DFT Calculations of Ammonia Oxidation Reactions on Bimetallic Clusters of Platinum and Iridium

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Abstract

Density functional theory calculations were performed on four platinum-iridium clusters, $\text{Pt}_{3-x}\text{Ir}_x$ ($x=0-3$) to examine ammonia oxidation in alkaline media. The adsorption of NH_{3-x} ($x=0-3$) on these clusters and the effect of cluster composition on the adsorption were investigated. The hybrid B3LYP level of theory was used in Gaussian 09 along with the LANL2DZ and 6-311++g basis sets.

The HOMO-LUMO energy gap on bare metal clusters showed that increasing the iridium concentration decreased the energy gap, a sign of a more reactive catalyst. The relative adsorption energy showed more stability of NH_{3-x} on the Ir_3 cluster and less stability as the number of platinum atoms increased in the cluster. These results combined with activation and dissociation energy calculations of sequential dehydrogenation reactions showed that Ir_3 is more active than Pt_3 for ammonia oxidation, and the addition of iridium to platinum makes a more favorable pathway for the ammonia oxidation reaction. The computational calculations suggest the possibility of two different mechanisms of ammonia oxidation on platinum and iridium electrocatalysts.

Keywords: Density Functional Theory, ammonia oxidation, ammonia electrolysis, platinum and iridium bimetallic catalyst, waste water remediation, hydrogen production.

Introduction

Population increase and growth of technology are the main reasons for increasing demand of energy sources and the consumption of fossil fuels as the main source of energy consequently increases. However, these fuels emit large amounts of toxic and greenhouse gases to the atmosphere. Moreover, they are not renewable resources. Wind and solar energy are clean and renewable but intermittent - they are not consistently available. Alternatively, hydrogen as an energy carrier is attractive because the only product of its combustion is water, but production and storage of hydrogen raises concerns about cost and safety. For hydrogen to become a viable energy source, these concerns will need to be addressed, and researchers in recent decades have proposed innovative solutions for those problems.

Water is abundant and can be electrochemically dissociated to produce hydrogen. However, the thermodynamics cell voltage of hydrogen production from water is 1.23 V at standard conditions and in practice is higher due to surface overpotential and other cell limitations. On the other hand, ammonia (NH₃) can be used as a hydrogen source as well and it requires about 5% of the thermodynamic cell voltage (0.059 V) needed to produce hydrogen from water [1-4]. This technology is known as ammonia electrolysis and can be summarized by the following equations:

Ammonia electrolysis can also be used to produce hydrogen from ammonia wastewater relying in an already natural source of ammonia while removing a water pollutant. High levels of

ammonia entering natural water resources can result in toxic conditions for wild life through eutrophication [5, 6]. Diaz and Botte have demonstrated that the electrolysis of ammonia offers a promising potential for the deammonification of wastewater with lower energy consumption than the conventional nitrification/denitrification process [7]. In summary, it is important to have a better understanding of the electrooxidation of ammonia in alkaline media for hydrogen production, storage, and as an alternative to clean water [8-11].

The ammonia oxidation reaction (equation (1)) has been investigated for more than five decades. The first intrinsic kinetics for this reaction was suggested by Oswin and Salamon in 1963. The authors proposed a step-by-step dehydrogenation mechanism of ammonia on a platinum surface [12]. Gerischer and Mauerer further modified this mechanism by considering the combination of dehydrogenated species and then oxidation of those molecules to form nitrogen [13]. Contrary to Oswin and Salamon who believed the combination of nitrogen atoms (N) is responsible for producing the nitrogen molecule (N_2), Gerischer and Mauerer considered it a catalyst poison. Later studies by de Voors *et al.* also confirmed that the formation of atomic nitrogen is the reason for catalytic deactivation [14].

Using ab initio methods, Garcia-Hernandez *et al.* [15] and Illas *et al.* [16] reported that NH_3 is preferentially adsorbed in the top position above the Pt atoms in a N-down orientation. However, they did not extend their research to other intermediates formed in the process (NH_2 , NH and N). Moreover, these calculations did not consider spin effects which have been shown to play an important role in calculating adsorption geometries and energies on Pt clusters [17]. Taking spin effects into consideration, Daramola and Botte [18] showed that the adsorption energy of ammonia and its dehydrogenated species on Pt(111) follow the sequence: $N_2 < NH_3 <$

$\text{NH}_2 < \text{NH} < \text{N}$. Furthermore, they reported that the dimerized intermediate species could not be responsible for surface blockage since their adsorption energies are far less than NH_2 [19].

Novell-Leruth *et al.* [20, 21] used density functional theory (DFT) calculations with a plane-wave basis to study the adsorption and decomposition of ammonia on the (111) and (100) surfaces of platinum-group metals (Pd, Rh, Pt). They concluded that NH_3 adsorbs preferentially on top sites, NH_2 on bridge sites, and NH and N on hollow sites. Also, they found out that Rh (100) is the most favorable surface overall; however based on experimental results, de Vooy and coworkers concluded that polycrystalline Ru and Rh provided the strongest affinity for N_{ads} which acts as a poison toward the production of N_2 [14]. Furthermore, de Vooy *et al.* showed that platinum and iridium are the most active catalysts in ammonia oxidation. However, they did not extend their research on the role played by bimetallic surfaces on these reactions.

The roles of bimetallic surfaces have been investigated mostly with experimental techniques. Vitse *et al.* [4] reported that Pt-Ir catalysts prepared by the electro-deposition technique showed higher activity than Pt. Boggs and Botte reported that Pt-Ir bimetallic surface is the best catalyst for ammonia oxidation in alkaline media [3]. They also concluded that concentration of Pt(IV) and Ir(III) of the plating bath strongly influence electrode surface atomic composition of the Pt-Ir alloy directly affecting the electro-oxidation behavior of ammonia. Bonnin *et al.* investigated the reaction at low concentration of ammonia with different substrates and noble metal [22]. They reported that Rh-Pt-Ir and Pt-Ir on carbon fiber substrate were the most promising electrodes for the ammonia oxidation process at low concentration of ammonia. The experiments carried out by Allagui *et al.* [23] on carbon-supported Pt-Ir nanoparticles with the nominal atomic ratio of 70:30, also demonstrated a 33% higher degradation rate of ammonia

on Pt-Ir than on Pt with N_2 as the main product, in addition to the emergence of some traces of NO_3 and NO_2 .

Le Vot *et al.* [24] performed several experiments of ammonia electro-oxidation with electrodeposited $\text{Pt}_{(x)}\text{-Ir}_{(1-x)}$ on graphite and glassy carbon substrates. They demonstrated that only Pt-rich (Pt at. % > 85-90) Pt-Ir binary electrodes could be considered as better catalysts for NH_3 oxidation such as low anode potential (< -0.4 V vs. Ag/AgCl) and/or for low ammonia concentration (< 0.02 M). Endo *et al.* [25, 26] prepared different Pt-Me (Ir, Ru, Ni, Cu) binary alloys on glassy carbon substrate. They reported that the saturated current density after 60 s at a high oxidation potential was apparently higher on $\text{Pt}_{1-x}\text{Ir}_x$ ($x \leq 0.8$) than on Pt. However, according to the Figure 1-I, the main oxidation peak on Pt is still higher than the other surfaces. Lomocso and Baranova [27] also studied ammonia electro-oxidation on carbon-supported Pt and bimetallic $\text{Pt}_y\text{M}_{1-y}$ ($\text{M} = \text{Pd}, \text{Ir}, \text{SnO}_x$ and $y = 70, 50$ at.%) nanoparticles. They determined that oxidation of ammonia is facilitated with addition of Pt nanoparticles to Pd and Ir, since no ammonia oxidation occurs on Pd and Ir nano particles showed low activity. Although, in their cyclic voltammograms the highest peak current density is found for pure Pt (Figure 1-II).

(I)

(II)

Figure 1 –Cyclic voltammograms of: (I) - $\text{Pt}_{1-x}\text{Ir}_x$ in 1 M NH_3 + 1 M KOH at 25°C. Scan rate 10 mV s^{-1} , the main oxidation peak on Pt is still higher than the other surfaces. (II) - Carbon supported PtM catalyst in 0.5 M NH_4OH + 1 M KOH at 30 mV s^{-1} scan rate. Catalysts: Pt (a), Pt_5Pd_5 (b), Pt_7Pd_3 (c), Pt_7Sn_3 (d), Pt_7Ir_3 (e), the highest peak current density can be seen for pure Pt. Reprinted from Endo *et al.* [25], and Lomocso and Baranova [27]. Copyright © 2004 and 2011, with permission from Elsevier.

In summary, the electro-oxidation of ammonia has been studied both experimentally and computationally. However, the effect of bimetallic surfaces has not been investigated thoroughly, and the ongoing controversy between researchers shows that aspects of this reaction remain misunderstood. In this study, we attend to address open questions on the mutual effect of bimetallic surfaces of iridium and platinum, which have been reported as the most effective catalyst for the electro-oxidation of ammonia [14], using numerical density functional theory analysis. Energetics studies on four different clusters of $\text{Pt}_{3-x}\text{Ir}_x$ ($x=0-3$) are presented, including adsorption of NH_{3-x} ($x=0-3$) species and stepwise ammonia dehydrogenation on these clusters.

Theoretical Methods

Previous studies on molecular scale ammonia oxidation simulation carried out in our research group were performed using cluster calculations [18, 19] which have been properly optimized for the system of interest. Moreover, analysis of prior results obtained by the cluster method for vibration modes have produced better agreement with experimental observations of vibrational modes than the slab calculations reported in the literature [18]. Thus, the same catalytic environment (cluster calculations) was used in this study via unrestricted spin calculations performed in Gaussian 09 [28, 29]. The hybrid B3LYP functional was the level of theory used for local correlation. Different basis sets were used to represent the heavy and light atoms with the pseudopotential-based LANL2DZ for platinum and iridium, and the 6-311++g**

basis set added for hydrogen and nitrogen [18]. The transition states (TS) for the dissociation of adsorbed ammonia were directly searched for by either the transit-guided quasi-Newton (STQN) method or the eigenvector method, following the Berny algorithm. Frequency analysis was done at the same level of theory as geometry optimization for all stationary points to incorporate zero point energy (ZPE) corrections. Density of state (DOS) calculations were performed using the program GaussSum 3.0 [30].

Models of various $\text{Pt}_{3-x}\text{Ir}_x$ ($x=0-3$) surface clusters and NH_{3-x} ($x=0-3$) molecules were created and geometrically optimized. In one of them, all three atoms were platinum (monometallic platinum cluster). The second surface contained two platinum atoms and one iridium atom making it a bimetallic cluster. For the third surface, a second platinum atom was changed to iridium, resulting in a bimetallic cluster with two iridium atoms and one platinum atom. Finally, the last surface consisted of fully iridium atoms, which make it a monometallic iridium cluster (Figure 2). The surfaces were geometrically optimized until the most stable configuration was reached. The multiplicity and binding energy of each surface were also examined. The binding energy (E_b) is defined according to equation (4) [31]:

$$E_b = \left(\sum_i E_i - E_{cluster} \right) / m \quad (4)$$

where, E_i is the energy of a single atom, $E_{cluster}$ is the energy for the cluster and m is the number of atoms in the cluster. The adsorption energy ($E_{adsorption}$) is defined according to equation (5):

$$E_{adsorption} = E_{system} - (E_{cluster} + E_{species}) \quad (5)$$

where, $E_{species}$ is the energy of the gas-phase species and E_{system} is the energy of the system formed by the cluster and adsorbed species. To calculate the adsorption energy, the species were initially attached to the cluster at various possible adsorption sites on the clusters (Figure 2) and geometrically optimized. The most stable optimized geometry (based on energy values) was chosen as the final configuration of the species-cluster system. Note that a more negative value for the adsorption energy is an indication of stronger adsorption.

Figure 2 – (a-d): Schematic of clusters, (a): three platinum, (b): two platinum and one iridium, (c): one platinum and two iridium, (d): three iridium – (e-g): adsorption of ammonia at different sites on three platinum cluster, (e): top, (f): bridge, (g): hollow

Results and Discussion

Clusters

Table 1 shows the binding energies and HOMO-LUMO gaps of the clusters. In monometallic clusters, the even distribution of spin densities was considered. In Pt_3 , the most

stable multiplicity (the singlet) has the closest spin densities. However, in the Ir₃ cluster, this is different. The two lowest electronic energies belong to the doublet and quartet spin multiplicities with 0.18 eV difference in electronic energy. Interestingly, the spin densities in the doublet state, which has the lower energy, are 1.24, -0.12 and -0.12 for each atom, while these values for the quartet state are 1.10, 0.95 and 0.95, respectively. As the quartet state has plausibly all spins aligned (all are close to 1.0), it is selected as the most stable configuration with a binding energy of 1.83 eV. To characterize the electronic structure of the cluster, the differences between the energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were calculated. It is worthwhile to note that the catalysts with smaller gap are more reactive [32, 33]. Pt₃ has the highest HOMO-LUMO gap energy, and as the number of iridium atoms increases in the cluster, this gap energy decreases which means that the catalyst is more reactive toward the formation of chemical bonds. It is worthwhile to mention that this reactivity depends on the species which are present on the surface of the catalyst as well.

Table 1 – Multiplicity, $E_{\text{cluster}}-E_{\text{ground}}$, binding energies and HUMO-LUMO gaps for four different metal atom-clusters Pt_{3-x}Ir_x (x=0-3). Pt₃ has the highest gap energy, and by increasing the number of iridium atom, this gap energy decreases as a sign of higher reactivity toward chemical bonds formation.

Cluster	Multiplicity	$E_{\text{cluster}}-E_{\text{ground}}$ (eV)	Binding energy (eV)	HOMO- LUMO gap (eV)
Pt ₃	1	0.00	1.76	0.068
	3	0.20		
	5	0.88		
Pt ₂ Ir ₁	2	0.09	1.82	0.064
	4	0.00		
	6	0.44		
Pt ₁ Ir ₂	1	0.36	1.82	0.062
	3	0.00		
	5	0.11		
Ir ₃	2	0.00	1.83	0.051
	4	0.18		

	6	0.22		
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Adsorption of NH₃

Adsorption of NH₃ on all of four clusters occurs on a top oriented configuration. The adsorption energy of the ammonia in the different cluster configurations and their orientation are summarized in Table 2. The adsorption energy on Pt₃ is -114.92 kJ mol⁻¹. All other investigated positions have higher energy. On Pt₂Ir₁, the adsorption of ammonia on the iridium atom produces the most stable configuration with an adsorption energy of -132.33 kJ mol⁻¹. However, if ammonia adsorbs on platinum, the energy is -130.10 kJ mol⁻¹. Note that this value is relatively close to the adsorption energy on iridium which means that there are no specific preferences for ammonia to be adsorbed on this cluster. On Pt₁Ir₂, adsorption of ammonia on the iridium atom is close to the previously discussed configuration (Pt₂*Ir₁) with the adsorption energy of -126.76 kJ mol⁻¹. However, adsorption on platinum makes the less stable configuration among all clusters with an adsorption energy of -109.08 kJ mol⁻¹. Finally, adsorption of NH₃ on Ir₃ appears as the most stable one among all clusters studied, with an adsorption energy of -149.85 kJ mol⁻¹. Briefly, when adsorption takes place on platinum, the trend in stability is Pt₂Ir₁ > Pt₃ > Pt₁Ir₂. Meanwhile, if adsorption happens on iridium, the trend is Ir₃ > Pt₂Ir₁ > Pt₁Ir₂ which means Pt₂Ir₁ shows more stability toward ammonia adsorption between bimetallic clusters and as mentioned earlier, there is no specific preferred adsorption site on this cluster.

Table 2 – NH₃ adsorption energies, multiplicity, atomic distances, and schematic of adsorption on four clusters of Pt_{3-x}Ir_x (x=0-3). The most and least stable clusters are Ir₃ and Pt₁*Ir₂, respectively.

Cluster	Pt ₃	Pt ₂ Ir ₁ *	Pt ₂ *Ir ₁	Pt ₁ Ir ₂ *	Pt ₁ *Ir ₂	Ir ₃
NH ₃ Adsorption	-126.23	-143.14	-140.88	-137.89	-120.02	-160.15

energy (kJ mol ⁻¹)						
Adsorption energy (ZPE corrected)	-114.92	-132.33	-130.10	-126.76	-109.08	-149.85
N-metal distance (Å)	2.1665	2.1878	2.1496	2.1445	2.1608	2.1871
N-H distance (Å)	1.0168 1.0168 1.0180	1.0177 1.0188 1.0170	1.0166 1.0166 1.0174	1.0177 1.0177 1.0202	1.0166 1.0166 1.0177	1.0174 1.0174 1.0187
Schematic of adsorption
Multiplicity	1	4	4	3	3	4

*: indicates the adsorption site

Adsorption of NH₂

NH₂ adsorption on these four clusters also occurs on a top position. The adsorption energy of the NH₂ in the different cluster configurations and their orientation are summarized in Table 3. The adsorption energy on Pt₃ is -238.65 kJ mol⁻¹. The most stable configuration of NH₂ on Pt₂Ir₁ appears to be on the iridium atom with a value of -311.60 kJ mol⁻¹. To compare the adsorption of NH₂ on Pt₃ and Pt₂Ir₁, the adsorption on platinum in Pt₂Ir₁ was considered. Contrary to NH₃, no significant change in the value of the energy (-243.94 kJmole⁻¹ on Pt₂*Ir₁ and -238.65 kJmole⁻¹ on Pt₃) was observed. The adsorption on iridium atom of Pt₁Ir₂ produces the most stable configuration on these clusters with an energy of -323.35 kJ mol⁻¹. Adsorption on the platinum atom increases this value to -235.58 kJ mol⁻¹, very close to the corresponding energy of the pure Pt₃ cluster. For Ir₃, the adsorption energy obtained is -323.02 kJ mol⁻¹, a value close to the adsorption energies obtained for adsorption on iridium atom in Pt₁Ir₂. Unlike adsorption of

ammonia on the most stable bimetallic cluster where there was no preference of platinum or iridium; here iridium is preferred on bimetallic clusters. This can be attributed to the higher number of unpaired electrons of iridium than platinum, which causes bonding with the unpaired electron of NH_2 .

Table 3 – NH_2 adsorption energies, multiplicity, atomic distances, and schematic of adsorption on four clusters of $\text{Pt}_{3-x}\text{Ir}_x$ ($x=0-3$). The most and least stable clusters are Ir_3 and Pt_1^*Ir_2 , respectively. Moreover, Pt_1Ir_2^* seems to be as stable as Ir_3 .

Cluster	Pt_3	Pt_2Ir_1^*	Pt_2^*Ir_1	Pt_1Ir_2^*	Pt_1^*Ir_2	Ir_3
NH_2 Adsorption energy (kJ mol^{-1})	-256.32	-329.25	-261.04	-340.29	-253.35	-338.94
Adsorption energy (ZPE corrected)	-238.65	-311.60	-243.94	-323.35	-235.58	-323.02
N-metal distance ($\text{\AA}$)	1.8866	1.8950	1.8980	1.9002	1.9089	1.8966
N-H distance ($\text{\AA}$)	1.0150 1.0150	1.0132 1.0170	1.0142 1.0142	1.0169 1.0129	1.0135 1.0135	1.0130 1.0188
Schematic of adsorption
Multiplicity	2	3	3	4	4	3

*: indicates the adsorption site

Adsorption of NH

Adsorption energies of NH on the four clusters and the illustration of the adsorbate-cluster systems are shown in Table 4. The most stable configuration of NH on Pt_3 is a bridge position with an energy of $-304.40 \text{ kJ mol}^{-1}$. However, our calculations suggest that the NH

species prefer a top position on the iridium atom in the Pt_2Ir_1 cluster with an energy of $-386.81 \text{ kJ mol}^{-1}$. In order to compare the effect of the presence of an iridium atom, the adsorption on a bridge position in this cluster was also performed. The adsorption energy of this configuration resulted in a value of $-293.22 \text{ kJ mol}^{-1}$ which is approximately 10 kJ mole^{-1} higher than the value obtained in Pt_3 . On Pt_1Ir_2 , the lowest energy corresponded to a top adsorption on one iridium atom with a value of $-381.30 \text{ kJ mol}^{-1}$. For comparison with Pt_3 , the calculations on the bridge position in this cluster were performed. In the bridge position, the NH radical is adsorbed on Ir and Pt atoms simultaneously. The adsorption energy in this case is equal to $-343.15 \text{ kJ mol}^{-1}$. Comparing the results for the clusters Pt_2^*Ir_1 and Pt_1^*Ir_2 , the effect of the presence of iridium in the adsorption is obvious; there is a net difference of $\sim 50 \text{ kJ mol}^{-1}$ in adsorption energies which means adsorption on iridium is more stable. Finally, it was found that the adsorption on Ir_3 is the most stable one among all the clusters –with an energy of $-407.43 \text{ kJ mol}^{-1}$. Like NH_2 , the preferred adsorption site for the NH radical is iridium due to a larger number of unpaired electrons in the iridium atom than in the platinum atom.

Table 4 – NH adsorption energies, multiplicity, atomic distances, and schematic of adsorption on four clusters of $\text{Pt}_{3-x}\text{Ir}_x$ ($x=0-3$). The most and least stable clusters are Ir_3 and Pt_2^*Ir_1 , respectively.

Cluster	Pt_3	$\text{Pt}_2 \text{Ir}_1^*$	$\text{Pt}_2^* \text{Ir}_1$	$\text{Pt}_1 \text{Ir}_2^*$	$\text{Pt}_1^* \text{Ir}_2$	Ir_3
NH Adsorption energy (kJ mol^{-1})	-323.82	-402.80	-312.49	-398.85	-361.87	-422.18
Adsorption energy (ZPE corrected)	-304.40	-386.81	-293.22	-381.30	-343.15	-407.43
N-metal distance ($\text{\AA}$)	1.9417 1.9412	1.7346	1.9475 1.9478	1.7231	Pt:1.9575 Ir: 1.9009	1.7282
N-H distance ($\text{\AA}$)	1.0311	1.0259	1.0310	1.0178	1.0300	1.0212

Schematic of adsorption
Multiplicity	1	2	2	3	3	4

*: indicates the adsorption site

Adsorption of N

Adsorption energies of N on the four clusters and the illustration of the adsorbate-cluster systems are shown in Table 5. On all four clusters, the most stable configurations are the bridge positions. For Pt_3 this energy is $-361.82 \text{ kJ mol}^{-1}$. For Pt_2Ir_1 the most stable is the bridge position where the iridium atom is present as one of the adsorbate sites with the energy of $-445.62 \text{ kJ mol}^{-1}$. To compare with Pt_3 , the calculation for bridge position with two platinum atoms which were present in bonding with adsorbed species was performed. This energy is $-337.37 \text{ kJ mol}^{-1}$, which is 25 kJ mol^{-1} higher than adsorption on Pt_3 . Here, the decreased tendency of Pt_2^*Ir_1 to adsorb N in preference to NH is evident. On Pt_1Ir_2 the adsorption energy decreases to $-485.14 \text{ kJ mol}^{-1}$, which is the most stable configuration among the clusters. This configuration is a bridge position; both atoms present in bonding are iridium (Pt_1Ir_2^* in Table 5). For comparison, the adsorption energy when one atom present in bonding is platinum and the other is iridium in this cluster (Pt_1^*Ir_2) was calculated. The adsorption energy is $-453.85 \text{ kJ mol}^{-1}$. Also comparison of the adsorption energy for Pt_2Ir_1^* and Pt_1^*Ir_2 in Table 5 shows that increasing the Ir concentration decreases the adsorption energy to near 8 kJ mol^{-1} . Like other species, adsorption on Ir_3 is the most stable configuration. This energy is $-519.40 \text{ kJ mol}^{-1}$.

Table 5 – N adsorption energies, multiplicity, atomic distances, and schematic of adsorption on four clusters of $\text{Pt}_{3-x}\text{Ir}_x$ ($x=0-3$). The most and least stable clusters are Ir_3 and Pt_2^*Ir_1 , respectively.

Cluster	Pt ₃	Pt ₂ Ir ₁ [*]	Pt ₂ [*] Ir ₁	Pt ₁ Ir ₂ [*]	Pt ₁ [*] Ir ₂	Ir ₃
N Adsorption energy (kJ mol ⁻¹)	-370.01	-454.75	-345.06	-494.83	-462.54	-528.73
Adsorption energy (ZPE corrected)	-361.82	-445.62	-337.37	-485.14	-453.85	-519.40
N-metal distance (Å)	1.8016 1.8016	Pt: 1.8770 Ir: 1.7267	1.8510 1.8510	1.7354 1.8037	Pt: 1.8775 Ir: 1.7331	1.7861 1.7899
N-H distance (Å)	-	-	-	-	-	-
Schematic of adsorption
Multiplicity	2	1	3	2 - 4 same energy	4	3

*: indicates the adsorption site

In order to facilitate the comparison, all the adsorption energies of NH_x on Pt_{3-x}Ir_x (x=0-3) are summarized in Figure 3. As can be seen, N is the most stable species on these clusters. It is worthwhile to note that the most stable configuration of NH_x (x=0-3) adsorption on platinum are hollow, hollow, bridge, and top positions as x increases from 0 to 3 (N, NH, NH₂, and NH₃, respectively) [15, 16, 20, 34]. However, as mentioned earlier, these stable configurations are bridge, bridge, top and top position in this study, and this difference can be attributed to edge effects caused by the limited number of atoms in the clusters.

Figure 3 – Adsorption energy of NH_x ($x=0-3$) on $\text{Pt}_{3-x}\text{Ir}_x$ – N is the most stable species on these clusters and as x increases, the adsorption energy increases as well.

Density of States

Density of states (DOS) calculations were performed to obtain further analyses of the electronic structure properties that determine the adsorption of NH_3 and its dehydrogenated species over the four studied clusters. In this study, DOS of bare clusters, clusters with adsorbed NH_3 and NH_2 have been considered. In Figure 4 plots of the partial DOS for the metal atoms that contribute to the favored NH_x adsorption (the platinum atom in Pt_3 and the iridium atom in Pt_2Ir_1 , Pt_1Ir_2 , and Ir_3 , that contributes in the adsorption process) are shown. The figure also includes the

DOS for N and Hs contained in the NH_3 molecule in its gas phase for four different clusters of Pt_3 , Pt_2Ir_1 , Pt_1Ir_2 and Ir_3 .

Figure 4 – Density of states calculations for the most stable configuration of bare clusters and NH_3 in gas phase before adsorption. The black vertical lines are cluster Fermi level. The green curves represent the metal atom where adsorption will take place, the blue curves are nitrogen atoms and the brown curves are hydrogen atoms. Cluster composition has a distinguishable effect on the local DOS of the atom analyzed; as the number of iridium atoms increases; the d-band is shifted toward higher energies.

The black vertical lines indicate the bare cluster Fermi level. Comparing the above plots for the metallic atoms, especially Pt_2Ir_1 , Pt_1Ir_2 and Ir_3 where the contributing atom is iridium, it can be concluded that the cluster composition has a distinguishable effect on the local DOS of the atom analyzed. As the number of iridium atoms in the cluster increases, the d-band is shifted

toward higher energies as reported by Hammer and Norskov [35]. When compared to the values obtained for the adsorption energies, this trend is in agreement with the results of Kitchin *et al.* [36] for hydrogen and oxygen adsorption on Pt (111), and Morrow *et al.* for the adsorption of carbon monoxide on a bimetallic surface of PtAu [37]. Also Figure 4 shows that these three clusters have a fully occupied top energy level (while it is less evident for Pt₁Ir₂ and Ir₃). However, Pt₃ has a partially occupied top energy level. For NH₃, the two bands below the cluster Fermi level are occupied and the one at around -0.5 eV is unoccupied. The calculations show the same qualitative results for NH₂ although with different values of bands energy level (NH₂ DOS data not shown).

In Figure 5, DOS for NH₃ adsorbed on the clusters is shown. The x axis corresponds to the cluster and adsorbed-molecule Fermi energy. The DOS plots change significantly compared to those obtained for isolated metal clusters and gas phase NH₃. For instance, the metal atoms significantly contribute to the DOS of two occupied bands of NH₃ which are at the two lowest energies. However, for the case of Pt₁Ir₂, this contribution is not the same as for the others; therefore, it is speculated that this could be the reason for a lower adsorption energy in the trend of Ir₃<Pt₂Ir₁< Pt₁Ir₂<Pt₃. In all cases, adsorption of NH₃ causes large changes in the structure of the metal's d-bands and also in the d-band position with respect to the cluster Fermi energy. In comparing the DOS plots of Figure 5, it can be seen that in the case of adsorption on Pt₃, the two occupied band of NH₃ are shifted to higher energy with a reduced occupancy. These differences may be attributed to the high adsorption energy of NH₃ on Pt₃.

Figure 5 – Density of states calculations for adsorbed NH_3 on four metallic clusters. The green curves represent the metal atom that is directly contributing in the adsorption process. The blue and brown curves are nitrogen and hydrogen atoms of adsorbed NH_3 . The energy is referenced to the cluster-adsorbed molecule complex Fermi level. In comparison to the DOS plots for isolated metal cluster and gas phase ammonia; here, the metal atoms significantly contribute to the DOS of two occupied bands of NH_3 .

To show the adsorption characteristic of NH_3 dehydrogenated species, the DOS for the NH_2 adsorption over the four clusters are compared in Figure 6. The major difference between NH_2 and NH_3 adsorption (comparison between Figure 5 and Figure 6) is the higher contribution of the N atom to the d-band. This could be the reason for the larger stability of adsorbed NH_2 on these metals. In the adsorption on the Pt_3 cluster, the two occupied bands of NH_2 are shifted the most, to the right among these four clusters. Additionally, the contribution fraction of N in the Fermi energy level is the least for the adsorption on Pt_3 . These observations along with a far

lower adsorption energy on Pt_3 in comparison to the three other clusters suggests the absence of strong interactions between NH_2 and Pt_3 .

Figure 6 - Density of states calculations for adsorbed NH_2 on four metallic clusters. The green curves represent the metal atom that is directly contributing in the adsorption process. The blue and brown curves are nitrogen and hydrogen atoms of adsorbed NH_2 . The energy is referenced to the cluster-adsorbed molecule complex Fermi level. The higher contribution of the N atom to the d-band may be attributed to the more stability of NH_2 than NH_3 on these clusters.

Dehydrogenation Process

The adsorption energies were recalculated with respect to a common reference system: the NH_3 molecule in the gas phase, shown in equation (6). These relative adsorption energies were used to compare the relative stabilities of different species. It was considered that the

adsorbed NH₃ and its dehydrogenated species and (3-x) H atoms do not interact; that is, they were calculated separately.

$$E_{rel} = E_{NH_x-surface} + (3-x)E_{H-surface} - \left((4-x)E_{Surface} + E_{gas-phaseNH_3} \right) \quad (6)$$

Using equation (6), Figure 7 shows the relative energy of different species in comparison to the NH₃ gas phase. As can be seen from this graph, the adsorption energies of NH₃ on all surfaces are close to each other, but for dehydrogenated species this energy dramatically changes. This relative adsorption energy increases for NH₂+H, NH+2H and N+3H in comparison to NH₃ on Pt suggesting that the interactions of these species and the cluster decreases accordingly. This behavior can be attributed to the fact that ammonia oxidation on Pt does not follow the consecutive dehydrogenation of ammonia, but it may be the case for iridium containing clusters. As it has been shown earlier [8, 38, 39], the ammonia oxidation process on platinum proceeds through dimerization of NH₂ to hydrazine and then this hydrazine can be oxidized to N₂.

Figure 7 - Relative adsorption energy (E_{rel} in kJ mol^{-1}) of the most stable configurations of the NH_{3-x} ($x=0-3$) species with respect to gas-phase NH_3 on $\text{Pt}_{3-x}\text{Ir}_x$ ($x=0-3$). Pt_3 shows the least reactivity especially for NH_2 , NH and N . As the number of Ir increases in the cluster, the reactivity increases as well.

The potential energy profiles for the more favorable pathway of ammonia decomposition over the surfaces are displayed in Figure 8, where an asterisk (*) represents an adsorbed species on the surface and pound (#) represents a transition state. The transition state geometry and frequency in addition to activation and dissociation energy of consecutive dehydrogenation reactions are shown in Table 6 and 7. The activation energy and dissociation energy are defined by equations (7) and (8), respectively.

$$E_a = E_{\#} - E_{\text{reactant}} \quad (7)$$

$$E_{diss} = E_{product} - E_{reactant} \quad (8)$$

Figure 8 - Potential energy profiles for the most stable configurations of ammonia and its dehydrogenated species, adsorption and dissociation on $Pt_{3-x}Ir_x$ ($x=0-3$). Pt_3 shows the least reactivity and as the number of Ir increases in the cluster, the reactivity increases as well.

Table 6 – Transition states and frequency calculations of consecutive dehydrogenation of NH_3 on $Pt_{3-x}Ir_x$ ($x=0-3$). Star superscript means adsorbed species.

	$NH_3^* \rightarrow NH_2^*.H^*$ Transition state		$NH_2^* \rightarrow NH^*.H^*$ Transition state		$NH^* \rightarrow N^*.H^*$ Transition state	
	Geometry	Frequency (cm^{-1})	Geometry	Frequency (cm^{-1})	Geometry	Frequency (cm^{-1})

Pt ₃		-266.32		-330.84		-1130.56
Pt ₂ Ir ₁		-1213.71		-1134.93		-992.71
Pt ₁ Ir ₂		-1227.77		-1162.91		-1064.84
Ir ₃		-1184.71		-1288.48		-1305.79

Table 7 – Activation and dissociation energy in kJ mol⁻¹ of consecutive dehydrogenation of NH₃. Star superscript means adsorbed species. For each step, the starting point was a NH_{3-x} species (x= 0-2) plus the energy of x adsorbed H atoms without any other species coadsorbed on the surface. The final state was taken as NH_{3-x-1} plus one H atom coadsorbed in their most stable configuration and the energy of x adsorbed H atoms in order to make the number of atoms consistent with NH₃.

Activation energy (kJ mol ⁻¹)			
	NH ₃ * → NH ₂ *.H*	NH ₂ *.H* → NH*.H*+H*	NH*.2H* → N*.H*.2H*
Pt ₃	139.84	175.05	170.77
Pt ₂ Ir ₁	104.60	132.00	114.46
Pt ₁ Ir ₂	72.97	131.83	82.38
Ir ₃	82.38	174.23	112.16
Dissociation energy (kJ mol ⁻¹)			
Pt ₃	23.55	52.47	21.03

Pt ₂ Ir ₁	-2.17	39.94	9.17
Pt ₁ Ir ₂	-51.67	15.85	-28.74
Ir ₃	-34.95	24.88	-47.97

For each step, the starting point (reactant) was NH_{3-x} species (x= 0-2) plus the energy of x adsorbed H atoms without any other species coadsorbed on the surface. The final state (product) was taken as NH_{3-x-1} plus one H atom coadsorbed in their most stable configuration and the energy of x adsorbed H atoms. Figure 8 and Table 7 show that Pt₃ has the highest energy in all the three dehydrogenation processes: NH₃ to NH₂, NH₂ to NH and NH to N. However, the difference between the activation energy in the first dehydrogenation step (NH₃ to NH₂) between Pt₃ and the nearest neighbor (which is Pt₂Ir₁) is 35 kJ mol⁻¹, while for the second (NH₂ to NH) and third (NH to N) dehydrogenation steps, they are 43 and 56 kJ mol⁻¹, respectively. The results from the relative adsorption energy in Figure 7 show that second and third dehydrogenation steps are not as favorable on platinum when compared to mixed clusters where iridium is present. These findings bolster the claim of different mechanisms for ammonia electro-oxidation on platinum and iridium especially after the first dehydrogenation step.

Conclusions

The HOMO-LUMO gap energy calculations showed that as the number of iridium atoms increases, the energy gap decreases, which can be interpreted as a sign of a more reactive catalyst toward chemical bond formation. This conclusion was also supported by the results of DOS studies of the clusters. Increasing the number of iridium atoms shifts the d-band toward higher energies. Adsorption of NH₃ and NH₂ caused large changes on d-bands and their position compared to Fermi levels. Additionally, the higher contribution of the nitrogen atom of NH₂ than

the nitrogen atom of NH_3 in the d-band may be interpreted as a more stable adsorption process of NH_2 in comparison to NH_3 on these clusters.

In agreement with the HOMO-LUMO and DOS calculations, the relative adsorption energy shows that NH_3 and its dehydrogenated species have lower energy (more negative) on iridium than platinum. In addition, as the number of platinum atoms increased in the cluster, this energy increased which can be interpreted as more stability on Ir_3 and this stability decreases toward Pt_3 . However, according to Sabatier principles, the interactions between the catalyst and the substrate should be "just right"; that is, neither too strong nor too weak. About the Ir, this interaction is stronger than Pt; it means that these intermediates may fail to dissociate from the surface and the catalyst would deactivate at lower energy than Pt.

A comparison on activation energy in the dehydrogenation process indicates that for all the clusters, the most favorable dehydrogenation step is the first one which shows the less sensitivity of this step to surface composition. However, in the second and third step, Ir containing clusters are more active than Pt_3 . This higher reactivity in bimetallic surfaces may be attributed to generated electronic effects between two metals in bimetallic clusters. In another perspective, this behavior would suggest that the mechanism of ammonia oxidation on platinum may differ from iridium. The previous studies also reported the possibility of dimerization of NH_2 to hydrazine and then oxidation of hydrazine to nitrogen on platinum [8, 38, 39]. Additionally, Pt_1Ir_2 shows the most favorability in all of dehydrogenation processes since the activation energies on this surface are minimum among all clusters.

The bond formation between N atoms to form molecular nitrogen has not been considered here. This is a very important step in ammonia oxidation since it has been reported to

be the rate determining step in this process [38-40]. For future studies, it is suggested that a thorough investigation be performed based on the formation of molecular nitrogen via binding between the dehydrogenated species on different clusters. Another simplification in this study is the absence of the hydroxide ion. The probable adsorption of OH^- on active sites of catalyst may affect the results as well.

In summary, the addition of iridium to platinum changes the characteristic of the catalyst and allows ammonia oxidation to occur in a more favorable pathway. The electronic effect generated between two metals could be the reason behind this higher activity. Finally, this work suggests that this reaction may follow two different mechanisms on platinum and iridium catalysts.

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