

Theoretical study of ammonia oxidation on platinum clusters – Adsorption of intermediate nitrogen dimer molecules

Damilola A. Daramola, Gerardine G. Botte *

Center for Electrochemical Engineering Research, Department of Chemical and Biomolecular Engineering, Stocker Center 165, Ohio University, Athens, OH 45701, United States

ARTICLE INFO

Article history:

Received 15 January 2013

Accepted 22 March 2013

Available online 11 April 2013

Keywords:

Density Functional Theory methods

Ammonia oxidation

Ammonia electrolysis

Hydrazine adsorption

Hydrazyl adsorption

Diazene adsorption

Platinum catalyst

Hydrogen production

ABSTRACT

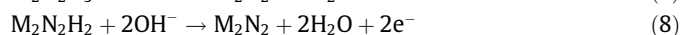
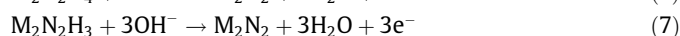
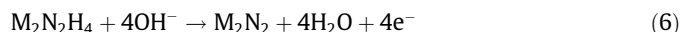
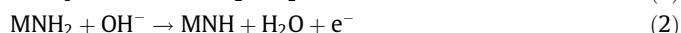
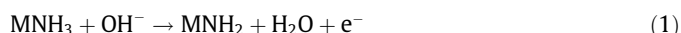
Density Functional Theory calculations with the hybrid B3LYP functional and the LANL2DZ and 6-311++g** basis sets were used to calculate the adsorption energies, geometries and vibration modes of N_2H_z ($z = 0-4$) molecules on a cluster of 20 platinum atoms. Based on calculated binding energies, the *trans* conformations of N_2H_4 and N_2H_2 were predicted to adsorb with one nitrogen in contact with the cluster; N_2H_3 and N_2H radicals adsorb with both nitrogen atoms in contact with the catalyst; while N_2 was not found to adsorb to any appreciable degree. Calculated frequencies showed N–N bond stretching frequency occurs at 913 cm^{-1} and 953 cm^{-1} for N_2H_4 and N_2H_3 , respectively and is blueshifted to 1603 cm^{-1} and 1631 cm^{-1} for N_2H and N_2H_2 , respectively. This trend suggests that the formation of this bond could indicate the presence of these species during ammonia oxidation as a shift from 900 to 1600 cm^{-1} is expected when the single bond becomes a double bond. Finally, this study combined with earlier studies predicts the following trend for the adsorption energies of species formed: $N_2 < H_2O < NH_3 < N_2H_2 < N_2H_4 < N_2H < N_2H_3 < OH < NH_2 < NH < N$.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

Electrolysis of ammonia, in the presence of platinum, has been considered as a plausible source of hydrogen for use in fuel cells [1–8], as well as a process for the deammonification of wastewater [9,10]. In the process, ammonia is electrochemically oxidized to nitrogen while water is reduced to hydrogen. It has been observed that during the ammonia oxidation, the platinum anode undergoes deactivation over time. As such, it is necessary to investigate the reaction mechanism so as to understand and enhance this technology for hydrogen production.

While two mechanisms have been proposed for the oxidation of ammonia to nitrogen in basic conditions [11,12], the more extensive mechanism suggests the recombination of oxidized ammonia fragments (NH_2 and NH) prior to complete removal of hydrogens [12] (where M is platinum):



A prior investigation was performed on adsorbed NH_x ($x = 0-3$) and OH_y ($y = 1$ and 2) molecules [5] on platinum clusters and it was concluded that while the adsorption of NH_3 and H_2O were relatively facile at adsorption energies of -119 and -66 kJ/mol , respectively, the adsorption of NH_2 , NH , OH and N yielded adsorption energies of -215 , -360 , -203 and -414 kJ/mol , respectively (these adsorption energies used the frozen cluster as the reference). This suggested that these latter molecules could cause the surface blockage and subsequent deactivation of the platinum catalyst. In addition, using different platinum clusters of 10, 15, 20 and 25 atoms, it was found that the cluster of 20 platinum atoms provided the best comparison to experimental values. This was based on the calculated spin densities of the platinum atoms and bond lengths of the adsorbed molecules [5]. However, the adsorption of nitrogen dimers formed according to the preceding equations i.e. N_2H_z ($z = 0-4$) have not been fully characterized on the platinum surface in any prior studies.

While the hydrazyl radical (N_2H_3) has not been isolated [13], hydrazine (N_2H_4) and diazene (N_2H_2) are found to occur naturally. Prior experimental studies on free hydrazine reported that the molecule exists in the *gauche* conformation [14,15], while diazene would mostly exist in the *trans* conformation although evidence for

* Corresponding author. Fax: +1 740 593 0873.

E-mail address: botte@ohio.edu (G.G. Botte).

the *iso* and *cis* conformations also exist [16]. Furthermore, experimental characterization of hydrazine adsorbed on other single crystal surfaces [17–21] expected both nitrogen atoms to be in contact with the surface i.e. side-on adsorption with N–N bond parallel to the surface as opposed to end-on adsorption with one nitrogen in contact with the surface and the N–N bond at an angle to the surface normal. However, a more recent computational study predicted that the side-on adsorption was preferred for adsorbed hydrazine on Pt(111) [22]. This surface is one of the types of platinum surfaces possible and it is the three-dimensional expansion along the (111) crystal plane in a unit cell of bulk platinum.

Recently, multiple Density Functional Theory (DFT) studies of hydrazine adsorption on metallic surfaces have yielded varying favored conformations for adsorbed N₂H₄. A study performed on Ni(100) by Agusta et al. [23] suggested that the end-on adsorption with a *trans* conformation was the most favored configuration with a adsorption energy of –80 kJ/mol, although the adsorption energy for the end-on *gauche* conformation was only higher by 2 kJ/mol. This Ni(100) study essentially suggests that within the end-on configuration, there is also a plausible rearrangement in the molecular geometry. Another study performed on copper surfaces [24] by Daff et al. calculated the most favorable configurations on Cu(111), Cu(110) and Cu(100) to be the end-on *gauche* (adsorption energy = –41 kJ/mol), side-on *gauche* (adsorption energy = –79 kJ/mol) and end-on *gauche* (adsorption energy = –55 kJ/mol) conformations, respectively. Finally, an investigation of adsorbed hydrazine and other N₂H₂ molecules in the Gerischer and Mauerer mechanism was performed by Zhang et al. on Ir(111) [25] predicting side-on adsorption for N₂H₄, N₂H₃, N₂H₂, N₂H while N₂ exhibited an end-on adsorption with the N–N axis perpendicular to the Ir surface.

These prior experimental and theoretical studies indicate the complexity in investigating the adsorption of N₂H₄ on metallic surfaces as the crystal surface, adsorbate position and molecular conformation play relevant roles in the analyses. Considering these molecules are also relevant in understanding the overall kinetics of ammonia oxidation in the presence of hydroxides, the investigation of the adsorption of these molecules is relevant and paramount.

Within this context, this paper seeks to investigate the adsorption of N₂H₄, N₂H₃, N₂H₂, N₂H and N₂ on Pt(111) based on adsorption energies, dihedral angle rotations and vibration analysis to highlight the expected configurations of these transient intermediates on the catalytic surface upon formation. This current study has only be preceded by a theoretical analysis of only hydrazine adsorption on Pt(111) [22] and as such the analyses presented in this paper expands the literature by studying all the molecules which could lead to nitrogen formation. The findings within this study predict a trend for the adsorption of the precursors for nitrogen formation from ammonia oxidation on platinum and therefore show the possible intermediates and reactants that could be responsible for the deactivation of platinum during ammonia electrolysis. These findings also examines prior experimental observations for hydrazine on Pt(111), Ni(111), Ru(0001), Si(111) and Si(100) and comments on the prior interpretation of the N(1s) XPS showing a disagreement based on vibrational analyses and comparison with hydrazine ligands on the same metals. Finally, the chosen surface [Pt(111)] is the most prominent crystal plane for a typical poly-crystalline platinum electrode and is expected to be mostly responsible for the experimental observations during ammonia oxidation.

2. Computational details

Prior characterization of NH_x and OH_y molecules on various cluster sizes representative of Pt(111) showed that Pt₂₀ yielded the best agreement with experimental measurements and this

was the cluster size used for all the N₂H₂ molecules [5]. In order to characterize the adsorption of N₂H₂ molecules, both the conformation of the molecule as well as the binding position were analyzed. Initial characterization of the potential energy surfaces of the free molecules was performed through angular rotations to predict the most favorable conformation of the individual molecules. Subsequently, the N₂H₂ molecules were placed with one nitrogen atom in one of the symmetrical positions of Pt(111) i.e. top, bridge, face-centered cubic hollow or hexagonal close-packed hollow, while the other nitrogen atom was placed in an adjacent symmetrical position on the platinum cluster (Fig. 1).

The methodology used in this study is the same used in describing the adsorption of the NH_x and OH_y molecules previously studied. As a summary, calculations were performed using DFT as applied in Gaussian 09 [26] and based on the hybrid B3LYP functional [27,28]. The Pople all electron basis set (6-311++g**) [29–32] was used for nitrogen and hydrogen atoms, while a pseudopotential-based basis set (LANL2DZ) [33–35] was used for platinum. The large 6-311++g** basis set was used in this study due to its similar performance in comparison with Dunning-type basis sets [36]. The interstitial electron model [37] was used in describing the electronic properties of the platinum cluster with prior analyses showing that the ground state had a multiplicity [5] of S = 14. All calculations (geometry optimization and frequency calculations) were performed at the default levels [38] found in Gaussian 09 and the vibration modes were visualized using GaussView 5 [39]. Based on a comparison of the effect of basis set and functional on molecular properties, the errors in bond lengths, bond angles, frequencies and conformational energies are approximately .01 Å, 1°, 80 cm⁻¹ and 15% respectively for a large Pople basis set and the hybrid B3LYP functional [36].

Finally, in the comparison of this work with experimental observation (where possible) and prior calculations, four atoms within the platinum cluster were allowed to relax (Fig. 1). Calculations performed with this configuration of the platinum cluster were thus referred to as the relaxed cluster and prior work in this group [5] has shown that this relaxation provides closer values to experimental observation. Based on both frozen and relaxed configurations, adsorption energies were calculated as follows:

$$\text{Adsorption energy (Frozen)} = E_{\text{frozen cluster+molecule}} - E_{\text{frozen cluster}} - E_{\text{molecule}} \quad (10)$$

$$\text{Adsorption energy (Relaxed)} = E_{\text{relaxed cluster+molecule}} - E_{\text{relaxed cluster}} - E_{\text{molecule}} \quad (11)$$

3. Results and discussion

3.1. Geometry of free molecules

The lowest energy configurations for N₂H₄, N₂H₃, N₂H₂ and N₂H were calculated (Fig. 2) with comparison to experimental bond angles and lengths where available (Table 1).

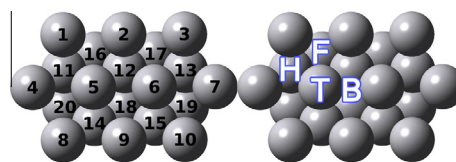


Fig. 1. The Pt(111) surface represented with a cluster of 20 platinum atoms. Numbers on the left image illustrate the labels used in differentiating the atoms when surface relaxation was induced on the cluster and when adsorbed molecules were present. The labels on the right image are the position of high symmetry on the platinum cluster surface: T, B, F and H represent top, bridge, face-centered cubic and hexagonal close-packed positions respectively.

Download English Version:

<https://daneshyari.com/en/article/6999664>

Download Persian Version:

<https://daneshyari.com/article/6999664>

[Daneshyari.com](https://daneshyari.com)