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Adsorption energies of NH$_3$ and NH$_4^+$ in zeolites corrected for the long-range electrostatic potential of the crystal

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The calculation of adsorption energies in zeolites in the cluster approximation has the advantage of a reduced computational effort compared to that of the periodic approach. However, in the cluster approximation, the long-range electrostatic effects of the infinite crystal are ignored and there are boundary effects. In order to remove a part of the disadvantages of the cluster approach, we developed a method to embed a cluster in a zeolite crystal by imposing an electrostatic potential on it. This potential adds the long-range electrostatic effects of the crystal and subtracts the electrostatic potential of the boundary of the cluster. It is calculated from the charge distribution of the crystal obtained with an ab initio calculation using the CRYSTAL program. We calculated the adsorption energies of NH$_3$ and NH$_4^+$ on three different clusters embedded in the potential of a chabazite crystal, and we have compared them with the adsorption energies of NH$_3$ and NH$_4^+$ in the crystal. If a cluster is used that has dangling bonds four, or more, bonds away from the adsorbate, i.e., the adsorption site is described well covalently, embedding the cluster reduces the error in adsorption energies (relative to the crystal calculations) from ~20 to ~2–3 kJ/mol.

INTRODUCTION

Zeolites are microporous alumino-silicates. They are applied widely because of their specific properties: a three-dimensional system of intersecting channels of molecular dimensions in which molecules can be adsorbed and the presence of various functional groups inside this channel system. Catalytically, the most important functional group is the acidic HOSiAl group. To obtain detailed information on the adsorption of small molecules on this acidic group and proton transfer from the acidic group to an adsorbate these processes have widely been studied quantum chemically.

The cluster approximation is widely used to describe a zeolite in quantum chemical calculations. In this approximation a group of atoms is cut from the zeolite crystal and the dangling bonds are saturated, usually with hydrogen atoms. The advantage of the cluster approximation is that adsorption processes can be described as a molecule–molecule interaction, with its computational advantages. The disadvantages of the cluster approximation are the absence of the long-range electrostatic forces of the crystal and the boundary effects of the cluster. Due to the saturation of dangling bonds with hydrogen atoms the chemical environment of the atoms in the cluster is different from the chemical environment of the corresponding atoms in the crystal. Because of these boundary effects, the atoms in the cluster behave differently towards an adsorbate than the corresponding atoms in the crystal.

A perfect zeolite crystal can also be used as a model. So far, one study has been reported in which adsorption energies are calculated in a zeolitic crystal. For the calculation of the electronic structure and the energy of the periodically repeating structure the CRYSTAL program was used. Such calculations have the advantage that the crystal model is more realistic than the cluster model because boundary effects are absent and the long-range electrostatic forces of the crystal are included. However, the computational effort that comes with a crystal calculation is much larger.

In order to combine the computational advantages of the cluster approximation with the better model for the zeolite provided by the crystal, we developed a method in which a zeolite cluster is embedded in a zeolite crystal by imposing an electrostatic potential onto the cluster. This electrostatic potential adds the long-range electrostatic forces of a crystal (the Madelung potential) and subtracts the electrostatic part of the boundary effects of the cluster. There is no correction for the covalent part of the boundary errors. With this embedding scheme we keep the computational advantage of the cluster approximation but we remove, at least a part of, its disadvantages.

There are two main differences in the present work with respect to other schemes in which a cluster is embedded in a potential representing in some way the long-range electrostatic potential. The first difference is that the potential in this scheme is obtained from a periodic calculation performed with the same Hamiltonian, basis set, and numerical accuracy as the (embedded) cluster calculations. In other schemes the long-range electrostatic potential is calculated from a lattice of point charges. These point charges are the full, half, or three-quarter formal charges of the atoms in the lattices, or they are obtained with Mortiers electronegativity equalization method. The second difference is that in this scheme the potential is not imposed on the complete cluster, but only on the central part of it. Embedding of the boundary of the cluster prevents a proper correction for the boundary errors.
The host crystal and the host cluster are divided into an inner zone and a outer zone. The charge distribution of the outer zones are used for the calculation of the correction potential. The central part of the adsorption cluster is the part that is corrected for the long-range electrostatic effects. It does not necessarily equal the inner zone.

We calculated the adsorption energies of NH$_3$ and NH$_3^+$ in a zeolite crystal and on three clusters embedded in the potential of the zeolite crystal. From the comparison between the adsorption energies on the embedded clusters and the crystal we can judge the validity of the embedding scheme and we can give some comments on the choice of the cluster.

**METHODS AND COMPUTATION DETAILS**

Our aim is to study adsorption and proton transfer processes on a zeolitic cluster that is embedded in a zeolitic crystal. The cluster is embedded by adding the long-range electrostatic potential of the zeolite crystal and subtracting the electrostatic potential of the boundary of the cluster. The starting point for our embedding scheme is a perfect zeolite crystal. This crystal is called the host crystal [Fig. 1(a)]. The second step in the embedding scheme is the creation of a cluster from the host crystal by cutting out a group of atoms around the adsorption site, in the present case the acidic HOSiAl group, and saturating the dangling bonds with hydrogen atoms. This cluster is called the host cluster [Fig. 1(b)] and it is used for the correction of the electrostatic part of the boundary errors. Apart from the dangling-bond hydrogen atoms, the host cluster must have the same chemical composition and the same geometry as the host crystal. From the host cluster we derive a second cluster: the adsorption cluster [Fig. 1(c)]. The adsorption cluster is the cluster on which we study the adsorption and proton transfer processes. The adsorption cluster may be equal to the host cluster, but in some cases it is desirable to make some changes in the adsorption cluster with respect to the host crystal and host cluster; atoms can be replaced by others and the geometry can be modified. However, the boundary of the adsorption cluster must remain equal to the boundary of the host cluster since the host cluster is used to correct for the boundary errors of the adsorption cluster.

The interaction between the adsorption cluster and the adsorbate can be calculated in the case the cluster is embedded, but also in the case it is not. In the latter case the cluster–adsorbate interaction is equal to a normal cluster–adsorbate interaction. The electrostatic potential that is imposed on the adsorption cluster, the correction potential ($V^{\text{corr}}$), adds the Madelung potential of the crystal to the Fock matrix of the adsorption cluster and subtracts the electrostatic potential of the boundary of the cluster. For the calculation of the $V^{\text{corr}}$ we have divided the host cluster and the host crystal into two complementary parts, the inner zone and the outer zone. The charge distribution in the inner zones of the host cluster and the host crystal are very similar if the boundaries of the host cluster are sufficiently far from the inner zone. The correction potential is the electrostatic potential of the outer zone of the host crystal minus the electrostatic potential of the outer zone of the host cluster. It is calculated as follows. The charge distributions of the host crystal and the host cluster, obtained with a relativistic Hartree–Fock (RHF) calculation, are partitioned through a Mulliken scheme. From the resulting atomic charge distributions the atomic multipoles are calculated, up to the hexadecapoles:

$$
V^{\text{corr}}(r) = V_{\text{outer zone}}(r) - V_{\text{host cluster}}(r)
$$

$$
= \sum_{A,L} \gamma_{L}^{\text{host crys}}(A) \sum_{h} \Phi_{L}(r - s_{h} - h)
$$

$$
- \sum_{A,L} \gamma_{L}^{\text{clus}}(A) \Phi_{L}(r - r_{d}),
$$

The $A$ summation extends to the atoms of each unit cell of the host crystal in the first summation and to the atoms of the outer zone of the host cluster in the second. The $h$ summation extends over all unit cells in the infinite crystal, excluding those identifying the atoms of the inner zone of the host crystal. $L=(l,m)$ are (spherical harmonic) quantum numbers; $\gamma_{L}^{\text{host crys}}(A)$ and $\gamma_{L}^{\text{clus}}(A)$ are the $(l,m)$ multipole moments of atom $A$ calculated according to a Mulliken partitioning from the host cluster and host crystal charge distribution (see Appendix A in Ref. 4). $X_{l}^{m}$ are real solid spherical harmonics (see Appendix A in Ref. 4). The position of atom $A$ in the reference cell is given by $s_{h}$, the position in the cluster by $r_{d}$. The question can be raised why in Eq. (1) only the outer zone is considered; in fact if the multipoles in the inner zone of the host crystal and the host cluster coincide, $V^{\text{corr}}$ would be exactly the same as resulting from Eq. (1). As we need a correction for the long-range effects, the differences in the charge distributions and thus in the multipoles of the inner zone should be negligible. However, the risk exists of magnification of minor differences by the multipole approximation or by numerical errors caused for example by small differences between the geometries of the host cluster and the host crystal. Therefore, the inner zones are ignored in the calculation of the correction potential. The correction potential is thus smooth in the inner zone of the adsorption cluster. We would like to repeat that since the host cluster is used to correct for the electrostatic boundary errors of the adsorption cluster the outer zones of the two clusters should...
be equal. Modification of the adsorption cluster with respect to the host cluster may only be made in the inner zone of the host cluster.

Only the part of the adsorption cluster that is of interest for the adsorption process is embedded, i.e., corrected with the \( V_{\text{corr}} \). The rest of the cluster remains unmodified. We will define the part of the adsorption cluster that is embedded as the central part. The correction potential must behave properly in the central part, therefore the central part must be completely inside the inner zone. The central part is defined by assigning a group of atoms around the adsorption site to the central part. An overlap distribution \( \mu \nu \) is said to belong to the central part if both atomic orbitals \( \mu \) and \( \nu \) are centered on nuclei belonging to the inner part.

\[
F_{\mu \nu} = F_{\mu \nu}^0 + \langle \mu | V_{\text{corr}} | \nu \rangle + V_0 S_{\mu \nu}, \tag{2}
\]

\( F \) is the modified Fock matrix, \( F^0 \) is the Fock matrix of the nonembedded adsorption cluster. The adsorption cluster is embedded by adding the integrals \( \langle \mu | V_{\text{corr}} | \nu \rangle \) to the Fock matrix of the adsorption cluster (2). This integral is set to zero if \( \mu \) or \( \nu \) do not belong to the inner zone. A second term is added to all matrix elements: \( V_0 S_{\mu \nu} \), where \( S_{\mu \nu} \) is the overlap element and \( V_0 \) a constant selected such that the host cluster and host crystal potential coincide. This term is necessary in order to fix the arbitrary zero of the potential in the periodic calculation.\(^{18}\) This arbitrary zero is caused by the expansion of the charge distribution into multipoles. It is to be noticed that the \( V_0 S_{\mu \nu} \) term has no influence on the energy of a neutral inner zone, if both electronic and nuclear terms are corrected. In our calculations we did not calculate the \( V_0 \) explicitly but it was set to zero for convenience.

From the previous discussion, and from general considerations, our model supposes that the long-range electrostatic potential has a minor influence on the wave function of the cluster, but a non-negligible effect on the adsorption energy. On the basis of this assumption the correction can be applied \textit{a posteriori}, once the convergence of the self-consistent cycle in the calculation of the wave function has been reached. This is the first-order embedding scheme since the effect of the correction is calculated as a first-order perturbation. If the correction, on the contrary, is applied to the Fock matrix at each cycle, the full embedding scheme is obtained. In the latter the wave function of the adsorption cluster can adjust itself to the correction potential. In the following these two corrections are compared.

The embedding of the central part of the adsorption cluster in the correction potential changes its total energy. The effect of the embedding on the adsorption energy is that of the adsorption cluster with respect to the host cluster may only be made in the inner zone of the host cluster.

\[
\Delta E_{\text{Embed}}^{\text{Ads}} = \sum_{\mu, \nu} P_{\mu \nu}'(\mu | V_{\text{corr}} + V_0 | \nu) \]

\[
- \sum_{Z} Z_i(r_i') [V_{\text{corr}}(r_i') + V_0] \tag{3a}
\]

\[
- \sum_{\mu, \nu} P_{\mu \nu}'(\mu | V_{\text{corr}} + V_0 | \nu) \]

\[
+ V_0 \int_{\text{central part}} (\rho(r) - \rho'(r)) V_{\text{corr}}(r) \]

\[
+ V_0 \int_{\text{central part}} (\rho(r) - \rho'(r)) \tag{3b}
\]

In Eq. (3a) the atomic positions, the nuclear charges, and the density matrix of the adsorption cluster with the adsorbate are indicated with \( r_i' \) and \( Z_i' \), and \( P_{\mu \nu}' \). For the adsorption cluster without the adsorbate the symbols are \( r_i \) and \( Z_i \), and \( P_{\mu \nu} \), respectively. In other words, in the first-order embedding, the effect of the embedding on the adsorption energy is the integral over the central part of the product of the correction potential and the change in the charge distribution due to the adsorption. This is the first term in Eq. (3b). The charge distributions \( \rho(r) \) and \( \rho'(r) \) also contain the nuclear charges. Although Eq. (3) is only correct for the first-order embedding scheme we also used it in the interpretation of the results of the full embedding scheme since, for the cluster we will discuss more extensively, there appears to be only a minor difference between the first and full embedding scheme. The second term in Eq. (3b) is the error made by ignoring the \( V_0 \) at the time we did our work. This error is equal to the constant \( V_0 \) multiplied by the charge in the charge of the central zone by the adsorption process, i.e., the flow of charge in or out of the central part as a result of the interaction with the adsorbate. Although we did not calculate the \( V_0 \) explicitly we made an estimate for it from the correction potential. Since for the zeolite system studied here the absolute value of the \( V_{\text{corr}} \) is below \( 10^{-3} \) and since the charge flow of the adsorption is at maximum a few tenths of an electron charge, the error maximally made by ignoring the \( V_0 = 1 \text{ kJ/mol} \). For other systems, in which either the charge flow or the \( V_0 \) is larger, the \( V_0 \) should be calculated explicitly.

We would like to make some comments on the choice of the inner zone in the hosts and the central part in the adsorption cluster. As the correction potential should correct for the electrostatic boundary errors the inner zone should be as small as possible because the correction potential only corrects for boundary errors outside the inner zone. On the other hand, a large inner zone has the advantage that more modifications can be made in the adsorption cluster and that the central part can be larger. In the latter case a larger part of the cluster is embedded and more changes in the electronic
FIG. 2. The structure of chabazite with NH$_4^+$. The view is perpendicular to the one of the eight-ring channels.

structure due to adsorption or changes in the geometry are embedded. We studied the effect of the size of the inner zone and the central part by varying their size in the calculation of the adsorption energies.

We calculated the adsorption energies of NH$_3$ and NH$_4^+$ on three zeolite clusters, both embedded and nonembedded, and we compared them with the adsorption energies as calculated in the host crystal. The host crystal is an acidic chabazite with a Si/Al ratio of three. Chabazite contains eight-ring channels in three different, almost perpendicular, directions. The geometry of the crystal was optimized with the shell model, using the parameter set of Schröder et al. The structure of the chabazite, with NH$_4^+$ adsorbed in it, is shown in Fig. 2. Three clusters were cut from the crystal. Cluster I, Si$_6$Al$_2$O$_{18}$H$_{16}$, contains the acidic HOSiAl site and the oxygens bonded to this group. Also the second shell of silicon and aluminum atoms around the acidic site is included. Two pairs of silicon atoms are connected with oxygen atoms to form rings containing four silicon and aluminum atoms. Cluster II, SiAlO$_7$H$_7$, is smaller than cluster I; only the acidic HOSiAl group and the oxygens bonded to them are included in the cluster (Fig. 4). Cluster III (Si$_{10}$Al$_2$O$_{28}$H$_{28}$) is an extension of cluster I; it contains the silicon and aluminum atoms that form an eight ring and the oxygen atoms that are bonded to these silicon and aluminum atoms. Cluster III is shown in Fig. 5. For all clusters the saturating hydrogen bonds are put in the direction of the bond they are saturating. Si–H and Al–H bond lengths are 1.49 Å and OH-bond lengths are 0.95 Å. For NH$_3$ and NH$_4^+$ experimental geometries were used. NH$_3$ and NH$_4^+$ were adsorbed in such a way that their symmetry axes coincided with the OH axis. All calculations are carried out at the RHF level with a STO-3G basis set. This basis set is used to facilitate the comparison between the embedded cluster and the crystal calculations. It is too much computer time consuming to carry out CRYSTAL calculations on the chabazite crystal with a larger basis set.

FIG. 3. Cluster I. The structure is shown from three mutually perpendicular directions.

The adsorption clusters were chosen equal to the host clusters.

RESULTS AND DISCUSSION

The comparison between the adsorption energies on the three embedded clusters and the adsorption energies in the crystal allows us to draw conclusions about the role of the cluster size in the embedding scheme. The clusters differ in two ways. First, they differ in the number of atoms directly interacting with the adsorbate and second, they differ in the quality of the covalent description. In both clusters I and II the main interaction is the interaction between the adsorbate
and the acidic OH group. Cluster III also describes the interaction between the adsorbate and the atoms in the eight ring. In Clusters I and II this interaction is described purely electrostatically.

Apart from the number of atoms interacting with the adsorbate the clusters also differ in the quality of the covalent description. Previously, we found that the quality of the covalent description can be estimated from the Mulliken charges of the atoms, if the atoms in the cluster have a charge that is close to the charge of the corresponding atom in the crystal the environment in the cluster and the crystal is very similar and the quality of the covalent description is good. Before we calculated the adsorption energies on the three clusters, we performed a RHF calculation on the host clusters, here equal to the adsorption cluster. From the resulting Mulliken charges on the atoms interacting with the adsorbate we made an estimate of the quality of the covalent description. In Table I the Mulliken charges of the atoms of the acidic group are given for the crystal and the three clusters. The charges of the atoms of the acidic site of clusters I
TABLE I. The net charges resulting from a Mulliken population analysis on the atoms of the acidic SiOHAl group and the oxygen atoms bonded to this group. The charges are given for the crystal and the three clusters. The charges for the embedded clusters are marked with an asterisk. In parentheses the central part and the inner zone that were used in the embedding scheme are indicated.

<table>
<thead>
<tr>
<th>Atom</th>
<th>H</th>
<th>O</th>
<th>Si</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal</td>
<td>0.213</td>
<td>-0.534</td>
<td>1.443</td>
<td>1.212</td>
</tr>
<tr>
<td>Cluster I</td>
<td>0.215</td>
<td>-0.532</td>
<td>1.449</td>
<td>1.224</td>
</tr>
<tr>
<td>Cluster I*</td>
<td>0.219</td>
<td>-0.533</td>
<td>1.473</td>
<td>1.203</td>
</tr>
<tr>
<td>(HOSiAIO₅/HOSiAIO₅)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cluster I*</td>
<td>0.220</td>
<td>-0.537</td>
<td>1.535</td>
<td>1.198</td>
</tr>
<tr>
<td>(HOSiAl/HOSiAl)</td>
<td>0.222</td>
<td>-0.522</td>
<td>1.612</td>
<td>1.275</td>
</tr>
<tr>
<td>Cluster I*</td>
<td>0.226</td>
<td>-0.527</td>
<td>1.586</td>
<td>1.173</td>
</tr>
<tr>
<td>(HOSiAl/HOSiAl)</td>
<td>0.219</td>
<td>-0.533</td>
<td>1.452</td>
<td>1.230</td>
</tr>
<tr>
<td>Cluster II</td>
<td>0.222</td>
<td>-0.522</td>
<td>1.612</td>
<td>1.275</td>
</tr>
<tr>
<td>Cluster II*</td>
<td>0.226</td>
<td>-0.527</td>
<td>1.586</td>
<td>1.173</td>
</tr>
<tr>
<td>Cluster III</td>
<td>0.219</td>
<td>-0.533</td>
<td>1.452</td>
<td>1.230</td>
</tr>
</tbody>
</table>

and III deviate less than 0.01 unit from the charges in the crystal, whereas the deviation for cluster II is larger. Clusters I and III give a correct covalent description of the zeolite OH group, whereas cluster II does not. Table II shows that in cluster III the atoms in the eight ring are not described well.

We calculated the potential energy curves of NH₃ and NH₄⁺ on the embedded and nonembedded cluster I. They are shown in Fig. 6. The embedding of the cluster shifts the potential energy curves of NH₃ and NH₄⁺ towards the potential energy curves as calculated in the crystal. However, the shape of the potential energy curve remains more or less the shape of the cluster curve. The reason for this is that, since the embedding is purely electrostatic, the embedded cluster describes the interaction between the adsorbate and the opposite wall of the zeolite channel purely electrostatically. In the case of NH₃, the N–O distance in the crystal is a little larger than in the embedded cluster, probably because of covalent bonding effects and polarization of the atoms of the opposite wall. Both of them are not included in the embedding scheme, and give rise to additional attraction between the opposite wall and the adsorbate. The potential energy curve of the cluster is shifted the least if the central part and the inner zone are equal to HOSiAIO₅. This combination of central part and inner zone also results in the smallest perturbation of the wave function of the cluster (see Table I). In the minimum the embedded cluster describes the crystal potential energy curve quite well; the crystal adsorption energies are reproduced within 6 kJ/mol for all combinations of central part and inner zone. The corresponding adsorption energies are given in Tables III and IV.

The error made by the cluster approximation is reduced largely by embedding the cluster. For the nonembedded cluster the errors with respect to the crystal calculations were 16
TABLE III. The adsorption energies and O–N equilibrium distances of NH$_3$ on cluster I. The adsorption energies obtained with the first-order embedding scheme are indicated with $\Delta E^{ads}(1)$, the adsorption energies obtained with the full embedding scheme are indicated with $\Delta E^{ads}$. The adsorption energies are given in kJ/mol, the equilibrium distances in Å. The adsorption energy of NH$_3$ in the crystal is $\sim 72$ kJ/mol, the corresponding equilibrium distance is 2.72 Å (Ref. 3). The calculated adsorption energies of the first line are the adsorption energies of the nonembedded cluster.

<table>
<thead>
<tr>
<th>Central part</th>
<th>Inner zone</th>
<th>$\Delta E^{ads}(1)$</th>
<th>$R_{N-O}$</th>
<th>$\Delta E^{ads}$</th>
<th>$R_{N-O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>...</td>
<td>...</td>
<td>$-56$</td>
<td>2.67</td>
<td>$-56$</td>
<td>2.67</td>
</tr>
<tr>
<td>NH$_3$ + HO</td>
<td>HOSiAl</td>
<td>-71</td>
<td>2.66</td>
<td>-70</td>
<td>2.65</td>
</tr>
<tr>
<td>NH$_3$ + HOSiAl$_6$</td>
<td>HOSiAl$_6$</td>
<td>-68</td>
<td>2.66</td>
<td>-67</td>
<td>2.66</td>
</tr>
<tr>
<td>NH$_3$ + HOSiAl</td>
<td>HOSiAl</td>
<td>-69</td>
<td>2.66</td>
<td>-68</td>
<td>2.65</td>
</tr>
</tbody>
</table>

and 23 kJ/mol for NH$_3$ and NH$_4^+$, respectively. By embedding the cluster the errors are 1–4 and 1–6 kJ/mol. The embedding scheme produces the crystal adsorption energies with a relatively small error for a smaller part of the computer time. On a Cray Y-MP4/464 the acidic form of the chabazite crystal costs 408 s. The nonembedded and embedded adsorption energies of the two central parts is caused in adsorption energy for the two central parts is about 1 kJ/mol. The adsorption energy of NH$_3$ in the crystal is $\sim 72$ kJ/mol, the corresponding equilibrium distance is 2.72 Å (Ref. 3). The calculated adsorption energies of the first line are the adsorption energies of the nonembedded cluster.

TABLE IV. The adsorption energies, and O–N equilibrium distances of NH$_3^+$ on cluster II. The first-order embedded adsorption energies are indicated with $\Delta E^{ads}(1)$, the full embedded adsorption energies by $\Delta E^{ads}$. The adsorption energies are given in kJ/mol, the equilibrium distances in Å. The adsorption energy of NH$_3$ in the crystal is $\sim 72$ kJ/mol, the corresponding equilibrium distance is 2.72 Å (Ref. 3). The calculated adsorption energies on the first line are the adsorption energies of the nonembedded cluster.

<table>
<thead>
<tr>
<th>Central part</th>
<th>Inner zone</th>
<th>$\Delta E^{ads}(1)$</th>
<th>$R_{N-O}$</th>
<th>$\Delta E^{ads}$</th>
<th>$R_{N-O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>...</td>
<td>...</td>
<td>$-57$</td>
<td>2.75</td>
<td>$139$</td>
<td>2.23</td>
</tr>
<tr>
<td>NH$_3$ + HO</td>
<td>HOSiAl</td>
<td>-82</td>
<td>2.63</td>
<td>89</td>
<td>2.23</td>
</tr>
<tr>
<td>NH$_3$ + HOSiAl</td>
<td>HOSiAl$_6$</td>
<td>-76</td>
<td>2.57</td>
<td>116</td>
<td>2.25</td>
</tr>
<tr>
<td>NH$_3$ + HOSiAl$_6$</td>
<td>HOSiAl$_6$</td>
<td>-90</td>
<td>2.06</td>
<td>92</td>
<td>2.26</td>
</tr>
<tr>
<td>NH$_3$ + HOSiAl$_6^*$</td>
<td>HOSiAl$_6^*$</td>
<td>$-85^*$</td>
<td>2.63*</td>
<td>92*</td>
<td>2.26*</td>
</tr>
<tr>
<td>NH$_3$ + HOSiAl$_6$</td>
<td>HOSiAl$_6$</td>
<td>$-118$</td>
<td>2.59</td>
<td>25</td>
<td>2.26</td>
</tr>
</tbody>
</table>

central part should be used. The effect of the size of the inner zone is investigated by keeping the central part constant at HOSiAl and changing the size of the inner zone. In the first case there is a correction for the boundary effects of the six oxygen atoms, in the second there is no such correction. The difference in adsorption energy, as calculated with the two inner zones, HOSiAl and HOSiAl$_6$ is small: 2 kJ/mol. This implies that the charge of the oxygen atoms bonded to the acidic site in the host crystal and the host cluster differs little, they are described well in the host cluster.

In Table I we showed that only the OH group itself is described well in cluster II. All other atoms have relatively large boundary effects, i.e., they have a charge deviating more than 0.1 unit from the charge of the corresponding atoms in the zeolite crystal. This means that cluster II does not give a good covalent description of the acidic site. Since the embedding scheme only gives an electrostatic correction cluster II will not produce good results. A correction potential that is not affected by boundary effects can only be obtained if the inner zone, and the corresponding central part, consist of just the OH group. This central part however is too small to give proper results in the embedding scheme. This becomes clear if we compare the adsorption energies calculated with the inner zone equal to the HOSiAl group. There is a large difference in adsorption energy for the central part equal to the HOSiAl group and just the OH group. As a consequence the embedded cluster II does not reproduce the adsorption energies of the crystal (Table V). Also there is a large difference in adsorption energy for the full and the first-order embedding energy.

The adsorption energies of NH$_3$ and NH$_4^+$ on cluster III are given in Table VI. Cluster III is an extension of cluster I; it includes the atoms of the eight ring, their charges however, differ from those they have in the zeolite crystal (see Table II). As in the case of cluster II the poor covalent description of the atoms in the eight ring will prevent proper adsorption energies in the embedding scheme. For the “small” inner zone and central part (the HOSiAl$_6$ group) the error in the adsorption energy is a result of the poor description of the eight ring. Because the inner zone is very large for the
The adsorption energy and O-N equilibrium distances of NH$_3$ and NH$_4^+$ on cluster III. The embedded adsorption energies are first-order embedded energies. Energies are in kJ/mol, bond lengths in Å. The adsorption energies denoted with small are calculated with the central part and the inner zone equal to the HOSiAlO$_6$ group. The adsorption energies denoted with large were obtained with the central part and the inner zone equal to HOSiAlO$_6$ group plus the silicon and oxygen atoms in the eight ring. The adsorption energy of NH$_3$ and NH$_4^+$ in the crystal are -72 and 117 kJ/mol, respectively, with equilibrium distances of 2.21 and 2.72 Å (Ref. 3). The calculated adsorption energies on the first line are the adsorption energies of the nonembedded cluster.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>NH$_3$</th>
<th>NH$_4^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Central part/Inner zone</td>
<td>$\Delta E^{\text{ads}}$</td>
<td>$R_{N-O}$</td>
</tr>
<tr>
<td>...</td>
<td>-77</td>
<td>2.66</td>
</tr>
<tr>
<td>Small</td>
<td>-65</td>
<td>2.69</td>
</tr>
<tr>
<td>Large</td>
<td>-78</td>
<td>2.66</td>
</tr>
</tbody>
</table>

"large" inner zone and central part (the HOSiAlO$_6$ group and the atoms in the eight ring) there is only a small correction to the adsorption energy.

Although cluster III is an extension of cluster I, the latter yields better adsorption energies. Apparently, the error made by the purely electrostatic description of the interaction between the adsorbate and the eight ring, as in cluster I, is smaller than the error caused by boundary errors in the eight ring, even if there is a correction for the electrostatic part of them. By comparing the three clusters it results that the embedding scheme only produces reasonable results if atoms with boundary effects are three or four bonds away from the adsorbate. In this embedding scheme the cluster must be relatively large because the embedding is purely electrostatic.

Even if the cluster is chosen well, some numerical errors will remain in the embedding scheme. For the systems studied in this paper a numerical error of a few kJ/mol is made by the truncation errors in the calculation of the matrix elements $\langle \mu | V^{\text{corr}} | \nu \rangle$ (see the Appendix). Another error is introduced by computing the adsorption energies on the embedded cluster with adsorption energies in the host crystal. In the crystal calculations the adsorbate is adsorbed periodically and there is an interaction between the adsorption sites and the adsorbates. In the embedded cluster there is only one adsorbate. The error introduced by this comparison is about 2 kJ/mol for NH$_4^+$ and smaller for NH$_3$ (the crystal adsorption energies were calculated with three NH$_3$ molecules per unit cell and one NH$_4^+$ cation per unit cell). Neglecting $V_0$ causes an error of less than 1 kJ/mol.

It is useful to make a comparison between our embedding scheme and other schemes in which a zeolite cluster is embedded in a potential representing in some way the long-range electrostatic effects. Allavena and co-workers$^{9,10}$ developed a method in which the potential is calculated from a lattice of point charges whose value is obtained with Mortiers electronegativity equalization method.$^{15,16}$ From this potential a correction for the potential of the dangling-bond hydrogens is subtracted. The latter is calculated in the Mulliken point-charge approximation. The cluster is embedded completely, not just a central zone. Allavena et al.$^{9,10}$ did not calculate the effect of the embedding on the adsorption energy of NH$_3$ or NH$_4^+$ but they calculated the effect of the Madelung potential on the proton transfer energy, i.e., the difference in adsorption energy between the adsorbed NH$_3$ and NH$_4^+$. They estimated the effect of the Madelung potential on the proton transfer energy to be $-197$ kJ/mol. We calculated this effect to be $-6$ or $-8$ kJ/mol for cluster I, depending on the size of the inner zone and the central part. The value produced by Allavena et al. seems a large overestimation of the effect of the long-range electrostatic potential since our values are consistent with the crystal calculations.

The overestimation of the effect of the embedding in the scheme of Allavena et al. can have two causes: the size of the cluster and the embedding scheme itself. Both groups of authors used a cluster in which the silicon atom of the HOSiAl group was saturated with hydrogen atoms. These cluster are too small to be embedded in an electrostatic potential representing the crystal. Already in cluster II, having the dangling-bond hydrogens even further away from the adsorbate than the clusters used by Allavena et al. and Cook et al. the effect of the embedding is overestimated. Another reason for the errors made may be in the embedding scheme itself. There can be two sources of errors in the method. The first is the error in the potential. Although some error will be made by using the electronegativity equalization method to calculate the potential instead of taking the potential from the crystal, this error will not cause a large overestimation. The charges obtained with this scheme do not deviate more than 35% from the Mulliken charges.$^{38}$ Probably more important errors in the scheme are the correction for the dangling-bond hydrogen atoms and the fact that the complete cluster, including the dangling bond hydrogen atoms is embedded. In the potential there is a correction for the dangling bond hydrogen atoms, i.e., the electrostatic potential of the hydrogen atoms is subtracted from the correction potential. Thus, at the position of the dangling bond hydrogen atoms, the potential will have very large values, possibly close to infinity. As such values for the potential strongly perturb the wave function the embedding of the complete cluster, including the hydrogen atoms, causes problems. In the work of Allavena et al. another error may be caused by the fact that for the geometry of the acidic site the geometry of the isolated HOSiAlH$_4^+$ and OSiAlH$_6^+$ clusters was used. In this way the link between the lattice of point charges and the orientation of the zeolite acidic site is not well defined.

The scheme used by Vetrivel et al. does not allow an estimation of the effect of the embedding since their cluster is charged.$^{11-13}$ However, some comments can still be made on the method. Probably as a result of the charge of the cluster the effect of the embedding can be largely overesti-
mated. For example, the Mulliken charges found in the clusters are strongly deviating from other cluster calculations, oxygen charges of $-1.5$, or in another case aluminum charges of $+0.8$. Also a deprotonation energy of more than 2600 kJ/mol was calculated. On nonembedded small clusters this was calculated to be about half this value. An overestimation of the effect of the long-range electrostatic potential will also be caused by the fact that the charges in this scheme are the full formal charges ($Si^{4+}, O^{2-}$), half the formal charge or three-quarters the formal charge. A general comment on the methods used by Allavena et al., Cook et al. and Vetrivel et al. to embed a cluster in a array of point charges,9–14 is that point charges are used to describe the ions in the zeolite lattice. By ignoring the higher electrical moments of the ions a relatively large error, about 20%–30%, is introduced in the calculation of the potential (see the Appendix).

CONCLUSIONS

We have calculated adsorption energies on three embedded clusters. Cluster I gives the best results, because the atoms close to the adsorbing molecule are properly described and their charges are very close those of the perfect zeolite crystal. On this cluster the error in adsorption energy with respect to the adsorption energy in the perfect crystal is very small; 1–6 kJ/mol. Roughly speaking, it results that in the present, simplified embedding scheme in which there is only an electrostatic correction, only reasonable results are obtained if the boundary of the cluster is three or four bonds away from the adsorbate. On clusters having the dangling bonds close to the adsorbate, such as clusters II and III, erroneous results are obtained.

The effect of the additional electrostatic field on the wave function of the cluster is negligible, as shown by the very small difference resulting from the a posteriori and self-consistent correction of the Fock operator. However, the corrective contribution is important in the calculation of the adsorption energy, in particular if charged species are considered.

The present scheme contains numerical approximations in the calculation of the corrective term to the Fock matrix; the numerical error as a result of the Taylor expansion (1A), although not negligible, is small enough to calculate precise adsorption energies.

By comparing the results of this work with other schemes in which there is a correction for the long-range electrostatic effects of the crystal we see that most of these methods tend to overestimate the effect of the long-range electrostatic potential.9–14 The reasons for this overestimation are several: the choice of the charges used to calculate the potential, the choice of the cluster and the method to correct for the dangling bond hydrogens. Probably also an error is caused by embedding the complete cluster instead of just a part.

ACKNOWLEDGMENTS


APPENDIX: THE CALCULATION OF THE MATRIX ELEMENTS

The integrals $\langle \mu | V_{\text{ion}} | \nu \rangle$ that are added to the Fock matrix of the nonembedded cluster (2) are calculated with a Taylor series truncated after the second step (A1).

$$\langle \mu | V | \nu \rangle = V S_{\mu \nu}^{0} + \frac{dV_{x}}{dx} \gamma_{x}^{\mu \nu} + \frac{dV_{y}}{dy} \gamma_{y}^{\mu \nu} + \frac{dV_{z}}{dz} \gamma_{z}^{\mu \nu}. \tag{A1}$$

$S_{\mu \nu}^{0}$ is the overlap between the atomic orbitals $\mu$ and $\nu$, $\gamma_{i}^{\mu \nu}$ are the transition dipole moments. The atomic orbitals (AOs) are linear combinations of Gaussians. The potential is expanded from the center of the product of the atomic orbitals $\mu$ and $\nu$. This center is determined with the Gaussian product theorem.28 The exponents used in this theorem are the most diffuse exponents of the atomic orbitals. Using only the most diffuse exponents of the contracted Gaussians gives a considerable saving in computer time but it does not introduce a large error since the largest overlap between two AOs comes from the most diffuse Gaussians. The potential and its derivatives are calculated from atomic multipoles, Eq. (1). The correction to the Fock matrix which is approximated in two ways, the truncation of the multipole series in the calculation of the potential and the truncation of the Taylor series, Eq. (A1). Both approximations are acceptable if the central part and the outer zone are not only not overlapping but also relatively apart form each other.

We studied the convergence of the potential as a function of the order of the multipole Eq. (1). We calculated the interaction of NH$_3$ with the Madelung potential of the chabazite crystal, without an inner zone created in it, for three O–N distances: 2.77, 3.19, and 3.62 Å. The first O–N distances are close to the O–N equilibrium distances, for the last one the NH$_3$ is in the middle of the cage. The order of the multipole is varied from the charge only up to the hexa-

![FIG. 7. Convergence of the multipole series. The interaction energy of NH$_3$ with the Madelung potential of the chabazite crystal is shown as a function of the order of multipole used to calculate the potential. This calculation has been carried out for three O–N distances: 2.67 Å ( – ), 3.19 Å ( – ), and 3.62 Å ( – ).](image-url)
TABLE VII. The effect of the truncation of the Taylor series on the interaction energy of NH$_3$ with the electrostatic potential of the cluster I (kJ/mol). The interaction energies are calculated in two ways. In the first the integral is approximated as the product of the overlap integral and the potential at the centroid of the overlap integral. In the second also the dipole contribution is included.

<table>
<thead>
<tr>
<th>O–N distance (Å)</th>
<th>2.97</th>
<th>3.97</th>
<th>4.97</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta V + \frac{dV}{dt}$</td>
<td>-28.17</td>
<td>-8.62</td>
<td>-1.83</td>
</tr>
<tr>
<td>$\Delta V$</td>
<td>-25.85</td>
<td>-8.27</td>
<td>-1.93</td>
</tr>
</tbody>
</table>

The effect of the truncation of the Taylor series on the interaction energy of NH$_3$ with the electrostatic potential of the cluster I (kJ/mol). The interaction energies are calculated in two ways. In the first the interaction energy of NH$_3$ with the electrostatic potential of the cluster I (kJ/mol). In the second also the dipole moment. The results of these calculations are shown in Fig. 7. For the shortest distance, as expected the convergence is slow. For an O–N distance of 3.62 Å the multipole expansion convergence is more satisfactory.

We have also studied the convergence of the Taylor series in Eq. (A1). We calculated the interaction energy between a NH$_3$ molecule and the potential of a cluster I in two ways. First the integral $\langle \mu | V | \nu \rangle$ is calculated according to Eq. (A1). Second the Taylor series is truncated after the first step, e.g., the integral is approximated as the product of the charge and the potential. The comparison is made for three O–N distances; 2.97, 3.97, and 4.97 Å. The first distance is a little bit larger than the equilibrium O–N distance, in the last one NH$_3$ is relatively far from the cluster. The interaction energies with the electrostatic potential of the cluster are given in Table VII. Table VII shows that if the adsorbate and the part of the zeolite that is described electrostatically, e.g., the atoms outside the inner zone are separated from the adsorbate by 4 Å as is the case in clusters I and III, the error we will make in the matrix elements will be at maximum 10%. For the calculation of the effect of the correction potential, in which the potential of the boundary effects is subtracted from the potential of the crystal, the error will be less since it can be expected that the errors made in the calculation of the host potential and the host crystal will be relatively similar. Although the integrals are approximated, they are sufficiently precise for our purposes.