaline earth metal exchanged beta zeolites using CO as a probe molecule to investigate the effect of exchanged cations on the electric field. Xie et al. [14] characterised the Lewis acidic (cations) and Lewis basic sites of alkaline earth exchanged X zeolites by studying pyrrole chemisorption with FTIR spectroscopic

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*Corresponding author. Email: ramesh@tezu.ernet.in

ISSN 0892-7022 print/ISSN 1029-0435 online

DOI: 10.1080/08927020802073032
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technique and determined the Lewis acidic and basic strengths by calculating charges of cations and oxygen atoms, respectively, using the electronegativity equivalence method. Brönsted acidity of zeolites can be well characterised by calculating the positive charge of acidic hydrogen [15,16]. However, the prediction of correct Lewis acidity trend of cation-exchanged zeolites has not been successful using positive charge of the cations [17]. In this respect, the density functional based reactivity descriptors have been found to be quite useful [18,19].

In the present study, we investigate the Lewis acid strength of different alkaline earth metal exchanged faujasite zeolites using density functional theory (DFT) based reactivity descriptors such as chemical hardness (η), chemical softness (S), chemical potential (μ), Fukui function (f_M^+ and f_M^-), etc. [20–22]. The global reactivity descriptors, η, S and μ give the reactivity of a system as a whole whereas the local parameter, Fukui function, represents the reactivity of an atom in a molecule. Fukui functions f_M^+ and f_M^- give the sites that are prone to nucleophilic and electrophilic attack, respectively. In most of the cases, Fukui function values are found to be successful in explaining experimental reactivity sequences of chemical species [23–25]. However, in some systems the atom with high electrophilicity, i.e. having higher value of f_M^+ may also show high nucleophilicity, i.e. having higher value of f_M^-. Then, their ratios 'relative electrophilicity', (f_M^+/f_M^-), and 'relative nucleophilicity', (f_M^-/f_M^+), express the reactivity of atoms in molecules in a better way [26]. Vos et al. [27,28] applied the DFT based local and global reactivity descriptors successfully to explain the mechanism for the electrophilic aromatic substitution reaction involving zeolites. Hemelsoet et al. [29] studied the dependence of global reactivity descriptors on electronic structure methods as well as basis set for typical reactions in zeolite catalysis. Parr et al. [30] proposed a new global reactivity parameter called electrophilicity index (ω) based on the chemical potential and chemical hardness of the system. Electrophilicity index measures the electrophilic power of molecular species. Domingo et al. [31] applied electrophilicity index to characterise quantitatively the electrophilic power of common diene/dienophile pairs used in Diels–Alder reactions. Padmanabhan et al. [32] also used electrophilicity index to explain toxicity and aromaticity of a series of chlorinated benzenes correctly. We have calculated global softness, global hardness, chemical potential and electrophilicity index of alkaline earth exchanged zeolites using a cluster model approach and determined their Lewis acid strength. We also derived the Lewis acidity trends of the model clusters by calculating the relative electrophilicity of the exchanged cations.

2. Method

2.1 *Theoretical aspects*

The global and local reactivity descriptors used in this study are derived from DFT. In DFT, the hardness (η) of an electronic system is defined as the second derivative of energy (E) with respect to the number of electrons (N) at constant external potential, $v(\vec{r})$ [33].

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

where μ is the chemical potential of the system.

The global softness is the inverse of the global hardness with a factor of half.

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

Using the finite difference approximation, global hardness, η and global softness, S can be approximated as

$$\eta = \frac{\mathrm{IP} - \mathrm{EA}}{2}, \tag{3}$$

$$S = \frac{1}{\mathrm{IP} - \mathrm{EA}}, \tag{4}$$

where IP and EA are the first vertical ionisation potential and electron affinity, respectively, of the system. In most numerical applications, chemical potential, μ and chemical hardness, η are calculated using finite difference approximation in terms of ionisation potential and electron affinity. Further approximations, involving the use of Koopmans' theorem [34], give access to μ and η in terms of the energies of frontier molecular orbitals HOMO and LUMO.

$$\mu = \frac{E_{\mathrm{LUMO}} + E_{\mathrm{HOMO}}}{2}, \tag{5}$$

and

$$\eta = \frac{E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}}{2}, \tag{6}$$

where E_{LUMO} is the energy of lowest unoccupied molecular orbital and E_{HOMO} is the energy of highest occupied molecular orbital.

Parr et al. [30] introduced global electrophilicity index (ω) as a measure of energy lowering due to maximal electron flow between a donor and an acceptor in terms of chemical potential and hardness as:

$$\omega = \frac{\mu^2}{2\eta}. \tag{7}$$

According to this definition, ω measures the ability of a molecular species to soak up electrons.

While global quantities take care of reactivity of the entire molecule, the selectivity of each atomic site in a molecule is characterised by local quantities like Fukui function, local softness, etc. The local softness $s(\vec{r})$ of atoms of a chemical system is defined as,

$$s(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial \mu}\right)_{v(\vec{r})}, \tag{8}$$

so that $\int s(\vec{r})\mathrm{d}r = S$ is satisfied. In Equation (8), $\rho(\vec{r})$ is the electron density at position $\vec{r}$. The local softness $s(\vec{r})$ then can be re-written as,

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

Here, $f(\vec{r})$ is the Fukui function originally proposed by Parr and Yang [35]. As seen from Equation (9), the definitions of $f(\vec{r})$ and $s(\vec{r})$ involve derivatives of $\rho(\vec{r})$ with respect to the number of electrons. A finite difference approximation can be applied to define three different types of local quantities for an atom 'M' in a molecule [36].

$$f_{\mathrm{M}}^{+} = [\rho_{\mathrm{M}}(N_0 + 1) - \rho_{\mathrm{M}}(N_0)], \quad \text{(for nucleophilic attack on the system)}, \tag{10a}$$

$$f_{\mathrm{M}}^{-} = [\rho_{\mathrm{M}}(N_0) - \rho_{\mathrm{M}}(N_0 - 1)], \quad \text{(for electrophilic attack on the system)}, \tag{10b}$$

$$f_{\mathrm{M}}^{0} = \frac{1}{2}[\rho_{\mathrm{M}}(N_0 + 1) - \rho_{\mathrm{M}}(N_0 - 1)], \quad \text{(for radical attack on the system)}, \tag{10c}$$

where $\rho_{\mathrm{M}}(N_0)$, $\rho_{\mathrm{M}}(N_0 + 1)$ and $\rho_{\mathrm{M}}(N_0 - 1)$ are electronic population on atom M for N_0, $N_0 + 1$ and $N_0 - 1$ electron systems, respectively. The 'relative electrophilicity' of an atom, M, in a molecule can be calculated from the ratios of Fukui function values as $(f_{\mathrm{M}}^{+}/f_{\mathrm{M}}^{-})$. Similarly, the 'relative nucleophilicity' can be expressed as $(f_{\mathrm{M}}^{-}/f_{\mathrm{M}}^{+})$ [26].

2.2 *Computational details*

The cluster model used in our study is generated from the crystalline structure of Faujasite [37] and it represents a six-member ring of the zeolite (Figure 1). Two of the Si atoms of the model cluster are isomorphously substituted by two aluminium atoms to generate the active sites. The negative charges of the cluster are compensated with alkaline earth metal cations namely Mg^{2+}, Ca^{2+}, Sr^{2+} or Ba^{2+}. The cations are located at $\mathrm{S_{II}}$ site of faujasite zeolites. The relative position of aluminium atoms in the cluster are chosen in such a way that the cluster obeys the Loewenstein rule [38]. In order to have more accurate description of the active site, the free valences of the silicon and aluminium atoms of the cluster are saturated with O—H groups. During optimisation of the clusters, the terminating hydrogen atoms were first optimised keeping all other atoms fixed at their crystallographic positions. The positions of the terminating hydrogen atoms thus obtained as well as those of silicon and aluminium atoms were kept fixed in all subsequent calculations, while the oxygen atoms of the cluster and the alkaline earth exchanged cations were allowed to relax freely. The terminal hydrogen atoms were kept fixed to avoid the unrealistic hydrogen bonding. Furthermore, the procedure of keeping the T atoms fixed during optimisation attempts to represent the real situation in the zeolite framework, where the motion of the T atoms is restricted because of the two additional bonds outside the ring, while the oxygen atoms are much more mobile. The unconstrained optimisation of zeolite

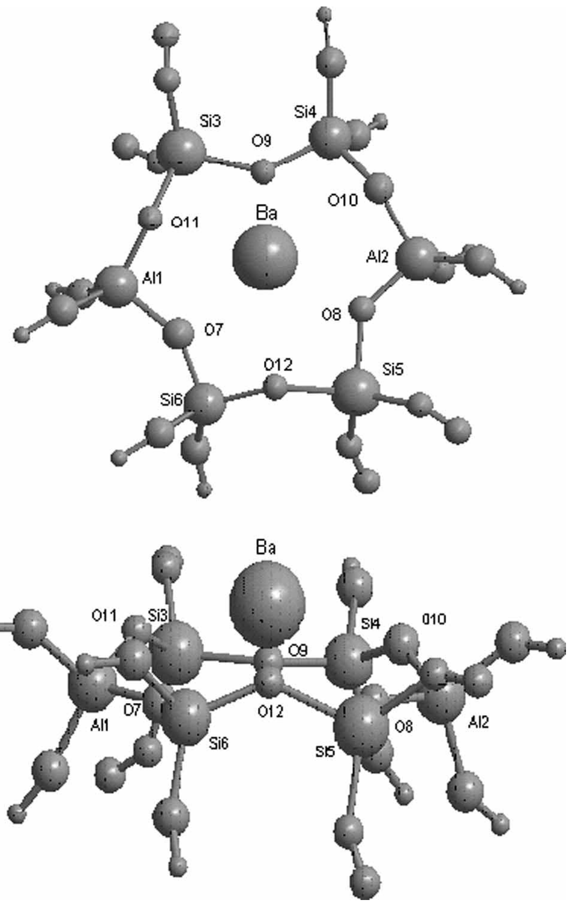

Figure 1. Top and side views of optimised structures of model Ba-exchanged 6T faujasite zeolite cluster with two aluminium atoms. Ring oxygen, silicon and aluminium atoms are numbered for easy reference in the discussion.

clusters leads to a structure which does not resemble the experimental geometry [39]. Hence, constrained optimisation is commonly used in zeolite modelling [40].

All calculations are performed using DMol^3 (Software from Accelrys Inc., www.accelrys.com) [41] program package. The geometry optimisations are performed at local density approximation level with Perdew–Wang functional (PWC) and generalised gradient approximation level with BP functional having local correlation replaced by Vosko–Wilk–Nusair (VWN) functional [42,43] (VWN-BP). We have used DNP basis sets for all the atoms in our calculations. The sizes of these DNP basis sets are comparable to the 6-31G** basis [44,45]. However, they are believed to be much more accurate than Gaussian basis sets of the same size [46]. The integration grid referred to as FINE in the software program has been used for optimisation of the clusters. The global reactivity descriptors, such as chemical potential (μ) chemical hardness (η) and electrophilicity (ω) have been calculated by using Equations (5)–(7), respectively. The local reactivity descriptors are evaluated using both Hirshfeld population analysis (HPA) [47] and Mulliken population analysis (MPA) [48] schemes.

3. Results and discussion

3.1 Structure

The top and side views of optimised structure for Ba^{2+} exchanged 6T ring cluster of faujasite zeolite are shown in Figure 1. Some of the selected geometric parameters of the optimised clusters for all the alkaline earth exchanged zeolites, derived at PWC/DNP and VWN-BP/DNP levels are given in Table 1. The location of the metal cation with respect to zeolite framework depends on the ionic radius of the cation. Different experimental and theoretical methods have been used to investigate the location of extra framework cations relative to zeolite framework and their interaction with guest molecules [49]. X-ray diffraction (XRD) [50] and neutron diffraction data have provided precise information regarding the location of extra framework cations. It is seen from Table 1 that the Mg^{2+} cation has three-fold coordination with framework oxygen atoms, O_7, O_8 and O_9, and stays at long distance from other oxygen atoms (O_{10}, O_{11} and O_{12}). The Mg—O distances for O_7, O_8, O_9 atoms are almost same (2.05–2.09 Å). The location of the Mg^{2+} ion is near the centre of the 6T ring, which is in agreement with the experimental XRD data for dehydrated MgNa—X zeolite [51]. In contrast to Mg^{2+}, larger cations, Ca^{2+}, Sr^{2+} and Ba^{2+} have six-fold coordination with framework oxygen atoms, O_7, O_8, O_9, O_{10}, O_{11} and O_{12}. The strength of interaction between the extra framework cation and framework oxygen atoms decrease in the series from Mg^{2+} to Ba^{2+} [52]. This sequence correlates quite nicely with the cation radii and corresponding internuclear distance X^{2+}—O as reported in Table 1. The deviation of cation position from the plane of T atoms can be explained by calculating O—X^{2+} distances and O—X^{2+}—O angles. For larger cations, O—X^{2+} distances are larger and O—X^{2+}—O angles are

Table 1. Variation of selected internal coordinates of the optimised alkaline earth metal exchanged 6T ring structure of faujasite zeolites cluster calculated at PWC/DNP and VWN-BP/DNP levels.

	Exchanged cations							
	PWC/DNP					VWN-BP/DNP		
Internal co-ordinates	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
X^{2+}—O_7^{a}	2.058	2.248	2.380	2.556	2.054	2.278	2.427	2.610
X^{2+}—O_8^{a}	2.074	2.258	2.386	2.563	2.069	2.286	2.437	2.619
X^{2+}—O_9^{a}	2.103	2.282	2.457	2.659	2.097	2.325	2.515	2.731
X^{2+}—O_{10}^{a}	2.592	2.479	2.591	2.724	2.623	2.535	2.655	2.809
X^{2+}—O_{11}^{a}	2.540	2.475	2.579	2.716	2.559	2.512	2.632	2.786
X^{2+}—O_{12}^{a}	3.131	3.025	2.981	3.059	3.166	3.098	3.096	3.179
⟨Al1—O⟩^{a}	1.793	1.781	1.781	1.780	1.805	1.799	1.798	1.798
⟨Al2—O⟩^{a}	1.781	1.769	1.767	1.768	1.797	1.789	1.788	1.789
⟨Si3—O⟩^{a}	1.646	1.641	1.642	1.643	1.663	1.658	1.660	1.661
⟨Si4—O⟩^{a}	1.657	1.652	1.653	1.654	1.672	1.668	1.670	1.671
⟨Si5—O⟩^{a}	1.671	1.662	1.661	1.663	1.688	1.681	1.682	1.683
⟨Si6—O⟩^{a}	1.661	1.653	1.652	1.653	1.677	1.671	1.671	1.672
O_7—Al_1—O_{11}^{b}	88.586	90.207	92.473	93.796	88.980	90.360	92.321	93.633
O_8—Al_2—O_{10}^{b}	92.483	93.648	96.285	97.597	93.082	94.072	96.203	97.612
O_7—X^{2+}—O_8^{b}	107.333	104.054	98.485	90.194	107.090	100.508	93.796	86.069
O_9—X^{2+}—O_{12}^{b}	176.709	161.252	145.559	130.945	174.445	152.270	137.974	125.032
O_{11}—X^{2+}—O_{10}^{b}	117.246	120.146	116.586	110.684	117.401	119.912	115.160	108.486

⟨⟩ Represent average.^{a} Values are in Å. ^{b} Values are in degrees.

smaller. It is noticed from Table 1 that with increasing ionic radii of the cations, the X^{2+}—O distances increase and O—X^{2+}—O angles decrease. Therefore, the exchanged cations move away from the plane of T atoms with the increase of their ionic radii. Plant et al. [53] performed quantum chemical study on the adsorption of carbon dioxide in alkali cation-exchanged Y faujasites and reported similar deviation of cation locations from the plane of the six-membered ring.

The interaction between cation and framework oxygen atoms leads to substantial deformation of zeolite structure around the cation. The interaction of a cation with framework oxygen atoms elongates Al—O and Si—O bond lengths and decreases O—Al—O bond angles. The elongation of Al—O and Si—O bond lengths is maximum for Mg^{2+} and minimum for Ba^{2+}. For Mg^{2+} the Al_1—O bond length is 1.793Å and Si_6—O bond length is 1.661 Å while for Ba^{2+} the Al_1—O bond length is 1.780 Å and Si_6—O bond length is 1.653 Å. Vayssilov and Rösch [54] performed computational studies on the influence of alkali and alkaline earth cations on Brönsted acidity of cation-exchanged faujasite zeolites and reported similar geometrical changes.

3.2 *Lewis acidity of alkaline earth metal-exchanged zeolites*

The catalytic activity of cation-exchanged zeolites depends upon the Lewis acidity of exchanged cations and Lewis basicity of framework oxygen atoms. To understand the Lewis acidity of alkaline earth cation-exchanged faujasite zeolites, we have calculated DFT based reactivity descriptors namely, global hardness, global softness, electrophilicity, Fukui function and relative electrophilicity.

3.2.1 *Global descriptors*

The calculated global reactivity descriptors, chemical hardness, chemical softness, chemical potential and electrophilicity of alkaline earth cation-exchanged zeolite clusters using PWC/DNP and VWN-BP/DNP basis set levels are presented in Table 2. The maximum hardness principle [55] states that at constant external potential, the higher the hardness, the higher is the stability, i.e. lower is the Lewis acidity. Conversely, the lower the softness value, the higher is the stability, i.e. lower is the reactivity. It is seen from Table 2 that the chemical hardness values of modelled clusters derived at PWC/DNP level increase in the order: $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$. The global softness values of the clusters derived using PWC/DNP level decrease from Mg^{2+} exchanged cluster down to Ba^{2+} exchanged cluster (Table 2). Hence, Lewis acidity of the exchanged cluster decreases in the order: $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$, which is in excellent agreement with experimental Lewis acidity trends [56]. However, chemical hardness and global softness values calculated at VWN-BP/DNP level fail to predict the systematic acidity sequence. The electrophilicity index computed using PWC/DNP and VWN-BP/DNP levels are also given in Table 2. Higher values of electrophilicity measure the electrophilic power of molecular species, i.e. higher Lewis acidity. Mg-exchanged zeolite cluster has maximum electrophilicity value and hence is the most reactive. The electrophilicity values decrease from Mg-exchanged cluster to Ba-exchanged cluster. Therefore, the Lewis acidity of alkaline earth metal exchanged faujasite zeolites decrease in the order: $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$.

3.2.2 *Local reactivity descriptors*

Lewis acidity of a cation depends on its positive charge, ionic radius and polarizability. Experimentally, it has been found that the Lewis acidity of alkali metal exchanged zeolite decreases in the order of $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. Deka et al. [16] have studied Lewis acidity of alkali cation-exchanged zeolites using DFT based local reactivity descriptors such as local softness (s_M^+) and the relative electrophilicity value

Table 2. Calculated chemical potential (μ), chemical hardness (η), chemical softness (S) and electrophilicity (ω) values of alkaline earth metal exchanged 6T ring faujasite clusters.

Exchanged cations	DFT functional	Chemical potential (μ)	Chemical hardness (η)	Chemical softness (S)	Electrophilicity (ω)
Mg^{2+}		−3.970	2.009	0.249	3.923
Ca^{2+}	PWC/DNP	−3.734	2.147	0.233	3.247
Sr^{2+}		−3.725	2.155	0.232	3.219
Ba^{2+}		−3.604	2.157	0.232	3.011
Mg^{2+}		−3.755	2.081	0.240	3.388
Ca^{2+}	VWN-BP/DNP	−3.525	2.222	0.225	2.796
Sr^{2+}		−3.485	2.185	0.229	2.779
Ba^{2+}		−3.415	2.174	0.230	2.682

These values are evaluated at PWC/DNP and VWN-BP/DNP levels.

Table 3. The MPA and HPA derived charge, nucleophilic Fukui function, electrophilic Fukui function and relative electrophilicity of cations in the alkaline earth metal cation-exchanged 6T ring faujasite cluster (Figure 1).

		MPA derived parameters				HPA derived parameters			
Exchanged cations	DFT functional	q_M	f_M^+	f_M^-	f_M^+/f_M^-	q_M	f_M^+	f_M^-	f_M^+/f_M^-
Mg^{2+}		1.166	0.487	0.007	69.571	0.689	0.240	0.008	30.000
Ca^{2+}	PWC/DNP	1.508	0.604	0.009	67.111	0.691	0.263	0.011	23.909
Sr^{2+}		1.321	0.605	0.013	46.538	0.736	0.359	0.016	22.436
Ba^{2+}		1.321	0.534	0.021	25.429	0.782	0.351	0.023	15.261
Mg^{2+}		1.236	0.475	0.008	59.375	0.715	0.241	0.008	30.125
Ca^{2+}	VWN-BP/DNP	1.574	0.573	0.010	57.300	0.734	0.279	0.011	25.364
Sr^{2+}		1.410	0.599	0.015	39.933	0.794	0.398	0.016	24.875
Ba^{2+}		1.422	0.564	0.023	24.522	0.847	0.421	0.024	17.542

The values are evaluated at PWC/DNP and VWN-BP/DNP levels.

(s_M^+/s_M^-) of the exchanged alkali cations and obtained similar acidity trend. Here, we have evaluated the charge (q_M^+), Fukui function for nucleophilic attact (f_M^+), Fukui function for electrophilic attact (f_M^-), and relative electrophilicity (f_M^+/f_M^-) of the exchanged cations. These values derived from MPA and HPA schemes at PWC/DNP and VWN-BP/DNP levels for alkaline earth metals are summarised in Table 3. It is seen from Table 3 that the Mulliken and Hirshfeld charges on the exchanged cation indicate no systematic trend of Lewis acidity of alkaline earth metal exchanged zeolites. Hence, we derive better local reactivity descriptors, Fukui functions (f_M^+) and (f_M^-) and their ratio, the relative electrophilicity (f_M^+/f_M^-) to study the correct acidity trend. The Fukui function (f_M^+) values of the exchanged cation evaluated using both MPA and HPA schemes at PWC/DNP and VWN-BP/DNP levels also do not give the correct result of acidity. The relative electrophilicity (f_M^+/f_M^-) and relative nucleophilicity (f_M^-/f_M^+) values have been found to be more reliable local reactivity descriptors compared to f_M^+ and f_M^- [18,19]. The superiority in favour of (f_M^+/f_M^-) and (f_M^+/f_M^-) is due to the fact that the individual values of Fukui functions are strongly influenced by the basis set and correlation effects whereas their ratios involving two differences of electron densities of systems differing by one in their number of electrons at constant nuclear framework are expected to be less sensitive to the basis set and correlation effects [26]. The relative electrophilicity, (f_M^+/f_M^-) values of exchanged cations are presented in Table 3. A larger value of relative elctrophilicity (f_M^+/f_M^-) of exchanged cations explains higher reactivity, hence, higher Lewis acidity. The reported relative electrophilicity, (f_M^+/f_M^-) values of the cations derived from MPA and HPA at PWC /DNP level decreases in the order of $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ (Table 3). Hence, the Lewis acidity of the alkaline earth metal cation-exchanged zeolite decreases in the order of $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$, which is in good agreement with the experimental acidity sequence. The relative eletrophilicity (f_M^+/f_M^-) values derived from MPA and HPA schemes using DNP basis set and VWN-BP functional also agree well with the experimental Lewis acidity sequence. In our calculation, the local reactivity descriptors evaluated using HPA and MPA schemes provide similar trends of Lewis acidity.

4. Conclusions

DFT calculations on 6T ring cluster of alkaline earth cation-exchanged faujasite zeolite show a significant change in geometric parameters of the cluster around the cations. Smaller cation Mg^{2+} has three-fold coordination while larger cations namely, Ca^{2+}, Sr^{2+} and Ba^{2+} have six-fold coordination with framework oxygen atoms of the zeolite cluster. The change in geometry is more prominent for smaller cations. The order of global electrophilicity values for modelled clusters calculated at PWC/DNP and VWN-BP/DNP levels is $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. Fukui function f_M^+ values of alkaline earth cations are found to be weak local reactivity descriptors to explain the correct Lewis acidity of exchanged cations. The relative electrophilicity (f_M^+/f_M^-) values for alkaline earth cations derived from HPA and MPA schemes at PWC/DNP and VWN-BP/DNP levels decrease in the order of $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. Therefore, we can conclude from global electrophilicity values and relative electrophilicity that the Lewis acidity of alkaline earth metal cation-exchanged faujasite zeolite decreases in the order of $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ which is in excellent agreement with experimental observations.

Acknowledgements

The authors thank Council of Scientific and Industrial Research, New Delhi for financial support.

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