



# Adsorption and decomposition of NH<sub>3</sub> on Ir(111): A density functional theory study

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## ABSTRACT

The adsorption and decomposition of NH<sub>3</sub> on Ir(111) have been studied using the density functional theory calculations. The recombinative nitrogen desorption has also been investigated. The configurations and stability of NH<sub>x</sub> ( $x = 0-3$ ) species have been performed using frequency analysis. The corresponding reaction energies, the activation energies and the structure of the transition states have been determined and analyzed in detail. Including the zero point energy correction, the calculated activation barrier energy for NH<sub>x</sub> ( $x = 1-3$ ) dehydrogenation is between 0.94 eV and 1.05 eV, and that for the recombination desorption of N<sub>2</sub> is 1.55 eV, which indicates that the N<sub>2</sub> recombinative desorption is the rate-limiting step for the NH<sub>3</sub> decomposition on Ir(111). The NH<sub>3</sub> desorption energy (0.82 eV) is lower than the NH<sub>3</sub> dehydrogenation barrier, which indicates that the ammonia rather desorbs than dissociates from a thermodynamic point of view, consistent with the experimental results. But the competition between desorption and dissociation can be controlled in practice via the applied pressure and temperature.

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## 1. Introduction

As an environmentally benign replacement for gasoline, heating oil, natural gas and other fuels, hydrogen attracts worldwide attention [1]. Searching sources and carriers of clean hydrogen have received considerable attention in recent years. So far, a huge amount of research has been performed regarding storage of hydrogen in a convenient, efficient, and safe manner. Conventional hydrogen production technologies such as steam reforming, partial oxidation, and autothermal reforming of hydrocarbons lead to a large amount of CO and CO<sub>2</sub> as byproducts. Both compounds are known greenhouse gases, which would result in many disastrous environmental effects. The carbon-free nature of ammonia makes itself as a pollution-free onboard carrier of hydrogen which can be released by ammonia catalytic decomposition [2–4]. It has a high hydrogen content (17 wt.%), and so it constitutes a promising storage medium for hydrogen [5]. Moreover ammonia being one of the largest volume chemicals in the world has already been produced on a large scale and an infrastructure exists for its distribution [5]. Thus, ammonia catalytic decomposition on transition metal surfaces has been one of the most extensively studied issues in recent years due to its great industrial and economic importance.

Iridium shows a wide variety of potential applications as a heterogeneous catalyst in the chemical industry, much like other late transition metals [6]. Recently, the Ir-based catalysts are found to be efficient for

the CO<sub>x</sub>-free production of hydrogen from ammonia [2–4,7–9]. The study of ammonia decomposition on the metal wires indicated that the rate of decomposition on Ir is faster than on Pd, Pt, Rh, and Ni [9]. Ammonia adsorption and decomposition have been investigated on Ir(100), Ir(110), Ir(510) and Ir(111) single-crystal surfaces [2,3,10–17]. The decomposition shows only a moderate structural sensitivity. It has been found that ammonia dissociates on Ir(100) [3], Ir(110) [12,14,18], and Ir(510) [11] in the absence of oxygen. On Ir(100), ammonia was found that the desorption and dissociation are very competitive using the temperature programmed desorption (TPD) [3], while in the presence of coadsorbed oxygen, the catalytic activity for the decomposition of NH<sub>3</sub> was greatly increased [2]. Liu et al. have also investigated ammonia on O- and OH-predosed Ir(100) surface using DFT method, they proposed that the ammonia dehydrogenation is significantly more active than its desorption on O- and OH-predosed Ir(100) surface [15]. In fast X-ray photoelectron study of NH<sub>3</sub> on Ir(110), the steady state decomposition reaction of NH<sub>3</sub> starts at 500 K, and the dissociation products, NH and N adsorbates, were observed but not for NH<sub>2</sub> adsorbate [12]. On a flat Ir(111) surface, NH<sub>3</sub> was found to be adsorbed molecularly at a saturated surface coverage via the angle-resolved photoemission [13]. Weststrate et al. [17] also confirmed that ammonia does not decompose on Ir(111) at 100 K under low-pressure ( $\sim 10^{-7}$  mbar) with TPD. Recently, this team reported that NH<sub>3</sub> dissociation can be induced by radiation with 60 eV photoelectrons and the dissociation product NH was found to be the most stable species [16]. Krekelberg et al. [7] predicted that NH<sub>3</sub> dissociation process is thermodynamically favorable using density functional theory calculations. However, theoretical understanding of NH<sub>3</sub> decomposition on Ir(111) surface is not reported in literature,

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and this is not clear for the micro scenario of  $\text{NH}_3$  adsorption and decomposition on Ir(111).

Experimental studies concentrate on the analysis of the product composition in relation to reactant composition, surface condition and surface intermediates. Due to the complex nature of the reaction intermediates adsorbed on these surfaces, many aspects concerning the reaction processes in atomic level are unclear. Recently, we discussed some fundamental aspects of adsorption and decomposition of ammonia on Ir(100) [19] and Ir(110) [20], as well as adsorption sites for corresponding fragments and reaction barriers of ammonia on both surfaces. These results demonstrated that desorption and dissociation of  $\text{NH}_3$  on the two surfaces are very competitive. It should be mentioned that the close-packed (111) facet is generally the dominant face in real fcc metal catalyst particles [21]. In order to understand comprehensively the interaction between ammonia and Ir(111), the nature of ammonia stepwise decomposition, we performed DFT calculations to investigate  $\text{NH}_3$  decomposition on Ir(111). The adsorption geometries and energies, site preference, relative stability of ammonia and its dehydrogenated species, interactions between adsorbates, and the reaction barriers were systematically characterized. The paper is organized as follows. Section 2 gives the details of the computational method. The calculated results are presented and discussed in Section 3. Section 4 concludes with a short summary.

## 2. Computational details

The electronic structure calculations were performed using periodic density-functional theory with Vienna ab initio Simulation Package (VASP) code [22,23], with a plane wave basis set. The electron-ion interactions were described with projector augmented wave (PAW) method [24,25]. In order to be consistent with our previous studies [19,20], the generalized gradient approximation (GGA) of Perdew and Wang (PW91) [26] for the exchange-correlation energies was used in the current work. It was noted that the long-range dispersion interaction should be considered in the DFT calculation. But our test calculation with DFT-D3 [27] showed that the dispersion correction only increases the adsorption energy of  $\text{NH}_3$  about 0.26 eV. Thus it could be anticipated that the calculations without including the dispersion corrections in this studying should not introduce large errors in the structures or adsorption energies. This choice without including the dispersion corrections is based on a compromise between accuracy and practicability. The first-order Methfessel-Paxton method [28] is employed for the Fermi surface smearing with a width of 0.1 eV and the energy was corrected by extrapolation to zero temperature. With the considered pseudopotentials, a cutoff energy of 400 eV for the plane-wave basis ensures a good accuracy. Tests showed that the spin contribution to the total energy of the adsorbated systems is negligible and hence a non-spin approach was used except for the atoms and molecules in gas phase. The calculated lattice constant for bulk Ir is 3.88 Å, which is in reasonable agreement with the experimental value of 3.84 Å [29].

We considered the  $2 \times 2$  unit cell corresponding to a molecular coverage of 0.25 ML. The adsorption energy of  $\text{NH}_3$  increases by 0.1 eV for the  $3 \times 3$  unit cell, which indicated that there has the little repulsive effect between the adsorbates for the  $2 \times 2$  unit cell. In fact, the  $2 \times 2$  unit cell is well suited to represent to the coverage (~0.25 ML) employed in the experiments [16]. For the Brillouin zone integration a Monkhorst-Pack  $5 \times 5 \times 1$  k-point mesh was used for all structures. It was found that the increase in k-points from  $5 \times 5 \times 1$  to  $7 \times 7 \times 1$  results in the difference between the adsorption energies of  $\text{NH}_3$  by less than 0.01 eV. The Ir(111) metal surfaces were modeled by 5 metal layers with a vacuum width of about 13.4 Å in normal direction to the surface. The adsorption energy of  $\text{NH}_3$  on Ir(111) surface with 6 metal layers decreases by 0.08 eV with respect to that on the 5 metal layers. The target molecule and atomic species were adsorbed on one side of the slab only. The geometry optimization includes all degrees of freedom of the adsorbates

and the first topmost Ir layers, while the bottom four layers were constrained to their bulk geometry. The relaxation of the top two metal layers gives almost the same adsorption energies of  $\text{NH}_3$  with the top one relaxation. The structure optimization was stopped until the forces acting on each atom converged to better than 0.01 eV/Å. The test results considering the number of k-points, the size of the unit cell and the slabs are presented in Table 1.

The adsorption energy ( $E_{\text{ads}}$ ) is calculated as follows:

$$E_{\text{ads}} = (E_{\text{surface}} + E_{\text{gas-phase molecule}}) - E_{\text{adsorbate-surface}} \quad (1)$$

where  $E_{\text{adsorbate-surface}}$ ,  $E_{\text{surface}}$ , and  $E_{\text{gas-phase molecule}}$  are the total energy of adsorbed system, the clean surface, and gas-phase species, respectively. A positive value of  $E_{\text{ads}}$  indicates an exothermic adsorption process. The climbing image nudge elastic band (CI-NEB) method [30,31] was used to search the various transition states (TSs). We used 8 images for a CI-NEB calculation. Saddle points and minima were considered converged when the maximum force in every degree of freedom was less than 0.03 eV/Å. Vibrational frequency calculations have been performed for the initial and final states as well as the transition states through the finite-difference method in the harmonic approximation.

## 3. Results and discussion

### 3.1. $\text{NH}_x$ and H adsorption on Ir(111)

We considered high-symmetry adsorption sites on Ir(111), i.e. the top, bridge, fcc, and hcp sites, as depicted in Fig. 1. The adsorption energies of  $\text{NH}_x$  ( $x = 0-3$ ) and H on Ir(111) at 0.25 ML are summarized in Table 2, where only stable adsorption sites are shown. The structural parameters of  $\text{NH}_x$  ( $x = 0-3$ ) and H for the preference adsorption are presented in Table 3.

Adsorbed  $\text{NH}_3$  was found to be favored on the top site, bound via the N atom and with the H atoms in the direction of bridge sites, which is consistent with the earlier DFT calculations [7]. However angle-resolved photoemission study of ammonia adsorption on Ir(111) showed that the fcc site is favored at a saturated surface coverage. The difference in coverages between that study and ours (0.25 ML) could be a reason for the different position preferences. The adsorption energy for  $\text{NH}_3$  on Ir(111) is 0.96 eV and is decreased to 0.82 eV if the ZPE is included, which is in line with the earlier DFT results of 0.84 eV on Ir(111) [7]. On Ir(111), the adsorption energies are also insensitive to rotation around the local molecular 3-fold axis. The barrier of rotation is very small (less than 1 meV). At the top site, the N-Ir bond length is 2.15 Å. The N-H bond lengths (1.02 Å) and the H-N-H cone angles ( $110^\circ$ ) do not significantly alter with respect to those in the gas phase (1.01 Å and  $107^\circ$ ) [32]. It is similar to the  $\text{NH}_3$  adsorption on Pt [33], Ir [19,20] and Rh [34] that the structure of the  $\text{NH}_3$  molecule is not significantly changed upon adsorption. This is due to the nonbonding lone pair of  $\text{NH}_3$  involved in the  $\text{NH}_3$ -substrate bond [34]. Compared to the adsorption

**Table 1**

The test results for the number of k-points and the size of the supercell.

Unit cell	Layers	k-Points	$E_{\text{NH}_3}$ (eV)
p( $2 \times 2$ )	5	$3 \times 3 \times 1$	0.92 <sup>a</sup>
		$5 \times 5 \times 1$	0.96 <sup>a</sup>
		$5 \times 5 \times 1$	0.96 <sup>b</sup>
		$7 \times 7 \times 1$	0.95 <sup>a</sup>
p( $3 \times 3$ )	6	$5 \times 5 \times 1$	0.88 <sup>a</sup>
		$3 \times 3 \times 1$	1.06 <sup>a</sup>

<sup>a</sup> The adsorption energies were calculated with the top one metal layer relaxed.

<sup>b</sup> The adsorption energies were calculated with the top two metal layer relaxed.

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