

Mechanism study of NH_3 adsorption and dissociation on a nano-sized iron cluster

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1 Introduction

Hydrogen is high in energy, yet an engine that burns pure hydrogen produces almost no pollution. A fuel cell combines hydrogen and oxygen to produce electricity, heat, and water is basically a pollution free process. Fuel cells are often compared to batteries. Both convert the energy produced by a chemical reaction into usable electric power. However, the fuel cell will produce electricity as long as fuel (hydrogen) is supplied. Fuel cells are a promising technology for use as a source of heat and electricity for buildings, and electric motors propelling vehicles. The smooth operation of fuel cells depends on continuous supply of clean hydrogen gas free from contaminant such as carbon monoxide or sulphur complexes to avoid poisoning of the anode catalyst. Due to these constraints, the fuel cell processes using carbonaceous fuels requires secondary units such as desulphurisation and reduction of CO.

Hydrogen generated from single step decomposition of ammonia represent an attractive alternative to hydrocarbons for fuel cells [1]. Ammonia has high hydrogen content (17% by weight) and more importantly, it provides a promising mode of storage of hydrogen for its on-site generation [2]. Hydrogen generated from ammonia decomposition is a straightforward process with CO-free product gases N_2 and H_2 . Decomposition of ammonia is an endothermic reaction $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$. Many metals, alloys, and compounds of noble metal have been tested for ammonia decomposition. Group VIII metals (Ni, Ru, Ir, Fe, Co and Rh) or metal carbides/nitrides (MoN_x , VC_x , MoC_x , VN_x , etc.) have been proved to catalyse the NH_3 decomposition [3]. Especially, Ru clusters on different supports such as alumina, silica, magnesia, Mg–Al spinel, active carbon and carbon nanotube (CNT), are proved to be the most active. Nevertheless, the restricted availability and high prices of Ru limit its usage. Recently, researchers have made great efforts to seek some inexpensive alternatives to Ru [4,5].

Beside the material, also the shape of the catalyst is very important [6]. Often the physical and chemical properties of nanoclusters differ significantly from the bulk properties, especially the catalytic properties are often unique. For these reasons, metal nanoparticles are widely used in several real-world catalytic applications, including nanoparticle-catalysed hydrolytic dehydrogenation of ammonia and its borane compounds for chemical hydrogen storage [7]. Recent studies have proved that iron nanoparticle play a key role in this scenario [7-10].

2 Objectives of the research

Though the commercial ammonia synthesis has reached its level of saturation for any radical development, the reverse reaction of ammonia decomposition has been an interest of research only during the last couple of decades. In order to understand the role of the cluster in this reaction, we have used first principle calculations to study the steps of this reaction on a small nanocluster (GPAW[11]). To our knowledge,

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there are only few ab-initio studies of nanosized clusters but these works do not address any chemical reactions. The nanoparticles have features that cannot be studied on the stepped surfaces, and this work will complement the existing studies of active sites.

3 Results

First principle DFT [11] calculations has been used to study NH_3 , NH_2 , NH , atomic H and N adsorption on icosahedral Fe_{55} . The geometry optimization has been started from the high symmetry adsorption sites of one the 20 triangular face of the cluster. To describe quantitatively the energetic of the adsorbed species on the surface, we introduce the binding energy term (B.E.), defined as $\text{B.E.} = E_{\text{Mol/CO}} - (E_{\text{Mol}} + E_{\text{CO}})$, where $E_{\text{Mol/CO}}$ is the total energy of the adsorbate-substrate system, E_{Mol} is that of Fe_{55} cluster, and E_{Mol} is that of the free adsorbate. B.E. describes the strength of the adsorbate-substrate interaction.

The stability of NH_3 on the cluster was considered. The molecule was located on the vertices, on the edge and on the centre of the icosahedral face of the cluster. For every adsorption site, the possible effect of the orientation was considered though optimization started from molecule placed in different orientation on the adsorption sites but only the interaction N-Fe is favourable, and only the top sites are the stable sites ($-0.73 \text{ eV} < \text{B.E.}(\text{NH}_3) < -0.60 \text{ eV}$).

Considering NH_2 , during the relaxations the molecule spontaneously moves, migrating on the bridge sites on the facet of the surface ($-3.10 \text{ eV} < \text{B.E.}(\text{NH}_2) < -2.52 \text{ eV}$). The arrangement presenting the nitrogen tetrahedral coordinate at two hydrogens and two iron atoms is clearly preferred. Similar behaviour has been observed considering the interaction of NH with the high symmetry adsorption site of the icosahedral Fe_{55} ($-4.64 \text{ eV} < \text{B.E.}(\text{NH}_2) < -3.18 \text{ eV}$). During the geometry optimization the fragment rearrange moving on the hollow site, where N can easily interact with three metal atoms.

A possible dissociation path for NH_3 has been studied as well with the Nudge Elastic Band method (NEB [12]). The obtained reaction energy is $-0.32 \text{ eV/molecule}$ with an overall barrier of of 1.00 eV (Figure 1). The complete dissociation reaction, to atomic nitrogen and hydrogen involve three steps: (I) $\text{NH}_3 \rightarrow \text{NH}_2 + \text{H}$; (II) $\text{NH}_2 + \text{H} \rightarrow \text{NH} + 2\text{H}$; (III) $\text{NH} + 2\text{H} \rightarrow \text{N} + 3\text{H}$. The reaction barrier for the overall process is 1.00 eV . The rate limiting step is the last hydrogen dissociation.

4 Relevance of the research

We have presented an ab initio study of NH_3 adsorption and dissociation on a small iron nanoparticle. Overall, we noticed that the natural ability of solid iron surfaces to make and break bonds to the ammonia-like molecules is enhanced if the metal is in the nano structured phase. For NH_3 , only the interaction N-Fe is favourable, and only the top sites are the stable sites ($-0.73 \text{ eV} < \text{B.E.}(\text{NH}_3) < -0.60 \text{ eV}$). Fe_3N conformations are the only stable for the atomic adsorption of nitrogen. These results are in agreement with the previous obtained calculations of H on flat Fe surfaces [9].

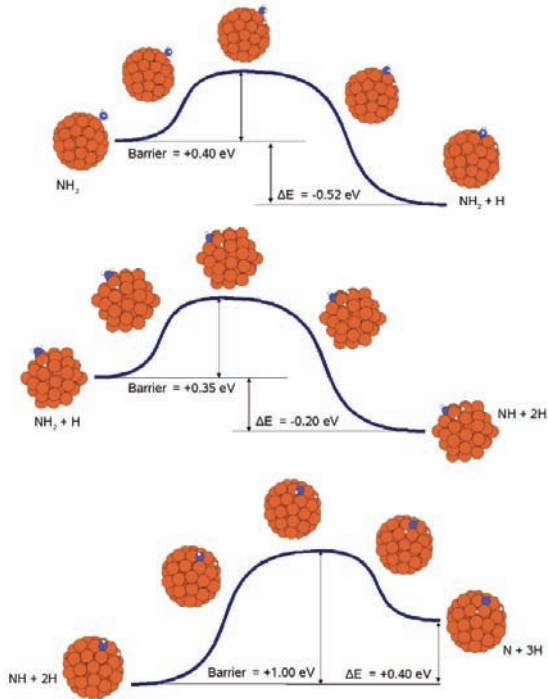


Figure 1 The proposed scheme for the NH_3 decomposition to atomic N and H on Fe_{55} .

A dissociation path for NH_3 were identified. The complete dissociation reaction, to atomic nitrogen and hydrogen involve three steps: (I) $\text{NH}_3 \rightarrow \text{NH}_2 + \text{H}$; (II) $\text{NH}_2 + \text{H} \rightarrow \text{NH} + 2\text{H}$; (III) $\text{NH} + 2\text{H} \rightarrow \text{N} + 3\text{H}$. The reaction barrier for the overall process is 1.00 eV. The rate limiting step is the last hydrogen dissociation. This is natural since the NH fragment is very strongly bonded to the surface and the metal-N interaction force the NH bond to be perpendicular at the surface, orientation unfavourable to the dissociation process. It is important to note that in order to achieve a similar value with catalyst not in nanoparticle phase, it is necessary to more expensive metal, as Ru.

References

- [1] A. Züttel, Hydrogen storage and distribution systems, **Mitig-Adapt-Strat-Glob-Change** 12 (2007): pp. 343–365.
- [2] M. Diwan, D. Hanna and A. Varma, Method to release hydrogen from ammonia borane for portable fuel cell applications, **International Journal of Hydrogen Energy** Volume 35 (2), (2010): pp. 577-584.
- [3] S.F. Yin, B.Q. Xu, X.P. Zhou and C.T. Au, A mini-review on ammonia decomposition catalysts for on-site

- generation of hydrogen for fuel cell applications, **Appl. Catal. A: Gen.** 277 (2004): pp. 1-9.
- [4] C.S. Lu, X.N. Li, Y.F. Zhu, H.Z. Liu and C.H. Zhou, Ammonia decomposition over bimetallic nitrides supported on γ - Al_2O_3 , **Chin. Chem. Lett.** 15 (1), (2004): pp. 105-108.
- [5] J. Zhang, H.Y. Xu, X.L. Jin, Q.J. Ge and W.Z. Li, Characterizations and activities of the nano-sized Ni/ Al_2O_3 and Ni/La- Al_2O_3 catalysts for NH_3 decomposition, **Appl. Catal. A: Gen.** 290 (2005): pp. 87-96.
- [6] B.C. Gates, Supported metal clusters: synthesis, structure and catalysis, **Chem. Rev.** 95 (1995): pp. 511-522.
- [7] J.M. Yan, X.B. Zhang, S. Han, H. Shioyama and Q. Xu, Iron-nanoparticle catalyzed hydrolytic dehydrogenation of ammonia borane for chemical hydrogen storage, **Angewandte Chemie International Edition** 47 (12), (2008): pp. 2287-2289.
- [8] R.Y. Chein, Y.C. Chen, C.S. Chang and J.N. Chung, Numerical modeling of hydrogen production from ammonia decomposition for fuel cell applications, **International Journal of Hydrogen Energy** Volume 35 (2), (2010): pp. 589-597.
- [9] K. Nishimaki, S. Ohmae, T.A. Yamamoto and M. Katsura, Formation of iron-nitrides by the reaction of iron nanoparticles with a stream of ammonia, **Nanostructured Materials** 12 (1-4), (1999): pp. 527-530.
- [10] A. Jedynak, Z. Kowalczyk, D. Szmigiel, W. Raróg and J. Zielinski, Ammonia decomposition over the carbon-based iron catalyst promoted with potassium, **Applied Catalysis A: General** 237 (1-2), (2002): pp. 223-226.
- [11] J. J. Mortensen, L. B. Hansen and K. W. Jacobsen Physical, Real-space grid implementation of the projector augmented wave method, **Review B**, Vol. 71 (2005): pp. 035109/1-035109/11.
- [12] G. Henkelman, B.P. Uberuaga, and H. Jonsson, A climbing image nudged elastic band method for finding saddle points and minimum energy paths, **J. Chem. Phys.** 113 (2000): pp. 9901/1-9901/4.

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