Density Functional Study of Hydrazine N—N Bond Cleaving on 3d Metal Surfaces

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Abstract

Theoretical calculations based on dispersion-corrected density functional theory (DFT-D2) has been performed to investigate hydrazine adsorption and N—N bond cleaving on closed packed surfaces of 3d metals: Fe(110), Co(0001), Ni(111), Cu(111), and Zn(0001). The activation energies of N—N bond cleaving of hydrazine on each surface are estimated using climbing-image nudged elastic band (CINEB) method. The results showed that the activation energies for this process have increasing trend from Fe(110) to Zn(0001). By examining the electronic structure of the adsorbed hydrazine, it is found that this trend is related to occupation of derived $6\sigma^*$ orbitals. It is also found that approximate linear relationship between reaction energy and activation energy (the Brønsted-Evans-Polanyi (BEP) relationship) holds for those surfaces.

Keywords: density functional theory, hydrazine, decomposition, N—N bond cleaving

1. Introduction

Hydrazine (N_2H_4) is an important inorganic chemical in various applications. In gas phase it has three conformations: *anti*, *cis*, and *gauche* as depicted in Figure 1. It is mainly used as propellant for rocket engines and satellites [1]. It is also used as reducing agent in chemical synthesis [2]. Recently, hydrazine has been investigated for hydrogen generation application [3, 4, 5] and precious-metal-free direct hydrazine fuel cell [6, 7, 8, 9, 10]. Catalytic decomposition of hydrazine on solid surfaces is an important process in these applications. An atomistic view of this decomposition is desirable for optimization of the catalytic process.

Figure 1: Conformations of hydrazine in gas phase

The decomposition of hydrazine gives nitrogen, hydrogen, and ammonia as products which stoichiometric

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amount may vary depending on the reaction conditions. The following reaction has been suggested to describe hydrazine decomposition [11]:

with parameter x has value between 0 and 1. Most of the previous studies of catalytic decomposition of hydrazine have been focused on finding the reaction pathways using various experimental techniques (for examples: [12, 13, 14, 15, 16, 17, 18, 19, 20]. Unfortunately, despite of those extensive studies, the reaction pathways of hydrazine decomposition are not convincingly established yet. Various theoretical studies of hydrazine interaction with solid surfaces also have been done. Most of these studies focus on adsorption process of hydrazine on clean transition metal surfaces such as Cu(111), Cu(100), Cu(110) [21], Ni(100) [22], Pt(111) [23], Ni(111) [24], Co(0001), and Pd(111) [25].

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[1], so it is expected that N—N bond cleaving is more favorable than N—H bond cleaving. Recent computational studies have indeed shown that hydrazine’s N—N bond cleaving is favored over the first N—H bond cleaving on Ir(111) [26] and Rh(111) [27].

In this article, a computational study based on density functional theory of N—N bond cleaving of hydrazine:

on close-packed surface (the most stable) of 3d metals: Fe(110), Co(0001), Ni(111), Cu(111), and Zn(0001) is presented. These surfaces are chosen mainly because of their simplicity and potential as non-precious-metal catalysts [6, 7, 8]. The main objective of this study is to find whether certain trends may be found in N—N bond cleaving of hydrazine on these surfaces and to investigate electronic structure aspects of this process. The discussion in this article will be divided into two parts. The first part discusses the adsorption energies and geometries while the second part deals with the electronic structure of adsorbed hydrazine as its N—N bond is cleaved.

2. Methods

The calculations were performed using density functional theory as implemented in Quantum Espresso [28] package. Ultrasoft pseudopotentials [29] were used to treat interaction between electron and ionic cores. Plane wave basis set with cutoff 30 Ry for wave function and 200 Ry for electronic density were used. The surfaces Fe(110), Co(0001), Ni(111), Cu(111), and Zn(0001) were modeled using 3-layer slab and 3×3 supercell constructed using their respective lattice bulk constants. Comparison of adsorption energies obtained by using 4-layer shows that the trend of adsorption energy is similar to that obtained by using 3-layer slab model. During geometry optimization, atoms at the bottom layer were fixed while other atoms were allowed to relax in any directions. A

vacuum layer of about 20 Å and dipole correction have been used to eliminate the interaction between periodic image of slab. Brillouin zone sampling was done using $3 \times 3 \times 1$ Monkhorst-Pack grid. The PBE [30] exchange-correlation functional has been used for all calculations. Recent studies [31, 32] showed that PBE functional gives balanced description of the bulk structure of various transition metal elements. Spin polarization has been included in all calculations. DFT-D2 method [33, 34, 35] was used to account for dispersion force. The inclusion of DFT-D2 was found to be important in Cu surfaces[36] and is also expected to be important for Zn(0001) surface that is considered here. Nudged elastic band (NEB) [37] calculations were used to estimate activation energies of N—N bond cleaving. The reaction path was discretized using 8 images. Climbing image version of NEB (CINEB) [38, 39] was used to improve the transition state search. Additional calculations of N—N bond stretching of hydrazine in gas phase is done by Gaussian09 package [40] using basis set 6-31G(d,p) and B3LYP level theory. The resulting energy levels of hydrazine obtained using this setting is qualitatively similar to the ones obtained using plane wave calculation.

3. Calculation results and analysis

3.1. Energetics and geometry

In this article, adsorption energy E_{ads} is calculated as

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

where $E_{\text{mol/surf}}$ is total energy of hydrazine adsorbed on surface, E_{surf} is total energy of clean surface, and E_{mol} is total energy of gas phase hydrazine molecule in *gauche* conformation.

Hydrazine adsorbed molecularly in *cis*-like structure (which will also be designated as bri-A) has been used as initial geometry for CINEB calculation for all surfaces. For final structure, adsorption structure with two NH_2 fragments adsorbed on two bridge sites is used for Fe(110), Co(0001), Ni(111), and Cu(111). For Zn(0001), adsorption structure with two NH_2 fragments adsorbed on two top sites is used as final structure because it was found that potential energy surface near this structure is relatively flat. Except for Zn(0001) such ontop structure is not found by geometry optimization on other surfaces. Figure 2 and 3 give initial, final, and transition state structure found from CINEB calculations on Ni(111) and Zn(0001). It can be observed that the transition states for N—N bond cleaving closely resemble initial structures, so they may be classified as early transition states.

The adsorption energies of these structures along with the activation and reaction energies for each surface are given in Table 1. The imaginary frequencies associated with N—N bond stretch at the transition state are also provided in Table 1. In Figure 4, adsorption energies of initial, transition, and final states are visualized. Except for Zn(0001), found to be exothermic process for all surfaces. The activation energy for this process has the lowest value for Fe(110) and highest for Zn(0001).

Figure 2: Initial, transition, and final structure for N—N bond cleaving on Ni(111). Similar structures are also obtained for Fe(110), Co(0001), and Cu(111).

Figure 3: Initial, transition, and final structure for N—N bond cleaving on Zn(0001).

As shown in Figure 5, the Brønsted-Evans-Polanyi relationship which is shown to hold for various systems [41, 42, 43, 44]. can be established for N—N bond cleaving of hydrazine. While the reaction energy ΔE is a good descriptor to predict activation energy, it is also possible that other descriptors such as adsorption energy of final product [45], i.e E_{fin} , might be a better descriptor for predicting activation energy of N—N bond cleaving of hydrazine. We are currently working to extend our investigation to other surfaces.

Table 1: Calculated adsorption energies of initial E_{ini} , transition E_{TS} , and final structure E_{fin} . ΔE is calculated as $E_{\text{fin}} - E_{\text{ini}}$. All energies are given in eV and calculated relative to gas phase hydrazine in gauche conformation. The imaginary frequencies are given in cm^{-1}

Surface	E_{ini}	E_{TS}	E_{fin}	ΔE	E_{act}	ν^{TS}
Fe(110)	-1.28	-1.05	-3.26	-1.96	0.23	504.4i
Co(0001)	-1.47	-1.08	-2.83	-1.36	0.39	337.0i
Ni(111)	-1.32	-0.83	-2.35	-1.03	0.49	334.6i
Cu(111)	-0.94	-0.35	-2.03	-1.09	0.59	516.8i
Zn(0001)	-0.29	0.62	0.42	0.71	0.91	168.1i

Two geometry quantities, *i.e.* distance between N—N atom of hydrazine $d_{\text{N-N}}$ and distance between N atom of hydrazine and bonded surface atom $d_{\text{N-M}}$ ($M = \text{Fe, Co, Ni, Cu, or Zn}$), are given in Table 2 and 3, respectively. It is observed that $d_{\text{N-N}}^{\text{IS}}$ has increasing trend from Fe(110) to Zn(0001), with very close values obtained for Co(0001), Ni(111), and Cu(111). $d_{\text{N-N}}^{\text{TS}}$ does not have similar trend as $d_{\text{N-N}}^{\text{IS}}$, however the lowest value is also obtained for Fe(110) and highest value for Zn(0001). Meanwhile, $d_{\text{N-M}}^{\text{IS}}$ has almost the same trend as adsorption energy E_{ini} . For all surfaces, $d_{\text{N-M}}^{\text{TS}}$ is found to be shorter than $d_{\text{N-M}}^{\text{IS}}$.

In order to find more insight to the N—N bond cleaving process, the activation energy E_{act} is analyzed by

Figure 4: Energy diagram for N—N bond cleaving of hydrazine

Table 2: N—N bond distance of adsorbed hydrazine in initial and transition state structure. The difference is calculated as $\Delta d_{\text{N-N}} = d_{\text{N-N}}^{\text{TS}} - d_{\text{N-N}}^{\text{IS}}$. All values are given in angstrom.

Surface	$d_{\text{N-N}}^{\text{IS}}$	$d_{\text{N-N}}^{\text{TS}}$	$\Delta d_{\text{N-N}}$
Fe(110)	1.486	1.803	0.317
Co(0001)	1.479	1.929	0.450
Ni(111)	1.479	2.046	0.567
Cu(111)	1.470	1.951	0.481
Zn(0001)	1.457	2.113	0.656

decomposing it into several parts according to the following equation [46, 47, 27]:

$$E_{\text{act}} = E_{\text{subs}} + E_{\text{deform}} + (E_{\text{A}}^{\text{TS}} + E_{\text{B}}^{\text{TS}} - E_{\text{int}}^{\text{TS}}) - E_{\text{AB}}^{\text{IS}} \quad (4)$$

This decomposition allows us to interpret activation energy as sum of various contributions from separate subsystems. E_{subs} is calculated as total energy difference between surface only part of transition and initial geometry. E_{deform} is calculated similarly as E_{subs} for N_2H_4 . E_{subs} and E_{deform} E_{A}^{TS} and E_{B}^{TS} are adsorption energies of fragment A and fragment B at the transition state. In the case of reaction $\text{N}_2\text{H}_4 \longrightarrow 2\text{NH}_2$, A and B are two different NH_2 fragments. $E_{\text{int}}^{\text{TS}}$ is interaction energy between A and B at transition state geometry. Finally, $E_{\text{AB}}^{\text{IS}}$ is adsorption energy of hydrazine molecule at initial state geometry. Note that the adsorption energies E_{A}^{TS} and E_{B}^{TS} are calculated with respect to half of the total energy of gas phase hydrazine in *gauche* conformation.

The result of activation energy decomposition is given in Table 4. First, it is observed that E_{subs} is relatively small (less than 0.05 eV) for all surfaces, except Zn(0001). This means that contribution of surface structure

Figure 5: Brønsted-Evans-Polanyi relationship for N—N bond cleaving of hydrazine on 3d metal surfaces. The equation of the BEP line is $y = 0.248x + 0.757$.

Table 3: N-M bond distance (M = Fe, Co, Ni, Cu, or Zn) of adsorbed hydrazine in initial and transition state structure. The difference is calculated as $\Delta d_{N-M} = d_{N-M}^{TS} - d_{N-M}^{IS}$. All values are given in angstrom.

Surface	d_{N-M}^{IS}	d_{N-M}^{TS}	Δd_{N-M}
Fe(110)	2.137	1.992	-0.145
Co(0001)	2.081	1.909	-0.172
Ni(111)	2.026	1.873	-0.153
Cu(111)	2.108	1.961	-0.147
Zn(0001)	2.377	2.034	-0.343

changes to the activation energy is relatively small. The largest value of E_{subs} is obtained for Zn(0001) which reflects the result that geometrical change of this surface is more noticeable compared to other surfaces (two Zn atoms which are bonded to NH_2 go upward as compared to their positions in initial geometry). E_{deform} is also found to be the largest for Zn(0001). The trend for this energy component is similar to the trend of Δd_{N-N} : the greater change in N—N bond length, the larger E_{deform} (see Table 2). The next energy contributions are adsorption energies E_A^{TS} and E_B^{TS} . Note that, because N—N bond cleaving process on the surfaces studied here is symmetric, E_A^{TS} and E_B^{TS} will have the same values. The trend of this component is similar to the trend of E_{act} . The stronger interaction between NH_2 with surface: the more negative value of E_A^{TS} the lower activation barrier. Adsorption energy of hydrazine at initial state E_{AB}^{IS} has opposite effect with E_A^{TS} . For similar adsorption energy at the transition state, the stronger interaction of hydrazine with surface (more negative E_{AB}^{IS}) the larger activation energy. This is found to

Table 4: Activation energy decomposition analysis for $\text{N}_2\text{H}_4 \longrightarrow 2\text{NH}_2$

Surface	E_{subs}	E_{deform}	E_{A}^{TS}	E_{B}^{TS}	$-E_{\text{AB}}^{\text{IS}}$	$-E_{\text{int}}^{\text{TS}}$	E_{act}
Fe(110)	0.01	0.68	-1.02	-1.02	1.28	0.30	0.23
Co(0001)	0.03	1.09	-0.82	-0.82	1.47	-0.56	0.39
Ni(111)	0.03	1.45	-0.62	-0.62	1.32	-1.07	0.49
Cu(111)	0.01	1.17	-0.51	-0.51	0.94	-0.51	0.59
Zn(0001)	0.14	1.69	0.30	0.30	0.29	-1.81	0.91

be the case for Fe(110) and Co(0001) which are found to have similar E_{A}^{TS} . However, $E_{\text{AB}}^{\text{IS}}$ for Co(0001) is more negative which result in higher activation energy as compared to Fe(110). $E_{\text{int}}^{\text{TS}}$ mainly originate from interactions of nitrogen atoms of different NH_2 fragments with surface. The largest value of $E_{\text{int}}^{\text{TS}}$ is obtained for Zn(0001) which may be taken as a sign for strong attractive interaction between N—N atoms of hydrazine.

3.2. Electronic structure

To investigate electronic structure aspect of N—N bond cleaving of hydrazine we start by analyzing charge density difference ρ_{diff} of adsorbed hydrazine. This quantity is calculated as:

$$\rho_{\text{diff}} = \rho_{\text{mol/surf}} - \rho_{\text{mol}} - \rho_{\text{surf}} \quad (5)$$

where $\rho_{\text{mol/surf}}$ is the charge density of hydrazine adsorbed on surface, ρ_{mol} and ρ_{surf} denote charge density calculated separately with same atomic positions as found in adsorbed state for hydrazine and surface, respectively. Contour plots of ρ_{diff} of adsorbed hydrazine at initial and transition state geometry are given in Figure 6. It can be observed that the charge density difference of adsorbed hydrazine has similar features for all surfaces considered here. Along the bond between N atom of hydrazine and surface atom negative charge difference (depletion) region is observed at both edges (of N and surface atom) with positive charge difference (accumulation) region at the center of the bond. This positive charge difference is less pronounced on Cu(111) and Zn(0001) as compared to Fe(110), Co(0001), and Ni(111) which reflects the magnitude of hydrazine adsorption energy. Meanwhile, along the N—N bond at initial state, there is relatively small charge density difference which indicates that, in terms of charge density, the interaction between two N atoms in hydrazine is weaker than the interaction between the individual N atom and surface atom. However, at the transition state, there is substantial change in the charge density along N—N bond of hydrazine. Charge depletion region is observed at the center of N—N bond and accumulation region at both sides of the bond. The most pronounced charge accumulation around this area is observed for Zn(0001). This might be an indication that N—N interaction of hydrazine at transition state is the strongest on Zn(0001) as also have been hinted by the $E_{\text{int}}^{\text{TS}}$ term of Table 4.

Figure 6: Contour plot of charge density difference of adsorbed hydrazine at initial (left) and transition geometry (right). From top to bottom: on Fe(110), Co(0001), Ni(111), Cu(111), and Zn(0001).

To investigate the origin of N—N activation trend across the investigated surface, molecular orbitals (MOs) of adsorbed hydrazine will be investigated. Before considering the MOs of adsorbed hydrazine, it is useful first to consider MOs of hydrazine in gas phase for *cis* conformation with normal N—N bond length and the one with elongated N—N bond. This is useful for investigating change of MOs during N—N bond cleaving. Alternatively, we can also investigate the change of the molecular orbitals of hydrazine during by plotting the molecular orbital energy levels as function of N—N bond length. In Figure 7 such plot is given. The MO energies of the elongated hydrazine is marked with the dashed lines in Figure 7. The comparison of MOs for both structures is given in Figure 8. Recall that hydrazine has 14 valence electrons which occupies 7 MOs. Figure 8 depicts the five highest occupied

and two lowest unoccupied MOs along with their labels which will be used in this discussion. Note that the $4\pi^*$ MO is the highest occupied molecular orbital (HOMO) while the 3π MO is second highest occupied molecular orbital (HOMO-1). Visualization of molecular orbitals at the initial N—N bond and the elongated hydrazine is given in Figure 7. From Figures 7 and 8, it can be seen that MOs of hydrazine and elongated hydrazine structure are very similar. However, two differences can be observed. First, for elongated *cis* 5σ is higher in energy than 2π . Second, the unoccupied $6\sigma^*$ also lower in energy, approaching HOMO. This pattern is also observed when N—N bond cleaving of hydrazine happens on metal surfaces.

Figure 7: Change of molecular orbital energy levels of hydrazine as function of N—N bond length. Hydrazine is initially at the *cis* structure. A vertical dashed line corresponds to the N—N bond length of 1.8 Å, which is the shortest N—N bond length among the transition states found in this work (see Table 2).

MO	1π	5σ	$2\pi^*$	3π	$4\pi^*$	5π	$6\sigma^*$

MO	1π	$2\pi^*$	5σ	3π	$4\pi^*$	$6\sigma^*$	5π

Figure 8: Gas phase molecular orbitals of hydrazine and hydrazine with elongated N—N bond ($d_{\text{N-N}} = 1.8$). These MOs are ordered according to their energy levels: from left to right energy level become higher. Highest occupied molecular orbital for both case is the $4\pi^*$ level.

In Figure 9 the electronic density of states (DOS) of initial and transition state projected to s , p_x , p_y , and p_z orbitals of nitrogen atom are given. Zero energy levels for all plots are set to Fermi energy. At the initial state,

Figure 9: DOS projected on N atom of adsorbed hydrazine at initial (left) and transition geometry (right). Several peaks related to $6\sigma^*$ derived orbitals at transition states have been marked by letters A-E. Visualization of such orbitals is given in Figure 11.

three sharp peaks can be identified for all surfaces around the energy range of -12 to -8 eV. Within the geometry that is used in this work, N—N bond lies in x axis, 1π and $2\pi^*$ will be composed almost entirely of nitrogen p_y while 5σ of nitrogen p_z and p_x . Using this geometry, these three sharp peaks can be identified as derived orbitals (Kohn-Sham electronic states) from 1π , 5σ , and $2\pi^*$. These orbitals still retain their gas phase characteristics. At the transition state, these three peaks lie higher in energy with 5σ peak located higher than $2\pi^*$. This is similar to what was observed when comparing MOs of hydrazine and elongated hydrazine (see Figures 7 and 8). Peaks that are located higher in energy correspond to the derived orbitals due to interaction between HOMO-1 and HOMO with surface orbitals. These orbitals are dominated by contribution from p_z orbitals of nitrogen. At transition state, HOMO will be shifted to lower energy, while HOMO-1 will be shifted to higher energy.

Figure 10: Visualization of Kohn-Sham orbitals which have $6\sigma^*$ character of elongated hydrazine on $3d$ surfaces, from left to right: Fe(110), Co(0001) and Ni(111). Aside from having N—N antibonding character, these orbitals also have bonding character. The energy of these orbitals lie at the position indicated by letters F-H in Figure 9

Figure 11: Visualization of Kohn-Sham orbitals which have $6\sigma^*$ character of elongated hydrazine on $3d$ surfaces, from left to right: Fe(110), Co(0001), Ni(111), Cu(111), and Zn(0001). Aside from having N—N antibonding character, these orbitals also have antibonding or nonbonding character with surface orbitals. As indicated by letters A-E in Figure 9, it can be seen that on Fe(110), Co(0001), and Ni(111) these orbitals are located above Fermi level while for Cu(111) and Zn(0001) they are located below Fermi level.

The N—N bond cleaving process is mainly caused by the population of $6\sigma^*$ -derived orbitals at transition state. These orbitals are dominated by nitrogen p_x and have N—N antibonding character. The interaction between gas phase $6\sigma^*$ MO of elongated hydrazine with surface d -orbitals (d -band) will result in bonding and antibonding orbitals with respect to surface atom in the case of sufficiently strong coupling between these orbitals. The $6\sigma^*$ -derived bonding orbitals lie at lower energies and are readily occupied. Examples of such states are given in the Figure 10. On Cu(111) and Zn(0001) the interaction between $6\sigma^*$ and d -orbitals due to large energy difference between them. However, the position of the peak of $6\sigma^*$ -derived antibonding states vary as we go from Fe(110) to Zn(0001). Examples of such states are given in Figure 11. For Fe(110), peaks that correspond to $6\sigma^*$ -derived

antibonding states with surface atom lie above Fermi level. This results in stronger bonding between elongated hydrazine (transition state) with surface, thus more negative adsorption energy which will lead to lower activation energy. As we go down from Fe(110) to Zn(0001) these antibonding states lie lower in energy and are occupied by electrons. This will result in weaker interaction. Thus, from electronic structure perspective, the trend of activation energy for N—N bond cleaving on the surfaces that are considered here can be attributed to this occupation of $6\sigma^*$ -derived orbitals.

4. Conclusion

In summary, N—N bond cleaving process of hydrazine has been investigated on close-packed 3d metal surfaces: Fe(110), Co(0001), Ni(111), Cu(111), and Zn(0001). Going from Fe(110) to Zn(0001) activation energy is found to have increasing trend. The transition state for this process is found to closely resemble the structure of initial state. The present study also has shown that the Brønsted-Evans-Polanyi relationship holds for N—N bond cleaving on 3d metal surfaces that are considered. By analyzing the orbitals of adsorbed hydrazine it is found that the trend of activation energy is related to the occupation of $6\sigma^*$ -derived orbitals of the elongated hydrazine (the transition state). On the surface where the interaction of $6\sigma^*$ orbital of the transition state is strong, the $6\sigma^*$ -derived bonding orbitals will be occupied and the derived antibonding orbitals will be unoccupied. However, on the surface where the interaction of $6\sigma^*$ orbital of the transition state is weak, the antibonding (or nonbonding) orbitals will be occupied and this will result in more positive adsorption energy of the transition state. This will eventually lead to higher activation energy for N—N bond cleaving.

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