Large Basis Sets and Geometry Optimizations in Embedded Cluster Calculations

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ABSTRACT

In the embedded cluster method, a cluster is embedded in a correction potential. This potential adds the long-range electrostatic forces of the crystal and subtracts the electrostatic potential of the boundary errors of the cluster. The correction potential is calculated from the wave function of the cluster and the crystal. So far, the method has only been used on a cluster having the same geometry and basis set as that of the crystal. Here, we calculated the adsorption energies of NH₃ and NH₄⁺ on an embedded zeolite cluster with different basis sets and modified geometries. We showed that a mixed basis set, a basis set having a large basis set on the atoms around the adsorption site and a minimal basis set on the atoms of the boundary of the cluster, yields adsorption energies close to that of the large basis set. The optimized geometries of the zeolite acidic site were almost equal for the nonembedded cluster, the embedded cluster, and the crystal. By combining the mixed basis set with a partial geometry optimization, an improved description of the adsorption process is obtained. © 1995 John Wiley & Sons, Inc.

Introduction

The adsorption of small molecules onto the acidic HOSiAl group in zeolites and the proton transfer from the zeolite to an adsorbate have been studied widely with various quantum chemical methods [1]. It appears that, for an accurate description of adsorption and proton transfer processes, it is necessary to use a relatively large basis set, to optimize the geometry, and to include the long-range electrostatic forces of the crystal [2–7]. Usually, the zeolite–adsorbate interaction is studied in the cluster approximation. In this approximation, a group of atoms is cut from the zeolite crystal and the dangling bonds are saturated with hydrogen atoms. The advantage of the cluster approximation is that large basis sets can be used. Furthermore, the geometry can be optimized relatively easy as standard molecular
packages such as GAMESS and Gaussian [8, 9] have implemented automatic geometry optimizations. The disadvantages of the cluster approximation are the absence of the long-range electrostatic forces of the crystal and the boundary errors of the cluster [6]. As a result of the saturation of the dangling bonds with hydrogen atoms, the atoms at the boundary of the cluster are in a different chemical environment than in the crystal. Consequently, they behave differently toward adsorbates [6].

So far, one study has been reported in which the adsorption and proton transfer processes were studied in a zeolite crystal [6]. In crystal calculations, the model representing the zeolite is better: There are no boundary effects and the long-range electrostatic forces of the crystal are present. However, the disadvantage of the crystal calculations is that for silicon–aluminum zeolites, because of the size of the system, the calculations are restricted to a minimal basis set. Furthermore, geometry optimizations are elaborate.

Another alternative for the calculation of adsorption energies in zeolites is the embedded cluster method that we described in [7]. An embedded cluster calculation has the computational advantages of a cluster, i.e., it requires hardly more computing time than does a cluster calculation. It provides a good model for the zeolite because the long-range electrostatic forces are included and a part of the boundary effects is removed [7]. An embedded cluster reproduces the adsorption energies of the crystal within a few kJ/mol, requiring less computer time. Until now, the embedded cluster method has only been used with clusters having the same basis set and geometry as used to calculate the long-range electrostatic potential of the crystal [7].

We studied the adsorption of NH$_3$ and NH$_4^+$ on an embedded cluster. NH$_3$ is adsorbed hydrogen-bonded onto the zeolite OH group; in the case of the adsorption of NH$_4^+$, the proton has been transferred and NH$_4^+$ interacts with a zeolite anion.

On a small cluster, keeping the geometry fixed, we calculated the adsorption energies of NH$_3$ and NH$_4^+$ with a minimal, a large, and a mixed basis set. The latter has a large basis set on the atoms around the adsorption site and a minimal basis set on the atoms at the boundary of the cluster. As an application of the mixed basis set, the adsorption energies of NH$_3$ and NH$_4^+$ were calculated on an embedded and a nonembedded larger cluster, using the minimal and the mixed basis set.

Using a minimal basis set, we optimized the geometry of the acidic OH group of the nonembedded cluster, the embedded cluster, and the crystal. We also calculated the changes in energy, with respect to a reference structure, as a result of the optimizations of the various structures. Finally, we calculated the adsorption energy of NH$_3$ and NH$_4^+$ using a mixed basis set and partially optimizing the geometry.

### Methods and Computational Details

We studied chabazite, a zeolite crystal with a relatively small unit cell. The geometry of the chabazite was optimized with the shell model [10, 11], using the parameters of Schröder et al. [12]. The shell model is a model in which the interaction between the atoms in the zeolite lattice is described with classical two-body potentials. Oxygen atoms are represented as a core and a charged shell connected to it with a harmonic potential; in this way, the oxygen is polarizable. The chabazite structure is shown in Figure 1; more details on it can be found in [6].

We calculated the adsorption energies of NH$_3$ and NH$_4^+$ on two clusters cut from the chabazite crystal. The small cluster contains the acidic HOSiAl group and the oxygen atoms bonded to it. The large cluster is an extension of the small cluster. It also contains the silicon and aluminum atoms bonded to the oxygen atoms bonding to the acidic

![FIGURE 1. The structure of chabazite. The view is perpendicular to the one of the eight-ring channels.](image-url)
HOSiAl group i.e., the second shell of aluminum and silicon atoms around the adsorption site. Two pairs of silicon atoms are linked together with an oxygen atom in rings containing four silicon or aluminum atoms. The dangling bond hydrogens are put in the direction of the bond that they are saturating. The O—H bond lengths are set to 0.95 Å; the Si—H and Al—H bond lengths are set to 1.47 Å. The small and large clusters are shown in the Figures 2 and 3, respectively. More details on the large cluster can be found in [6]. For NH₃ and NH₄⁺, experimental geometries were used [13,14]. They are adsorbed onto the acidic OH group with their symmetry axes coinciding with the OH axis. The ON distance is the only parameter optimized in the calculation of adsorption energies.

The embedded cluster method is described in [7]; a cluster is embedded in the zeolite crystal by imposing an electrostatic potential, called the correction potential, onto the cluster. This correction potential adds the long-range electrostatic potential of the crystal and subtracts the electrostatic potential of the boundary of the cluster. It is calculated from the RHF wave function of the cluster and the crystal. The wave functions of the cluster and the crystal are calculated with the CRYSTAL program [15–19], using a minimal STO-3G basis set [20]. There is a correction for the boundary errors of all the atoms in the cluster except for the atoms of the HOSiAlO₆ group and the correction potential is only added to the HOSiAlO₆ group. We used two embedding schemes: the first-order embedding scheme giving an a posteriori correction to the energy of the cluster and the full embedding scheme in which the wave function of the cluster can adjust itself to the correction potential [7].

On the small cluster, we compared the results of three different basis sets: The first basis set was the standard minimal STO-3G basis set. The second basis set was called the large basis set. In this basis set, the silicon and aluminum atoms of the acidic HOSiAl group had a 6-31G(d) basis set [21,22] and the oxygen atom of the acidic group had a 6-311G(d) basis set [23]. All other atoms had a 6-31G basis set [24,25]. The third basis set is the mixed basis set. In this basis set, the adsorbate and the HOSiAl group had the same basis set as in the large basis set. All other atoms had the minimal STO-3G basis set. The minimal basis set requires little computer time but does not yield precise adsorption energies. The large basis set, requiring more computer time, produces the adsorption energies of NH₃ with an error of 10 kJ/mol and underestimates the adsorption energy of NH₄⁺ by about 50 kJ/mol [2,26–28].
We used a mixed basis set for several reasons: First, to embed the cluster properly, the atoms in the boundary of the cluster must have the same basis set as that of the corresponding atoms in the crystal [7]. As we can use only a minimal basis set in the crystal calculations, the atoms in the boundary of the cluster should have a minimal basis set as well. Second, a large basis set on all atoms of a relatively large cluster would increase the number of basis functions, such that the calculations are not feasible any more. The disadvantage of the mixed basis set is that it is unbalanced; one part of the cluster is described well, whereas another part is not. This imbalance may cause a flow of electronic charge to the part that is described better, thus perturbing the calculation of adsorption energies.

Using a minimal sto-3G basis set, we optimized the $x$, $y$ and $z$ coordinates of the oxygen and the hydrogen atom of the OH group of the crystal, the embedded cluster, and the nonembedded cluster with the CRYSTAL program [15–19]. A parabolic interpolation algorithm [29] was used, as analytical derivatives are not implemented in CRYSTAL. The start for the optimizations was the shell-model geometry.

In CRYSTAL, not all the Coulomb and exchange integrals are calculated exactly. If the overlaps between the involved $AOs$ are below a threshold, the integral is approximated with multipolar expansions [15,19]. The thresholds were $10^{-5}$ for Coulomb integrals and $10^{-6}$ for exchange integrals. The convergence criteria in the geometry optimization are affected by the approximations in the calculation of the integrals; the potential energy surface is slightly discontinuous. We decided to stop the optimizations when the changes in energy became of the order of magnitude of the numerical noise due to the approximation of the integrals. In practice, this means that the energy was converged below $10^{-6}H$ ($2.5 \cdot 10^{-3}kJ/mol$), corresponding to a step size of about $5 \cdot 10^{-4}\AA$.

The OH group in the nonembedded cluster was also optimized with the Berny algorithm [30], an algorithm using analytical derivatives and implemented in the Gaussian 92 program package [9]. Here, all Coulomb and exchange integrals are calculated exactly. As the result of the two criteria

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>The adsorption energies (in kJ/mol) of NH$_3$ and NH$_2^+$ on the small cluster, calculated with the minimal sto-3G basis set, the mixed basis set, and the large basis set.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbate</td>
<td>Large</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>$-58$</td>
</tr>
<tr>
<td>NH$_2^+$</td>
<td>$6$</td>
</tr>
</tbody>
</table>
LARGE BASIS SETS IN EMBEDDED CLUSTER CALCULATIONS

TABLE I

The adsorption energies (in kJ/mol) of NH₃ and NH₄⁺ on the nonembedded and embedded large cluster calculated with the STO-3G basis set [7].

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Nonembedded</th>
<th>First-order embedded</th>
<th>Full embedded</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>-56</td>
<td>-67</td>
<td>-68</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>140</td>
<td>123</td>
<td>122</td>
</tr>
</tbody>
</table>

for the convergence, the step size \((2 \cdot 10^{-4})\) and the forces on the atoms, the energy converges below \(10^{-8} \text{H} \) \((2.5 \cdot 10^{-5} \text{kJ/mol})\). With the result of this optimization, the accuracy of the parabolic interpolation algorithm can be estimated since the optimization with the Berny algorithm is more accurate.

We calculated the adsorption energies of NH₃ and NH₄⁺ on the embedded and nonembedded large cluster using the mixed basis set and optimizing the geometry of the OH group and the adsorbate. The optimizations were carried out with the Gaussian program package. During the optimizations, the \(\text{O-H-N}\) angle was kept fixed at 180°. For NH₄⁺ there was an additional restriction: The N-H distance of the proton bonding to the anionic oxygen atom was kept fixed at the experimental value of 1.03 Å [14].

Results and Discussion

COMPARISON OF THE THREE BASIS SETS

The adsorption energies of NH₃ and NH₄⁺ on the small cluster calculated with three basis sets are given in Table I. As found earlier, the adsorption energy of the hydrogen bonding NH₃ is relatively independent of the basis set [2]. The adsorption energy of NH₄⁺ depends more strongly on the basis set as a result of the diffuse nature of the anionic oxygen atom in the zeolite cluster [2]. If the large basis set is taken as a reference, the minimal basis set underestimates the stability of the ionic structure by more than 120 kJ/mol.

With respect to the large basis set, the mixed basis set slightly overestimates the adsorption energies of NH₃ and NH₄⁺. This overestimation is probably caused by the imbalance in the small cluster as a result of the mixed basis set. Because of the better description of the acidic site, its electronic population is increased. The imbalance stabilizes the adsorbate and causes an overestimation of the adsorption energies by about 5–10 kJ/mol on the small cluster. In the large cluster, this overestimation is smaller, probably because it is more buffered in the large cluster. Thus, with the mixed basis set, adsorption energies on the large basis set can be calculated well.

The adsorption energies of NH₃ and NH₄⁺ for the nonembedded, the first-order embedded, and the full embedded large cluster are given in Tables II and III. On the large cluster, the difference between the adsorption energies calculated with the STO-3G and the mixed basis set are larger than for the small cluster. This larger difference is probably not the result of the imbalance in the basis set, but most probably the result of the larger basis-set superposition error (BSSE) [31,32]. The BSSE is larger because there are more atoms in the large cluster. Thus, the adsorbate and the cluster have more possibilities to use each other's orbitals to lower their own energy.

TABLE III

The adsorption energies (in kJ/mol) of NH₃ and NH₄⁺ on the nonembedded and embedded large cluster, calculated with the mixed basis set.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Nonembedded</th>
<th>First-order embedded</th>
<th>Full embedded</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>-69</td>
<td>-80</td>
<td>-80</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>-8</td>
<td>-27</td>
<td>-29</td>
</tr>
</tbody>
</table>
Although the mixed basis set gives a much better adsorption energies than does the minimal basis set, the charge distribution is not strongly affected [7]. This is illustrated by the fact that the difference between the effect of the embedding for the minimal and the mixed basis set is at most 3 kJ/mol. Also, there is a very small difference between the full and the first-order embedding scheme. This was seen before for the STO-3G basis (Table II).

GEOMETRY OPTIMIZATIONS WITH THE STO-3G BASIS SET

The results of the geometry optimizations of the OH group of the nonembedded and embedded large cluster and the crystal, all with a minimal basis set, are shown in Figure 4 and Table IV. The shell-model structure is different from the structures in which the OH group is optimized quantum chemically. Especially, the O—H bond is predicted too long. The quantum chemical optimized structures are similar to each other: Bond lengths for the various structures are equal within 0.01 Å and the Si—O—Al angles within 0.2°. The geometries of the acidic group of the nonembedded cluster as optimized with Gaussian and CRYSTAL differ only slightly. This difference can be caused by the approximation of the integrals in CRYSTAL, but it is more likely that it is caused by the less strict convergence criteria used in the CRYSTAL optimizations.

The results of the optimizations of the nonembedded cluster, the embedded cluster, and the crystal show a large resemblance to each other. We concluded before that in the large cluster the atoms of the acidic HOSiAl group are in the same chemical environment as in the crystal [6,7]. Here, this is illustrated by the very similar bond lengths. Although the long-range effects of the crystal affect the relative weak interaction with adsorbates, they hardly affect the covalent binding between the atoms in the acidic site of the cluster. For more extensive geometry optimizations, one could expect larger deviations, since, in the cluster, the boundary effects are getting more important. However, more extended geometry optimizations are not feasible for the crystal at this moment.

In Table V, the lowerings in energy of the cluster as a result of the optimization with respect to the shell-model geometry, the $\Delta E^{opt}$, are given. We calculated the $\Delta E^{opt}$ for all geometries obtained from the various optimizations. The $\Delta E^{opt}$ is relatively independent of the method used to optimize the geometry. The difference are never larger than 0.5 kJ/mol. The differences between the optimizations on the cluster with the Berny algorithm with Gaussian and the parabolic interpolation with CRYSTAL are not negligible, but, rather, constant. They seem to be caused more by the approximations in CRYSTAL than by the

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Shell-model geometry</th>
<th>Geometry-optimized with Gaussian</th>
<th>Geometry-optimized on the nonembedded cluster</th>
<th>Geometry-optimized on the embedded cluster</th>
<th>Geometry-optimized in the crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>r$_{0-H}$</td>
<td>0.999</td>
<td>0.975</td>
<td>0.975</td>
<td>0.976</td>
<td>0.976</td>
</tr>
<tr>
<td>r$_{0-Si}$</td>
<td>1.712</td>
<td>1.738</td>
<td>1.742</td>
<td>1.742</td>
<td>1.748</td>
</tr>
<tr>
<td>r$_{0-Al}$</td>
<td>1.884</td>
<td>1.829</td>
<td>1.825</td>
<td>1.825</td>
<td>1.820</td>
</tr>
<tr>
<td>[\alpha]</td>
<td>138.1</td>
<td>140.7</td>
<td>140.7</td>
<td>140.7</td>
<td>140.5</td>
</tr>
</tbody>
</table>
The gain in energy, $\Delta E^{opt}$ due to the optimization, given in respect to the shell-model geometry.

<table>
<thead>
<tr>
<th>$\Delta E^{opt}$ calculated on</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV</td>
<td>-10.797</td>
<td>-11.179</td>
<td>-11.183</td>
<td>-11.277</td>
</tr>
</tbody>
</table>

The $\Delta E^{opt}$ has been calculated for four geometries of the OH group. In column A, the $\Delta E^{opt}$ is calculated for the geometry obtained with the geometry optimization on the nonembedded cluster using the Berny algorithm. In the columns B, C, and D, the $\Delta E^{opt}$ is calculated for the geometries obtained with the parabolic interpolation geometry optimization of the nonembedded cluster, the embedded cluster, and the crystal, respectively. In row I, the $\Delta E^{opt}$ is calculated for the nonembedded cluster, using Gaussian. In rows II, and III, $\Delta E^{opt}$ is calculated with CRYSTAL on the nonembedded cluster, the embedded cluster, and the crystal, respectively.

The difference in the accuracy of the parabolic interpolation algorithm. Probably, the $\Delta E^{opt}$ for the CRYSTAL calculation on the cluster are about 0.3 kJ/mol larger because the energy of the shell-model geometry cluster was calculated 0.3 kJ/mol higher in energy as a result of the approximations used in CRYSTAL.

For each structure, the $\Delta E^{opt}$ as a result of the various optimizations is similar. This means that, for the geometries investigated here, the potential energy surfaces seem parallel. On the other hand, the $\Delta E^{opt}$ of a geometry differs for each structure. The $\Delta E^{opt}$ in the embedded cluster is 0.3 to 0.4 kJ/mol lower than is the $\Delta E^{opt}$ in the nonembedded cluster. Although the geometries found with the optimization in the embedded and nonembedded cluster are similar, the $\Delta E^{opt}$ in the former is larger. Apparently, the potential energy surfaces are similar in the sense that the minima are in the same position but that the depths of the potential energy well are different. The same is true for the crystal, in which the $\Delta E^{opt}$ are even larger. The covalent binding and the long-range electrostatic effects of the crystal seem to enforce the bonds in the acidic site.

### ADSORPTION OF NH$_3$ AND NH$_4^+$ WITH THE MIXED BASIS SET AND OPTIMIZED GEOMETRY

The geometry and adsorption energies of NH$_3$ and NH$_4^+$ on the embedded and nonembedded large cluster augmented with the mixed basis set are given in Tables VI and VII. With this basis set, the OH distance is shorter than in the shell-model geometry and the STO-3G geometry. For the OH form of the cluster, the Al—O and Si—O distances are relatively close to those of the shell model.

The adsorbates are more stable on the geometry-optimized cluster than on the shell-model geometry cluster (Tables III and VII). Previously, we saw that NH$_3$ is adsorbed less strongly if the geometry is optimized: The zeolite is more stable and less reactive [2,6]. Apparently, the effect of the optimization on the adsorption is dependent on the starting geometry. In this case, the shell-model geometry provided a good model for the OH form of the cluster; the Al—O and Si—O bond lengths are very similar. With respect to the shell-model geometry, the cluster with NH$_3$ adsorbed on it could, during the optimization, stabilize itself by elongating the Al—O bond length and shortening the Si—O bond length. NH$_4^+$ is stabilized by the geometry optimization by shortening the Si—O and Al—O distances after proton transfer. The stabilization of NH$_4^+$ is larger than for NH$_3$ because its adsorption energy is more sensitive to the geometry than that of NH$_3$ [2,5–7]. Moreover, the optimized geometry of the NH$_4^+$ adsorbed on the zeolite differs more from the shell-model optimized structure than that of NH$_3$ (compare Tables IV and VI). With respect to the minimal basis set, the

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>OH</th>
<th>NH$_3$</th>
<th>NH$_4^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{OH}$</td>
<td>0.953</td>
<td>0.996</td>
<td>1.468</td>
</tr>
<tr>
<td>$R_{O-Si}$</td>
<td>1.713</td>
<td>1.700</td>
<td>1.670</td>
</tr>
<tr>
<td>$R_{O-Al}$</td>
<td>1.894</td>
<td>1.900</td>
<td>1.886</td>
</tr>
<tr>
<td>$\angle_{Si-O-Al}$</td>
<td>137.2</td>
<td>137.7</td>
<td>141.7</td>
</tr>
</tbody>
</table>
TABLE VII
The adsorption energies of NH$_3$ and NH$_4^+$ on the partially geometry-optimized, nonembedded, and embedded large cluster, calculated with the mixed basis set.

<table>
<thead>
<tr>
<th></th>
<th>Nonembedded</th>
<th>Full embedded</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_{NO}$</td>
<td>$\Delta E$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>2.76</td>
<td>-79</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>2.48</td>
<td>-14</td>
</tr>
</tbody>
</table>

mixed basis set stabilizes the anionic oxygen. This is illustrated in the elongation of the O—N bond with respect to the minimal basis-set calculations [6]. The enlargement of the cluster, with respect to the calculations in which a small cluster and a larger basis set was used, also seems to stabilize the anion as the O—N bond is elongating [2, 5]. As the charge separation is larger, the large O—N distance is enlarging the effect of the embedding [6].

Conclusion

We calculated the adsorption energies of NH$_4^+$ and NH$_3$ on the small cluster with three different basis sets: a minimal basis set, a large basis set, and a mixed basis set. The mixed basis set has a large basis set on the atoms around the adsorption site and a minimal basis set on the rest of the cluster. We deduced that there was some imbalance in the small cluster as a result of the use of the mixed basis set, as it showed a slight overestimation of the adsorption energies with respect to the large basis set. This error is 4 kJ/mol for the adsorption of NH$_3$ and 10 kJ/mol for the adsorption energy of NH$_4^+$. The minimal basis set underestimates the stability of NH$_4^+$ by more than 120 kJ/mol. The imbalance, and thus the overestimation of adsorption energies, is smaller for the large cluster.

Using a minimal basis set, we optimized the positions of the atoms of the OH group in the nonembedded cluster, the embedded zeolite cluster, and the crystal. The resulting geometries were very similar in all cases. The $\Delta E_{opt}$, the change in energy with respect to the reference geometry, was almost the same for all optimized geometries. The potential energy surfaces for the OH group, a group relatively far from the boundary, are parallel for the nonembedded cluster, the embedded cluster, and the crystal.

We calculated the adsorption energies of NH$_3$ and NH$_4^+$ with a partial optimization of the cluster and the mixed basis set. With respect to the fixed geometry calculations, the adsorbates are stabilized.

The calculations presented here are an important step toward the calculation of accurate adsorption energies as they showed that we can use mixed basis sets and geometries optimized in clusters in an embedded cluster. The deficiencies in these calculations, such as the limited optimization, the low coordination of NH$_4^+$ toward the zeolite lattice, and the absence of electron correlation and a correction for the BSSE, are not likely to cause problems in the embedded cluster scheme and will be included in future calculations.

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