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First-principles calculations of ammonia decomposition on Ni(110) surface

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ABSTRACT

First-principles calculations based on density functional theory (DFT) have been performed to study the adsorption and decomposition of NH_3 on Ni(110). The adsorption sites, the adsorption energies, the transition states and the activation energies of the stepwise dehydrogenation of NH_3 and the associative desorption of N are determined, and the zero point energy correction is included, which makes it possible to compute the rate constants of the elementary steps in NH_3 decomposition. Combined DFT calculations and kinetic analysis at 350 K indicate that the associative desorption of N has a reaction rate lower than NH_x dehydrogenation and is therefore the rate determining step. The distinctly different rate constants over Ni(110), Ni(111) and Ni(211) imply that ammonia decomposition over Ni-based catalyst is a structure-sensitive reaction.

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1. Introduction

During the past two decades, ammonia decomposition has attracted extensive interests from both academia and industry [1–7]. Previous studies on NH_3 decomposition over various supported metals (Ru, Ni, Fe, Pt, Pd, etc.) indicate that Ru is the most active for the reaction, but its expense and scarcity are prohibitive to large scale commercialization [8,9]. In terms of the cost and the activity for NH_3 decomposition, Ni is more attractive than other transition metals. The catalytic performance of Ni-based catalysts for NH_3 decomposition has been widely investigated. More recent studies have focused on the selection of supports and promoters to improve the catalytic activity and the high temperature stability of the Ni-based catalysts [4,5,8,10,11]. However, few theoretical studies have been carried out to determine the mechanism of NH_3 decomposition on Ni surfaces.

Recently, some researchers have used surface science techniques to identify the surface species of NH_3 decomposition on Ni surfaces [12–18]. For example, Gundry et al. reported that Ni films could decompose NH_3 into $NH_{2ad} + H_{ad}$ at 195 K and $NH_{2ad} + NH_{ad} + H_{ad}$ at 293 K and above, and the formation of atomic nitrogen on Ni films was not detected [12]. Seabury et al. showed that Ni(111) did not activate NH_3 at 200 K and dissociate NH_3, and only after electron beam exposure did it decompose NH_3 into $NH_{ad} + H_{ad}$ [13]. Grunze et al. confirmed that Ni(110) would decompose NH_3 into $NH_{ad} + H_{ad}$ at 150 K and $N_{ad} + H_{ad}$ at above 350 K [14]. These results indicate that Ni(110) has an ammonia decomposition activity higher than Ni (111). Despite the detailed experimental studies of the surface species of NH_3 decomposition on Ni surfaces, a generally accepted atomic level description of the adsorption of the key intermediates and the barriers and heats of the elementary reactions has not been provided.

In this work, we focus our attention on the mechanism of NH_3 decomposition on Ni(110) surface. We perform DFT calculations to systematically investigate the NH_3 decomposition on Ni(110) surface. The adsorption geometries, transition states geometries, adsorption energies and activation energies are identified. The decomposition of the activation energy is carried out to analyze the factors governing the reaction barrier. The zero point energy correction is included and the rate constants of the elementary steps involved in NH_3 decomposition are calculated. Moreover, kinetic analysis of NH_3 decomposition over Ni(110) is performed. By combining DFT calculations and kinetic analysis, the most abundant reaction intermediate and the reaction rates of the elementary steps involved in NH_3 decomposition are determined. Moreover, the structure sensitivity analysis of NH_3 decomposition on different Ni crystal surfaces is presented, and the possible reaction mechanism of ammonia decomposition on Ni nanoparticles is discussed. To the best of our knowledge, first-principles calculations of NH_3 decomposition on Ni(110) surface have not been reported previously in the literature.

2. Computational details

Ni(110) is an open surface, and a schematic representation of the adsorption sites is displayed in Fig. 1. In this work, all the DFT calculations were performed using the VASP code [19-21], in which the wave functions at each *k*-point are expanded in terms of a plane wave basis set with a cutoff kinetic energy of 400 eV. The interaction between valence electrons and ion cores was treated by the PAW

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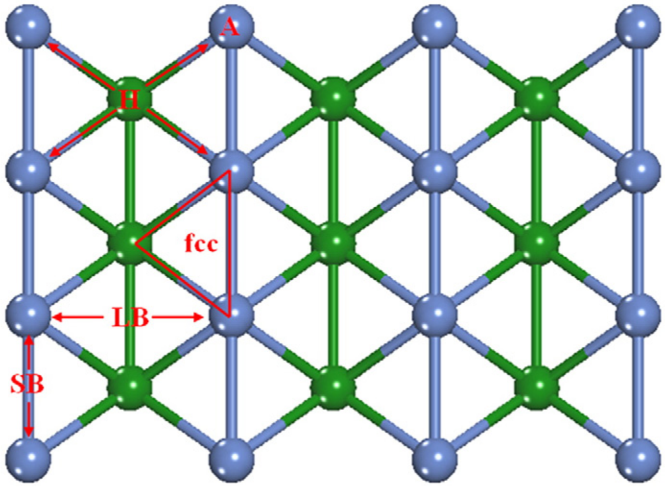

Fig. 1. Typical adsorption sites of NH_x (x = 0–3), N_2 and H on Ni(110). Only the two upper layers of the Ni atoms are shown. The blue and green balls correspond to the Ni atoms in the first and second layer, respectively. SB, LB, H and A indicate short bridge, long bridge, hollow and atop sites, respectively.

method [22,23]. Exchange and correlation of Kohn–Sham theory was treated with the GGA-PBE functional [24,25]. Step sites were modeled as a five-layer Ni(110) slab and a $p(3\times3)$ unit cell. The bottom two layers were fixed at their bulk-like positions and the top three layers as well as the adsorbates were allowed to relax during geometry optimization and transition state search. The optimized bulk lattice constant of Ni, 3.532 Å, agreed very well with the experimental value, 3.524 Å. To ensure numerical convergence, a $(3\times3\times1)$ Monkhorst–Pack *k*-point grid was used. A vacuum spacing of 12 Å was used to reduce the interactions between repeating slabs. As the magnetic element Ni was involved in the system, spin-polarized effect was considered.

Table 1
Adsorption energies of the NH_3 decomposition reaction intermediates on Ni(110) surface at 1/9 ML (eV)[a].

Species	Atop	Short bridge	Long bridge	4-fold hollow
NH_3	−0.90 (−0.80)	Atop	Atop	Atop
NH_2	Short bridge	−3.18 (−2.99)	−2.75	Long bridge
NH	Short bridge	−3.82	−4.11 (−3.93)	−3.95
N	Short bridge	−4.52	−5.46 (−5.37)	−5.07
H	−2.18	−2.63	−2.66	−2.70 (−2.53)[b]
N_2	−0.06	−0.51	−0.57	−0.57 (−0.53)

[a] The ZPE corrected energies are shown in parenthesis.
[b] H sits at the fcc site.

The Dimer method [26] was used to determine the transition states of the elementary steps of ammonia decomposition. In all the calculations, a force-based conjugated-gradient method was used to optimize the geometries [27]. The saddle points and minima were considered to be converged when the maximum force in every degree of freedom was less than 0.03 eV/Å. To verify the configurations of adsorption and transition states, vibrational frequency calculations were carried out by the numerical finite difference method. These calculations made it possible to include the zero point energies ($ZPE=\sum_i(1/2)h\nu_i$, where ν_i are the computed real frequencies of the system) of the adsorption energy and the activation energy. The adsorption energies of absorbates were calculated by $E_{ad}=E_{adsorbate+surface}-E_{adsorbate}-E_{surface}$.

3. Results and discussion

3.1. Adsorption of NH_x, H and N_2

DFT calculations of adsorption energies and geometries were performed for NH_x (x = 0–3), H and N_2 on Ni(110) at 1/9 ML, and the results are summarized in Table 1. Only geometrical parameters of the most stable adsorption configurations (as shown in Fig. 2) are listed in Table 2.

Clearly, NH_3 preferentially adsorbs at the atop site, with the N atom bonding to Ni and the H atoms pointing outward. Any attempt to find a minimum of energy in the other symmetric sites leads to the atop site after complete optimization, which is in agreement with previous theoretical studies of NH_3 adsorption on transition metals [6,7,28–31]. The adsorption energy of NH_3 is −0.90 eV and decreased to −0.80 eV if ZPE is included. In the preferred atop geometry, the N atom is 2.01 Å above the surface. The N–H bond length and the H–N–H cone angle are 1.03 Å and 107.9°, respectively, which are close to those of NH_3 in gas phase (the calculated values are 1.02 Å and 106.3°, while the experimental values are 1.02 Å and 106.7° [32]). This indicates that the structure of the NH_3 molecule is not significantly changed upon adsorption and the NH_3-substrate bond is the non-bonding lone pair of NH_3 [33].

For NH_2, the most stable site is the short bridge site. The adsorption energy of NH_2 is −3.18 eV, which decreases to −2.99 eV if ZPE is included. At the short bridge site, the N–Ni bond length is 1.92 Å and the perpendicular distance of N to the Ni surface is 1.46 Å. The N–H bond lengths decrease slightly from 1.04 Å of gas-phase NH_2 to

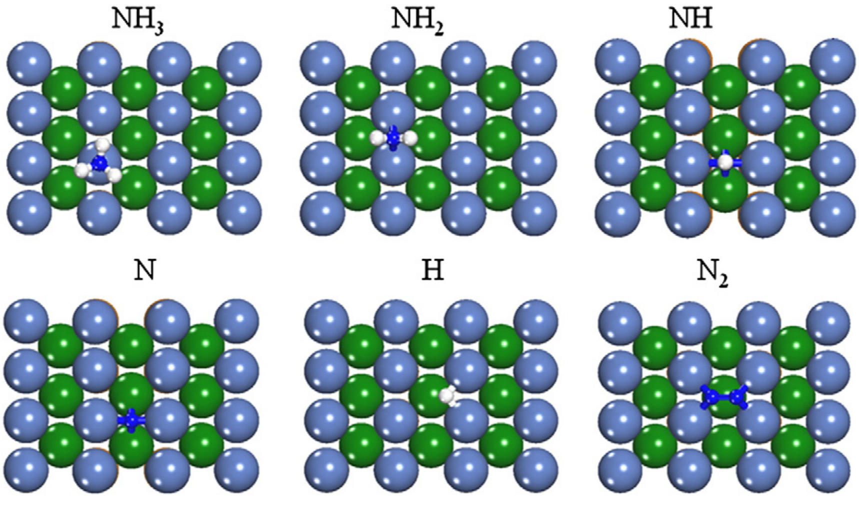

Fig. 2. Schematic representations of the most stable adsorption configurations of NH_x, H and N_2 on Ni(110) surface. The small blue balls and white balls correspond to nitrogen atoms and hydrogen atoms, respectively. The large blue balls and green balls correspond to the Ni atoms in the first layer and the second layer, respectively.

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