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Decomposition of NH_3 on Ir(110): A first-principle study

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ABSTRACT

The adsorption and dehydrogenation of NH_3 on Ir(110) have been investigated using periodic density functional calculations. The adsorption sites, the adsorption energies, the predominant adsorption configurations and the transition states of the stepwise dehydrogenation of NH_3 were identified. The results show that the NH_3 prefers the top site with inclining 68.6° of N—Ir bond relative to the surface, while NH_2, NH, N and H favor the short bridge position. The NH decomposition to N and H or recombination with H to form NH_2 shares the similar and relatively high reaction energy barrier, implying that NH will be the main surface species in the NH_3 dehydrogenation processes. N—N bond formation possesses the highest energy barrier of 1.75 eV, indicating that it is the rate-limiting step for NH_3 decomposition. Barrier decomposition analysis reveals that the deformation and the binding to the surface of the reactants and the interaction among binding species in transition states will increase the activation energy while the bonding to the surface of the species in transition state will decrease the energy barrier.

1. Introduction

NH_3 is a very important industrial chemical; most of it are converted into solid fertilizers or directly applied to arable soil [1]. It can also be catalytically oxidized to prepare nitric acid by the Ostwald process [2]. As a toxic component in gaseous and aqueous waste streams, its decomposition to N_2 is an important topic in environmental catalysis. In the selective catalytic reduction process (SCR) a stoichiometric amount of NH_3 is used to reduce the NO_x in flue gasses in a catalytic reaction of the nitrogen oxides [3,4]. Recently, the increasing attention is focused on the catalytic decomposition of NH_3 for pure hydrogen production [5–13]. Normally the steam reforming, partial oxidation and autothermal reforming of hydrocarbons are used as technologies for hydrogen production which is unwillingly producing a large amount of CO_x as a by-product [14]. Reducing of CO_x to ppm levels from the hydrogen stream makes the process extremely complex and unwieldy, and therefore hindering the use of existing hydrogen production technologies in vehicular and small-scale fuel cell applications. As an alternative way, the catalytic decomposition of NH_3 provides a hopeful route for CO_x-free hydrogen production. Papapolymerou et al. [15] have reported that Ir catalysts have much higher activity to decompose NH_3 than the other transition metals, such like Pd, Pt and Rh. Weststrate and his coworkers have investigated the NH_3 behavior on Ir(110) surface using XPS, they found that NH_3 and NH were decomposed at 225~300 K and 400~500 K respectively, the desorption of formed N_2 through N recombination was observed under 500~700 K, NH_2 on Ir(110) surface was found to be the most unstable species, but the experiments were suffering from the thermal and X-ray radiation effects [16]. By using TPD techniques, Goodman *et al.* have studied the adsorption and decomposition of NH_3 on Ir(100), they show that the desorption and decomposition of NH_3 are rather competitive [17]. Moreover, Xie et al. have studied the decomposition of NH_3 on Ir(100) surface using DFT method, they proposed that the first dehydrogenation of NH_3 is a rate-limiting step based on the pretext that the first transition state for H depletion is not stable [18]. Krekelberg et al. have investigated the adsorption of NH_3 on Ir(111) surface by employing DFT method, the results indicate that the NH_3 adsorbs molecularly on the top site with N-end down to the surface, the adsorbed NH_3 does not dissociate in this case [19], but surface defects and co-adsorbed O facilitate the NH_3 decomposition [20]. However, there are still some questions remained, for example, theoretical understanding of NH_3 physics and chemistry on Ir(110) surface is not reported in literature, the micro scenario of adsorption and decomposition of NH_3 on Ir(110) is not clear, the factors that dominate the N—H bond breaking and the N—N bond forming are not known.

In this paper, we will perform DFT calculations to characterize adsorption geometries, adsorption site preference and relative stability of NH_3 and the derived species on Ir(110) surface, we will explore the reaction mechanism and identify the transition states, and finally we will include energy analysis to shed light on the relative importance of the factors governing the reaction barrier. The paper is organized as follows. After the introduction, the computational details are given in Section 2. The calculated results and discussions are presented in Section 3. A short summary is concluded in Section 4.

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2. Computational details

All calculations were based on density functional theory (DFT) method as implemented in VASP package [21–23]. The electronic states were expanded by using a plane wave basis set with a cutoff energy of 400 eV, the projected augmented-wave method was employed to describe the inner cores [24,25], and the GGA-PW91 was used to model the exchange and correlation effects [26]. The calculated total energy was extrapolated to 0 K. A 5-layer slab, separated by a vacuum spacing of 15 Å, was used to imitate the Ir (110) surface. A (2 × 2) supercell, corresponding to the coverage of 1/4 ML, was truncated from the bulk with an optimized lattice constant of 3.88 Å (The experimental value of Ir lattice constant is 3.84 Å [27]). A 3 × 5 × 1 k-point sampling within the surface Brillouin zone was adopted using Methefessel–Paxton method [28]. The adsorbate was arranged on one side of the slab and fully relaxed together with the top-layer metal atoms. The adsorption energy was calculated using $E_{ads} = E_{gas} + E_{surf} - E_{gas/surf}$, where E_{gas}, E_{surf} and $E_{gas/surf}$ are the energies of adsorbate in gas, the clean surface and the adsorbed system respectively. Transition states (TS) were identified using the Lanczos method [29] and verified by vibration analysis with only one imaginary frequency corresponding to the bond forming or breaking. Zero-point energy (ZPE) corrections were considered in the barrier calculations: $ZPE = 0.5\sum_i h\nu_i$, where ν_i are the frequencies of the system.

3. Results and discussion

3.1. The adsorption of NH_x ($x = 0 \sim 3$), H and N_2 on Ir(110)

Ir(110) is an open surface, typical adsorption sites for NH_3 and the derivatives were considered, which consists of the top (T), short bridge (SB), long bridge (LB) and 4-fold hollow (H) sites, as were displayed in Fig. 1.

DFT calculations of adsorption energies and geometries were performed for NH_x ($x = 0 \sim 3$), H and N_2 on Ir(110) at 1/4 ML and the results are summarized in Tables 1 and 2. Two predominant adsorption configurations for NH_3 are identified, one is the NH_3 binding to the top site with the C_3-axis perpendicular to the surface, as was seen in the left panel of Fig. 2, the other is the NH_3 anchoring near to atop position (displaces 0.81 Å off the top site in a <100> azimuth), 68.6° tilting of the N—Ir bond relative to the surface, very much like that NH_3 on Cu(110) surface at coverage above ~0.20 ML [30,31], as was displayed in Fig. 2 (right panel). In the perpendicular configuration, the N—H bond length and the H—N—H angle are 1.02 Å and 108.8° respectively, very close to those of NH_3 in gas phase (1.02 Å and 107.3°). The N—Ir bond length is 2.19 Å. The adsorption energy of NH_3 is 1.05 eV. In the tilted configuration, the C_3-symmetry of NH_3 was broken, one of the N—H bonds (the N—H^1 bond, right panel in Fig. 2) elongated to 1.04 Å while the other two N—H bond lengths remained the same as in the gas phase. The H—N—H angles are increased by ~2° (relative to the angle in gas phase), which implies that the NH_3 structure was perturbed due to the adsorption, this also agrees with the changes of N—Ir bond length and adsorption energy, 0.03 Å shorter and 0.06 eV larger than those in the perpendicular configuration (left panel, Fig. 2), indicating that the tilted adsorption structure is more stable than the perpendicular one. Booth [30] and Mocuta [31] speculated that the off-top site adsorption was owing to the attraction between neighboring NH_3 molecules and the tilting configuration was caused by the dipole–dipole repulsion between the interacting molecules. In our case, the separation between NH_3 molecules is ~5.49 Å, molecular interactions should be very weak. The physical origin for the stability difference of the two configurations was mainly due to the interactions between NH_3 orbitals and surface electronic states. In the perpendicular case, NH_3 binds to the surface chiefly through the mixing of the $3a_1$ orbital with the $5d_z^2$ state of the metal atom. In the tilting configuration, NH_3 adsorbs on the surface not only through the mixing of $3a_1$–$5dz^2$ but also through the recombination of NH_3 1e orbital with metal $5d_{xz}$ state, these cooperative interactions fortified the NH_3 adsorption on one hand and on the other hand they shifted the d-band center from −2.27 eV (the clean surface) to −3.02 eV, which is 0.20 eV lower than that in the perpendicular case.

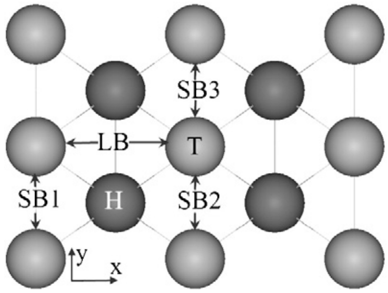

Fig. 1. Typical adsorption sites of NH_x ($x = 0 \sim 3$), N_2, H on Ir(110). Light and dark gray atoms represent the top and lower layers respectively. H, T, SB and LB indicate hollow, top, short bridge and long bridge sites respectively. Only the two upper layers of the Ir atoms are shown.

Table 1
Adsorption energies of NH_3 and the derivatives on Ir(110) at 1/4 ML (eV)*.

Species	Top	Short bridge	Long bridge	4-fould hollow
NH_3	1.11(0.92)	0.36	–	0.07
NH_2	2.82	3.55(3.21)	3.13	0.97
NH	3.53	4.72(4.47)	3.68	3.10
N	4.63	5.69(5.53)	4.49	4.29
H	2.71	2.83(2.54)	2.38	2.34
N_2	–	0.65	0.97(0.96)	–

*NH_x ($x = 1 - 3$) are binding with the N-end to the surface. The ZPE corrected energies for the adsorption on most stable sites are given in parenthesis. For NH_3 in perpendicular configuration, the adsorption energy is 1.05 eV and the ZPE corrected value is 0.85 eV.

NH_2, NH, N and H favor the short bridge site. In NH_2/Ir(110), the NH_2 bonded chemically to the surface with its C_2-axis perpendicular to the surface and N-end down, the adsorption energy is 3.55 eV, the N—Ir bond length is 2.10 Å. The N—H bond length is close to the values of the gas phase (1.02 Å), the H—N—H angle is increased from 103.2° (NH_2, in gas phase) to 110.5°. In NH/Ir(110), different from the case in NH/Ir(100) (NH favors the 4-fold hollow site) [18], the NH adsorbed at the SB site with N—H bond perpendicular to the surface, the adsorption energy is 4.72 eV, ~1 eV more stable than on the other sites. The N—Ir bond length is 1.96 Å and the N atom is 1.44 Å high above the surface. In N/Ir(110), the N atom prefers the SB site with an adsorption energy of 5.69 eV, the N—Ir bond length is 1.86 Å, and the distance from N to the surface is 1.21 Å. In H/Ir(110), the adsorption energy of H is 2.83 eV on the most stable adsorption site (the SB site); the energy difference among different sites is less than 0.5 eV,

Table 2
The predominant geometries of NH_X ($x = 0 \sim 3$), H and N_2 on Ir(110) surface.

Species	d_{Ir-N} (Å)	d_{A-B} (Å)	h_v (Å)	∠HNH (°)
NH_3(T)	2.16(2.19)	1.02/1.04(1.02)	2.04(2.19)	109.5/109.2(108.8)
NH_2(SB)	2.10	1.02	1.73	110.5
NH(SB)	1.96	1.02	1.44	–
N(SB)	1.86	–	1.21	–
H(SB)	1.80	–	1.11	–
N_2(LB)	2.02	1.17	1.60	–

d_{Ir-N}: the Ir-N bond length. d_{A-B}: the N—H bond length for NH_x ($x = 1 \sim 3$) and N—N bond length for N_2. h_v: the vertical height of the species, it is the N height above the surface for NH_x ($x = 1 \sim 3$). Values in parentheses are the parameters in perpendicular configuration.