

A Systematic Density Functional Theory Study of the C–N Bond Cleavage of Methylamine on Metals

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The C–N bond cleavage for the relative large molecule of methylamine on Cu(111), Ag(111), Au(111), Ni(111), Rh(111), Pd(111), Pt(111), and Mo(100) has been systemically studied using the DFT-GGA method; the reaction energy changes and the activation energies were obtained. The calculated results show that the activation energy of C–N bond cleavage decreases as the metal element goes up and to the left across the periodic table, which is in general agreement with the experimental observation. Moreover, it was found that the steric effect should be considered for the metals with high activity and small radius such as Ni, which is much different from the case for the small molecule decomposition in which the steric effect may be ignored. The linear relationships between the activation energies and electronic properties (d-band center) are presented. It is expected that such a rule can be used to predict the reactivity of metal for other dissociative adsorption systems.

1. Introduction

The decomposition of simple molecules such as H_2 ,^{1,2} CO ,³ NO ,⁴ and N_2 ⁵ on metal surfaces has recently received extensive attention due to its importance in many metal-catalyzed reactions. It has been found that both the electronic and the geometrical factors affect the dissociation reactions. The trends in atomic and molecular adsorption energies and the mechanism of simple chemical reactions on the transition metal surfaces can be understood on the basis of the theoretical model of Hammer and Nørskov;^{6–8} that is, the more close to the Fermi level is the d-band center, the more active is the molecular decomposition. However, it should be pointed out here that such a rule is just examined for the small molecule, and it is unclear whether this model is suitable for more complicated systems, that is, the relative large molecule. In the present work, we intend to investigate the complicated decomposition reactions of C–N bond cleavage for methylamine (CH_3NH_2) on the transition metal surface to further understand the molecule dissociation mechanism and examine the above theoretical model. One of the reasons for choosing CH_3NH_2 as an example is that the surface chemistry of molecules containing carbon and nitrogen is interesting in the oil industry⁹ and relatively little is known about reactions of the C–N bond on surfaces.

2. Calculation Details

The methylamine adsorption on transition metal surfaces, such as Cu(111), Ag(111), Au(111), Ni(111), Rh(111), Pd(111), Pt(111), and Mo(100), was studied using DFT-GGA calculations within the package of STATE¹⁰ (Simulation Tool for Atom Technology), to obtain some general knowledge of the reactivity of transition metals for C–N bond cleavage in the periodical table. The Perdew, Burke, and Ernzerhof (PBE) functional¹¹ was used to treat the electron exchange and correlation. Ionic

cores were described by Vanderbilt's ultrasoft pseudopotentials,¹² and the valence electrons were expanded in a basis of plane waves. The cutoffs energies are 25 and 400 Ry for wave functions and augmentation charge density, respectively. In the surface Brillouin zone, a Monkhorst–Pack mesh¹³ with $4 \times 4 \times 1$ k-point sampling was used. The periodical slabs including four metallic layers were employed with ~ 10 Å of vacuum region between slabs. The slab model of $p(2 \times 2)$ four layers with the first two layers relaxed was used.

The transition states of all reactions were searched using the nudged elastic band (NEB) method.^{14,15} In fact, to increase the density of images near the transition state and to locate the TS more accurately, the modified NEB method, that is, the ANEBA method,¹⁶ was used. In the ANEBA method, we choose three movable images connecting two local minima on the potential energy surface and use the NEB method as a starting level. After the calculation converges to some given accuracy, we choose the two images adjacent to the one that has the highest energy as our new starting points for the next level NEB calculation. Through several iterations, at the last level, the ANEBA calculation will locate three images so that the total energy of each of them is almost the same and then the one in the middle is considered as the TS. Although this approach does not employ the frequency analyses, it has been shown in many cases to give excellent convergence to saddle points on an analytical potential energy surface.^{17,18}

In our investigation on the methylamine decomposition mechanism on Pd(111), the transition state for the reaction of $\text{AB} = \text{A} + \text{B}$ is searched using two approaches with the same initial state (IS): one is that every adsorbate in the final state (FS) is placed on the most stable adsorption site, and the other is that the final state is optimized from IS in which the two dissociated parts are not in the most stable site. The calculated results show that the activation energy obtained from the former (i.e., in the most stable site) is much lower as compared to the case of products from IS.¹⁹ Therefore, adsorbates in the IS and FS are optimized at its most stable adsorption site.

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TABLE 1: Calculated Adsorption Energies of Every Adsorbate on Investigated Transition Metal Surfaces (Energy Units in eV)

	CH ₃ NH ₂	CH ₃		NH ₂	
	top	hollow	top	hollow	bridge
Mo(100)	1.12	2.00(2.41) ^a			4.82
Ni(111)	0.57	2.04	1.75	3.64	3.79
Rh(111)	0.74	1.79	1.72	3.54	3.58
Pd(111)	0.79	1.78	1.84	3.09	3.31
Pt(111)	0.73	1.28	2.00	3.21	3.20
Cu(111)	0.27	1.33	1.20	3.04	3.06
Ag(111)	0.53	1.05	1.29	3.27	3.15
Au(111)	0.31	0.55	1.16	2.27	2.31

^a Bridge site result.**TABLE 2: Energetics of C–N Bond Cleavage of Methylamine on the Investigated Transition Metal Surfaces (Energy Units in eV)**

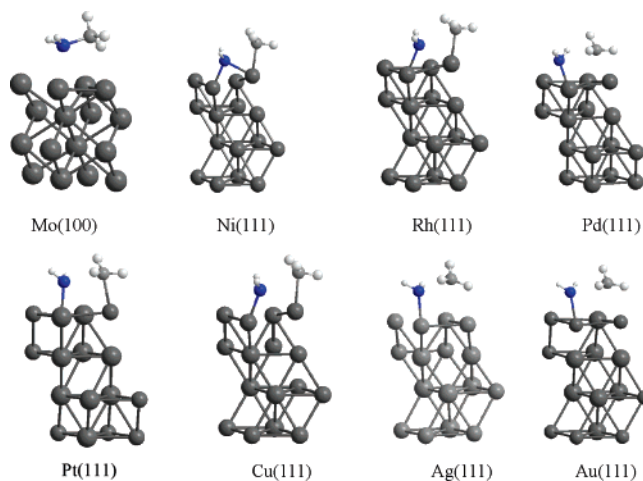
	E_{dis}	ΔH	ϵ_d	V_{ad}^2
Mo(100)	0.33	−1.08	0.35	6.62
Ni(111)	1.49	0.24	−1.29	1.16
Rh(111)	1.50	0.39	−1.73	3.32
Pd(111)	2.20	0.48	−1.83	2.78
Pt(111)	2.37	0.64	−2.25	3.90
Cu(111)	2.50	1.07	−2.67	1.00
Ag(111)	3.09	1.20	−4.30	2.26
Au(111)	3.53	1.82	−3.56	3.35

3. Results and Discussion

Before searching the transition state of C–N bond cleavage of CH₃NH₂ into CH₃ and NH₂ on metal surfaces using the ANEBA method, the adsorption behaviors of every adsorbate should be investigated. For the much heavier adsorbate of methylamine, the adsorption at the top site is considered as the most stable state. In our previous investigation on methyl adsorption, the results show that methyl is preferentially adsorbed at the hollow site on Ni, Rh, and Cu, at the top site on Pd, Pt, Ag, and Au,²⁰ and at the bridge site on Mo.²¹ For NH₂, it is also mainly adsorbed at the hollow and bridge sites, and the difference in adsorption energies is small at the two sites. Furthermore, the bridge site adsorption is slightly preferred for most surfaces (Table 1). Interestingly, for IB metals, the adsorption energy of NH₂ on Ag(111) is largest, and it may be induced by the surface relaxation. In addition, when NH₂ adsorbed on the Mo(100) hollow site, we find that it is not so stable and moves to the bridge site (Table 1).

Next, we determine the initial state (IS) and final state (FS) using its most stable adsorption site approach. In the IS, methylamine is adsorbed on the top site. In the coadsorption FS, CH₃ and NH₂ are placed on their most stable adsorption site. After optimizing the configurations, we start to interpose images between them to find the reaction path.

The activation energies (E_{dis}) and reaction energy changes (ΔH) have been calculated and listed in Table 2. At the same time, Figure 1 displays the corresponding transition state structures (TSs). It can be seen that E_{dis} varies considerably from 0.33 to 3.53 eV among these metals. For each row of the periodical table investigated, one can also find that the order of the activation energy of C–N bond cleavage is that Ni < Cu (3d metals), Mo < Rh < Pd < Ag (4d metals), and Pt < Au (5d metals). The activation of C–N bond cleavage during methylamine adsorption on these transition metal surfaces decreases in the order of Mo(100) > Ni(111) \approx Rh(111) > Pd(111) > Cu(111) > Pt(111) > Ag(111) > Au(111) (Table 3), which in general agrees well with the experimental observation made by Hwang et al.²² The C–N bond of methylamine

**Figure 1.** Possible TS structures of C–N bond cleavage during methylamine adsorption on the investigated transition metal surfaces.**TABLE 3: Important Structural Parameters in the TS for the C–N Bond Cleavage during Methylamine Adsorption on the Investigated Transition Metal Surfaces (Units in Å)**

	$R_{\text{N–M}}$	$R_{\text{C–M}}$	$R_{\text{C–N}}$
Mo(100)	2.240	2.999	1.529
Ni(111)	1.846	2.018	2.250
Rh(111)	1.969	2.403	2.080
Pd(111)	1.956	2.610	2.234
Pt(111)	1.966	2.247	2.308
Cu(111)	1.924	2.114	2.333
Ag(111)	2.152	2.310	2.967
Au(111)	2.138	2.690	2.588

adsorbed on Pd(111) remained intact and without N or C residues detected by 500 K.²³ On Ni(111), Chorkendorff et al.²⁴ found that CN residues decomposed at \sim 530 K (ca. 1.45 eV based on the Redhead analysis), which is similar to our calculated value of 1.49 eV. It has been shown that the C–N single bond on Rh and Pt is highly resistant to cleavage and the species containing the C \equiv N bond are the major products by Cordonier et al.²⁵ The C–N bond in methylamine on Rh(111) is stable at least at 700 K, but on Pt(111) remains stable at \sim 1000 K. Maseri et al.²⁶ found no significant decomposition reactions for methylamine adsorption on Cu(110). Up to now, the surface chemistry of methylamine on the Ag and Au surface has not been fully studied, and one can believe that the activation energy of C–N bond cleavage is very high and it is difficult to dissociate on Ag(111) and Au(111). The high decomposition temperature shows that the C–N bond on these metal surfaces is stable, and only a little dissociates and is detected at the defects on the crystal surface.²⁵

In heterogeneous catalysis, Brønsted–Evans–Polanyi (BEP) is one of the classical approaches that could provide the means to correlate the activation energy and reaction heat or energy change, and allows one to predict the variations in reactivity from one metal to the next.²⁷ By checking the TSs for the different metals as shown in Figure 1, we find that the structures of TSs for C–N bond breaking of methylamine on almost metals are more like product (i.e., “late barrier”) with the exception of metal Mo(100) (“early barrier”). For the TSs of “late barrier”, a good linear correlation was found between the reaction barriers and the reaction energy changes (Figure 2). From Figure 2, one can know that the more positive is the reaction energy change, the higher is the activation energy. Thus, one can predict the reactivity of the transition metal surface following this relationship to some extent.

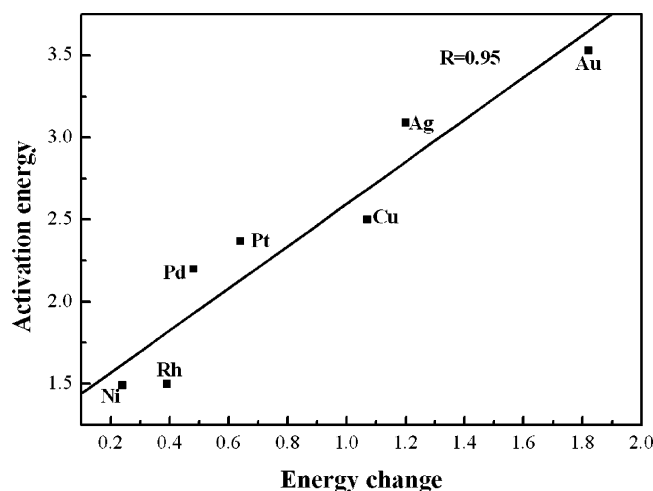


Figure 2. Relationship between the activation energy of C–N bond cleavage and reaction energy change.

To better understand the physical origin of such catalytic activity order, electronic property analysis is necessary. According to the theoretical model of Hammer and Nørskov,⁶ the formation of the bond between adsorbate and the metal surface is divided into two steps (as shown in Figure 3): coupling to metal *s* band first, then coupling to the metal *d* states. The contribution from coupling to the *s* band of any metal is dominant on the A–M binding energy (A denotes adsorbed atom), which was also suggested by Yang and Whitten,²⁸ and, what is more, is almost the same. The coupling of the second step reflects the trend of changes and determines the special properties of the metal, due to different *d* electron states. Therefore, we mainly discuss the interaction between the adsorbate and metal *d*-band, from which we can predict the trend of the adsorption energy on metal surface. We know that both the *d*-band center (ϵ_d) and the coupling matrix element square (V_{ad}^2) reflect the properties of the metal *d*-band, but their influence is quite different for the different metals, and we must

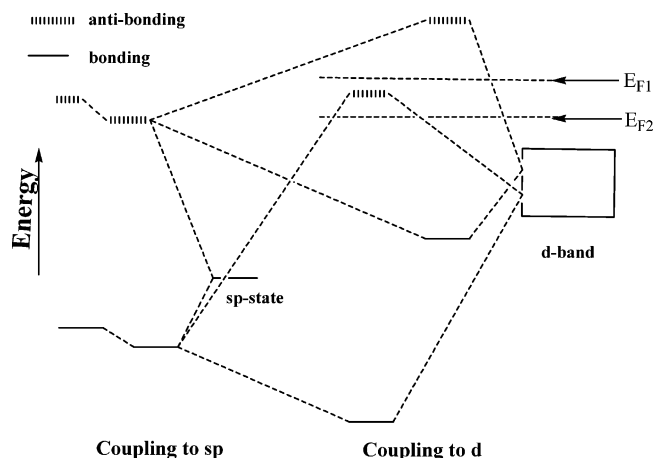


Figure 3. Schematic illustration of the interaction between two electronic states; E_{F1} and E_{F2} are the Fermi level of noble metals and transition metals, respectively.

determine which effect is the dominant factor for a given metal. In general, in the periodical table, the *d*-band center decreases generally from the left to the right and from the top to the bottom. On the other hand, V_{ad}^2 generally decreases within a row and increases down the groups.^{6,20,29} For the noble metals (group IB), copper, silver, and gold, they have a filled and deep-lying *d*-band, well below the Fermi level, so the coupled antibonding state is completely filled, and is difficult to push above the Fermi level. It has been shown that the variation in adsorption strength from copper to gold is given mainly by the Pauli repulsion;^{6,20,29} that is, the larger is V_{ad}^2 , the stronger is the overlap between the orbital, and the larger is the repulsion. For the transition metals, because the *d*-band is unfilled, its interaction with the adsorbed species is mainly attractive. Moreover, the narrower is the *d*-band (or the *d*-band center is more close to the Fermi level), the stronger is the interaction with the adsorbed species. Figure 4 shows the correlations between activation barrier and ϵ_d or V_{ad}^2 . (The electronic

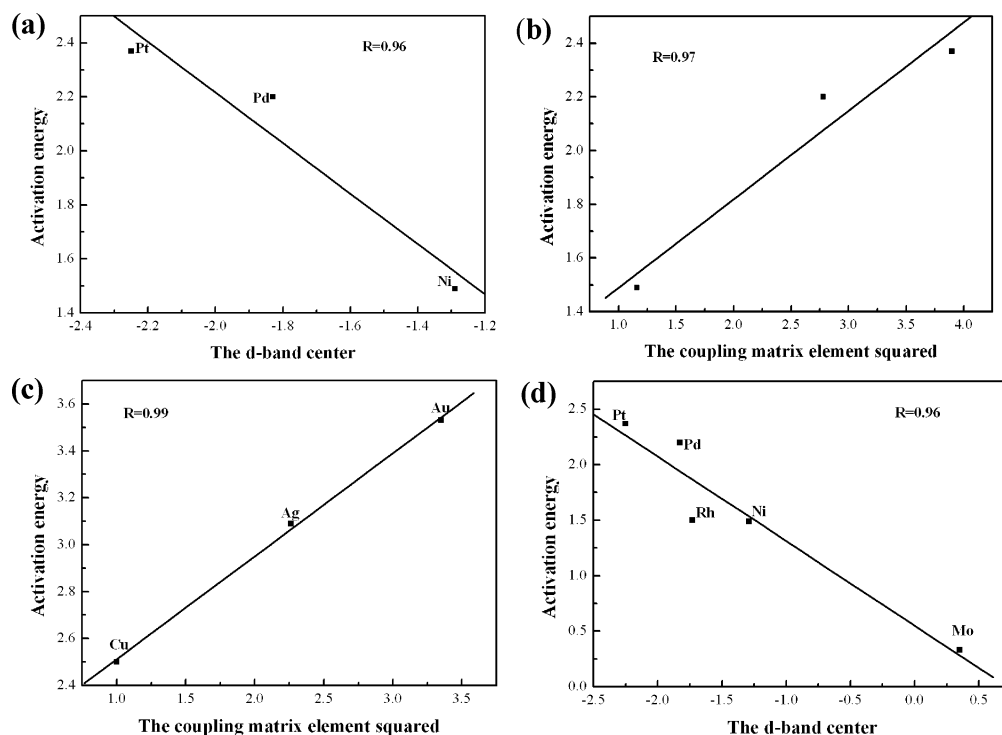


Figure 4. Relationship between the activation energy of C–N bond cleavage and the electronic properties.

structure characters (ϵ_d and V_{ad}^2) are obtained from the data of Andersen et al.³⁰ In Figure 4, for Ni, Pd, and Pt of group VIII, a clear linear correlation between E_{dis} and ϵ_d or V_{ad}^2 was found. However, only the correlation with V_{ad}^2 is suitable for the IB group metals. Additionally, to further confirm the above theoretical analysis, the metal surfaces investigated here are divided into two kinds: transition metals and noble metals, and a good linear relationship was observed between the activation energy and the square of the coupling matrix element for Cu, Ag, and Au (group IB) metals or the d-band center for Ni, Rh, Pd, Pt, and Mo transition metals (Figure 4c,d), which is consistent with the theory model of Hammer and Nørskov as well as our previous results.^{21,22} From Table 1, one can find that the Mo(100) surface is the most active among them based on the above activation energies. The reason is that Mo(100) surface has more unpaired d-electrons, leading to the narrower d-band, and the smallest absolute value of the d-band center relative to the Fermi level. The general rule is that the higher is the d-band center, the more reactive is the metal (i.e., the lower is the transition state energy). According to the values of the d-band center, Ni(111) should be more active than Rh(111); however, the activation energy of the C–N bond broken on Rh(111) is similar to that on the Ni(111) surface. Why does it happen? If we analyze their TS structures in detail, we can see that the two dissociated species (CH_3 and NH_2) in the TS structure on Rh(111) do not share bonding with metal atoms (Figure 1); however, for the Ni(111) surface, the bonding competition exists, which increases the C–N bond dissociation barrier. The possible reason may due to the fact that the metal Ni has the narrow d-band and the small radius, which results in stronger interaction between two coadsorbed species, as compared to that of metal Rh. To confirm such a point, the interaction between CH_3 and NH_2 at TS is estimated by the formula of $E_{CH_3NH_2} = E_{CH_3} + E_{NH_2} + E_{inter}$ (where E is the calculated total energy for each species at TSs), and the calculated interaction energies (E_{inter}) for the Ni(111) and Rh(111) are 24.65 and 13.99 kcal/mol, respectively, indicating that a stronger repulsion energy exists on the Ni(111) metal. The dissociation barriers are affected jointly by two important factors, both electronic and geometrical factors, which is different from the case for the small molecule decomposition in which the dissociate activation barrier is mainly determined by the metallic activity alone.

4. Conclusions

In summary, the present work shows that for the more complicated system of C–N bond cleavage during methylamine adsorption on the metal surfaces, the theoretical model of Hammer and Nørskov is still suitable to interpret the reactivity of the metals. The linear relationships appear between the electronic properties and the activation energies. Therefore, the

electronic properties (ϵ_d or V_{ad}^2) can be used to predict the reactivity of metals to some extent. In addition, the BEP relationship was also found between the reaction barriers and the reaction energy changes.

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