

Lewis acidity and basicity of cation-exchanged zeolites: QM/MM and density functional studies

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Received 24 January 2001; received in revised form 14 May 2001; accepted 27 June 2001

Abstract

The structure of Li⁺, Na⁺ and K⁺-exchanged faujasite (FAU) zeolite is studied by means of cluster model and QM/MM approach at HF/6-31G** level of calculations. When CO molecule interacts with cation, “hard” site present in the zeolite channel, the CO bond length decreases compared to the free CO molecule and this decrease in CO bond length depends on Lewis acid strength of the cation. The strength of Lewis acidity of the cations and basicity of framework oxygen atoms is investigated using density functional (DF) methods. We used local reactivity descriptors based on hard–soft acid–base concept as acidity and basicity parameters. The calculated ‘relative electrophilicity’ and ‘relative nucleophilicity’ values are found to be better descriptors of acidic and basic sites, respectively. From relative electrophilicity (s_k^+/s_k^-) value the Lewis acidity of the cation-exchanged faujasite zeolite is found to decrease in the order: [Li-FAU] > [Na-FAU] > [K-FAU], and from relative nucleophilicity (s_k^-/s_k^+) value of the framework oxygen atom, the Lewis basicity is found to increase in the order: [Li-FAU] < [Na-FAU] < [K-FAU]. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Zeolite; QM/MM; Lewis acidity; Lewis basicity; Reactivity descriptors

1. Introduction

Cation-exchanged zeolites have been frequently implicated as active sites in zeolite catalysis. The extraframework cation compensates the negative charge of the zeolite framework that is created due to substitution of a silicon atom by an aluminium atom. In alkali cation-exchanged zeolites the cation behaves as Lewis acid centre, while the framework oxygen bearing partial negative charge behaves as Lewis base centre. The presence of both acidic and basic sites in zeolites makes the material a unique type of catalyst in hydrocarbon reaction [1–10]. The most widely

used reactions are side-chain alkylation of toluene [4,5], condensation reactions [6] and selective alkylation of aromatic compounds that contain oxygen or nitrogen [7,8]. The formation of ethylbenzene and styrene were linked to basic sites in X and Y type zeolites exchanged with K⁺, Rb⁺ and Cs⁺ cations [9]. The production of xylenes was related to the acidic character of Li⁺ and Na⁺-exchanged zeolites [10].

The importance of cation-exchanged zeolites, both from a fundamental and an applied point of view, suggests that a better understanding of the parameters that determine the acidobasic character of zeolites is certainly requisite. Precise knowledge of strength and structure of Lewis acidic centres is mandatory for the successful description of the catalytic and sorption capabilities of alkali-exchanged zeolites. This requires a method of assessing the effect of the size, charge, and

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location of cations on the electric field created by the cations. The electric field around the extraframework cations has been investigated by studying the interaction of CO molecule with the cation-exchanged zeolites [11,12] and shift of the vibrational frequency of adsorbed CO molecule is related to the Lewis acidity of the cations. However, choice of a good probe for the measurement of basicity of framework oxygen is a major problem. The probe molecule should react specifically with the basic sites under consideration, while at the same time the probe should not decompose or polymerize. Theoretical methods can help significantly in understanding the reactivity of acidic and basic centres of zeolites.

So far, several quantum chemical studies have been undertaken by adopting cluster models which are cut out from the zeolite and saturated with hydrogen atoms [13–20]. The cluster models, however, do not reflect a specific zeolite framework and neglect the long-range electrostatic interactions. To include the effects of the zeolite framework, a periodic Hartree–Fock method may be ideal. However, this method is computationally expensive for most of the zeolites due to their relatively large unit cells. In order to overcome such limitation, embedded cluster techniques have been suggested at various levels [21–24]. We have adopted a hybrid quantum mechanical/molecular mechanical (QM/MM) method which is called surface integrated molecular orbital molecular mechanics (SIMOMM) [24]. This method is an extension of the original IMOMM method developed by Maseras and Morokuma [22]. In SIMOMM method, the embedding environment is described by a molecular mechanical potential (MM) and the active site is described by quantum mechanical method (QM). Thus, the QM/MM method is used to obtain reliable structures and these geometries are taken for calculating reactivity descriptors based on hard–soft acid–base (HSAB) principle described below.

In recent years, the global and local reactivity descriptors based on density functional theory (DFT) appeared as powerful tools to describe reactivity of various chemical systems [25]. By calculating the local softness values, Gazquez and Mendez [26] proposed a local HSAB principle and predicted the reactive centre of two interacting molecules. Krishnamurty et al. [27] showed the validity of this principle in the case of interaction of small gaseous molecules with zeolite

clusters. Geerlings and coworkers [28] studied the feasibility of this principle in various organic reactions such as Diels–Alder reactions, 1,3-dipolar cyclo addition, (2 + 1) cyclo addition, etc. They also proposed two more reactivity descriptors from the ratios of local softness values for nucleophilic and electrophilic attack on the system and its inverse [29]. These two reactivity descriptors are called ‘relative electrophilicity’ and ‘relative nucleophilicity’, respectively. In our previous studies, we investigated the Brønsted acidity of isomorphously substituted zeolites and Lewis basicity of alkali and alkaline earth-exchanged zeolites by calculating the local reactivity descriptors in a representative cluster model of the zeolites [30,31]. In this paper, we focus on the Lewis acidity and basicity of alkali cation-exchanged faujasite zeolites.

2. Method

2.1. The QM/MM scheme

In SIMOMM [24] method, the entire system (S) of the surface is divided into two regions, the inner region (I) and the outer region (O). The inner region is the part of chemical interest and is treated quantum mechanically. The outer region is chemically inactive and thus is adequately modelled using molecular mechanics. Creation of inner part (I) from the entire system possesses unpaired electrons (dangling bond) and the dangling bonds on the subsurface atoms in the inner region must be terminated; otherwise, the chemical behaviour of the inner region will be dramatically different from the real surface. The dangling bonds are saturated with hydrogen atoms, the so-called linked atoms. The inner region (I) and the link atoms (L) then form the cluster, $C = I + L$. Energy of the entire system is obtained by the following scheme:

$$E(S, L) = E_{QM}(C) + E_{MM}(O) + E_{MM}(I-O) \quad (1)$$

The last two terms are not evaluated separately, but the potential function is used for calculations on the whole systems:

$$E_{MM}(S) = E_{MM}(I) + E_{MM}(O) + E_{MM}(I-O) \quad \text{or} \\ E_{MM}(O) + E_{MM}(I-O) = E_{MM}(S) - E_{MM}(I) \quad (2)$$

Therefore, the actual working equation for total energy is

$$E(S, L) = E_{\text{QM}}(\text{C}) + E_{\text{MM}}(\text{S}) - E_{\text{MM}}(\text{I}) \quad (3)$$

For simplicity, we will drop the “L” in the symbol for QM/MM energy, $E(S, L)$.

The link atoms are moved according to the forces obtained from Eq. (3):

$$\frac{\delta E(S)}{\delta L_i} = \frac{\delta E_{\text{QM}}(\text{C})}{\delta L_i} \quad (4)$$

The forces on the I and O atoms are obtained by differentiating Eq. (3):

$$\frac{\delta E(S)}{\delta I_i} = \frac{\delta E_{\text{QM}}(\text{C})}{\delta I_i} + \frac{\delta E_{\text{MM}}(\text{I-O})}{\delta I_i} \quad (5)$$

$$\frac{\delta E(S)}{\delta O_i} = \frac{\delta E_{\text{MM}}(\text{S})}{\delta O_i} \quad (6)$$

The SIMOMM method was implemented using TINKER [32] and GAMESS [33] programs. The interaction energy of a molecule with the zeolite framework can also be calculated using QM/MM method and it is defined as

$$\begin{aligned} \Delta E(\text{reaction}) = & \{E_{\text{QM}}(\text{products}) - E_{\text{QM}}(\text{reactants})\} \\ & + \{E_{\text{MM}}(\text{products}) - E_{\text{MM}}(\text{reactants})\} \end{aligned} \quad (7)$$

2.2. Local reactivity descriptors

In DFT, the global hardness and global softness are defined as the second derivative [34] of energy and its inverse.

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(\vec{r})} = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{v(\vec{r})} \quad (8)$$

$$S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial \mu} \right)_{v(\vec{r})} \quad (9)$$

Using a finite difference approximation to the E versus N curve, one obtains

$$\eta = \frac{\text{IP} - \text{EA}}{2} \quad (10)$$

$$S = \frac{1}{\text{IP} - \text{EA}} \quad (11)$$

The local softness finds its origin within DFT and describes the reactivity of an atom in a molecule [35].

Using the finite difference approximation, for an atom k in a molecule, local softness values are defined as

$$s_k^+ = [\rho_k(N_0 + 1) - \rho_k(N_0)]S \quad (12a)$$

(for nucleophilic attack on the system),

$$s_k^- = [\rho_k(N_0) - \rho_k(N_0 - 1)]S \quad (12b)$$

(for electrophilic attack on the system),

$$s_k^0 = \frac{1}{2}[\rho_k(N_0 + 1) - \rho_k(N_0 - 1)]S \quad (12c)$$

(for radical attack on the system), where $\rho_k(N_0)$, $\rho_k(N_0 + 1)$ and $\rho_k(N_0 - 1)$ are electronic population of atom k in N_0 , $N_0 + 1$ and $N_0 - 1$ electron systems, respectively.

The condensed local softness values have been used successfully to explain a variety of experimentally observed phenomenon. The ‘relative electrophilicity’ (s_k^+/s_k^-) and ‘relative nucleophilicity’ (s_k^-/s_k^+) are defined from the ratios of the local softness values defined above (Eqs. (12a)–(12c)). These two newly defined local reactivity parameters describe Brønsted acidity and Lewis basicity of zeolite framework atoms in a much better way compared to charges of the atoms [30,31].

2.3. Computational details

We performed cluster model and QM/MM calculations to determine structure and energetics of Li, Na, and K-exchanged faujasite zeolite. The quantum cluster of both the models consists of three tetrahedral (T3) sites ($\text{H}_3\text{SiOAl}(\text{OH})_2\text{XOSiH}_3$, X = Li, Na or K), as shown in Fig. 1a and we refer it as [X-FAU]. In the QM/MM model, the entire system of zeolite contains 199 atoms and it is shown in Fig. 1b. Cations are mostly found at sites I, II and III of faujasite zeolite. The sites I and II are present in the sodalite cage, while site III is present in the supercage. We have considered site III in our calculations. The quantum chemical calculations were performed using the GAMESS program [33]. Geometry optimization is carried out at HF level using the 6-31G** basis set. In QM/MM studies, the outer region of the cluster is minimized with MM3 parameters [36]. We also studied the interaction of CO molecule with the zeolite cluster and the adsorption complex is represented as [X-FAU]/[CO]. Although

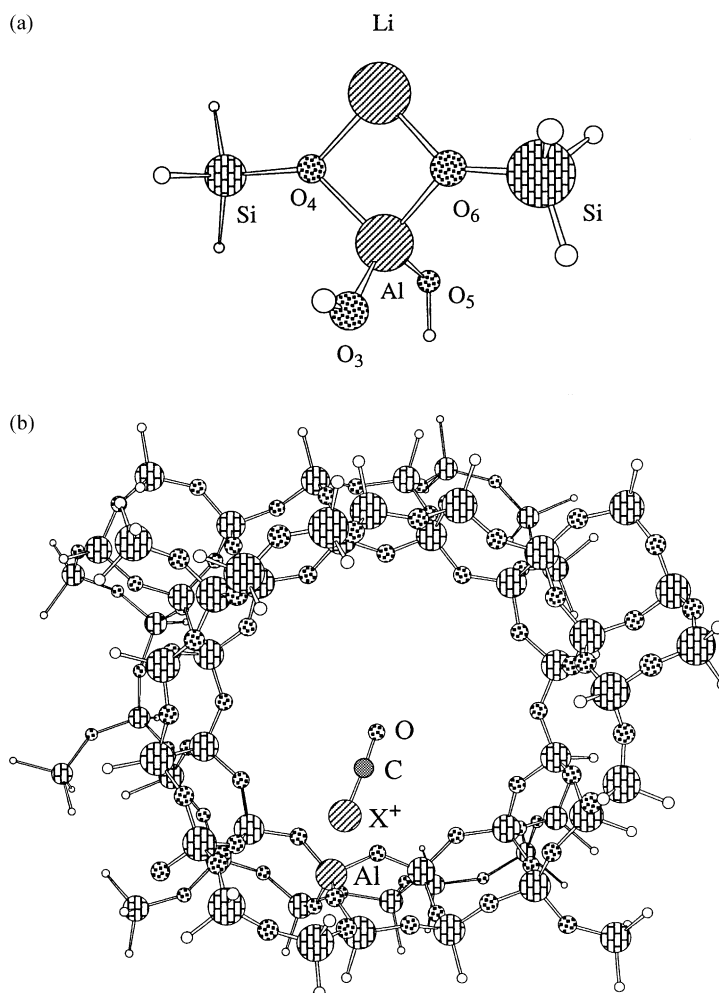


Fig. 1. The T3 cluster (Fig. 1a) to model the active site of zeolite and the cluster used in the QM/MM calculations (Fig. 1b).

CO molecule can interact with both C and O-ends, we consider here the interaction via the C-end.

The acidity and basicity of zeolites can be studied from the charges of the atoms. However, it has been found that the local reactivity descriptors based on DFT are more reliable [30,31] compared to atomic charges for predicting experimental reactivity trends. Since a fully optimized cluster does not represent a specific zeolite, we performed single point DFT calculations at the QM/MM optimized geometry and evaluated the local softness, relative electrophilicity and relative nucleophilicity values. We use DMol program [37] for DFT calculations.

3. Results and discussion

3.1. Structure

The trimer cluster used in our calculations is shown in Fig. 1a. The geometrical parameters and bonding characteristics of bare quantum cluster and QM/MM cluster models employed to represent the cationic, “hard” sites evaluated at HF/6-31G** level are given in Table 1. As reported in our earlier cluster model calculations [31], the small cations, Li^+ and Na^+ , have twofold coordination while the large cation, K^+ , has threefold coordination. Li^+ and Na^+

Table 1

Selected optimized geometrical parameters of [X-FAU] zeolite calculated at HF/6-31G** level

	[Li-FAU]		[Na-FAU]		[K-FAU]	
	QM	QM/MM	QM	QM/MM	QM	QM/MM
X ⁺ -Al	2.560	2.572	2.903	2.909	2.990	3.040
X ⁺ -O ₄	1.828	1.819	2.185	1.184	2.765	2.784
X ⁺ -O ₆	1.825	1.820	2.185	2.173	2.767	2.698
X ⁺ -O ₅					2.626	2.656
Al-O ₄	1.819	1.816	1.807	1.801	1.777	1.773
Al-O ₆	1.821	1.828	1.807	1.813	1.778	1.783
Si-O ₄	1.645	1.645	1.634	1.634	1.619	1.616
Si-O ₆	1.643	1.641	1.643	1.630	1.619	1.620
O ₄ -X ⁺ -O ₆	90.4	89.6	75.6	74.6	59.3	58.6
O ₄ -Al-O ₆	90.9	89.4	95.7	93.8	100.7	98.1
Si-O ₄ -Al	130.2	125.6	130.8	125.0	138.9	129.7
Si-O ₆ -Al	131.6	132.0	130.5	132.6	138.9	135.2
X ⁺ -O ₄ -O ₆ -Al	173.5	168.0	161.7	156.7	110.0	112.9
qx ⁺	0.635	0.640	0.771	0.771	0.828	0.810
qo	-1.001	-0.997	-0.983	-0.977	-0.944	-0.923

lie at long distance from the O₃ and O₅ oxygen atoms, whereas K⁺ cation is bonded to O₃, O₄ and O₆ atoms but lies at long distance from O₅ atom (Table 1). Interaction of a cation with the zeolite framework leads to deformations of the zeolite cluster around the cationic site. By comparing the structure between the cluster model and QM/MM model (Table 1), it is seen that the cluster environment imposed in the QM/MM calculations has little effect on bond lengths of the active site. In QM/MM model, X⁺-Al, Al-O₆ and X⁺-O₅ bond lengths increase slightly compared to bare cluster model. On the other hand, the X⁺-O₆, and Al-O₄ bond lengths decrease slightly. The QM/MM model shows a slight decrease of X⁺-O₄ bond length for [Li-FAU] and [Na-FAU] but the bond increases slightly in [K-FAU]. The large X⁺-Al distances indicate that the cluster environment weakens the attachment of the cations to the zeolite framework. There is a slight decrease in the O₄-X⁺-O₆ and O₄-Al-O₆ bond angles compared to the bare cluster model. The most significant difference is noticed in the decrease of Si-O₄-Al bond angle in the QM/MM model compared to the bare cluster model. In Li⁺ and Na⁺-exchanged clusters, the Si-O₆-Al angle increases slightly, whereas it decreases in K⁺-exchanged QM/MM model. A large difference between bare cluster and QM/MM model is also observed in X⁺-O₄-O₆-Al dihedral angle. In

bare cluster model, the Li⁺, Na⁺ and K⁺ cations lie out of the O₄, O₆ and Al plane by 6.5°, 18.3° and 70.0°, respectively, whereas in the QM/MM model, the corresponding angles are 12°, 23°, and 67.1°, respectively. Large differences may also be observed in other dihedral angles.

3.2. Interaction with CO molecule

The interaction of CO molecule with the cation-exchanged zeolite is studied via the carbon end and the calculated properties of [X-FAU]/[CO] complex are summarized in Table 2. The structure of Lewis acid sites does not change significantly upon CO adsorption because of weak interaction. The X⁺-C distance increases with increasing radius of the cations in both cluster and QM/MM models. The CO bond distance is shortened with respect to the free molecule by 0.007 Å for Li⁺ down to 0.003 Å for K⁺. This shortening of CO bond length is due to the reduction in the antibonding character of the 5σ carbon lone pair which is engaged in coordination to the cationic sites. Based on this argument, the CO → X⁺ (X⁺ = Li⁺, Na⁺, K⁺) σ charge transfer leading to a depopulation of the slightly antibonding CO 5σ orbital might be expected to increase the force constant of the adsorbed CO. Because of the shortening of CO bond length, a blue shift of CO vibrational frequency of decreasing extent from

Table 2

Selected optimized geometrical parameters of the adsorption complex [X-FAU]/[CO] calculated at HF/6-31G** level

	[Li-FAU]/[CO]		[Na-FAU]/[CO]		[K-FAU]/[CO]	
	QM	QM/MM	QM	QM/MM	QM	QM/MM
X ⁺ -Al	2.574	2.593	2.913	2.933	3.009	3.058
X ⁺ -O ₄	1.841	1.830	2.194	2.190	2.807	2.805
X ⁺ -O ₆	1.839	1.833	2.194	2.182	2.804	2.718
X ⁺ -O ₅					2.622	2.670
X ⁺ -C	2.357	2.346	2.751	2.733	3.232	3.212
C-O (1.114 Å)	1.107	1.107	1.108	1.108	1.111	1.111
Al-O ₄	1.816	1.810	1.806	1.799	1.777	1.773
Al-O ₆	1.817	1.824	1.806	1.812	1.777	1.783
Si-O ₄	1.642	1.642	1.632	1.633	1.620	1.617
Si-O ₆	1.641	1.638	1.632	1.629	1.620	1.621
O ₄ -X ⁺ -O ₆	89.6	88.7	75.2	74.3	58.5	58.1
O ₄ -Al-O ₆	91.1	90.0	95.8	93.9	100.9	98.0
Si-O-Al	130.7	124.0	131.4	124.7	137.7	129.5
Si-O ₆ -Al	132.3	131.5	131.4	132.2	137.8	135.2
O ₄ -X ⁺ -C	131.9	135.4	129.5	138.3	64.4	68.4
O ₆ -X ⁺ -C	138.8	134.8	140.2	144.7	67.9	68.6
Si-O ₄ -X ⁺ -C	-30.4	-10.0	-57.6	-5.8	-114.4	-82.9
X ⁺ -O ₄ -O ₆ -Al	173.0	171.9	161.7	160.6	108.8	112.6
Interaction energy (kcal/mol)	-8.05	-10.81	-5.96	-8.25	-3.89	-5.77
qx ⁺	0.484	0.489	0.676	0.681	0.778	0.828

Li⁺ to K⁺ is observed when it is adsorbed in alkali cation-exchanged zeolites [11,12]. It is also seen that adsorption of CO decreases the charges of the cations. The decrease in charge of alkali cations can also be assigned due to the σ charge transfer from 5 σ orbital to the cation. Similar results were observed in recent studies for the adsorption of CO in zeolites [38,39].

More interesting in the present context is the energy of the adsorption complexes. The interaction energies of the CO molecule exhibit a distinct trend to decrease from Li⁺ to K⁺. Cluster environment present in QM/MM calculations increases the binding energy of CO by 2.76, 2.29 and 1.88 kcal/mol in [Li-FAU], [Na-FAU] and [K-FAU], respectively. The binding energy for [Na-FAU] (8.25 kcal/mol) is in reasonable agreement with the experimental binding energy of 6.7 kcal/mol for adsorption of CO on Na-Y zeolite [40]. The calculated binding energy may become more close to the experimental values if BSSE correction is used. The enhanced binding energy of CO molecule in [Li-FAU] was also observed by Limtrakul et al. [38] using a different embedded cluster approach. They compared the binding energy of CO molecule of embedded cluster models with cluster model and the

naked alkali-metal ions and observed that the binding energy of the embedded cluster model lies between those of the bare quantum cluster and the simple naked ion/CO system. The naked ion system overestimated the structure and adsorption energy because of too large electrostatic field generated by the ion compared to the bare cluster model, where the electrostatic field is reduced by the surrounding oxygen atoms. The embedding environment improves the results of small cluster model.

3.3. Acidity and basicity of zeolites

We calculated the strength of Lewis acidity of the exchanged cations and framework basicity of oxygen atom using DF-based reactivity descriptors such as local softness, relative electrophilicity and relative nucleophilicity. We have performed single point calculations at the optimized geometry of the trimer cluster obtained from QM/MM calculations. The nucleophilic local softness, s_k^+ , electrophilic local softness, s_k^- , and the relative electrophilicity, s_k^+/s_k^- , of the cations are given in Table 3. Initially, we used Mulliken population analysis (MPA) to derive the

Table 3

The MPA and HPA nucleophilic local softness, electrophilic local softness, and relative electrophilicity of the exchanged cation of the zeolite cluster, $\text{H}_3\text{SiOX}^+\text{Al}(\text{OH})_2\text{OSiH}_3$, obtained from QM/MM calculations. The values are evaluated using single point calculations at DNP/BLYP level

Exchanged cations	Basis set	MPA-derived parameters			HPA-derived parameters		
		s_k^+	s_k^-	s_k^+/s_k^-	s_k^+	s_k^-	s_k^+/s_k^-
[Li-FAU]	DNP	3.1004	1.3405	2.3129	1.1143	0.5232	2.1296
[Na-FAU]		3.0328	1.5415	1.9675	1.5273	0.8781	1.7393
[K-FAU]		2.2113	1.0062	2.1978	1.2277	0.8470	1.4495

local reactivity parameters. The s_k^+ values calculated using MPA are in the order [Li-FAU] > [Na-FAU] > [K-FAU], indicating the maximum Lewis acidity of [Li-FAU]. Experimental studies by Barthomeuf [41] showed that the Lewis acidity of alkali-exchanged zeolites decreases in the order: $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. This acidity trend is also supported by the blue shift of vibrational frequencies of adsorbed CO molecule in cation-exchanged zeolites [11,12]. Although the MPA derived s_k^+/s_k^- value indicates the higher acidity of [Li-FAU], it does not support the acidity trend of [Na-FAU] and [K-FAU]. It has been observed that the reactivity parameters calculated using various population analyses sometimes predict different trends in selectivity and reactivity of atoms in a molecule. The Hirshfeld population analysis (HPA) is found to be quite stable in predicting reactivity based on relative electrophilicity and relative nucleophilicity values. It is seen from Table 3 that the HPA-derived s_k^+/s_k^- values are in the order: $\text{Li}^+ > \text{Na}^+ > \text{K}^+$, supporting the experimental acidity trend [41].

The basic strength of cation-exchanged zeolites can be derived from negative charge of framework oxygen, electrophilic local softness and relative nucleophilicity values. However, the negative charge on oxygen atom of the cation-exchanged zeolites remains

constant irrespective of the exchanged cations [39]. Recently, we have shown that relative nucleophilicity is very efficient to predict the basicity of alkali and alkaline earth-exchanged zeolites [31].

The calculated s_k^+ , s_k^- and s_k^-/s_k^+ values for framework oxygen atom (O_4) of the zeolite cluster are presented in Table 4. The MPA-derived s_k^+ values are negative. However, it has been shown by Hirao and coworkers [42] that the Fukui function used in calculating the local softness should always be positive. Due to negative s_k^+ values, it is difficult to use the MPA-derived reactivity parameter for predicting the basicity of framework oxygen. The MPA-derived s_k^- values are positive and they increase from [Li-FAU] to [K-FAU] indicating a basicity trend: [Li-FAU] < [Na-FAU] < [K-FAU], which is in agreement with experimental observations [41]. Absolute values of MPA-derived s_k^-/s_k^+ support the same trend.

HPA-derived s_k^+ , s_k^- and s_k^-/s_k^+ values for framework oxygen atom are also presented in Table 4, and in contrast to MPA-derived s_k^+ values, the HPA-derived s_k^+ values are found to be positive. Higher basicity of an atom in a molecule is indicated by a higher s_k^- and a lower s_k^+ value. The s_k^+ values predict the correct basicity trend. Although s_k^- values are not in agreement with the experimental

Table 4

The MPA and HPA nucleophilic local softness, electrophilic local softness, and relative nucleophilicity of the framework oxygen atom (O_4) of the zeolite cluster, $\text{H}_3\text{SiOX}^+\text{Al}(\text{OH})_2\text{OSiH}_3$, obtained from QM/MM calculations. The values are evaluated using single point calculations at DNP/BLYP level

Exchanged cations	Basis set	MPA-derived parameters			HPA-derived parameters		
		s_k^+	s_k^-	s_k^-/s_k^+	s_k^+	s_k^-	s_k^-/s_k^+
[Li-FAU]	DNP	-0.0784	0.0862	-1.1000	0.0921	0.2450	2.6596
[Na-FAU]		-0.0835	0.1044	-1.2500	0.0702	0.2285	3.2560
[K-FAU]		-0.1352	0.2215	-1.6389	0.0544	0.2166	3.9793

basicity trend, the ratio, s_k^-/s_k^+ , shows the correct trend of basicity of the framework oxygen (increase in order: [Li-FAU] < [Na-FAU] < [K-FAU]).

4. Conclusion

The structure of alkali cations (Li^+ , Na^+ , K^+)-exchanged faujasite zeolite is studied using QM and QM/MM methods. The cluster environment imposed in QM/MM method affects geometry of the active centre. A large difference between QM cluster and QM/MM model is observed in bond angles and the dihedral angles. Inclusion of cluster environment is found to noticeably improve the binding energy of adsorbed molecule and leads to better agreement with experimental observation. The acidity and basicity trends derived from calculated relative electrophilicity and relative nucleophilicity values for exchanged cation and framework oxygen, respectively, are in agreement with the experimental acidity and basicity trends. HPA-derived reactivity descriptors are found to be more reliable to compare the acidity and basicity trends of cation-exchanged zeolites.

Acknowledgements

The present research is supported in part by the Grant-in-Aid for Scientific Research on Priority Areas “Molecular Physical Chemistry” from the Ministry of Education, Science and Culture of Japan and by the grant from the Genesis Research Institute. RCD thanks the Intelligent Modeling Laboratory (IML), The University of Tokyo, for providing post-doctoral research fellowship.

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