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Theoretical Investigation of the Electro-oxidation of Ammonia

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Introduction

In a lot of ways, ammonia is an ideal fuel for fuel cells and certainly shows some advantages as a precursor for hydrogen production. Ammonia represents a convenient way of securing supplies of hydrogen with one cylinder of ammonia yielding the equivalent to nine or ten cylinders of hydrogen [1]. The fact that ammonia is easily condensed makes it a good choice for transportation and storage. Ammonia is readily available and its decomposition by electro-oxidation in alkaline media is environmentally friendly with nitrogen and water as main products of reaction. It appears that considerable current densities can be obtained from the oxidation of ammonia on noble metals but this electrode process is far less reversible than the oxidation of hydrogen [2,3]. Platinum-based catalysts are well-known for the electro-oxidation of organics molecules and perform well for ammonia oxidation. However, they are subject to poisoning due to adsorption of molecules over Pt surface, which reduces drastically their catalytic activity [4]. Therefore, addition of other metals (M) such as Ru, Ir, or Rh is necessary to improve the catalytic activity of the catalyst, Pt-Ir being the most promising bimetallic alloy [5,6].

To date, no molecular modeling study that deals with the ammonia interactions with Pt-based surfaces for the electro-oxidation of ammonia is available in the open literature. Few theoretical studies have been focused on the interactions of ammonia with some transition metals. [7,8] The oxidative addition reaction of ammonia in the catalytic alkene hydro-amination, and the solvation of Yttrium atoms with ammonia was studied for the physisorption and chemisorption on metals surfaces. [7,8]

The objective of this work is to investigate the feasibility of the mechanisms proposed in the literature for the electro-oxidation of ammonia on Pt-based electrodes. Well established computational chemistry techniques such as first principle calculations (quantum chemistry), combined with transition state theory were used to fulfill the objective. The most feasible mechanism for ammonia oxidation and the reaction rates and kinetics constants associated with the mechanism are presented. This work is important for the development of new alloys that will improve the electro-oxidation of ammonia for fuel cell applications, and will establish a base case for further development and research in this field.

Theoretical Calculations

Two mechanisms [2,4] are considered for ammonia oxidation on Pt-based electrodes, which propose identical adsorbed intermediates of reaction. However, they differ in the role played by adsorbed nitrogen (intermediate of reaction or poison of reaction). Mechanism 1 (derived by Oswin [2]):

$$NH_3(aq) \Leftrightarrow NH_{3,ad} \quad (1)$$

$$NH_{3,ad} + OH^- \Leftrightarrow NH_{2,ad} + H_2O + e^- \quad (2)$$

$$NH_{2,ad} + OH^- \Leftrightarrow NH_{ad} + H_2O + e^- \quad (3)$$

$$NH_{x,ad} + OH^- \Leftrightarrow N_{ad} + H_2O + e^- \quad (4)$$

$$2N_{ad} \Leftrightarrow N_{2,ad} \quad (5)$$

$$N_{2,ad} \Leftrightarrow N_2(g) \quad (6)$$

The first 3 steps of Mechanism 2 (derived by Gerischer [4]) are identical to Mechanism 1. The alternative termination proposed is:

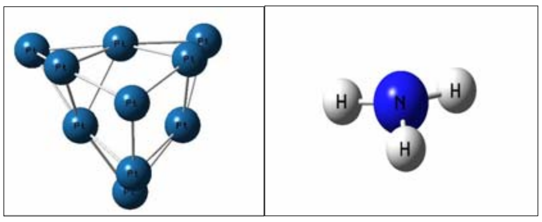
$$NH_{x,ad} + NH_{y,ad} \Leftrightarrow N_2H_{(x+y)} \quad (4bis)$$

$$N_2H_{(x+y)} + (x+y)OH^- \Leftrightarrow N_{2,ad} + (x+y)H_2O + (x+y)e.^- \quad (5bis)$$

$$N_{2,ad} \Leftrightarrow N_2(g) \quad (6bis)$$

$$NH_{ad} + OH^- \Leftrightarrow N_{ad} + H_2O + e^- \quad (7bis)$$

The feasibility of the mechanisms was evaluated using computational chemistry. The structures of the molecules involved in different paths were optimized in gas phase at 0 K and 1 atm at the B3PW91/LANL2DZ level of theory [9-11]. Gaussian 03 was the first principle calculations software used for the calculations [9]. A frequency analysis of the optimized structures was performed to determine the nature of the stationary point found by the optimization and to calculate the thermochemistry of the molecules. The STQN method was used to determine the structures for the transition states between the products and the reactants. {9} The Pt-based electrode surfaces were simulated by using clusters of Pt atoms (see Fig. 1). Further analysis and results will be presented.



(a) **(b)**

Figure 1. Optimized structures of the Pt-cluster and the ammonia molecule (a) Pt-10 cluster; (b) NH_3 molecule.

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