Theoretical Study of NH$_3$ Adsorption on Fe(110) and Fe(111) Surfaces

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With the aim of understanding the nature of the interactions between organic molecules and metal surfaces, the adsorption of NH$_3$ onto model Fe(110) and Fe(111) surfaces has been studied with use of the molecular orbital and density functional theories. B3LYP calculations have revealed that the on-top site is most suitable for adsorption of NH$_3$ both on Fe(110) and on Fe(111). Mulliken population analysis in terms of the MO's of the two fragment systems suggested that electron delocalization from NH$_3$ to the Fe surface should play a key role in the adsorption. Then, our transformation scheme of fragment orbitals has demonstrated that the electron delocalization is represented well only by a pair of interaction orbitals. The NH$_3$ molecule provides the occupied interaction orbital bearing a close resemblance to the highest occupied (HO) MO, whereas the Fe surface prepares the paired unoccupied orbital that is localized at the adsorption site and overlaps in-phase with the orbital of NH$_3$. Not only the lowest unoccupied (LU) MO but also other unoccupied MO's have been shown to participate significantly in the interaction. The reason the on-top site is the most preferable position for NH$_3$ attack has been elucidated by investigating the interaction orbitals.

Introduction

There is a long history of study for rust prevention and control.[1,2] Some organic compounds are effective inhibitors for aqueous corrosion of metals, being adsorbed on the metal surfaces.[3,4] Selection of these inhibitors has been based on an empirical approach to date. For proper selection of inhibitors, mechanistic information on corrosion and inhibition processes is needed. Some studies on the inhibitors from a quantum chemical point of view have been reported.[5−10] Most of these studies have focused, however, only on properties of the organic inhibitor molecule by taking some particular molecular orbitals (MO's), for instance, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Specific chemical interaction of polar groups with the metal may account for the reason a given compound is a good inhibitor for one sort of metal but not for other metals.[11] A need exists for a theoretical approach to clarify interactions between organic inhibitor molecules and metal surfaces. Therefore, we aim in this study to obtain useful information on the interaction between an organic molecule and model metal surfaces using the molecular orbital and density functional theories.

Chemical interactions are local by nature. If the substrate is very large in size, it may be difficult to interpret the interaction between the reagent and the substrate with only the frontier orbitals. On the other hand, we have shown in our previous papers that the local characteristics of chemical interactions can be displayed more properly by some sort of localized interaction orbitals.[12−19] They have been derived as the hybrids of canonical MO's by means of a pair of transformations of fragment orbitals for each given interaction. This theoretical treatment will be of great use when we discuss chemical interactions of large systems, such as the binding of molecules to surfaces.

In this work, we study the adsorption of an ammonia molecule onto the iron surface. Ammonia was employed as a simplified model of organic amines, which are used as inhibitors to prevent and control corrosion on iron and steel surfaces by acid aqueous solution.[20] As for the iron surface, we examine the Fe(110) and Fe(111) surfaces. While Fe(110) is a density packed surface, the Fe(111) surface has a relatively open structure. Experimental research of the adsorption has been reported in detail by Ertl and co-workers.[21−23] They examined the ammonia catalytic process at Fe(110), Fe(100), and Fe(111) surfaces and reported that the adsorption energies were in the range of 10−17 kcal/mol (42−71 kJ/mol). On the other hand, theoretical study of the ammonia adsorption on the Fe(100) surface has been reported by Cheng and co-workers, by applying the density functional theory and the tight binding extended Hückel method.[24] But it focused on the relative order of binding strength of ammonia on Fe(100), Ni(100), and Cr(100) surfaces with a certain specific adsorption pattern, namely on-top site, and paid little attention to characterization of the interaction between the ammonia molecule and the iron surface. Therefore, in the present paper, we estimate first the relative activity of adsorption sites on each above-mentioned iron surface based on the accurate total energy calculation and discuss the relative activity of various sites by means of Mulliken population analysis[25] to obtain useful information about the bonding. Then, by applying our transformation scheme of fragment orbitals, we derive the orbitals that participate actively in chemical interactions in these systems and disclose basic features of the interaction between the ammonia molecule and the iron surface.

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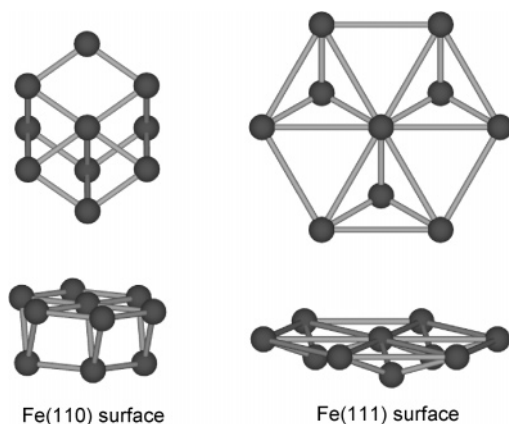§ Kyoto Institute of Technology.
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Figure 1. Fe₁₀ cluster models utilized for representing Fe(110) and Fe(111) surfaces.

Method of Calculation and Models

The hybrid Hartree−Fock and density-functional (DF) method (B3LYP) was used in this work.[26,27] This method was implemented with the Gaussian 98 program.[28] Parametrization was the method suggested by the Pople et al.,[27] i.e., 0.2, 0.8, and 0.72 for the Hartree−Fock, Slater,[29] and Becke[30] exchange functionals, and 0.19 and 0.81 for the Vosko−Wilk−Nusair[31,32] and Lee−Yang−Parr[33] correlation functionals. The Los Alamos effective core potential was used for the Fe atom[34−36] to replace the Ne core. As for the corresponding valence basis set, we employed (8s5p5d)/[3s3p2d]. For H and N atoms, the 6-311G** basis set was used.

All the calculations were performed for rigid iron surfaces. Throughout this work, the Fe₁₀ cluster with a lattice constant of 2.86 Å for body-centered-cubic Fe[37] was used to represent each of the Fe(110) and Fe(111) surfaces, as shown in Figure 1. The size and shape of the cluster especially affect the adsorption energy.[38] Therefore, we do not intend to discuss the absolute value of the adsorption energy. Instead, we aim to study the most suitable adsorption pattern of NH₃ on each iron surface to gain characterization of the interaction. The present model of the iron surface may be used to estimate the relative activity among possible adsorption sites on each iron surface, as will be demonstrated later. For the spin multiplicity of the Fe₁₀ cluster, we employed the value of 23, which is in most reasonable agreement with the experimental magnetic moment per atom, 2.22 μ_B.[39,40]

Throughout this work, the structure of NH₃ was fixed because we are interested in characterization of the interaction between NH₃ and the iron surface. The geometric parameters of NH₃ were optimized with the 6-311G** basis set in an isolated state, the N−H bond length being 1.016 Å and the H−N−H bond angle being 106.45°. Benndorf and co-workers have shown, in the study of the interaction of NH₃ with a stepped Fe(100) surface by using electron stimulated desorption ion angular distributions (ESDIAD), that NH₃ is bonded via the N atom and the H atoms (with random azimuthal orientation) are pointed away from the surface.[41] Therefore, we placed the NH₃ molecule on the iron surfaces modeled by an Fe₁₀ cluster with the lone-pair orbital directing toward a surface and the three hydrogen atoms pointing away from a surface. Then, the bond distance of the iron surface and the nitrogen of NH₃ at each adsorption site were optimized, as shown later, by making use of the assumption that the total energy would be insensitive to the rotation about the principal axis of NH₃.

All the SCF calculations were performed without the use of molecular symmetry. Moreover, to ensure that desorption leads
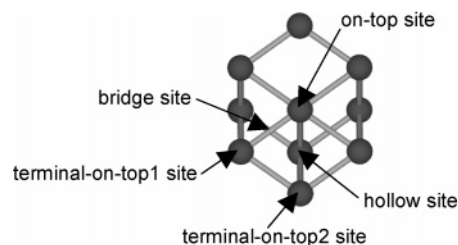

Figure 2. Adsorption patterns on the Fe(110) surface examined.

TABLE 1: Optimized Bond Distances and the Corresponding Adsorption Binding Energies for Each Adsorption Pattern on the Fe(110) Surface

absorption pattern	optimized bond distance (Å)	optimized adsorption binding energy (kJ/mol)
on-top	2.31	−45
bridge	2.41	−28
hollow	4.65	−9
terminal-on-top 1	2.23	−65
terminal-on-top 2	2.30	−39

adequately to the two fragment species with the initial electronic structures, the electron configuration in the composite system comprised of an Fe₁₀ cluster surface and an NH₃ molecule at the bond distance of 100 Å was calculated by employing the electron configuration at the optimized bond distance as an initial guess, in each case. Then, it was confirmed that the electron configuration at the bond distance of 100 Å gave the electronic structures of the two fragment molecules in an isolated state, in all cases. The adsorption binding energy was defined as ΔE = E(composite system) − {E(Fe₁₀) + E(NH₃)}, where E(Fe₁₀) was the total energy of the Fe₁₀ cluster, E(NH₃) the total energy of NH₃, and E(composite system) the total energy of the system that comprises of the two fragments. ΔE is shown to give negative values for active adsorption.

Results and Discussion

Adsorption Patterns of NH₃ on Iron Surfaces Modeled by Fe₁₀ Cluster. *Fe(110) Surface.* Three possible adsorption patterns on the Fe(110) surface examined are shown in Figure 2: on-top site, bridge site, and hollow site. Figure 2 displays not only these three possible patterns but also two terminal on-top sites: terminal-on-top 1 site and terminal-on-top 2 site. In Figure 2, the bridge site is located in the middle of the (central) on-top site and the terminal-on-top 1 site. On the other hand, the hollow site is located in the middle of the on-top site and the terminal-on-top 2 site. We also examined these two terminal on-top sites to see the difference between the central and terminal Fe atoms in adsorption.

The optimized bond distances of the Fe(110) first layer and the nitrogen of NH₃ at these adsorption sites and the corresponding adsorption binding energies are summarized in Table 1. The on-top site gives the largest, in negative value, optimized adsorption binding energy of −45 kJ/mol and the shortest bond distance of 2.31 Å in the three possible patterns. On the other hand, the bridge site and the hollow site give the negative but smaller optimized adsorption binding energies of −28 and −9 kJ/mol, respectively. As for the hollow site, a shallow energy minimum was found at a considerably long distance. The present computational method may not be able to give a reliable result at that distance, but it seems very likely that the chemical interaction is very weak at the hollow site. Incidentally, the interaction has been shown to become strongly repulsive at a shorter distance of ∼2.2 Å. On the other hand, the binding energies at the terminal-on-top 1 and terminal-on-top 2 sites
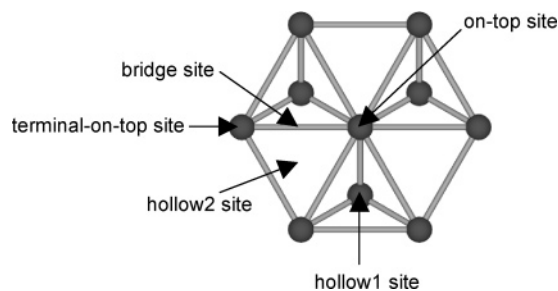
Figure 3. Adsorption patterns on the Fe(111) surface examined.

TABLE 2: Optimized Bond Distances and the Corresponding Adsorption Binding Energies for Each Adsorption Pattern on the Fe(111) Surface

adsorption pattern	optimized bond distance (Å)	optimized adsorption binding energy (kJ/mol)
on-top	2.20	−91
bridge	2.96	−11
hollow 1	4.24	−9
hollow 2	4.08	−9
terminal-on-top	2.16	−76

are −65 and −39 kJ/mol, respectively. We see that the adsorption energies at both the bridge site and the hollow site are smaller not only than that at the (central) on-top site but also than those at the terminal on-top sites. The on-top adsorption is concluded, therefore, to be the most favorable mode of NH_3 adsorption on the Fe(110) surface.

Fe(111) Surface. Four possible adsorption patterns on the Fe-(111) surface examined are shown in Figure 3: on-top site, bridge site, hollow 1 site, and hollow 2 site. Here, the hollow 1 site is located just on the second layer Fe atom. On the other hand, the hollow 2 site is located just on the third layer Fe atom that is not displayed in our Fe_{10} cluster. Figure 3 shows not only these four possible patterns but also another on-top site: terminal-on-top site. We examined also the terminal-on-top site to make a comparison between the central and peripheral Fe atoms in their activities for adsorption.

The optimized bond distances of the Fe(111) first layer and the nitrogen of NH_3 at these adsorption sites and the corresponding adsorption binding energies are summarized in Table 2. The on-top site gives the largest optimized adsorption binding energy at a negative value of −91 kJ/mol and the shortest bond distance of 2.20 Å among the four possible patterns. On the other hand, the binding energy at the terminal-on-top site has been calculated to be smaller in negative value, being −76 kJ/mol. All the other adsorption patterns have been shown to give the negative but smaller optimized adsorption binding energies of only −9 to −11 kJ/mol. Figure 3 shows that the bridge site is located in the middle of the (central) on-top site and the terminal-on-top site, and that each hollow site, namely hollow 1 site and hollow 2 site, is located in the center of an equilateral triangle comprised of one central Fe atom and two peripheral Fe atoms. The calculation indicates, however, that an effective chemical interaction between the Fe(111) surface and NH_3 can be generated only at the on-top site, and that all the other adsorption sites do not give chemical interactions of significance.

The hollow 1 site on the Fe(111) surface may be regarded as the "on-top site" of the Fe(111) second layer, because the Fe-(111) plane appears to be sparse. However, when the distance between the Fe(111) second layer and the nitrogen of NH_3 is taken to be 2.20 Å, which is the optimized bond distance for the on-top site adsorption on the first layer, the adsorption binding energy is shown to become very large, but positive in value. The same tendency has also been found in the hollow 2

model and in the hollow-site adsorption on the Fe(110) surface. These results indicate that the second layer is shielded by the electron cloud of the first-layer Fe atoms when it is viewed from the approaching NH_3 molecule and, consequently, the existence or absence of the second-layer Fe atoms in the direction of the approach of NH_3 is of little significance in the adsorption to the hollow sites.

In summary, our calculations have revealed that the most favorable adsorption pattern is "on-top" in both cases. The relative order of activity among possible adsorption sites is on-top site, bridge site, and hollow site, in the case of the Fe(110) surface. The adsorption to the hollow site should be very weak on the Fe(110) surface. As for the Fe(111) surface, adsorption to the on-top site is preferred to the other three types of adsorption. Bridge site, hollow 1 site, and hollow 2 site are not so active as to provide an effective chemical interaction with NH_3.

Experimentally, Ertl and co-workers have reported that the adsorption energies of NH_3 on Fe(110), Fe(100), and Fe(111) surfaces are in the range of 10−17 kcal/mol (42−71 kJ/mol).[21−23] On the other hand, our calculated energy of adsorption to the on-top site was 45 kJ/mol on the Fe(110) surface and 91 kJ/mol on the Fe(111) surface, in accordance with their definition of the sign of the adsorption energy. Our clusters are too small to evaluate the absolute value of the adsorption energy.[38] In addition, we did not take the relaxation of the NH_3 structure into account. Though we do not intend to discuss the absolute value of the adsorption energy, it seems that our calculated adsorption energies are not so far from experimentally observed values.

We perform next the Mulliken population analysis to obtain information that will be useful in characterizing the interaction between the Fe surface and NH_3, and in clarifying where the differences in the adsorption energy presented above come from.

Population Analysis and Electrostatic Attractions. *Mulliken Population Analysis.* We study next the changes in electron population associated with the interaction by comparing the Mulliken population of the system composed of an Fe cluster surface and an NH_3 molecule with those of the two species in an isolated state.[25] Electron populations are given in terms of the atomic basis set that has been utilized in the B3LYP calculation of the $Fe_{10}-NH_3$ combined system. It is possible then to represent the electron populations of $Fe_{10}-NH_3$ by utilizing the occupied and unoccupied MO's of the two fragment species, Fe_{10} and NH_3. We try to look at the changes within the fragments and at the change between the two fragments. Interactions between the occupied MO's of one fragment and the unoccupied MO's of the other fragment have apparently two important outcomes. That is, a part of the electron population donated from the electron-donor fragment remains in the region between the two fragment species through the overlap between the occupied MO's of the donor part and the unoccupied MO's of the acceptor part to form new bonds. Another part of electron population supplied from the electron-donor part is transferred to the electron-acceptor part, by partially filling the unoccupied MO's of the latter. This represents transfer of an electronic charge. At the same time, a part of the electron population is shifted from the occupied MO's to the unoccupied MO's within the reagent or within the substrate to lift the bias in electron distribution caused by the interaction. This may be termed polarization. Then, assuming that all of the electron population delocalized from the surface to NH_3 is retained in the region between the two fragments, the change in electron

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TABLE 3: Changes in Electron Populations for Each Adsorption Pattern on the Fe(110) Surface

	on-top	bridge	hollow
polarization in Fe surface	0.249	0.670	0.007
electron delocalization from Fe surface to NH₃	−0.003	−0.007	0.001
utilized for new bonds	−0.003	−0.007	0.001
transferred to NH₃[a]	0.000	0.000	0.000
polarization in NH₃	0.022	0.016	0.000
electron delocalization from NH₃ to Fe surface	0.231	0.203	0.060
utilized for new bonds	0.159	0.142	0.045
transferred to Fe surface	0.073	0.060	0.016

[a] Zero by assumption.

TABLE 4: Changes in Electron Populations for Each Adsorption Pattern on the Fe(111) Surface

	on-top	bridge	hollow 1	hollow 2
polarization in Fe surface	1.077	0.275	0.021	0.024
electron delocalization from Fe surface to NH₃	0.018	0.013	0.001	0.002
utilized for new bonds	0.018	0.013	0.001	0.002
transferred to NH₃[a]	0.000	0.000	0.000	0.000
polarization in NH₃	0.010	−0.001	−0.001	−0.001
electron delocalization from NH₃ to Fe surface	0.212	0.090	0.060	0.057
utilized for new bonds	0.126	0.064	0.043	0.042
transferred to Fe surface	0.085	0.026	0.016	0.015

[a] Zero by assumption.

population associated with the interaction can be decomposed into several terms, as given in Tables 3 and 4.

Tables 3 and 4 show clearly that the change in electron population is interpreted mainly in terms of electron delocalization from NH₃ to the surface to make new bonds and of the associated polarization in the Fe surface. The part that is transferred to the surface is smaller than the part that is utilized for the formation of bonds between NH₃ and the surface. In case of the on-top and bridge sites in the Fe(110) surface as well as the on-top site in the Fe(111) surface, a considerable amount of electron population is donated from the NH₃ part upon adsorption. Thus, NH₃ has a significant bonding interaction with the on-top and bridge sites of Fe(110) and with the on-top site of Fe(111). On the contrary, NH₃ is not disturbed significantly in its electronic structure in the other adsorption patterns. It is important for the adsorption that the surface shares electrons with the adsorbate in the region between two fragment species.

Our population analysis indicates that electron delocalization from NH₃ to the Fe surface plays the important role in the adsorption. Bagus and co-workers showed, from the study of the bonding of NH₃ to the Cu₅ cluster as a model of Cu(100) surface by means of the constrained space orbital variation (CSOV) method, that the interaction of NH₃ with the Cu surface is electrostatic since the interaction of the frozen orbitals of the separated units is attractive.[42] Then, we try next to estimate the role of electrostatic attractions in the interaction of NH₃ with the Fe surfaces.

Electrostatic Attractions. The interaction between reagent and substrate can be decomposed apparently into several terms, involving the electrostatic interaction, the exchange repulsion, polarization, and electron delocalization. Assuming then that NH₃ approaches the surface each retaining the charge distribution in an isolated state, we have calculated the energy of the classical electrostatic interaction, $E_{es(classical)}$, at the optimized bond distance by utilizing the point-charge approximation. It is negative but not large in all the models, being −3.7, −2.2, and

−0.5 kJ/mol for the on-top, bridge, and hollow site of the Fe-(110) surface, respectively. It is −0.8, −1.0, −0.3, and −0.2 kJ/mol for the on-top, bridge, hollow 1, and hollow 2 site of the Fe(111) surface, respectively. That is, the electrostatic interaction is attractive, but does not appear to be strong enough to bind NH₃ to the surfaces.[43]

In summary, our population analysis and evaluation of electrostatic attractions indicate that electron delocalization plays a key role in bringing the binding of NH₃ to the Fe surfaces. NH₃ is a hard base, and the Fe surface (bulk metals) is a soft acid and, accordingly, the present system is not a simple hard acid−hard base interaction in which the electrostatic attraction prevails.[44,45]

Orbital Interactions. Now, we would like to see how NH₃ interacts with the Fe surface from the viewpoint of orbital interactions. In particular, we are interested in clarifying what orbitals of the Fe surface participate in the interaction. The orbital interaction scheme based on perturbation theory is very useful in understanding chemical bondings and reactivities of small molecules.[46,47] Our surface model consists of 10 Fe atoms, giving 91 occupied and 129 unoccupied orbitals for the α-spin part and 69 occupied and 151 unoccupied orbitals for the β-spin part. Thus, we try to look at the orbital interactions between NH₃ and the Fe surface in terms of the paired interaction orbitals which are derived by applying the unitary transformations of the fragment canonical MO's simultaneously within the occupied MO space of one fragment and within the unoccupied MO space of the other fragment, referring to the bond-order matrix elements between the occupied MO's of the former and the unoccupied MO's of the latter as the measure of strength of orbital interactions.[12−14]

Electron delocalization takes place between the occupied MO's of one part and the unoccupied MO's of the other part. Here, we denote the occupied canonical MO's of the electron-donor fragment by ϕ_i ($i = 1, 2, ..., m$) and the unoccupied canonical MO's of the electron-acceptor fragment by ψ_j ($j = 1, 2, ..., n$), respectively. Then, electron delocalization between these species is expressed in terms of $m \times n$ orbital interactions. On the other hand, by the present transformation scheme, electron delocalization is represented compactly by a few pairs of the fragment interaction orbitals (ϕ'_f, ψ'_f), including not only the HOMO of the donor fragment and the LUMO of the acceptor fragment, but also all the occupied MO's of the former and all the unoccupied MO's of the latter that are relevant for the interaction. The orbital ϕ'_f is given by a linear combination of the occupied canonical MO's of donor fragment, and the paired orbital ψ'_f is given by a linear combination of the unoccupied canonical MO's of acceptor fragment.

In the present system, we may focus on electron delocalization from the occupied MO's of NH₃ to the unoccupied MO's of the Fe₁₀ cluster. The contribution of electron delocalization in the reverse direction is of little significance, as has already been demonstrated above. Here, we deal with the MO's with α-spin and with β-spin separately, because the system has an open-shell structure. We have obtained 5 occupied orbitals for the NH₃ fragment and, therefore, electron delocalization from NH₃ to the Fe₁₀ cluster is represented by five paired orbitals both for the α- and β-spins. One will find shortly that the description of interaction is simpler, represented practically by still fewer orbital pairs, only one pair in the present system.

Table 5 presents the bond-order matrix elements of paired interaction orbitals corresponding to electron delocalization from NH₃ to the Fe surface for each NH₃ adsorption pattern on Fe-(110) at the above-optimized bond distance. The sum of the

TABLE 5: Bond-Order Matrix Elements of Paired Interaction Orbitals Corresponding to Electron Delocalization from NH₃ to the Fe Surface for Each Adsorption Pattern on the Fe(110) Surface

| adsorption pattern	spin	pair 1	pair 2	pair 3	pair 4	pair 5
on-top	α	0.202	0.031	0.027	0.008	0.001
	β	0.184	0.021	0.019	0.018	0.002
bridge	α	0.197	0.022	0.017	0.012	0.001
	β	0.177	0.027	0.022	0.019	0.002
hollow	α	0.108	0.005	0.004	0.001	0.000
	β	0.105	0.005	0.004	0.001	0.000

bond-order matrix elements of paired interaction orbitals describing electron delocalization from NH₃ to the Fe surface is closely related to the electron population that is utilized for the formation of new bonds, presented in Table 3. It is very interesting to see that the number of paired interaction orbitals participating significantly in electron delocalization from NH₃ to the Fe surface is only one for both the α- and β-spins in all cases. That is, Pair 1 predominates and, in fact, a good correlation is found to exist between the sum of bond orders for the α- and β-spin parts of Pair 1 and the electron population that is utilized for the formation of new bonds between the two fragments.

Figures 4−6 illustrate Pair 1's which represent electron delocalization from NH₃ to the Fe₁₀ cluster surface for the on-top, bridge, and hollow-site models of the Fe(110) surface, respectively. The occupied interaction orbital of the NH₃ fragment is shown above and the unoccupied orbital of the Fe₁₀ cluster fragment is given below in each case.

The occupied interaction orbital of the NH₃ fragment consists mainly of the HOMO of NH₃ and overlaps in-phase with the paired unoccupied interaction orbital of the Fe₁₀ cluster fragment in all cases. In each model, the paired interaction orbital of the Fe₁₀ cluster for the α-spin part looks very similar to that for the β-spin part. Figure 4 indicates that a combination of the 4p functions extending normal to the surface, which belong to the Fe atom located right under the adsorbed NH₃, is the dominant constituent of the unoccupied interaction orbital of the Fe₁₀ cluster fragment in the on-top model. A combination of the 4s functions of the same Fe atom is the secondary component, mixed with the 4p function to magnify the overlap with the paired occupied interaction orbital of the NH₃ fragment. The contribution of d-type functions of the reaction center to the interaction orbital is small. In the bridge-site model, the unoccupied interaction orbital of the Fe₁₀ cluster is localized to the two Fe atoms closest to the adsorbed NH₃, as shown in Figure 5. The 4p and 4s functions of the two atoms are the major constituents.[48]

On the other hand, the orbitals of the surface part given in Figure 6 look very different from those for the on-top or bridge site. The orbital shows the maximum amplitude in the region away from the first layer of the surface, both in the α- and β-spin parts. Orbital interactions as have been found in the on-top model or in the bridge model do not appear in this case and, therefore, the basis functions allotted to the Fe cluster are utilized to stabilize the lone pair of electrons of NH₃ in the vicinity of the N atom. Thus, the orbital pair obtained for the interaction at a long distance has little chemical significance in describing a bond. The Fe(110) surface does not bind NH₃ tightly to its hollow site.

Electron delocalization from NH₃ to the surface is also represented well by a single pair of interaction orbitals, Pair 1, both for the α- and β-spin parts, in the adsorption to the Fe-(111) surface. Figures 7 and 8 illustrate the unoccupied interaction orbitals of the Fe₁₀ cluster fragment which predomi-
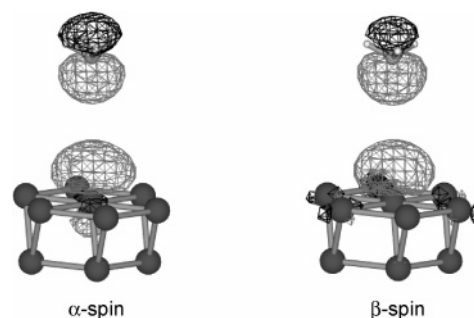
Figure 4. Pair 1's which represent electron delocalization from NH₃ to the Fe₁₀ cluster surface for the on-top model of the Fe(110) surface.
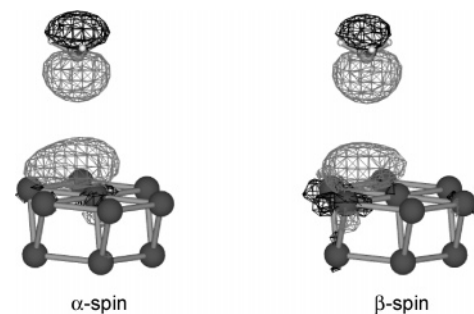
Figure 5. Pair 1's which represent electron delocalization from NH₃ to the Fe₁₀ cluster surface for the bridge model of the Fe(110) surface.
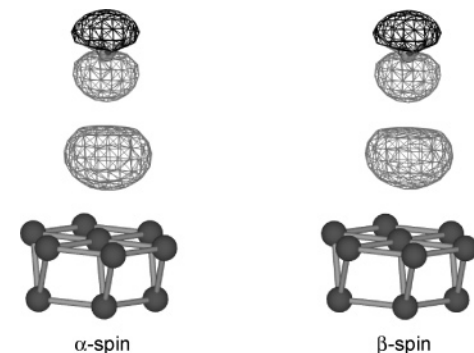
Figure 6. Pair 1's for the hollow model of the Fe(110) surface.
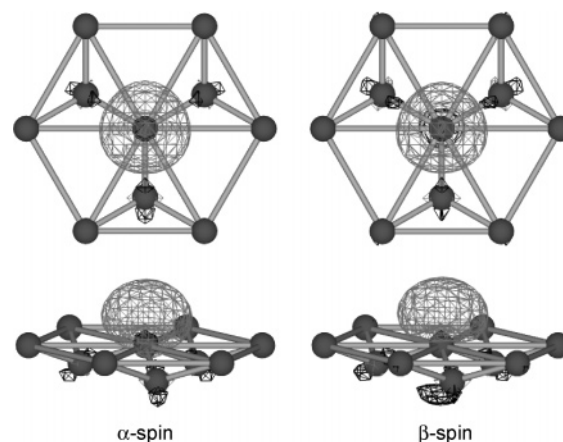
Figure 7. Unoccupied interaction orbitals of the Fe₁₀ cluster fragment which predominate electron delocalization from NH₃ to the Fe₁₀ cluster surface in the on-top model for the Fe(111) surface.

nate electron delocalization from NH₃ to the Fe₁₀ cluster surface in the on-top and bridge-site models for the Fe(111) surface, respectively. Here, we do not show the occupied interaction orbital of the NH₃ fragment, since the orbital looks much the same as that in the case of adsorption to Fe(110). The occupied
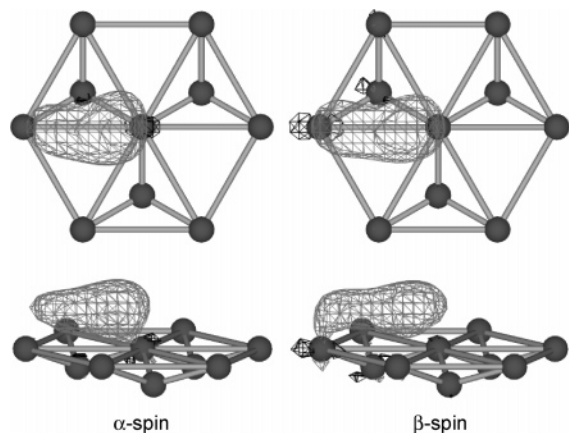
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Figure 8. Unoccupied interaction orbitals of the Fe$_{10}$ cluster fragment which predominate electron delocalization from NH$_3$ to the Fe$_{10}$ cluster surface in the bridge model for the Fe(111) surface.
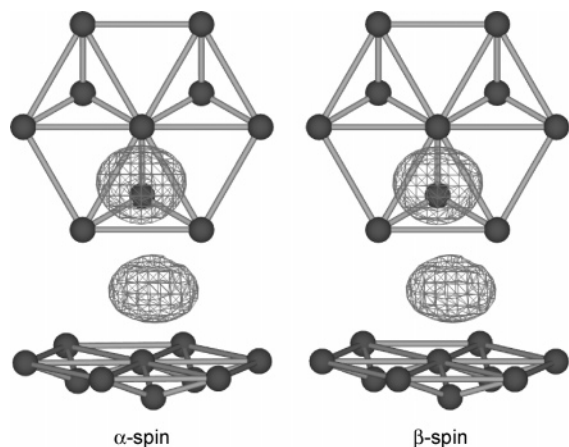

Figure 9. Unoccupied interaction orbitals of the Fe$_{10}$ cluster fragment in the hollow 1 model for the Fe(111) surface.

interaction orbital of NH$_3$ overlaps in-phase with the paired unoccupied orbital of the Fe$_{10}$ cluster fragment shown in Figures 7 and 8. In both cases, the paired interaction orbital of the Fe$_{10}$ cluster with α-spin is almost the same in shape as that with β-spin, as has been the case in the adsorption to the Fe(110) surface. It is also seen that the unoccupied interaction orbitals of the Fe$_{10}$ cluster in the on-top or bridge-site model for the Fe(111) surface bear a close resemblance to those in the corresponding adsorption model for the Fe(110) surface.

The hollow 1 and hollow 2 site models gave the interaction orbitals that look similar to those for the hollow site model for Fe(110). The orbitals do not show their maximum amplitude in the vicinity of some specific Fe atoms in these cases, as illustrated for the hollow 1 model in Figure 9. A small portion of electron population is shifted from NH$_3$ to the surface and to the region between the two fragments in each of these models, as has been demonstrated in Table 4. These orbitals suggest, however, that this shift of electron population from NH$_3$ is not brought about by electron delocalization of the usual sense, but simply by the use of Fe orbital functions to make up the orbital functions for NH$_3$. The hollow sites are not suited again to chemically bind NH$_3$ to the Fe(111) surface.

The interaction orbital of the NH$_3$ part is almost the same in the interactions discussed above and, therefore, the strength of adsorption depends for the most part on the extent of localization of the interaction orbital on the adsorption site.[15] Stronger orbital interactions at an early stage of adsorption yield interaction orbitals of the surface that are localized more effectively on the adsorption site. Interaction orbitals localized well will strengthen further orbital interactions to allow the adsorbate to reach a closer proximity. The on-top site can recombine the unoccupied canonical MO's to provide the interaction orbital that is localized well and extends directly from the adsorption site to the approaching NH$_3$. The interaction orbital of the NH$_3$ part is tight and strongly oriented and, accordingly, electron delocalization from NH$_3$ to the Fe surface is of σ type. This demands that the interaction orbital of the Fe surface is highly localized on the adsorption site, making the on-top site most active toward NH$_3$. The orbital delocalized over two Fe atoms is less effective to interact with the NH$_3$ orbital, making the bridge-site less active. The atomic orbital (AO) components of a greater number of Fe atoms tend to participate in electron delocalization at the hollow sites, but the resultant interaction orbitals are less oriented. It is difficult for the adsorbate to come into close proximity of the surface in this case.

Conclusion

To explore characterization of the interaction between an organic inhibitor molecule and a metal surface, we have studied the adsorption of NH$_3$ onto Fe(110) and Fe(111) surfaces. We have shown that the on-top site is most suited for adsorption in both cases based on the accurate total energy calculations. Then, we have pointed out that electron delocalization from NH$_3$ to the Fe surface plays the most important role in the adsorption by applying the Mulliken population analysis and by evaluating electrostatic attractions. In addition, our transformation scheme of fragment orbitals has demonstrated that the electron delocalization is represented well only by a pair of interaction orbitals. That is, NH$_3$ provides the occupied interaction orbital that looks like a lone-pair orbital, whereas the Fe surface prepares the paired unoccupied orbital, which is localized at the adsorption site and overlaps in-phase with the orbital of NH$_3$. The latter is constructed mainly by a combination of 4p and 4s functions of the Fe atom or atoms in the adsorption to the on-top and bridge sites. Not only the LUMO but also other unoccupied MO's have been shown to participate significantly, but in different ways, in the construction of the interaction orbitals for different adsorption sites.[49] The interaction orbital of NH$_3$ is tight and strongly oriented and, accordingly, the on-top site that can provide the unoccupied interaction orbital that is localized well and directed to the NH$_3$ orbital should be preferred both on the Fe(110) and the Fe(111) surfaces.

From the present study of adsorption of NH$_3$ onto Fe(110) and Fe(111) surfaces, as a model of the inhibition of Fe surface with organic amines, we deduce that organic amine acts as electron donor and is adsorbed onto the Fe surface, which behaves as an electron acceptor. It is strongly suggested that the Fe surface and larger organic amines in real systems provide the interaction orbitals that are very similar to those of the Fe cluster and NH$_3$ derived in the present study. On the basis of the results obtained here, we will investigate further the relationship between the inhibition and the strength of adsorption in our future works.

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(49) The LUMO of the Fe cluster surface is delocalized over many Fe atoms. In particular, the LUMO in the β-spin part has a small or no lobe on the central Fe atom of the first layer where the interaction with NH_3 is most preferred both on the Fe(110) and Fe(111) surfaces.