Theoretical study of adsorption and dissociation of NH$_3$ on pentanuclear Fe(111) surface

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Abstract. Theoretical study regarding the adsorption and dissociation of NH$_3$ molecule on Fe(111) surface has been carried out. The method used was DFT-B3LYP, and the basis sets used were ECP and 6-311G**. This research aimed at giving the theoretical understanding of adsorption and dissociation of NH$_3$ molecule on Fe(111) surface. The adsorption and dissociation were studied based on the energetic parameter, bond length, electron population, vibration and orbital interaction. The result of theoretical calculation revealed that the on top position is the interaction position with the minimum energy for the adsorption of NH$_3$ molecule on Fe(111) surface. The analysis of electron population of the two composing molecular orbitals indicated that the transfer of electron has an important role in the mechanism of adsorption. The visualization of molecular orbital showed that the transfer of electron occurred in the electron pairs of the interacting orbital. Relating to the adsorption mechanism and the overlapping of interaction orbitals, NH$_3$ molecule provides the Highest Occupied Molecular Orbital (HOMO) as the interaction pair for the Lowest Unoccupied Molecular Orbital (LUMO) on Fe surface. The insignificant difference between the oxidation state of N and H atoms as well as the higher hemolytic N-H bond dissociation energy (compared to heterolytic dissociation) cause the adsorption mechanism of NH$_3$ on Fe(111) model to occur through homolytic-dissociative chemisorption.

1. Introduction
Iron (Fe) is known as the heterogenic catalyst in NH$_3$ (ammonia) synthesis through Haber-Bosch process. Initially, the iron oxide form used as a catalyst in NH$_3$ synthesis is Fe$_2$O$_3$·nH$_2$O. It is known that the factor affecting the catalytic activity of Fe in NH$_3$ synthesis is the magnetic properties/magnetic moment of the surface which is represented by the crystallographic surface field of Fe [1].

Theoretically, by using ab initio DFT (Density Functional Theory) method, the calculation regarding the catalytic activity of Fe and its mechanism can be carried out. The calculation mechanism is performed by observing the structural model and the electronic properties of the crystal as well as the effects of magnetic properties on the occurring reaction.

Blonski and Kiejna [2] have carried out the theoretical study using ab initio method on the structure, electronic and magnetic properties of various types of single crystal Fe. It is found that single crystal Fe(111) has the highest surface energy as well as the highest magnetic properties among each type of Fe crystal which consists of 4 – 10 composing atoms. Satoh [3] has conducted the theoretical calculation for the catalytic activity of Fe(110) and Fe(111) as the adsorbent of NH$_3$ molecule. The optimum position for NH$_3$ adsorption on Fe surface is ‘on top’ position.

The model of NH$_3$ molecule could be adsorbed on Fe surface with 3 possible positions: on top of the apical atom, on top of the bridge site and on the three-fold site, known as on top, bridge and hollow positions. Adsorption of a molecule or an atom on the metal surface is dependent on the type and the crystallographic surface field of metal as well as the type of adsorbed matter [4].
Ammonia adsorption on Fe surface can be explained by the bonding formation between electron pair of NH$_3$ and Fe orbital, forming a donor-acceptor bonding. Confirmation of donor-acceptor bonding formation is carried out by observing the bond length of NH$_3$ molecular model when adsorbed on Fe surface as well as the magnetic and vibration properties of Fe-NH$_3$ interaction. The bond length will change and will be expressed as the bond-length correction of the addition of bonding with Fe [5]. GGA method with GENECP-6-311G** combination basis sets has a validation for Fe(10) system, giving the result which is similar to the experimental data. Therefore, the basis sets can be used in the calculation of energy and the structure of Fe-NH$_3$ complex [3].

2. Methods
The research was conducted in the Austrian-Indonesian Centre (AIC) for Computational Chemistry in Universitas Gadjah Mada, Yogyakarta. The hardware used consists of a computer with the specification as follows: Intel Dual Core 2.66 GHz processor with 4 GB Random Access Memory (RAM) and the software consist of GaussView version 5.08, Gaussian 09 [6], GaussSum version 2.2 [7], and Chemcraft 1.6 [8]. Windows platform was used for formulating the data of bond length and cluster geometry of the molecule under study (input) as well as the visualization of the result (output).

3. Results and Discussion
3.1. Adsorption Model of NH$_3$ Molecule on Fe(111)
Validation analysis of B3LYP/ECP basis sets in the calculation of Fe(111) field model was shown in Table 1. Spencer et al. [12] have given the evaluation of experimental data of crystal lattice constant of various metals. The crystal lattice constant of Fe(111) was 2.86Å. Doan [10] and Kittel [11] have given the evaluation of experimental data of magnetic moment and binding energy of each atom in various crystals. The magnetic moment of Fe(111) crystal was 2.22µ$_B$ and the binding energy of each atom was 18 kcal.mol$^{-1}$. Data resulted from computational calculation showed that the evaluation of crystal lattice constant, magnetic moment and lattice bonding energy are similar to the experimental data.

|               | Lattice constant (Å) | Magnetic moment ($\mu_B$) | Bonding energy of each atom (kcal·mol$^{-1}$) |
|---------------|----------------------|---------------------------|-----------------------------------------------|
| B3LYP/ECP     | 2.86                 | 2.22                      | 18.54243                                      |
| Experimental data | 2.86 [12]           | 2.22 [10,11]              | 18 [10,11]                                    |

Figure 1 showed that there is a shifting of electron density from NH$_3$ model molecule to Fe(111) surface. NH$_3$ molecule used its lone pair electrons to interact with Fe(111) surface. According to Figure 1, it can be known that the adsorption of NH$_3$ molecule in various interacting positions on Fe(111) surface occurred due to the shifting of electron density from NH$_3$ molecule to Fe(111) surface.

Fielicke et al. [12] generated the equation to evaluate the adsorption energy of the metal-ligand complex system as follows: $\Delta E_{M,X} = E_{M,X} - E_M - E_X$ in which, $E_{M,X}$ is the total energy of metal-ligand complex, $E_M$ is the metal energy and $E_X$ is the ligand energy. It is known that the adsorption energy is the binding energy between metal and ligand, therefore, the lower the adsorption energy; the more stable the metal-ligand complex.

Adsorption energy of on top position is -20.37 kcal·mol$^{-1}$. The interaction of NH$_3$ molecule and Fe(111) surface in on top position is an ideal interacting position. On top position has the lowest interaction distance which enables the low coverage. The low coverage is preferred in the adsorption process.

Evaluation of Fe bond length in Fe(111) model and N atom in NH$_3$ model showed that on top position provided the most dominant interaction sites of all positions. The decrease of interaction distance of Fe$_2$NH$_3$ from on top position to bridge and hollow caused the increase of high coverage in the catalytic reaction. This could decrease the active site of the catalyst and increase the residence time of the adsorbate. Thus, the optimum distance of adsorption process in the catalyst is needed [9].
Figure 1. Interaction model of NH$_3$ adsorption on Fe(111) surface: (a) on top, (b) bridge, (c) hollow 1 and (d) hollow 2.

Table 2. The distance and energy of NH$_3$ adsorption on Fe(111) surface.

| Adsorption position | The optimum bond distances of Fe-NH$_3$ (Å) | Adsorption energy (kcal.mol$^{-1}$) |
|---------------------|---------------------------------------------|-----------------------------------|
| on top              | 2.40                                        | -20.37                            |
| bridge              | 2.82                                        | -13.76                            |
| hollow 1            | 3.24                                        | -8.43                             |
| hollow 2            | 3.18                                        | -9.39                             |

The decrease of interaction bond length up to the optimum distance eased the transfer of an electron from NH$_3$ molecule to Fe(111) surface, thus, increasing the adsorption interaction energy. The lowest interaction distance between Fe and N in on top position makes the electron transfer in this position to be the highest of all other interacting positions.

3.2. Electron Population Analysis

Once the evaluation of electron calculation on Fe(111) surface and NH$_3$ molecule, as well as the interaction area between those two molecules, are conducted, electron changes related to the interaction could be known and could be elaborated as given in Table 3.
Table 3. Electron population change in the adsorption of Fe$_5$-NH$_3$ complex, given in electron per volume (m$^3$).

| Electron density | on top | bridge | hollow 1 | hollow 2 |
|------------------|--------|--------|----------|----------|
| 1. Fe surface    | 1.007  | 0.275  | 0.021    | 0.024    |
| 2. Electron transfer from Fe surface to NH$_3$ molecule | 0.018 | 0.013 | 0.001 | 0.002 |
| a. new bond formation | 0.018 | 0.013 | 0.001 | 0.002 |
| b. transfer to NH$_3$ | 0.000 | 0.000 | 0.000 | 0.000 |
| 3. NH$_3$ molecule | 0.010 | -0.001 | -0.001 | -0.001 |
| 4. Electron transfer from NH$_3$ molecule to Fe surface | 0.212 | 0.090 | 0.060 | 0.057 |
| a. new bond formation | 0.126 | 0.064 | 0.043 | 0.042 |
| b. transfer to Fe surface | 0.085 | 0.026 | 0.016 | 0.015 |

Electron population analysis using electron population approach could not explain the effect of Fe(111) surface on its composing atoms in electron transfer. The evaluation of electron population showed that electron transfer is the main factor in the adsorption of NH$_3$ molecule on Fe(111) surface.

### 3.3. Orbital Interaction

An initial study of electron transfer is based on the orbital interaction of Fe(111)-NH$_3$ complex system from the occupied molecular orbital of NH$_3$ to the empty molecular orbital of Fe(111). It is known that the electron transfer with a reversed direction is not significant as shown in Table 3. From the result of structural calculation, 4 pairs of occupied-unoccupied orbital were obtained. The electron transfer from NH$_3$ molecule to Fe(111) surface was represented by 4 orbital pairs for either alfa or beta spins.

Table 4 showed the charges of the orbital interactions which are suitable for the transfer of an electron from NH$_3$ molecule to Fe(111) surface at an optimum distance in various interacting positions. The value of each pair of interaction orbital demonstrated the electron transfer and electron population that participated in the formation of a new bond.

Table 4. Orbital interaction from NH$_3$ molecule to Fe(111) surface, given in electron per volume (m$^3$).

| Adsorption position | Spin | Pair 1 | Pair 2 | Pair 3 | Pair 4 |
|---------------------|------|--------|--------|--------|--------|
| on top              | A    | 0.202  | 0.031  | 0.027  | 0.008  |
|                     | B    | 0.184  | 0.021  | 0.019  | 0.018  |
| bridge              | A    | 0.197  | 0.022  | 0.017  | 0.012  |
|                     | B    | 0.177  | 0.027  | 0.022  | 0.019  |
| hollow 1            | A    | 0.108  | 0.005  | 0.004  | 0.001  |
|                     | B    | 0.105  | 0.005  | 0.004  | 0.001  |
| hollow 2            | A    | 0.107  | 0.005  | 0.004  | 0.001  |
|                     | B    | 0.106  | 0.005  | 0.004  | 0.001  |

From Table 4, it is known that the interacting orbital pair 1 participated most significantly in the transfer of an electron from NH$_3$ molecule to Fe(111) surface in each position. Electron population which is dominant in the formation of the new bond between NH$_3$ and Fe(111) surface is pair 1. Orbital interaction demonstrated that a small part of electron population shifted from NH$_3$ molecule to Fe(111) surface and to the area between the two molecules. This shows that the electron population shifting from NH$_3$ molecule was caused not only by the electron transfer but also affected by the function of Fe orbital in forming the interaction with the orbital function of NH$_3$ molecule. The orbital interaction also theoretically explains that hollow interacting position is insignificant in the bonding formation between NH$_3$ molecule and Fe(111) surface.

The adsorption strength is dependent on how far the orbital interaction in the adsorption process is. In the adsorption model, the stronger orbital interaction in the initial stage of adsorption results in the more effective orbital interaction on the surface. The local interaction orbital can also strengthen the further orbital interaction, thus, enables NH$_3$ molecule to achieve the optimum distance in the structural calculation.
3.4. Homolytic and Heterolytic Dissociative Adsorption of N-H in NH₃ Molecule

Figure 2 (a and b) showed the homolytic and heterolytic dissociative adsorption of Fe-N and Fe-H in Fe₅NH₃ complex. The result if geometric calculation showed that the dissociation of Fe-N and Fe-H occurred homolytically by forming the N atom radical for Fe-N and by forming H atom radical for Fe-H. The calculation showed that NH₃ heterolytic dissociation did not occur due to the insignificant difference of the oxidation states of N and H atoms. In addition, the homolytic dissociation energy of N-H bond is more negative than the heterolytic one. Therefore, the adsorption of NH₃ molecule on Fe(111) surface occurred through homolytic-dissociative chemisorption.

![Graph showing homolytic and heterolytic dissociation energies](image)

**Figure 2.** Homolytic and heterolytic dissociations of (a) Fe-H and (b) Fe-N on Fe(111) model.

Figure 2 (a) and (b) showed that based on the total dissociation energy, the dissociation of Fe-N on Fe₅-NH₃ complex occurred homolytically. The homolytic dissociation of Fe-N and Fe-H was preferable in on top position, followed by bridge and hollow positions.
Figure 3. Homolytic and heterolytic distance of (a) Fe-H and (b) Fe-N bond dissociations on Fe(111) model.

The easiness of the dissociation of N and H atoms is affected by the difference of oxidation state and the interaction distance that affects the energy of interaction model of Fe-N and Fe-H in Fe₅-NH₃ complex. Figure 3 (a) and (b) gave both homolytic and heterolytic bond dissociation distance of Fe-H and Fe-N in Fe(111) model. The formed interaction distance is the representation of bond interaction energy. The greater the interaction distance causes the electron transfer to occur insignificantly, lowering the interaction energy and making the dissociation process become easier. The low
interaction distance will facilitate the electron transfer and will make Fe-N and Fe-H bonds stronger, thus, the dissociation process becomes difficult to occur.

The evaluation of the value of the dissociation energy stated the easiness of bond breaking process both symmetrically and asymmetrically. The breaking in which one electron resulted from the interaction is attracted to each interacting atom (symmetry breaking) is easier to occur than the breaking in which two interaction electrons are attracted only to one atom (asymmetry breaking).

4. Conclusions
The most stable position of NH$_3$ adsorption on Fe(111) surface is on top position with the energy of -90.56 kcal mol$^{-1}$. Bond length of Fe-N in Fe$_5$NH$_3$ in various adsorption positions decreases in the order: hollow > bridge > on top. Electron transfer in on top position is the highest of all positions. The vibrational frequency of N-H bond in NH$_3$ molecule decreases in the order: hollow > bridge > on top. The low vibrational frequency of Fe-N caused the strong NH$_3$ adsorption on Fe$_5$ field (111) and the dissociation process of N-H in NH$_3$ become easy to occur.

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