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Adsorption and dissociation of ammonia on small iron clusters

Xilin Zhang ^a, Zhansheng Lu ^{a,*}, Dongwei Ma ^b, Zongxian Yang ^{a,*}^a College of Physics and Electronic Engineering, Henan Normal University, Xinxiang 453007, China^b School of Physics, Anyang Normal University, Anyang 455000, China

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ABSTRACT

The stepwise dehydrogenation of NH_x on small iron clusters is investigated from the density functional theory (DFT) calculations. The results indicate that the fewer the H atoms of the NH_x ($x = 0-3$) species, the higher the adsorption energies of NH_x on the same Fe cluster are. Also the larger the cluster size, the stronger the adsorption for the same NH_x species is. The catalytic activity of small Fe clusters for NH_3 dehydrogenation is comparatively studied, and the rate-limiting steps for the reactions are addressed. It is found that the rate-limiting steps for the dehydrogenation of NH_x on the Fe and Fe_3 are that for the NH decomposition, and those on the Fe_2 and Fe_4 are that for the NH_2 dissociation. The barriers for the rate-limiting steps are 1.06, 1.49, 1.43 and 1.51 eV for the dehydrogenation of NH_x on the Fe, Fe_2 , Fe_3 and Fe_4 clusters, respectively. The results suggest that the small Fe clusters can be regarded as the potential candidates for NH_3 dehydrogenation reactions and can serve as a reference for further investigations on the catalytic activity of small Fe clusters supported by various catalytic materials.

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Introduction

Ammonia (NH_3) is considered to be an important industrial chemical owing to its wide potential applications, which is known as a nitrogen feedstock for agriculture [1] and a refrigerant [2,3]. More importantly, it has also been used as a source and storage substance for hydrogen fuel cells [4–7]. Hydrogen generated from single step decomposition of ammonia represents an attractive alternative to hydrocarbons for hydrogen fuel cells [6,8,9] and also is a straightforward process with CO-free product gases N_2 and H_2 . At the same time, NH_3 is an undesirable byproduct of industrial catalytic reactions [10], which can cause pollution of lakes and

seas, and its emissions into the environment need to be avoided. Because of these and other technological, economical, and environmental factors, numerous researches on the decomposition and oxidation reactions of ammonia have been performed [4–6].

It is often reported that the iron nanoparticles play a key role in hydrolytic dehydrogenation of ammonia for chemical hydrogen storage [11–13]. For example, Yan and co-worker [11] have recently developed a simple but efficient method for preparing amorphous Fe nanoparticles with high catalytic activity for the generation of H_2 from ammonia-like molecule. Ammonia decomposition on iron particles of various grain sizes with an ammonia stream has been observed by Nishimaki and co-workers [12]. Lanzani and

* Corresponding authors.

E-mail addresses: zslu@henannu.edu.cn (Z. Lu), yzx@henannu.edu.cn (Z. Yang).

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Laasonen [14] studied the bonding and dissociation of NH_3 and its fragment on a nanosized icosahedral Fe_{55} cluster using spin-polarized density functional theory (DFT) calculations. Their results suggest that the catalytic activity of iron surfaces towards ammonia-like molecules is enhanced when the metal is in the nanostructured phase. Some researches also showed that the catalytic properties of small iron clusters show large deviation with cluster size. It is testified by the results of Sun et al. [15,16], who observed that the iron dimer has a stronger catalytic effect on the activation of methane, a species of ammonia-like molecule, than the iron atom by DFT calculations. They also studied the activation reactions of methane on Fe_4 cluster with different spin states. However, whether or not the iron clusters with different size have similar phenomenon on the activation of NH_3 is undefined owing to the lack of researches on the catalytic effect of smaller iron clusters, such as iron atom, iron dimer, Fe_4 and so on. Motivated by this, we employ the first-principles DFT calculation to investigate the NH_3 adsorption and dissociation on smaller Fe clusters (from Fe_1 to Fe_4) and catalytic activity dependence on the cluster size. The simulation results indicate that the iron atom has the highest catalytic effect on the NH_3 dehydrogenation, which is followed by Fe_3 . The Fe_4 and iron dimer have the relative lower activation, while also comparable with the Fe_{55} . We also find that the catalytic effect of Fe clusters is stronger than some noble and transition metals surfaces, such as Au(111) [17], Pt(111) [18] and Fe(111) [19,20], indicating that the smaller iron clusters can also be regarded as excellent candidates for NH_3 dehydrogenation reactions.

Through the comparison of the activated dehydrogenation of NH_3 by iron clusters of different sizes, even atomic scale, and iron bulk, the study will provide useful information to tune the relative reaction rates of the different steps during the activation of NH_3 by controlling the cluster size, which is very important for understanding the NH_3 dehydrogenation process from both environmental protection and the continuous supply of clean hydrogen gas for fuel cells.

Computational details

The periodic DFT calculations are performed using the Vienna Ab-initio Simulation Package (VASP) [21,22]. For improving the calculation efficiency, core electrons are replaced by the projector augmented wave (PAW) pseudo-potentials [23] and the generalized gradient approximation of the Perdew, Burke, and Ernzerhof (PBE) functional [24] is used for the exchange and correlation. The Kohn–Sham orbitals are expanded using plane-waves with the well converged cutoff energy of 450 eV and the convergence criterion for the electronic self-consistent iteration is set to 10^{-5} eV. The iron clusters and the adsorbates are free to relax until the self-consistent forces drop below $0.02 \text{ eV} \text{ \AA}^{-1}$. Spin polarization is taken into account in the calculations and the Gaussian smearing method is employed to determine electron occupancies with a smearing parameter of 0.2 eV. With the purpose of avoiding the interactions due to the artificial periodicity, a vacuum layer of 15 \AA is used to separate the periodic images in the direction

perpendicular to the surface. The Brillouin zone integration is performed with a $1 \times 1 \times 1$ Γ -centered Monkhorst–Pack (MP) grid. The different K-points, including $3 \times 3 \times 1$ and $5 \times 5 \times 1$, are tested for comparison and only tiny changes in energy are found.

The most stable geometric structures of iron clusters are obtained firstly based on the above calculation parameter settings. The optimized Fe_2 dimer has a bond length of 2.02 \AA . The result is well comparable with previous theoretical [25] and experimental works [26]. The equilateral triangle is the most stable configuration for Fe_3 cluster, which is in agreement with the previous DFT calculation [27,28]. However, the bond length (2.24 \AA) is slightly longer than the result of Alemany et al. (2.14 \AA) [29]. The linear structure for the Fe_3 cluster is found to be less stable (higher in energy by about 2.00 eV) than the equilateral triangle configuration. For Fe_4 , the tetrahedral structure is lower in energy than the rhombic structure by 0.16 eV , which agrees with the result of Chen et al. [27]. The bond lengths (2.31 \AA) of the present calculation are longer than those obtained by Yin et al. [30]. Although all the possible geometric configurations of iron clusters are discussed here, we will mainly present the results based on the most stable geometric structures of iron clusters in the following. The geometric configurations of NH_x in gas phase are also obtained. Take the NH_3 as an example, we find that the N–H bonds are 1.02 \AA , which is in good agreement with the previous results [31]. Our calculated H–N–H cone angle (106.33°) is the same as the calculated value of Xie et al. [31].

The climbing image nudged elastic band method (CI-NEB) [32,33], a method for finding saddle points and minimum energy paths between known reactants and products, is employed to investigate the saddle points and minimum energy paths for NH_x dissociation on the iron clusters. In this work, the spring force between adjacent images is set to $5.0 \text{ eV} \text{ \AA}^{-1}$. Images are optimized until the forces on each atom drop below $0.02 \text{ eV} \text{ \AA}^{-1}$. The energy barriers are calculated using the initial state as a reference.

Vibrational frequency analysis is carried out for all the optimized geometries and the transition states. It is found that the reactant complexes have all real frequencies, while each transition state has a single imaginary frequency. The detailed results can be found in the [Supporting information](#).

The adsorption and coadsorption energies are defined by the formulas (1) and (2), respectively.

$$E_{\text{ads}} = E_{\text{Cluster}} + E_{\text{NH}_x} - E_{(\text{NH}_x/\text{Cluster})} \quad (1)$$

$$E_{\text{coads}} = E_{\text{Cluster}} + E_{\text{H}} + E_{\text{NH}_x} - E_{(\text{NH}_x+\text{H})/\text{Cluster}} \quad (2)$$

The $E_{(\text{NH}_x/\text{Cluster})}$ and $E_{(\text{NH}_x+\text{H})/\text{Cluster}}$ are the spin-polarized total energies for the optimized equilibrium configurations of iron cluster with a single molecule (NH_x) and two coadsorbed molecules (NH_x and H), respectively. E_{Cluster} is the spin-polarized total energy for the optimized bare iron cluster, and E_{NH_x} and E_{H} are the spin-polarized total energies of the corresponding isolated gas molecules in the ground state. The x represents 0–3 in (1) and 0–2 in (2), respectively. Bader charge analysis method [34] is used to evaluate the atomic charges, which are further used to calculate the number of electrons transferred in the adsorption process.

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