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Theoretical study of the adsorption and dissociation mechanism for methylamine on Pd(1 1 1)

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ABSTRACT

The decomposition mechanisms of methylamine on Pd(1 1 1) has been systematically investigated with the DFT-GGA method using the repeated slab model, and the decomposition network has been mapped out. The adsorption energies under the most stable configuration of the possible species and the energy barriers of the possible elementary reactions involved are obtained in this work. Desorption is preferable for adsorbed methylamine and hydrogen, while for the other species decomposition is preferred. Through systematic calculations for the reaction mechanism of methylamine decomposition on Pd(1 1 1), we found the most likely decomposition path is $H_3CNH_2 \rightarrow H_2CNH_2 \rightarrow HCNH \rightarrow HNC + HCN \rightarrow CN + H_2$. The decomposition products are in general agreement with the previous experimental observations.

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1. Introduction

The adsorption of organonitrogen compounds on metal surfaces is very important not only for its industrial implications but for its catalytic reactions. It is known that organic amines are able to improve the selectivity of hydrogenation [1]. Methylamine is the simplest organic amines. The chemical interaction between methylamine and metal surfaces is studied to understand the fundamental reactions of organonitrogen compounds and metal surfaces.

Many investigations have been performed experimentally into methylamine on metal surface, such as Ni [2–8], Cr [2–4], Ru [9], W [10], Pt [11–13], Mo [14], Cu [15], and Pd [16]. All the results showed that methylamine was adsorbed through the lone pair electrons on the nitrogen atom and stable on metal surfaces below 300 K. For the different metals or the different surfaces for a given metal, the decomposition products are different. Baca et al. [2] found that methylamine was adsorbed molecularly on the (1 0 0) and (1 1 1) surfaces of Ni and Cr at 300 K using electron energy loss spectroscopy (EELS). The C—N bond scission was observed for H_3CNH_2 on Cr, while C—N bond cleavage was not found for H_3CNH_2 on Ni at this temperature [2]. Complete dehydrogenation of H_3CNH_2 on Ru(0 0 1) [9] and W(1 0 0) [10] have been observed to the formation of gaseous phase H_2, N_2 and NH_3. On Pt(1 1 1), Thomas et al. [11] found that the chemisorbed H_3CNH_2 dehydrogenate to produce H_2, HCN and C_2N_2 without C—N bond cleavage, whereas C—N bond scission was observed on Pt(1 0 0). To test the effect of surface modifiers on the decomposition pathway of H_3CNH_2 on transition metal surface, Pearlstine and Friend [10] found that H_3CNH_2 decomposes completely to yield H_2, N_2, and NH_3 on W(1 0 0)-(5 × 1)-C and clean W(1 0 0) surface using temperature programmed reaction spectroscopy (TPRS). However, the desorption energies on the two surfaces are significantly different. The adsorption and decomposition of H_3CNH_2 on a Mo(1 0 0)—$c(2 \times 2)$N [14] surface was studied using temperature-programmed desorption (TPD) and auger electron spectroscopy (AES), and the results showed that C—N bond cleavage occurred first. At 210 K, TPD studies showed that adsorbed H_3CNH_2 undergoes desorption and concurrent decomposition. Maseri et al. [15] found no significant decomposition reactions occurred for methylamine adsorption on Cu(1 1 0). Chen and Winograd [16] have investigated the thermal decomposition of methylamine on the clean Pd(1 1 1) surface based on X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), and thermal desorption spectrometry (TDS). They found that methyl-hydrogens (H—CH_2NH_2) are more stable than amino-hydrogens (H_3CNH—H), and no C—N bond activation is observed.

Although the adsorption and decomposition of methylamine on metal surfaces have been extensively studied, the theoretical work related to the reaction mechanism is rather scarce. The theoretical investigations of methylamine mainly focus on the silicon [17,18], nickel [19,20] and molybdenum [21,22] surfaces.

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The N—H and C—N bond cleavages on Si(1 0 0) surface have been investigated [17] theoretically, and the authors found that the N—H bond scission is preferential to C—N bond scission under milder conditions owing to the charge transfer from the surface to N atom weakening the N—H bond. Oliva et al. [19] found that the C—H bond breaking is slightly favored over the N—H bond cleavage on Ni(1 1 1). We also [20] investigated the initial activation of the C—H, N—H, and C—N bond on Ni(1 0 0), Ni(1 1 0), Ni(1 1 1), stepped Ni(1 1 1), and nitrogen atom modified Ni(1 0 0). The results indicate that the C—H bond is favorable to break on Ni(1 1 1) and Ni(1 0 0), whereas the N—H bond is preferred to cleave on stepped Ni(1 1 1) and N—Ni(1 0 0). Moreover, the C—N bond is the most difficult to break on the investigated surfaces. Besides on nickel surface, we have investigated the methylamine decomposition on the molybdenum surface [21,22]. We found the surface C, N and O atom reduces the reactivity of molybdenum for the C—N bond cleavage of methylamine forming methyl and amino [21], and the most likely decomposition path is $H_3CNH_2 \rightarrow H_2CNH_2 + H \rightarrow HCNH_2 + H + H \rightarrow CNH_2 + H + H + H \rightarrow C + NH_2 + H + H + H \rightarrow C + NH_3 + H_2 \rightarrow C + NH_3\ (g) + H_2\ (g)$ on the nitrogen atom modified Mo(1 0 0) surface [22].

Despite the experimental investigations, to our knowledge, there are no any theoretical works relevant to the methylamine decomposition on palladium surface. In this work, the decomposition of methylamine on Pd(1 1 1) is investigated in detail using the periodic density functional theory (DFT) calculation. Our aim is to map out the decomposition network of methylamine, and the structures and energies of the intermediates involved as well as the decomposition potential energy surface (PES) are included.

2. Calculation details

DFT-GGA calculations are performed using the VASP [23,24] software package. The exchange-correlation energy and potential are described by generalized gradient approximation (PW91) [25]. The electron-ion interaction is described by the projector-augmented wave (PAW) scheme [26,27], and the electronic wave functions are expanded by plane waves up to a kinetic energy of 400 eV. In the surface Brillouin zone, a Monkhorst-Pack mesh [28] with 3 × 3 × 1 k-grid samplings is used. The periodical slabs including four metallic layers are employed with ∼10 Å of vacuum region between the successive slabs. The $p(2 \times 2)$ unit cell is chosen, corresponding to 1/4 monolayer (ML) for a single adsorbate on the surface. During the calculation, the top two layers and the adsorbed species are allowed to be relaxed. The molecules in the gas phase have been calculated using a box with the size of $17 \times 18 \times 19\ Å^3$, and only a Γ-point was used during the calculation. Spin-polarized calculations were performed when needed. The adsorption energy (E_{ads}) of adsorbate is calculated in terms of equation of $E_{ads}(A) = E_{A/M} - E_M - E_A$, where $E_{A/M}$ is the total energy of the adsorbate–substrate system, E_M is the total energy of the substrate, and E_A is the energy of the adsorbate in the gas phase. In this work, for a reaction like $AB = A + B$, the calculated total energy change or reaction enthalpy (ΔH) is defined by the formula of $\Delta H = E(A+B)/M - E(AB)/M$, where $E(A+B)/M$ and $E(AB)/M$ are the total energy for the coadsorption system of the product and of the reactant, respectively. Activation energy, E_a, is calculated based on the equation of $E_a = E_{TS} - E_{(AB)/M}$, where E_{TS} is the total energy of the transition state (TS). Furthermore, to examine the coverage effect on the calculation results, the adsorption energy of methylamine on $p(3 \times 3)$ unit cell was also calculated. It was found that the methylamine adsorption energy on $p(3 \times 3)$ unit cell is 0.20 eV large than that on $p(2 \times 2)$ unit cell. This discrepancy was within the error range of DFT method.

The reaction paths are calculated using the climbing-image Nudged Elastic Band method (CI-NEB) [29]. The image of the highest energy is the TS. Moreover, all the TSs are identified by exhibiting the existence of a single normal mode associated with a pure imaginary frequency. Then the zero point energy (ZPE) into the activation energy is included [30]:

$$\mathrm{ZPE} = \sum_i \frac{1}{2} h\nu_i,$$

where ν_i is the calculated real frequencies of the system.

3. Results

3.1. Adsorption of reactants and possible intermediates

Adsorption of the reactants and all possible intermediates involved in the decomposition of methylamine on Pd(1 1 1) were considered. The stable configurations are displayed in Fig. 1, and the corresponding energetic data are listed in Table 1.

Analogous to the experimental results of Ni [2] and the DFT results for Mo [21] and Ni [20], H_3CNH_2 binds with the metal surface at the top site through the lone-pair electrons of nitrogen atom with the C—N bond tilting 56.8° from the surface normal (Table 1). The calculated adsorption energy is −0.81 eV for H_3CNH_2 on Pd(1 1 1), which agrees well with the experimental data of −0.72 eV [16] based on the Redhead analysis. And the calculated value is larger than that of −1.12 eV on Mo(1 0 0) and smaller than that of −0.58 eV on Ni(1 1 1). The H_2 molecule also prefers the top site perpendicularly with the adsorption energy of −0.07 eV. H_3CNH, NH_2, and $HCNH_2$ all prefer the bridge site via the N, N, and C atoms, and the adsorption energy is −2.38, −2.76, and −4.25 eV, respectively. For H_3CNH and NH_2, the N atoms interact with two Pd surface atoms, and the C atom locates at the hcp site for H_3CNH. For $HCNH_2$, the C atom interacts with two Pd surface atoms and N atom locates at the hcp site, which is different to the H_3CNH. CH_3, CH_2, CH, C, CNH_2, HNC, and CN all adsorb on a fcc site through the C atom interacted with surface Pd atom, and the adsorption energy is −1.88, −4.26, −6.85, −7.46, −4.53, −2.34, and −4.14 eV, respectively. The C—N bond is perpendicular to the surface and has a C—N distance of 1.35, 1.24, and 1.20 Å for CNH_2, HNC, and CN. H_2CN, NH, and N all adsorb via the N atom on a fcc site with the adsorption energy of −2.43, −4.53, and −5.19 eV, respectively. The C—N bond in H_2CN is approximately perpendicular to the surface and the tilting angle for C—N bond relative to the surface normal is 0.4°. H_2CNH_2 is adsorbed by a near μ–η^2 structure with the adsorption energy of −2.24 eV. The HCNH and HCN adsorb flat with the C—N bond almost parallel to the surface with the adsorption energy of −3.08 and −1.18 eV, and the center of the C—N bond is located at a hcp and a fcc site for HCNH and HCN.

3.2. Dissociative reaction paths

After getting the preferred adsorption sites for each possible species involved in the processes of methylamine decomposition, we can explore the details of reaction mechanism by calculating the activation energy. We first investigated the initial decomposition of methylamine by breaking its C—H, N—H, and C—N bonds individually and then walked through "likely" decomposition of involved species. For each reaction, the initial states (IS) and final states [6] of the reaction are taken to be the most stable states of adsorption/coadsorption of the involved intermediate(s) and the coadsorption/adsorption of the product species. The calculated barriers, Ea, and the total energy change, ΔH, for every possible mechanism on Pd(1 1 1) surface are listed in Table 2. At the same time, we also give the corresponding TS structures for each reaction

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