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Amines adsorption on Li- and Na-exchanged MOR: An ONIOM2 Study

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Abstract

The two-layered ONIOM method (B3LYP/6–31G(d,p):HF/3–21G) has been used to investigate the structure and energy of Li- and Na-exchanged MOR with amines (NH_3, NH_2Me, $NHMe_2$ and NMe_3). It is shown that the coordination of amine nitrogen to the zeolite alkali cation dominates the overall interaction. In addition, the adsorption complexes are further stabilized by weak hydrogen bonding between the negatively charged zeolite framework oxygen atoms and the hydrogen atoms of amines. The Lewis basicity based on the calculated adsorption energies in the order of $NMe_3 < NH_3 < NHMe_2 < NH_2Me$ is different from their relative Brønsted basicity derived from the adsorption on H-MOR. The adsorption energy of amines on Li- and Na-MOR only amounts to about 63–72 and 71–87% of the binding energy of the naked Li^+ and Na^+ with amines, respectively.

Keywords: MOR; Amines; Adsorption; ONIOM; Hydrogen bond

1. Introduction

Alkali metal cation-exchanged zeolites are widely used in many important industrial processes, such as gas separation, drying [1–3] and hydrocarbon reactions [4–7]. The location and nature of the alkali cations determine unique properties and applications of the zeolite catalysts [8,9]. Therefore, a deep understanding on the location of cations and the interaction of the adsorbates with the zeolite framework will benefit the design of new adsorbents and catalysts with advanced performance.

Alkali cations in zeolite cavities act as Lewis acid centers and interact with the basic group of the adsorbed molecules [10–12]. Several probe molecules have been used to characterize this kind of zeolites, for example, CO [13,14], CH_3OH [12], NH_3 [15,16] and NH_2CH_3 [17,18]. All these works demonstrated that the main interaction between the adsorbates and the alkali-exchanged zeolites is the binding of the guest molecule to the active center derived from the coordination of the electron-donating center of guest molecule to the alkali cations. Therefore, it is important to study the strength and structure of Lewis acid centers of alkali-exchanged zeolites.

Experimentally, a well-established technique for adsorption strength is microcalorimetry [10,19]. IR spectroscopy is used to elucidate the location and properties of alkali cations in zeolites [14,20–22]. However, a good choice of probe molecules is the major problem. Since the probe molecule should react specifically with the basic sites under consideration, while at the same time, it should not decompose or polymerise [23]. An effective solution is the theoretical method which will be helpful in understanding the reactivity of acid and base centers of the zeolites.

So far, theoretical calculations are devoted to introducing large clusters in order to include all the long-range electrostatic interactions. However, accurate calculations of large clusters are computationally very expensive or impos-

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sible. To overcome such limitation, embedding techniques [24,25] have been used at various levels. The combination of quantum mechanical and molecular mechanical (QM/MM) methods provides a fair tool to model the interaction between zeolites and other molecules with high accuracy and low computational costs [23,26]. Based on QM/MM, Morokuma and co-workers [27–29] developed an ONIOM method in which the whole system can be divided into two or three layers, being treated at different levels of theory. Roggero et al. [30] have successfully used the ONIOM method to model the adsorption of NH_3 at the isolated OH groups on a highly dehydrated silica surface. It was also applied successfully to the study of the catalytic reactions on HZSM-5 [31].

Using IR spectroscopy, Su et al. [17,18] have studied the interaction of NH_3 and NH_2Me in several large pore cationic zeolites and claimed that there are three types of interaction between host–guest molecules, which are the interaction between alkali cations and lone electron pair of nitrogen atom, the interaction between negatively charged oxygen atoms of the zeolite framework and the hydrogen atoms bonded to nitrogen and carbon atoms.

In this work, we report a study of adsorption of a series of amines (NH_3, NH_2Me, $NHMe_2$ and NMe_3) on Li- and Na-MOR. The structure of the bare clusters representing the zeolite framework is firstly investigated. On this basis, the structure of the amine adsorption complexes and the adsorption energies are obtained, as in our previous works [32,33].

2. Models and methods

2.1. Models

The coordination of the structure of zeolite was taken from the unit cell of Na-MOR [34]. As shown in Fig. 1, there are two types of cavities: one is the main channel surrounded by 12-membered rings and the other is the side channel circumscribed by 8-membered rings. The eight-membered ring channels only allow a diffusion of rather small molecules and most of the organic reactions take place in the main channels. In this work, the model employed to represent the pore structure of MOR (as shown in Fig. 2) contains 20 SiO_4 (or AlO_4) tetrahedron centers (20T) and includes a complete two-layered 12-membered ring. In this 20T model, one of the Si atoms was replaced by an Al atom, and the resulting negative charge was balanced by a Li^+ or Na^+ cation to produce Li- and Na-exchanged MOR. Terminal hydrogen atoms were employed to saturate each peripheral oxygen atom in the clusters with the O–H distances being 1.0 Å. The initial clusters of Li- and Na-MOR are shown in Fig. 2a-1 and b-1. In order to form the adsorption complexes, the amines were introduced. The distance between the nitrogen of the amines and the Li^+ and Na^+ in the zeolite framework is about 2.1 and 2.5 Å, which are the sum of the van der Waals radius of nitrogen and Li^+ or Na^+ ion [35].

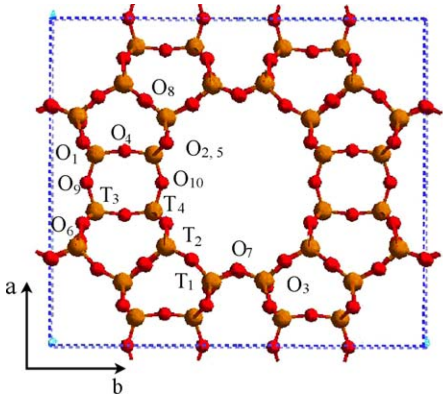

Fig. 1. The structure of mordenite unit cell viewed down the c-axis (T_1–T_4 and O_1–O_{10} are designated. Note that O_2 and O_5 sites are superposed in a projection along the c-axis).

2.2. Methods

All the calculations of this work were performed by using the Gaussian 03 program [36]. In order to better understand the interaction of amines with Li- and Na-MOR, the interaction of amines with naked Li^+ and Na^+ are firstly investigated. The amine–Li^+ and amine–Na^+ complexes were optimized by using B3LYP functional with 6–31G(d,p) and 6–311+ G(d,p) basis sets.

The structure of the amine adsorption complexes on Li- and Na-MOR was optimized by using the ONIOM2 [28] method. In this ONIOM method, the whole system was divided into two layers, which was described by two different methods. In this work, the 6T model (shown as ball and stick in Figs. 2–4) around the active site of zeolite formed the high-layer, which was treated at the B3LYP/6–31G(d,p) level, and the rest of the clusters forming the low-layer was described by the HF/3–21G method. In the adsorption complexes, the adsorbates were also included in the high-layer. Four linking H atoms between the two layers were introduced to avoid the chemically unrealistic model and they replaced four Si atoms in the clusters.

The bare 20T clusters for the structure of Li- and Na-MOR are partially optimized with the alkali cation and its neighboring Si and Al as well as the oxygen atoms surrounding Al relaxed, while the rest atoms are fixed to their crystal positions. For the adsorption complexes, the adsorbate probes were relaxed in addition to the above-mentioned atoms in the bare clusters.

The adsorption energy (ΔE_{ads}) is defined as the energy difference between the adsorption complex and the sum of the separated 20T cluster and the free amine probe [$\Delta E_{\text{ads}} = (E_{\text{adsorbate}} + E_{\text{20T}}) - E_{\text{adsorbate-20T}}$]. It is worth noting that the common practice of running a higher level single-point energy calculation at the geometry generated by using a cheaper method is as effective as performing all calculations at the higher level of theory [37]. To obtain more

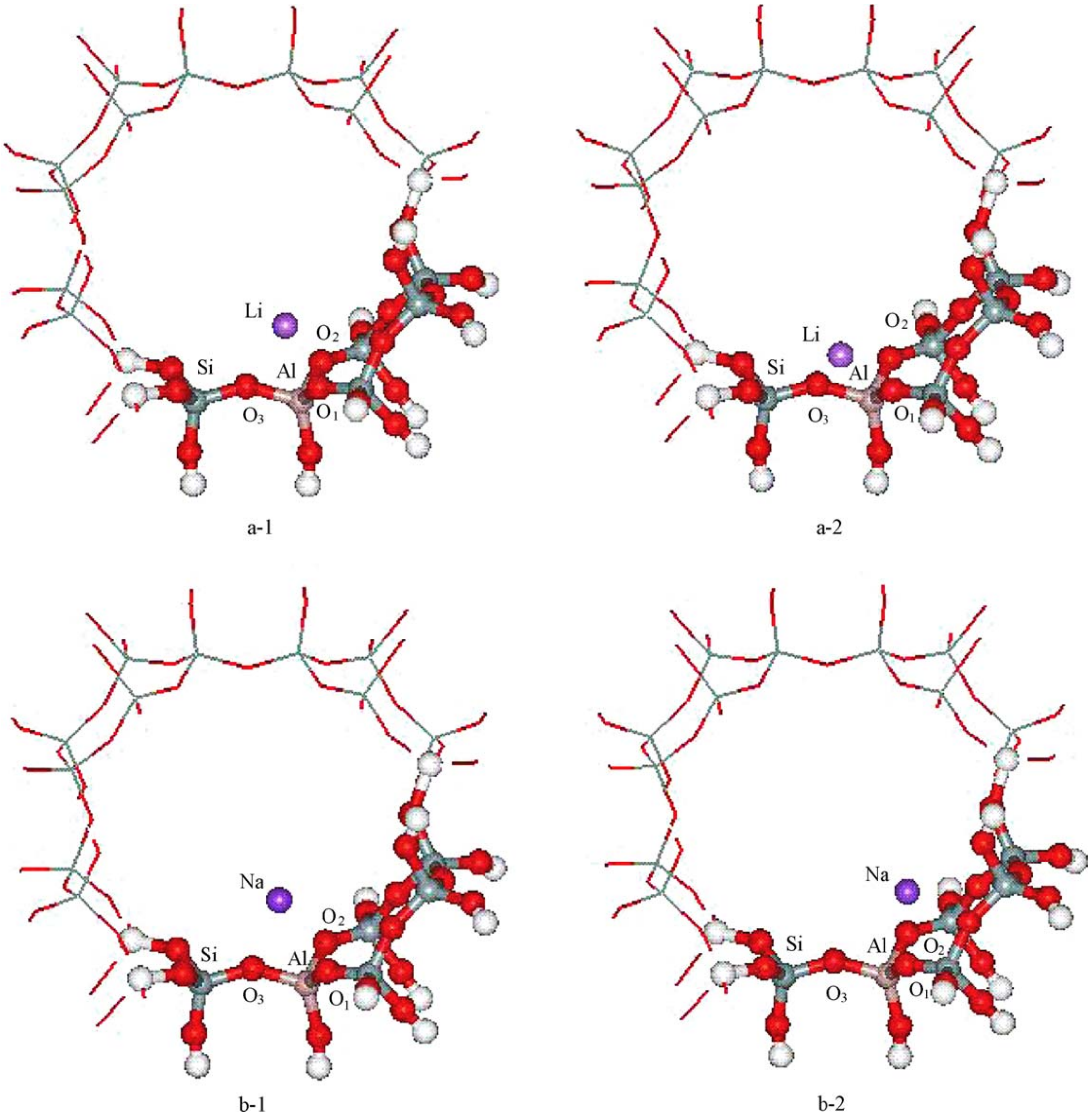

Fig. 2. The initial and optimized configuration of 20T models simulating the Li- and Na-MOR (a-1 and b-1, initial; a-2 and b-2, optimized).

precise energy data, we carried out single-point energy calculations at the ONIOM (B3LYP/6–311+ G(d,p):HF/3–21G) level by using the cluster structures optimized at the ONIOM (B3LYP/6–31G(d,p):HF/3–21G) level.

3. Results and discussion

3.1. Interaction of free amines with naked Li^+ and Na^+

The calculated binding energies (BE) for the amines coordinated to naked Li^+ and Na^+ are given in Table 1, and the atomic charges estimated by Mulliken populations of the adsorption complexes are also presented. Due to the interaction, the charges on Li^+ and Na^+ reduced from 1.0 to 0.760–0.798 and 0.814–0.842, while the adsorbed amines are positively charged by 0.202–0.240 and 0.158–0.186, respec-

Table 1

Binding energies (BE, kJ/mol) of amines to Li^+ and Na^+ and Mulliken charges on Li, Na and the amine molecules in the adsorption complexes as well as the corresponding pK_a of the conjugate acid of amines

	NH_3	$MeNH_2$	Me_2NH	Me_3N
Amine–Li^+				
q(Li)	0.798	0.778	0.765	0.760
$q(Me_nNH_{3-n})$	0.202	0.222	0.235	0.240
BE	170.4	176.9	177.4	174.6
Amine–Na^+				
q(Na)	0.842	0.825	0.816	0.814
$q(Me_nNH_{3-n})$	0.158	0.175	0.184	0.186
BE	119.2	122.3	122.7	116.9
pK_a [18]	9.3	10.6	10.7	9.7

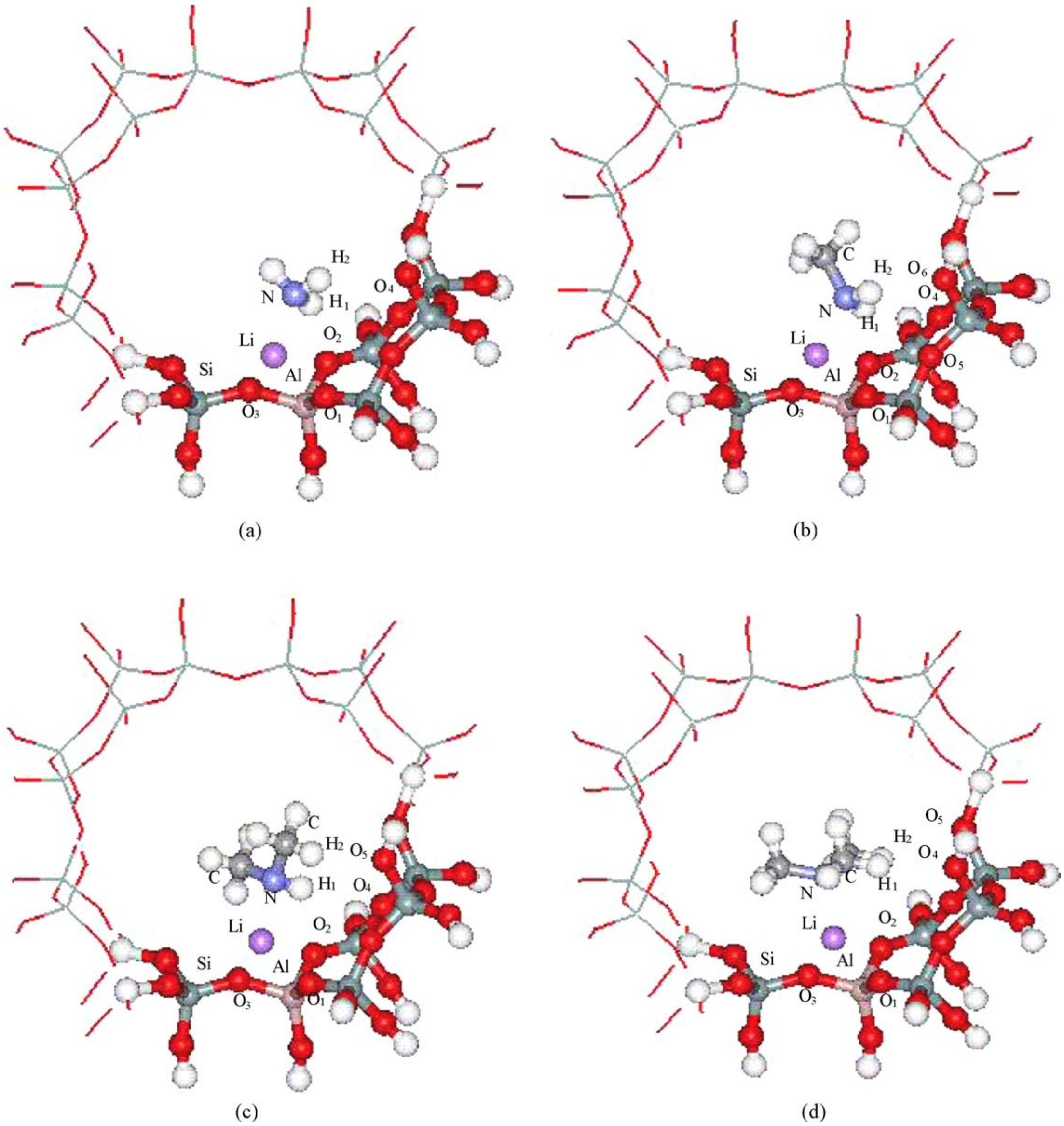

Fig. 3. The structure of the amines adsorption complexes on Li-MOR: (a) NH_3; (b) NH_2Me; (c) $NHMe_2$; (d) NMe_3.

tively. This indicates charge transfer from the amines to Li^+ and Na^+. In addition, because Li^+ exhibits stronger Lewis acidity than Na^+, the amount of transferred charge is more in amine–Li^+ complexes than that in amine–Na^+ complexes, and in turn leading to less positive charge on Li^+ than on Na^+ in the complexes. It is worth noting that such interaction was also found for the interaction of CH_3OH [38] and N_2 [39] with alkali-exchanged molecular sieves by Vayssilov et al., and they claimed that the electrostatic interaction between the negatively charged nitrogen atom and the alkali cations provides a significant contribution to the adsorption energy. In addition, due to the inductive effect of alkyl groups, the amine molecule with more methyl groups shows more charge transfer between the adsorbate and the alkali cation, lessening the charge populations on Li^+ and Na^+ in the adsorption complexes.

It is well known that the electron-donating methyl could increase the negative charge population on nitrogen atom in the amine molecules, which will strengthen the electrostatic interaction between nitrogen and Li^+ or Na^+ and then increase their binding energies. The binding energies of amines to the Li^+ follow the order of $NH_3 < NMe_3 < NH_2Me < NH\ Me_2$, which is consistent with the pK_a of their conjugate acids. However, their binding energies to the naked Na^+ increase in the order of $NMe_3 < NH_3 < NH_2Me < NHMe_2$, which is slightly different from the order of pK_a.

The binding energy of NH_3–Li^+ and NH_3–Na^+ calculated at the B3LYP/6–311+ G(d,p) level is 170.4 and 119.2 kJ/mol, respectively, which is very close to the experimental enthalpy values of 166.1 and 124.2 kJ/mol [40] and other theoretical results of 169.0 and 119.6 kJ/mol [41], respectively. This validates the reliability of our calculations.

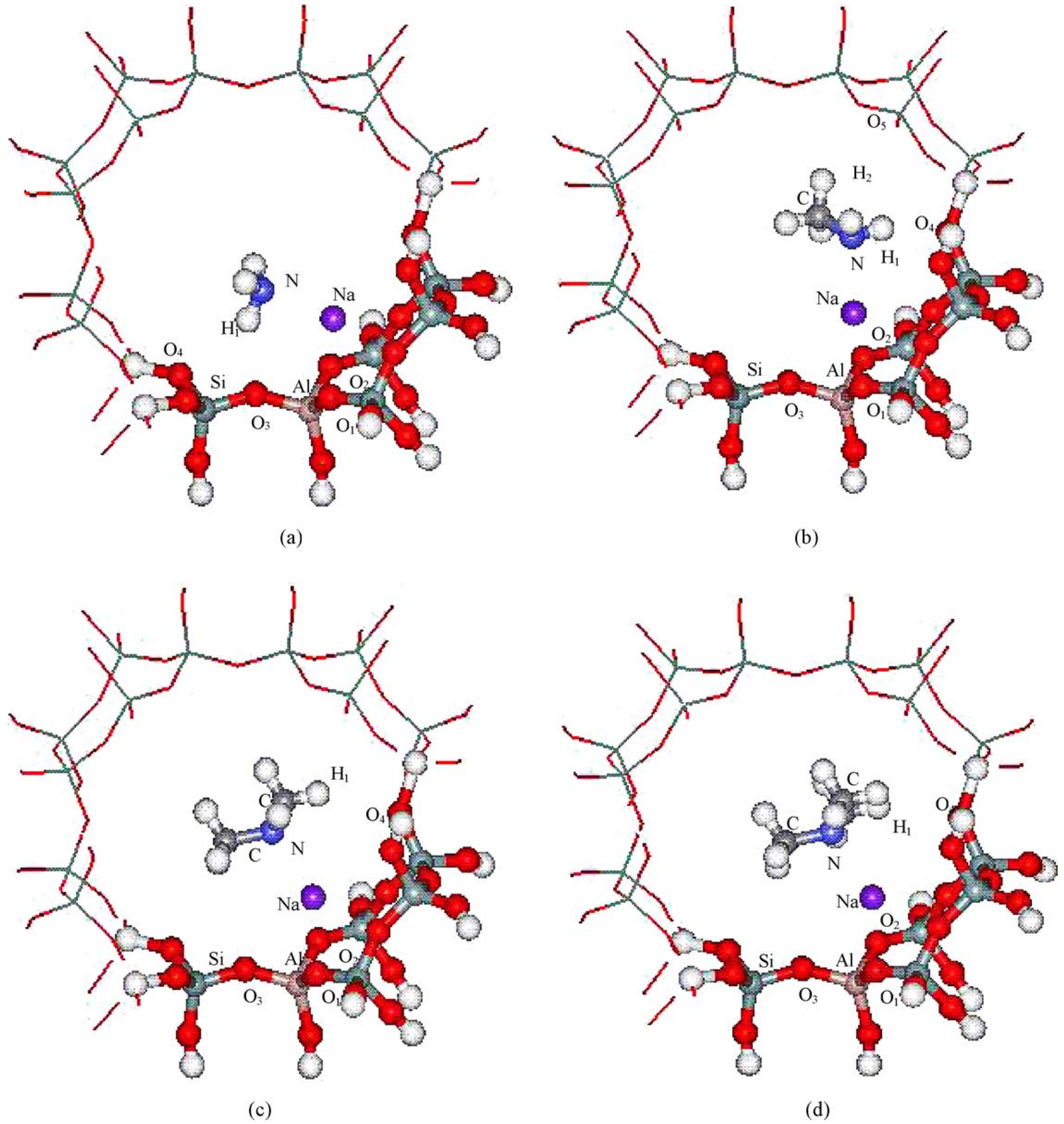

Fig. 4. The structure of the amines adsorption complexes on Na-MOR: (a) NH_3; (b) NH_2Me; (c) $NHMe_2$; (d) NMe_3.

Table 2 lists the structural parameters of the amine–Li^+ and amine–Na^+ complexes. In the adsorption complexes, the N–Li and N–Na distances range from 1.971 to 1.985 Å and from 2.328 to 3.337 Å, respectively, the N–H and N–C bonds in the amines are elongated and the C–H bonds are somewhat shortened, which is associated with the effect of hyper-conjugation. For a given amine, the binding energies and the changes on N–H, N–C and C–H bond lengths are larger for amine–Li^+ than those for amine–Na^+ complexes due to the stronger Lewis acidity of Li^+ than Na^+.

3.2. Amines adsorption on zeolite clusters

The optimized Li- and Na-MOR bare clusters are shown in Fig. 2a-2 and b-2, and the geometrical parameters are given in Tables 3 and 4. As found previously [32,33], the charge-compensating proton bonds to a particular bridging oxygen atom around Al center in the H-typed MOR, while in alkali cation-exchanged MOR, both Li^+ and Na^+ has a two-fold coordination to the zeolite oxygen. As shown in Tables 3 and 4, Li^+ bonds to O_1 and O_3 with bond length of 1.900 and 1.758 Å, and Na^+ bonds to O_1 and O_2 in the distance of 2.395 and 2.339 Å. The symmetrical binding of Li^+ and Na^+ cation to $[AlO_4{}^-]$ of other zeolites has also been confirmed by ESR experiment [42] and other theoretical studies [38,43,44].

The amine adsorption complexes on Li- and Na-MOR are illustrated in Figs. 3 and 4, and the selected geometrical parameters are listed in Tables 3 and 4. In a similar manner to amine adsorption on Li^+ and Na^+, the amine interacts with the zeolite by coordinating nitrogen to Li^+ and Na^+ with Li–N

Table 2
The optimized bond parameters (Å and degree) of adsorbed amine complexes on Li^+ and Na^+

	NH_3	NH_2Me	$NHMe_2$	NMe_3
Amine–Li^+				
R(Li—N)	1.985	1.979	1.975	1.971
R(N—H)[a]	1.022 (1.018)	1.022 (1.017)	1.022 (1.017)	–
R(N—C)[a]	–	1.500 (1.465)	1.492 (1.457)	1.488 (1.455)
R(C—H)[a]	–	1.092 (1.098)	1.094 (1.099)	1.095 (1.099)
A(Li—N—C)	–	114.0	111.2	109.4
Amine–Na^+				
R(Na—N)	2.337	2.333	2.331	2.328
R(N—H)[a]	1.021 (1.018)	1.021 (1.017)	1.021 (1.017)	–
R(N—C)[a]	–	1.494 (1.465)	1.486 (1.457)	1.483 (1.455)
R(C—H)[a]	–	1.093 (1.098)	1.095 (1.099)	1.096 (1.099)
A(Na—N—C)	–	114.9	111.6	109.3

[a] The average length of N—H, N—C, C—H bonds in the adsorption complexes, and the data in parenthesis are the values of the free molecules.

Table 3
Bond lengths (Å) in Li-MOR cluster and the amine–Li-MOR complexes[a]

	Li-MOR	NH_3–Li-MOR	NH_2Me–Li-MOR	$NHMe_2$–Li-MOR	NMe_3–Li-MOR
R(Li—O_1)	1.900	1.982	2.004	1.999	1.978
R(Li—O_3)	1.758	1.965	1.972	1.974	1.947
R(Al—O_1)	1.800	1.806	1.806	1.810	1.808
R(Al—O_2)	1.719	1.759	1.757	1.756	1.751
R(Al—O_3)	1.750	1.761	1.763	1.761	1.762
R(Li—N)	–	2.010	2.032	2.036	2.044
R(O_2—H_1)	–	2.358	2.454	2.528	–
R(O_4—H_1)	–	2.967	2.758	2.912	2.486
R(O_5—H_2)	–	–	2.822	2.516	2.900
R(O_6—H_2)	–	–	2.752	–	–
R(N—H, av.)[b]	–	1.021 (1.018)	1.022 (1.017)	1.022 (1.017)	–
R(N—C, av.)[b]	–	–	1.481 (1.465)	1.478 (1.457)	1.477 (1.455)
R(C—H, av.)[b]	–	–	1.094 (1.098)	1.095 (1.099)	1.096 (1.099)

[a] The numbering of the atoms follows those designated in Fig. 3.

[b] The average length of all N—H, N—C or C—H bonds, respectively, in the adsorbed state, and the data in parenthesis are the values of the free molecules.

or Na–N distance ranging from 2.010 to 2.044 Å and from 2.350 to 2.405 Å, respectively. In addition, there are weak interactions between the negatively charged framework oxygen atoms and the hydrogen atoms at nitrogen and at carbon of amines, with the O–H bond lengths being in the range of 2.180–2.967 Å. This finding further confirms the IR experimental results of Su et al. [17,18].

It is also seen that the adsorption of the amines affects the structure of the zeolite framework significantly due to the large dipole moment of amines. The coordination of N to Li^+ or Na^+ weakens the Li–O and Na–O bonds by elongating the Li–O_1, Li–O_3 and Na–O_1, Na–O_2 distances, and the hydrogen bond formation between amine hydrogen atoms and the framework oxygen atoms affects the Al–O bonds in

Table 4
Bond lengths (Å) in Na-MOR cluster and the amine–Na-MOR complexes[a]

	Na-MOR	NH_3–Na-MOR	NH_2Me–Na-MOR	$NHMe_2$–Na-MOR	NMe_3–Na-MOR
R(Na—O_1)	2.395	2.497	2.428	2.447	2.447
R(Na—O_2)	2.339	2.399	2.392	2.376	2.377
R(Al—O_1)	1.812	1.804	1.808	1.814	1.809
R(Al—O_2)	1.812	1.820	1.805	1.756	1.814
R(Al—O_3)	1.728	1.741	1.737	1.736	1.735
R(Na—N)	–	2.350	2.376	2.387	2.405
R(O_3—H_1)	–	2.242	–	–	–
R(O_4—H_1)	–	2.944	2.180	2.660	2.620
R(O_5—H_2)	–	–	2.618	–	–
R(N—H, av.)[b]	–	1.020 (1.018)	1.020 (1.017)	1.019 (1.017)	–
R(N—C, av.)[b]	–	–	1.484 (1.465)	1.478 (1.457)	1.479 (1.455)
R(C—H, av.)[b]	–	–	1.094 (1.098)	1.095 (1.099)	1.096 (1.099)

[a] The numbering of the atoms follows those designated in Fig. 4.

[b] The average length of all N—H, C—N or C—H bonds, respectively, in the adsorbed state, and the data in parenthesis are the values of the free molecules.

MOR. In addition to these changes, the N–H and N–C bonds are elongated and the C–H bonds are shortened as compared to the free amines, due to the weakening of N–H and N–C bonds. As compared with the amines adsorption on naked Li^+ and Na^+, the Li–N and Na–N distances are longer in the amine–Li(Na)-MOR complexes, which is due to the binding of Li^+ and Na^+ to the zeolite framework oxygen atoms. This indicates that the Li–N and Na–N bonds are weaker in the zeolite adsorption complexes than those in the naked cation complexes. As a result, it can be found that the bond lengths of the amine molecules are less affected by adsorbing on zeolite framework (see N–H, N–C and C–H bond lengths in Tables 2–4).

The weaker interaction of Li–N and Na–N in the amine–Li(Na)-MOR than in the amine–Li^+(Na^+) complexes can also be confirmed by the Mulliken charge populations on amines presented in Table 5. The net charge transfer of 0.099–0.107 to the adsorbed amines in amine–Li-MOR is less than that of 0.202–0.240 (Table 1) in amine–Li^+ complexes. This is the same situation as for amine–Na-MOR and amine–Na^+ complexes. It is also shown that in the existence of the zeolite framework, the Lewis acidity of Li^+ and Na^+ are weakened, as indicated by the less positive charge populations on Li and Na in Table 5 as compared to Table 1.

The calculated adsorption energies of amines on Li- and Na-MOR are also given in Table 5. It can be seen that the adsorption energy follows the increasing order of $NMe_3 < NH_3 < NHMe_2 < NH_2Me$ for these amines, indicating the increasing Lewis basicity of theses amines for alkali-exchanged zeolites, which is different from their Lewis basicity to naked Li^+ and Na^+. This reflects the contribution of hydrogen bond interaction to the adsorption energies. Our previous theoretical works [32,33] on the amines adsorption in H-MOR showed that when they act as Brønsted bases and interact with the zeolite Brønsted acidic sites, the basicity of these amines increased in $NH_3 < NH_2Me < NMe_3 < NHMe_2$, which differs from their Lewis basicity in Li- and Na-MOR. This different amine basicity order in alkali-exchanged and H-typed mordenite indicates the importance of the effect of counterpoise on zeolites, and with the larger radius of Na^+ than Li^+, the size of adsorbates have more significant effect on the adsorption of amines. As shown in Table 5, for a given amine, the adsorption energies follow the order of amine–Na-MOR < amine–Li-MOR, which is in agreement with the relative Lewis acidity of Li^+ and Na^+. In addition, the calculated adsorption energy of NH_3 in Na-MOR is 85.0 kJ/mol, which agrees well with the experimental result of 80.0 kJ/mol [45,46], validating our calculation methods again.

Table 5
Adsorption energies of amines on Li- and Na-MOR and the Mulliken charges on Li, Na and the amine molecules in the adsorption complexes[a]

	NH_3	$MeNH_2$	Me_2NH	Me_3N
Amine–Li-MOR				
q(Li)	0.440	0.439	0.402	0.357
$q(NH_{3-n}Me_n)$	0.107	0.105	0.101	0.093
ΔE_{ads} (kJ/mol)	117.6	128.1	120.4	109.9
Amine–Na-MOR				
q(Na)	0.453	0.355	0.303	0.265
$q(NH_{3-n}Me_n)$	0.045	0.044	0.043	0.063
ΔE_{ads} (kJ/mol)	85.0	106.9	91.7	82.9

[a] The Mulliken charges on Li and Na in the bare Li- and Na-MOR clusters are 0.5323 and 0.5522, respectively.

The adsorption energies of amines on Li- and Na-MOR only amount to about 63–72 and 71–87% of their binding energies to the naked Li^+ and Na^+, respectively, which further confirms the destabilizing role of the zeolite framework to the coordination of amine nitrogen to Li^+ or Na^+. In the amine–Li-MOR and amine–Na-MOR complexes, the Li–N and Na–N bond lengths are longer than those in amine–Li^+ and amine–Na^+ complexes, which is consistent with the lower adsorption energies of amines in Li- and Na-MOR than that in naked Li^+ and Na^+ cation and indicated that the dominant interaction between the amines and the alkali-exchanged zeolites is the coordination of amine nitrogen to the alkali cation.

4. Conclusion

The structure of Li- and Na-MOR and their interaction with amines including NH_3, NH_2Me, $NHMe_2$ and NMe_3 have been studied by using the ONIOM2 (B3LYP/6–31G(d,p):HF/3–12G) method. It was shown that besides the dominant interaction between amine nitrogen and the alkali cations of Li^+ and Na^+, there is weak hydrogen bonding between the negatively charged framework oxygen atoms and the hydrogen atoms of amines. The relative amine Lewis basicity in Li- and Na-MOR indicated by their adsorption energies on these zeolites are in the order of $NMe_3 < NH_3 < NHMe_2 < NH_2Me$, which is different from their relative Brønsted basicity derived from the adsorption on H-MOR. In addition, it is found that the adsorption energy of amines on Li- and Na-MOR only amounts to 63–72 and 71–87% of the binding energies to the naked Li^+ and Na^+ ion, respectively.

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