Density Functional Study of Hydrazine Adsorption and Its N-N Bond Cleaving on Fe(110) Surface

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Abstract

We report density-functional-theory-based calculations of hydrazine adsorption and its N-N bond cleaving on clean Fe(110) surface. It is found that hydrazine may adopt several adsorption configurations among which the most energetically stable is the bridging configuration. Adsorption on short bridge site generally has larger adsorption energies than those on long bridge site. N-N bond cleaving is an exothermic process with reaction energies of 1.90 and 1.67 eV on long and short bridge site, respectively. Nudged elastic band method is used to estimate the activation energies of N-N bond cleaving. Our results indicate that N-N bond cleaving on long bridge site has lower activation energy (0.27 eV) compared to that of short bridge site (0.36 eV). By examining the molecular orbitals of the initial state it is found that this difference stems from stronger bond between the two NH₂ fragments adsorbed on short bridge site as compared to long bridge.

Keywords: density functional calculations, hydrazine adsorption, hydrazine decomposition, N-N bond cleaving

1. Introduction

Adsorption and reactions of hydrazine (N₂H₄) on solid surfaces are important phenomena because of their relevance in several energy-related applications. As an example, hydrazine recently has been investigated as fuel in direct hydrazine fuel cell (DHFC) [1, 2, 3, 4, 5]. This type of fuel cell is interesting because it uses non-precious metal catalyst and has potential application in automotive industry. Hydrazine has been also investigated in carbon-free hydrogen storage and generations because of its high hydrogen content [6, 7, 8]. Moreover, hydrazine is also used widely as propellant for rocket engines [9] and as a reducing agent in chemical synthesis [10]. Most of those applications involve interaction between hydrazine and solid surface which usually act as a catalyst. Therefore, understanding the interaction between hydrazine and solid surfaces is required for better catalyst design.

On solid surfaces, hydrazine generally decomposes into ammonia, nitrogen, and hydrogen. This decomposition reaction is a central aspect in the aforementioned applications. Depending on reaction conditions and nature of the catalyst surface, the stoichiometric amount of each decomposition product might vary. Audrieth [11] suggested the following general equation for hydrazine decomposition

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with $0 \leq x \leq 1$. The reaction path of hydrazine decomposition as described by 1 is complex and involves a lot of possible elementary steps. It has been reported previously in [9] that in gas phase dissociation energy of N-N bond of hydrazine is about 2.96 eV while that of N-H is 3.73 eV. Thus in this study we only investigate adsorption and N-N bond cleaving of hydrazine:

Most of previous studies of hydrazine are of experimental nature (see review by [9] and references therein) while computational studies are limited in comparison. Our group has done several theoretical investigations of hydrazine adsorption on transition metals Ni(100) [12], Pt(111) [13], Ni(111) [14], Co(0001), Cu(111), and Pd(111) [15]. It was found that interactions between hydrazine and transition metals are characterized by the repulsive interaction between *d*-bands of metals with adsorbate states.

Iron surface is known to be active for N-N bond cleaving of dinitrogen (see for example [16]), thus we might expect that this surface is also active for hydrazine decomposition. Grunze [17] investigated hydrazine decomposition on Fe(111) surface using UV and X-ray photoelectron spectroscopy. His results confirmed the presence of NH_2 radicals on surface and thus N-N bond cleaving of hydrazine. A recent computational study of hydrazine decomposition path on Fe(211) surface also has been done by McKay [18]. However, there is no theoretical study of interaction between hydrazine and the most abundant surface (110). The objective of the present study is to investigate the adsorption configurations, electronic structure and reactive sites for N-N bond cleaving of hydrazine on Fe(110).

The outline of present article is as follows. First, minima of hydrazine adsorption configurations are identified and discussed. The electronic structure of several adsorption configurations and comparison with that of gas phase are also given. Two different sites of Fe(110) are investigated for their activity in N-N bond cleaving. Finally, qualitative explanation of the difference in activity is given by examining molecular orbitals of adsorbed hydrazine.

2. Method

All calculations are performed using Quantum Espresso [19] package. We use ultrasoft pseudopotentials [20] with cutoff 30 Ry for wave function and 200 Ry for electronic density. Using this cutoff value, adsorption energy change is less than 0.005 eV. Fe(110) surface is modeled using 3-layer slab and 3×3 supercell. Trend of adsorption energies among various adsorption configurations for 4-layer slab is similar to 3-layer slab, so we decide that 3-layer slab is sufficient for this study. Experimental bulk bcc iron lattice parameter of 2.87 Å has been used when constructing the slab. During geometry optimization, atoms in the the lowest layer of the slab are fixed while other atoms are allowed to relax. A vacuum layer of about 20 Å and dipole correction have been used to eliminate spurious interaction between periodic images of the slab. Brillouin zone sampling is done using $3 \times 3 \times 1$ Monkhorst-Pack grid. PBE functional [21] has been used as exchange-correlation functional. Spin polarization also has been taken into account for all calculations. Nudged elastic band (NEB) [22] calculations are used to estimate the activation energies of N-N bond cleaving. The reaction path is discretized using 8 images. Climbing image (CI) NEB [23, 24] has been used to improve the transition state search.

Figure 1: Conformations of hydrazine in gas phase

3. Calculation results and discussions

3.1. Adsorption geometry

Hydrazine can be thought as combination of two NH_2 groups bonded by a N-N sigma bond. Each of the NH_2 fragments in hydrazine has lone pair electrons. This configuration allows hydrazine to undergo rotation around its N-N axis resulting in three stationary conformations: *anti*, *cis*, and *gauche*. The *gauche* conformation is the most stable one in gas phase. These three conformations of hydrazine can be viewed in Figure 1. When adsorbed on surface, hydrazine may adopt adsorption geometries that are similar to its gas phase configurations.

From geometry optimization calculations, several stationary points of hydrazine adsorbed on Fe(110) can be identified. It is found that hydrazine adsorption configurations can be classified into *top* configurations, where one N atom of hydrazine is bonded to one surface metal, and *bridging* configurations where both N atoms of hydrazine are bonded to surface atoms. Letters A and B have been used to further differentiate variation in adsorption configurations based on their relative hydrogen atoms arrangement. For example, *top-A*, *top-B*, *bri-A* are analogous to *anti*, *gauche*, *cis* conformations in gas phase, respectively. Adsorption configuration *bri-B* is a slight distortion from *bri-A* configuration, where NH_2 groups are rotated in opposite direction about N-N axis. These configurations are differentiated further based on their locations on two different bridge sites of Fe(110) surface, namely long bridge (*lb*) and short bridge (*sb*) site. These adsorption geometries can be viewed in Figure 2.

Figure 2: Top view of adsorption geometries of hydrazine on Fe(110) on long bridge (upper figures) and short bridge (lower figures)

Adsorption energy E_{ads} is calculated using the following formula:

$$E_{\text{ads}} = E_{\text{surf+mol}} - (E_{\text{surf}} + E_{\text{mol}}) \quad (3)$$

where $E_{\text{surf+mol}}$, E_{surf} , and E_{mol} denote total energy of adsorbed molecule and surface, isolated surface, and isolated hydrazine molecule in *gauche* conformation, respectively. Table 1 shows the calculated adsorption energies and hydrazine absorbed bond lengths on Fe (110). It is found that adsorption energy differences among different configurations are relatively small. The maximum value of energy differences is about 0.11 eV, between *bri-A-lb* and *bri-B-sb*. However, in general it can be said that short bridge configuration is slightly preferable than long bridge site state.

Note that, the adsorption configurations might change especially in the case of high coverage of hydrazine. For such case, top configurations might be energetically more favorable than bridging configurations as has been shown before in [15]. There is also possible complication due to hydrogen bonds between hydrazine. This is an interesting topic for further investigations which is however beyond the scope of the present study. Results in the present study should be taken as the case of weak or no interaction between hydrazine molecules.

Table 1: Calculated adsorption energies and bond lengths of hydrazine adsorbed on Fe(110)

Quantity	top-A-lb	top-B-lb	bri-A-lb	bri-B-lb	top-A-sb	top-B-sb	bri-A-sb	bri-B-sb
E_{ads} (eV)	-0.71	-0.71	-0.69	-0.75	-0.72	-0.70	-0.75	-0.80
N-N distance (Å)	1.47	1.44	1.48	1.46	1.47	1.44	1.47	1.45
Fe-N distance (Å)	2.12	2.16	2.16	2.20	2.13	2.17	2.14	2.18

Several geometry parameters of adsorption configurations are given in Table 1. N-N bond length of hydrazine is found to become longer upon adsorption to Fe(110) surface compared to its value in gas phase (1.43 Å). Adsorption configurations *bri-A-lb* and *bri-A-sb* generally have longer N-N bond lengths compared with the other configurations. Thus, it is very probable that these configurations are the precursor states for N-N bond cleaving. It is also interesting to note that configurations with largest adsorption energy, in this case *bri-B-lb* and *bri-B-sb*, have the longest Fe-N bond.

Adsorption energy can be divided into two contributions: attractive contribution due to orbital interactions and repulsive contribution which proportional to overlap between the molecule and the surface atoms (see for examples [25] and [15] for its application to hydrazine adsorption). Bridging configurations such as *bri-B* have larger overlap, and thus larger repulsion as compared to top configurations. To minimize repulsion, the bond length will be greater as compared to top configurations. However, bridging configurations also allow for the possibility of more attractive orbital interaction with surface as hydrazine now interacts with two surface atoms as opposed to only one atom as in the case of top configurations. For the case of hydrazine on Fe(110), it turns out that this attractive interaction can overcome the repulsive and adsorption energy of *bri-B* is the largest one.

3.2. Electronic structure of adsorbed hydrazine

In this subsection, electronic structure of adsorbed hydrazine on Fe(110) is discussed, specifically focusing on the *top-A-lb* and *bri-B-lb* configurations. Except for *bri-A-lb* and *bri-A-sb*, any significant differences of the electronic states were not found between adsorption in long bridge and short bridge configurations. The discussion of the electronic states of *bri-A-lb* and *bri-A-sb* in connection with N-N bond cleaving process will be given in the next subsection.

Before discussing the electronic structure of adsorbed hydrazine, electronic structure of hydrazine in gas phase will be reviewed briefly for *anti* and *cis* conformations. Hydrazine has 14 valence electrons which occupy 7 molecular orbitals. Five of them are visualized in Figure 3 each for *anti* and *cis* conformations. The following notations are used to label the molecular orbitals: 1π , 5σ , $2\pi^*$, LP, and LP*. Note that LP and LP* are lone pair orbitals which are also HOMO-1 and HOMO of hydrazine. The density of states (DOS) of gas phase hydrazine in *anti* and *cis* conformations projected on the atomic states s , p_x , p_y , and p_z of nitrogen are plotted in Figure 4. N-N bond is chosen to lie along x direction. With this choice, it is found that the most dominant atomic state contribution to HOMO and HOMO-1 is nitrogen p_z with some contributions from p_x and s . Orbitals 1π and $2\pi^*$ are composed of only nitrogen p_y and the orbital 5σ is dominated by p_x and smaller contribution from p_z .

Figure 3: Molecular orbitals of hydrazine in *anti* (upper figures) and *cis* conformation (lower figures). Color red and blue differentiate the sign (+/-) of the orbital.

Figure 4: Density of states of hydrazine in gas phase projected to one N atom of hydrazine in *anti* and *cis* conformations. Unit of energy is eV. The levels have been broadened with smearing of 0.01 eV and shifted such that HOMO is located at 0 eV.

In Figure 5 DOS projected on adsorbed nitrogen atom of hydrazine in *top-A-lb* is given. Several peaks or

Figure 5: DOS projected to N atom for adsorption configuration top-A-lb and visualization of several adsorbed hydrazine molecular orbitals at several energy levels.

states have been labeled by letters A-J. Figure 5 also gives the visualization of the molecular orbitals corresponding to the peaks or states labeled in DOS plot. Contour plot of these molecular orbitals is also given to show the interaction between Fe and nitrogen atoms. we can see that state A is essentially the same as 1π orbital of gas phase hydrazine. No contribution from surface atoms is observed for this state. State B is the same as 5σ of gas phase molecular orbitals. Also, no contribution from surface atoms is observed. Thus for state A and B, no mixing or hybridization of hydrazine molecular orbitals with surface orbitals. However, state C has contribution from surface atoms, presumably delocalized sp -states of Fe. Thus, state C can be regarded as result of interaction between 5σ of hydrazine and sp states of Fe surface. State D is the same as $2\pi^*$ of gas phase molecular orbital. Just like states A and B, this state also does not mix with orbitals from surface atoms. State E is analogous to LP orbital of gas phase. However, polarization of this molecular orbitals toward surface atoms can be observed. Thus, this state can be identified as dative bonding of hydrazine to surface atom via the lone pair. Meanwhile, states F-J are mainly dominated by interaction between HOMO of hydrazine with surface orbitals, mainly the d states, resulting in bonding and antibonding orbitals. Some of them clearly show the symmetry of surface orbitals. For instance, state F shows bonding orbital due to d_{xy} and state I and J show antibonding orbital due to d_{z^2} . The mixing between atomic orbitals are very strong as can be seen by more balanced contribution between hydrazine and surface atoms.

In Figure 6 the projected DOS for *bri-B-lb* configuration is given and several peaks or states have been labeled by letters A-J. States A and B of this configuration have same features as states A and B of top-A-lb because they represent a π and σ bonding, respectively. They also do not hybridize with surface atomic orbitals. State C is not a π antibonding orbital because it shows bonding characteristic between two NH_2 fragments of hydrazine. State D shows bonding characteristic with surface. It has a similar feature as state C of top-A-lb that they both interact with sp states of surface. State E is HOMO-1 of hydrazine which has a dative bonding characteristic with surface. This state is analogous to state E of top-A-lb. State F has the same characteristic as state E, however with contribution of delocalized surface orbitals. States G,H, and I interact strongly with surface orbitals. They are the result of the interaction between HOMO of hydrazine and the d -orbitals of surface atoms. Just like in the case of top-A-lb, symmetry of surface orbitals which contributes in the interaction can be clearly seen from the contour

Figure 6: DOS projected to N atom for adsorption configuration bri-B-lb and visualization of several adsorbed hydrazine molecular orbitals at several energy levels.

plot: state G has bonding contribution from d_{z^2} of Fe, state H has bonding contribution from d_{xz} , and state I has antibonding contribution from d_{z^2} . State J does not have any recognizable character with occupied hydrazine molecular orbitals in gas phase. It is probably the result of the interaction between unoccupied molecular orbital of hydrazine and surface orbitals. It does not have significant bonding characteristic with surface.

From the preceding discussion, several points regarding the interactions between hydrazine and Fe(110) can be made. First, besides interaction with the delocalized sp orbitals of the surface, HOMO of hydrazine interacts strongly with surface d -orbitals and forms derived bonding and antibonding orbitals with respect to surface atoms. Second, HOMO-1 mainly interacts with surface atom via a dative bond. Third, lower molecular orbitals, such as 5σ , only interact with the delocalized sp orbitals of the surface.

3.3. Activation energy for N-N bond cleaving

In this subsection the calculation results of the activation energy of hydrazine's N-N bond cleaving are presented. Initial, transition state, and final structures of this process for long and short bridge are shown in the Figures 7 and 8, respectively. Note that configuration bri-A is chosen as initial structure because this is the optimum configuration (require minimum geometry change) for N-N bond cleaving. The obtained transition state structure can be classified as an early transition state since it is closer to the initial structure than to final structure.

Figure 7: Initial, transition, and final structures (long bridge)

The activation energies and associated energy changes for N-N bond cleaving can be seen in Table 2. From the table it can be seen that the N-N bond cleaving of hydrazine on Fe(110) surface is exothermic and has a relatively low activation energy. Difference in activation energy of about 0.09 eV is also found between long and short bridge

Figure 8: Initial, transition, and final structures (short bridge)

Table 2: Activation energies and energy change of N-N bond cleaving process on Fe(110)

Site	E_{act} (eV)	ΔE (eV)
Long bridge	0.27	-1.90
Short bridge	0.36	-1.67

adsorption site.

Figure 9: Charge density difference for hydrazine adsorbed on long bridge sites. Blue and red color signify region with positive and negative charge difference, respectively. Isosurface value is taken to be 0.002.

To find additional information about N-N bond cleaving process, we will use charge density difference analysis. This charge density difference is calculated as:

$$\Delta\rho = \rho_{\text{surf+mol}} - \rho_{\text{surf}} - \rho_{\text{mol}}$$

where ρ_{surf} , ρ_{mol} , and $\rho_{\text{surf+mol}}$ denote charge density of surface, hydrazine, and surface with adsorbed hydrazine calculated at fixed or static geometry. Figure 9 shows charge density difference comparison between initial state (bri-A-lb) and transition state for N-N bond cleaving process on long bridge site. Similar plot also can be made for adsorption on short bridge site, however it is not shown here because they have similar features with that on long bridge site. On Figure 9 region with positive (excess) charge difference is colored blue, while red color is used for negative (depletion) charge density difference. At initial state, region with negative charge density difference dominates. Meanwhile, region of positive charge difference can be observed at center N-Fe bond region. There is very little charge density difference along N-N bond at initial state. At transition state, however, there is significant difference at the N-N bond region as it elongates. Region of negative charge difference is observed at the center of

Table 3: Charges (number of electrons) of hydrazine molecule obtained as sum of atomic charges obtained from Löwdin partitioning scheme. Difference is calculated as charge at transition minus charge at initial geometry. Ideal value of hydrazine charges is 14 (number of valence electrons in hydrazine).

Site	Initial	Transition	Difference
Long bridge	13.31	13.47	0.16
Short bridge	13.30	13.49	0.19

N-N bond.

Sum of atom-centered charges based on Löwdin partitioning for initial and transition states of N-N bond cleaving of hydrazine for each for long and short bridge site are given in Table 3. From the table it can be observed that during geometry change from initial to transition state some electrons move to hydrazine molecule. This is found both for adsorption on long and short bridge. The atom-centered charge difference for short bridge site is found to be larger than that for long bridge site. This is probably can be related to larger activation energy on short bridge as compared to long bridge site.

Figure 10: DOS projected to bonded nitrogen atom for initial state on long bridge site (*bri-A-lb*).

In order to find the origin of this activation energy difference, the electronic structure of configurations *bri-A-lb* and *bri-A-sb* will be analyzed and compared. Figure 10 and 11 show the density of states projected on p_x , p_y and p_z of N atom when the adsorption configuration is *bri-A-lb* and *bri-A-sb*. It is found that both DOS have very similar features. There is no much difference in the p_z component (blue line), so the activation energy difference should be related to the p_x and p_y components of DOS. Four peaks (states) of DOS for each *bri-A-lb* and *bri-A-sb* are given labels A, B, C, and D. The corresponding molecular orbitals of on these peaks are also given in Figure 10 and 11.

It can be seen that the peak A of *bri-A-lb* corresponds to the σ bonding between the p_x orbitals of N atoms. The second peak correspond to the π antibonding between the two NH_2 fragments. These two orbitals are essentially the same as 5σ and $2\pi^*$ orbitals of gas phase hydrazine in *cis* conformation. The third and fourth peak both has N-N

Figure 11: DOS projected to bonded nitrogen atom for initial state on short bridge site (*bri-A-sb*).

bonding characters. They are the result of the interaction between HOMO-1 and surface atom orbitals. Thus, on long bridge site there are three bonding and one antibonding states among the 4 states that were considered. First peak of *bri-A-sb* has the same character as in the long bridge, i.e. it is a σ bonding between N-N atoms, although now it has been composed not purely of p_x but also by p_y orbitals. However the second peak of this configuration is not π antibonding as we can see slight bonding character between H atoms belonging to different NH_2 fragments. Similarly to the case of long bridge, third and fourth peaks are also result of the interaction between HOMO-1 and surface atom orbitals which have bonding characteristic. Thus, on the short bridge site all four states that were considered have bonding characteristic. Qualitatively, it can be said that the bonding between two NH_2 fragments of adsorbed hydrazine in short bridge is stronger as compared to the long bridge site. This will eventually result in higher activation energy of N-N bond cleaving for short bridge.

It is interesting to note that this kind of electronic structure is also expected to be found in interaction between hydrazine and other bcc(110) surfaces such as Mo(110) and Nb(110). Our initial investigation shows that activation energy for N-N bond cleaving of hydrazine on short bridge is indeed higher than long bridge. Similar molecular orbital characteristics with the one we have just mentioned here are also observed for hydrazine adsorbed on Mo(110) and Nb(110). These systems will be one subject of our future studies.

4. Conclusions

On Fe(110), hydrazine may adopt several adsorption geometries. The largest energy difference among those adsorption geometries is about 0.11 eV and the most stable geometry is found to be the bridging configuration on short bridge site (*bri-B-lb*). HOMO and HOMO-1 of hydrazine are found to dominate the interaction between hydrazine and surface. N-N bond cleaving of hydrazine is an activated process on Fe(110), with energy barriers of 0.27 eV for the long bridge and 0.36 eV for the short bridge site. The transition state of this process can be classified as early transition state because it closely resembles the initial state. By analyzing the electronic structure of the

bri-A-lb and *bri-A-sb* configurations it is found that they have different orbitals mixing. This difference results in stronger bonding between NH₂ fragments, thus higher activation energy on short bridge as compared to long bridge.

5. Acknowledgment

Some of the numerical calculations presented here were done using the computer facilities at the following institutes: CMC (Osaka University), ISSP, KEK, NIFS, and YITP. This work is supported in part by: MEXT Grant-in-Aid for Scientific Research on Innovative Areas Program (2203-22104008) and Scientific Research (A)(26248006); JST ALCA Program "Development of Novel Metal-Air Secondary Battery Based on Fast Oxide Ion Conductor Nano Thickness Film"; JSPS Core-to-Core Program "A. Advanced Research Networks: Computational Materials Design on Green Energy"; and the Osaka University Joining and Welding Research Institute Cooperative Research Program.

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