



## QUANTUM CHEMICAL STUDY OF CHEMISORPTION OF NITRIC OXIDE ON ALUMINUM (111) SURFACE

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### ABSTRACT

The interaction of Nitric Oxide (NO) with Al (111) surfaces including clusters has been studied by means of semi-empirical AM1 method. Metal cluster models (up to 51 atoms) with different sizes and geometries have been used to describe the atop, bridge and three-fold sites. The binding energies of NO in different geometries are calculated and compared with the results from the experimental data available and the previous study. GAMESS and OpenMX quantum chemical programs were used to compute the binding energies of the system and the geometrical properties of the initial and optimized clusters obtained from MOLDEN and RasMol packages respectively. The NO tilted upright with respect to the surface normal axis when adsorbed on top, bridge and three-fold sites and nitrogen atom is pointing towards the surface. The cluster model approach is discussed in terms of its reliability to determine the adsorption energies and the favored site of adsorption. Based on the results, the more negative value of binding energy obtained for small clusters ( $Al_{19}$  and  $Al_{21}$ ) in all on top, bridge and three-fold site adsorptions. The most negative value of binding energy was obtained for binding in bridge form in some cases and three-fold sites adsorption in all the other clusters. Therefore it is concluded that the NO adsorbs preferentially on bridge and also three-fold sites in all the cluster models. Since the geometry optimization of on top converged to bridge, close to bridge and the three-fold site geometry after geometry optimization, it can be concluded that on top adsorptions are comparatively unstable.

**Keywords:** Cluster, Adsorption, Binding energy, Geometry optimization

### INTRODUCTION

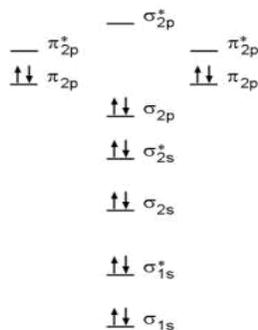
#### Chemisorption of NO on metal system

There are many reasons for studying the NO chemisorption on metal system. The oxidation of metal and semiconductor surfaces plays a central role in heterogeneous catalytic oxidation<sup>2</sup>. The catalytic reduction of NO is of great technological importance, one of the most common and important processes in which one tries to reduce the discharge of NO is the car exhaust catalysis. For this reason automobiles are currently produced with a catalytic converters, which greatly reduce the nitric oxide and carbon monoxide emissions. This is due to the fact that NO is one of the strongest oxidizing agents, which can affect air pollution with detrimental effects on the global environment<sup>3</sup>. In recent years, more stringent air quality regulations have been imposed on automobile manufacturers, which makes detailed understanding of the catalytic reduction of NO even more urgent. Especially  $NO_x$  pollutants are related to the production of

acid rain and human respiratory problems. Therefore, to reduce the emission of various nitrogen oxides, a number of catalysts, such as Rh, Pd and Pt are used in the automobile industry. The adsorption and reactivity of NO on metal surfaces is also important from a fundamental point of view<sup>3</sup>.

### Bonding of NO to metal surfaces

The commonly accepted idea of the bonding of NO with metals is one of  $\sigma$  donation and  $\pi$  back-donation. The NO oriented with N toward the metal atom and the NO  $5\sigma$  (N lone pair) orbital donates charge to and bonds with the metal. This  $\sigma$  donation leads to a  $\pi$  back-donation into the NO  $\pi^*$  level weakening the NO bond.



**Figure 1: Molecular orbital diagram of NO**

In order to separate the effects due to the  $d$  and  $sp$  electrons, It has been considered that the model studies of the adsorption (or interaction) of NO with aluminum cluster, a metal cluster which does not have occupied  $d$  shells. Also aluminum cluster have comparatively small numbers of electrons making it a simpler system to study.

### COMPUTATIONAL METHODS

In this cluster model study, the Al (111) surface is modeled using small and large clusters containing two layers of atoms. The crystal type of aluminum is face centered cubic. The crystal parameters that were used to generate the Al (111) surface are  $a = b = c = 4.05 \text{ \AA}$  and  $\alpha = \beta = \gamma = 90^\circ$ . The following aluminum bare clusters  $Al_{19}$ ,  $Al_{21}$ ,  $Al_{22}$ ,  $Al_{23}$ ,  $Al_{25}$ ,  $Al_{31}$ ,  $Al_{40}$ ,  $Al_{41}$ ,  $Al_{49}$  and  $Al_{51}$  have been investigated in this study. The cluster model calculations were performed at the AM1 semi-empirical level of theory using the GAMESS (General Atomic and Molecular Electronic Structure System) software package<sup>1</sup>. To view and draw the molecules and the clusters the graphic programmes such as RASMOL, MOLDEN, BABEL and ORTEP were used<sup>1</sup>. The total energy of bare clusters containing even number of Al atoms were calculated using the restricted Hartree-Fock (RHF) method<sup>1</sup> whereas bare clusters with odd number of Al atoms were treated with the unrestricted Hartree-Fock (UHF) method. RHF and UHF calculations were performed with the spin multiplicity of 1 and 2 respectively. The modeled structures have been optimized by using restricted open shell Hartree-Fock (ROHF)<sup>1</sup> with spin multiplicity one. In all cluster calculations the Al-Al distance was fixed at a bulk value of  $2.863 \text{ \AA}$  and N-O and Al-N bonds were optimized.

The HF (Hartree-Fock)-binding energy of  $Al_nNO$  clusters is calculated using the equation (XX)

$$BE = E_{HF}(Al_nXO) - E_{HF}(Al_n) - E_{HF}(XO) \dots \dots \dots (XX)$$

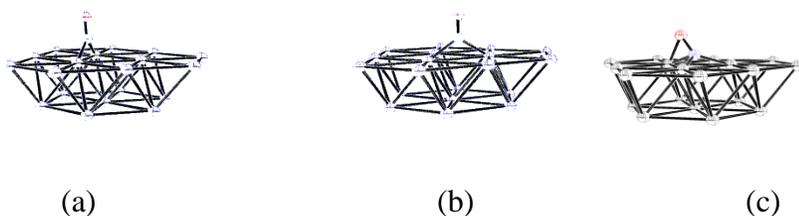
Where  $BE$  indicates binding energy,  $Al_n$  indicates aluminum bare cluster and 'n' is an integer

## RESULTS AND DISCUSSION

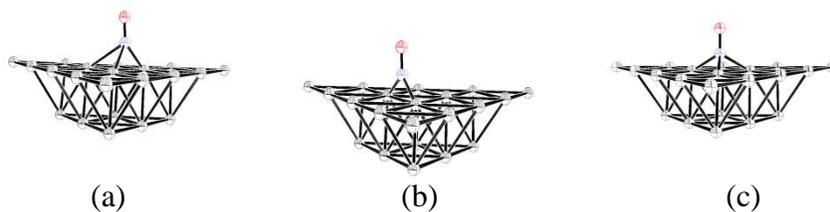
With the consideration of that NO adsorbed by different adsorption sites, the geometry optimization was done by the semi-empirical AM1 method. The graphical computer soft wares picked the bond distances of Al-N, and N-O from the optimized structure and the total energy also read from the output files of the different cluster calculation. The total energy of the bare cluster was calculated by semi empirical single point energy calculation with the spin multiplicity of 2. From these values binding energy of the NO with aluminum clusters was calculated.

### Aluminum cluster models for NO adsorption on the Al (111) surface

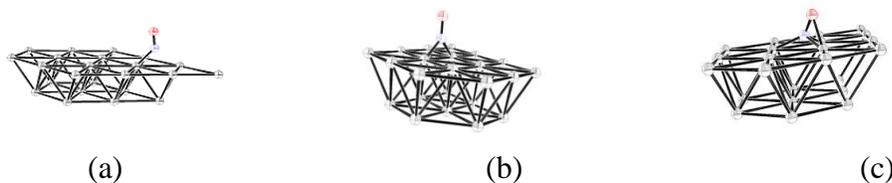
The number of electrons involved in NO molecule is 15 (odd number). Therefore it is called as an open-shell system. Multiplicity of one used for cluster contains an even number of aluminum atoms.



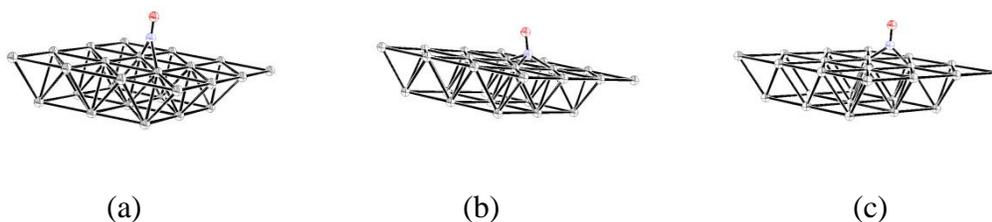
**Figure 1: NO adsorption on Al<sub>19</sub> cluster, (a) Adsorption on on-top site, (b) adsorption on bridge site and (c) adsorption on three-fold site**



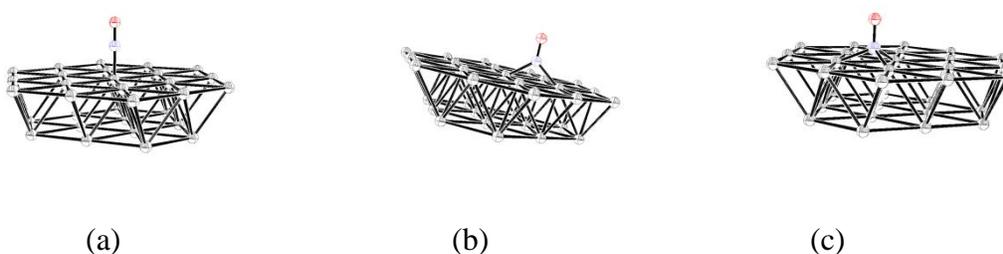
**Figure 2: NO adsorption on Al<sub>21</sub> cluster, (a) Adsorption on on-top site, (b) adsorption on bridge site and (c) adsorption on three-fold site**



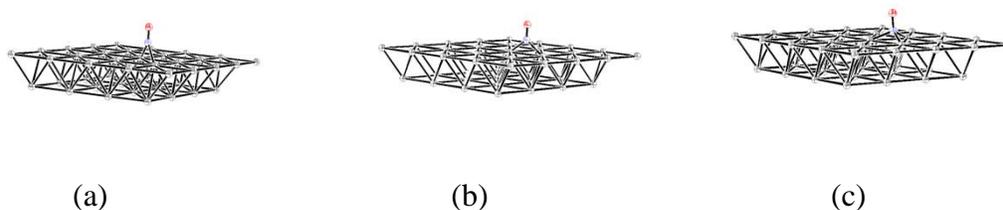
**Figure 3: NO adsorption on Al<sub>23</sub> cluster, (a) Adsorption on on-top site, (b) adsorption on bridge site and (c) adsorption on three-fold site**



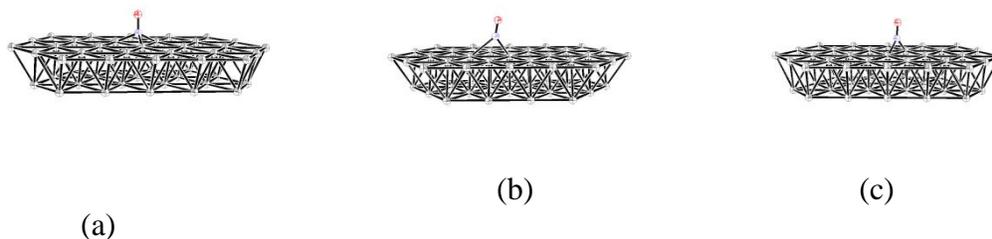
**Figure 4: NO adsorption on Al<sub>25</sub> cluster, (a) Adsorption on on-top site,(b) adsorption on bridge site and (c) adsorption on three-fold site**



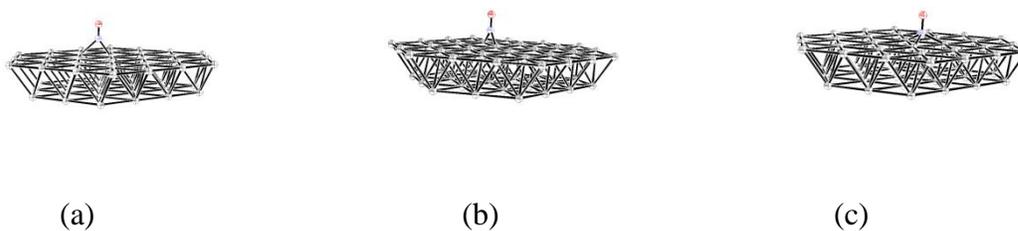
**Figure 5: NO adsorption on Al<sub>31</sub> cluster, (a) Adsorption on on-top site,(b) adsorption on bridge site and (c) adsorption on three-fold site**



**Figure 6: NO adsorption on Al<sub>41</sub> cluster, (a) Adsorption on on-top site,(b) adsorption on bridge site and (c) adsorption on three-fold site**



**Figure 7: NO adsorption on Al<sub>49</sub> cluster, (a) Adsorption on on-top site (b) adsorption on bridge site and (c) adsorption on three-fold site**



**Figure 8: NO adsorption on Al<sub>51</sub> cluster, (a) Adsorption on on-top site, (b) adsorption on bridge site and (c) adsorption on three-fold site**

**Table1: Total energy of bare cluster in eV**

Bare cluster	Total energy
Al <sub>19</sub>	-927.06
Al <sub>21</sub>	-1022.09
Al <sub>23</sub>	-1122.90
Al <sub>25</sub>	-1220.74
Al <sub>31</sub>	-1517.49
Al <sub>41</sub>	-2008.01
Al <sub>49</sub>	-2402.41
Al <sub>51</sub>	-2501.07

Table 2: Binding energy of different sites of NO adsorption

Cluster	On top	Bridge site	Hollow site
Al <sub>19</sub>	-1.71*	-1.71	-1.50
Al <sub>21</sub>	-1.09**	-1.88	-1.56
Al <sub>23</sub>	-1.31****	-1.41	-1.23
Al <sub>25</sub>	-1.12***	-1.39	-1.15
Al <sub>31</sub>	-0.71	-1.03	-0.81
Al <sub>41</sub>	-0.84***	-1.06	-0.94
Al <sub>49</sub>	-0.90***	-1.42	-1.18
Al <sub>51</sub>	-1.06***	-1.39	-1.20

\*Indicates NO moves to the bridge site after the geometry optimization.

\*\*Indicates NO adsorbed closer to the three-fold site after the geometry optimization.

\*\*\*Indicates NO adsorbed closer to the bridge site after the geometry optimization.

\*\*\*\* Indicates NO adsorbed bent like manner after the geometry optimization.

**Table 3:** Al-N Bond length for the different sites of NO adsorption on different aluminum clusters in Angstrom.

Cluster	On top	Bridge site	Hollow site
Al <sub>19</sub>	1.788	1.788	1.759
Al <sub>21</sub>	1.739	1.800	1.887
Al <sub>23</sub>	1.751	1.778	1.795
Al <sub>25</sub>	1.777	1.790	1.800
Al <sub>31</sub>	1.780	1.811	1.811
Al <sub>41</sub>	1.775	1.813	1.808
Al <sub>49</sub>	1.775	1.798	1.811
Al <sub>51</sub>	1.775	1.812	1.822

**Table 4:** N-O Bond length for the different sites of NO adsorption on different aluminum clusters

Cluster	On top	Bridge site	Hollow site
Al <sub>19</sub>	1.180	1.181	1.319
Al <sub>21</sub>	1.161	1.179	1.208
Al <sub>23</sub>	1.162	1.181	1.267
Al <sub>25</sub>	1.155	1.180	1.282
Al <sub>31</sub>	1.151	1.172	1.253
Al <sub>41</sub>	1.154	1.177	1.256
Al <sub>49</sub>	1.155	1.178	1.263
Al <sub>51</sub>	1.153	1.172	1.248

**Table 5:** Electron density for the different sites of NO adsorption on different aluminum clusters

Cluster	On top	Bridge site	Hollow site
Al <sub>19</sub>	10.97	10.97	11.37
Al <sub>21</sub>	11.05	10.10	11.25
Al <sub>23</sub>	10.90	10.94	11.01
Al <sub>25</sub>	10.94	10.95	11.31
Al <sub>31</sub>	11.12	10.97	11.35
Al <sub>41</sub>	11.01	11.03	11.31
Al <sub>49</sub>	11.02	10.99	11.41
Al <sub>51</sub>	11.02	10.98	11.37

The binding energy and the geometry were appreciably different for the atop, bridging and hollow site adsorption on different cluster models. The large binding energy differences observed in atop adsorption was about 1.00 eV (i.e.  $E_b$  difference between Al<sub>19</sub> and Al<sub>31</sub>) and the difference in the bond distances of Al-N and N-O are 0.049 Å and 0.029 Å respectively. The most negative value of binding energy of -1.71 eV in respect of on top adsorption was obtained for Al<sub>19</sub> cluster. However, the NO molecule moved to a bridging position after optimization. The large binding energy differences observed in bridging site adsorption is about 0.85 eV (i.e.  $E_b$  difference between Al<sub>21</sub> and Al<sub>31</sub>) and the difference in the bond distances Al-N and the N-O are 0.035 Å and 0.009 Å respectively. The more negative value of binding energy of -1.88 eV obtained from the Al<sub>21</sub> cluster model. The large binding energy differences observed in hollow site adsorption is about 0.75 eV (i.e.  $E_b$  difference between Al<sub>21</sub> and Al<sub>31</sub>) and the difference in the bond distances Al-N and the N-O are 0.128 Å and 0.111 Å respectively. The more negative values of binding energies of -1.56 eV and -1.50 eV obtained from the Al<sub>21</sub> and the Al<sub>19</sub> cluster model.

In all cases of cluster the higher coordinate adsorptions (bridge and three-fold) were more favoured than the on top adsorption. This could be explained by the terms of steric and molecular orbital components.

Based on the molecular orbital theory, the shift of NO to higher coordinate sites takes place as a result of the destabilization of the metal valence band due to charge transfer from the adsorbed substrate (NO). This shift of the metal valence  $sp$  band closer in energy to the empty NO  $\pi^*$  orbital energy level leads to increased  $\pi^*$  orbital mixing and stabilization of metal  $sp$  band orbitals and decreased donation stabilization from the  $5\sigma$  orbital of substrates (NO). As a result, strong  $\pi^*$  mixing favors high coordinated sites and strong  $5\sigma$  mixing favors the on top site which explains the shift to higher coordinate sites when NO chemisorbed by different Al (111) surfaces. Based on the steric effect, one might expect that the metal chemisorbate steric interaction would be larger in the hollow and the bridge site than the on top sites. This apparent anomaly is resolved by recognizing that the greater steric repulsion associated with hollow and bridge site bonding is more than offset by a decrease in the intramolecular bond repulsion caused by greater N-O bond elongation in the higher coordination sites (bridge and hollow). This also shows that higher coordinated adsorption sites more for NO adsorption on Al (111) surfaces.

When the bond distance of N-O is compared with the bond distance of equilibrium separation for free NO (1.151 Å) it was more elongated for three-fold and bridge site adsorption. This could be explained by the formation of chemical bond formed by chemisorption is strong for higher coordinated adsorption site rather than lower coordinated site (i.e. more negative binding values indicate which adsorption site is favoured and also stronger surface chemisorbed binding with metals). The bond distance of Al-N also increase with the coordination of the adsorption site (calculated value of Al-N obtained from previous studies is around 1.80 Å).

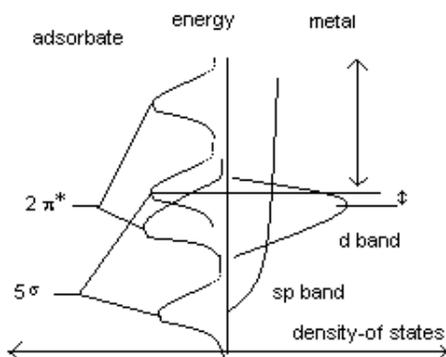
When the total HF (Hartree-Fock) -energy of bare cluster obtained in Table 1 was compared, the more negative values assigned to large aluminum clusters. The reason is in large clusters have high electron density around the cluster due to its higher number of valence electrons. This can be reduced the repulsion effects engaging in modeled clusters.

Some optimized cluster models M-NO (where M is transition metal) show a bent like configuration rather than the linear. This is due to the mechanism for reducing the  $5\sigma$  repulsion of the NO on M-NO. Blanchard<sup>15</sup> pointed that the transition metals in right side of the periodic table generally show this type of behavior.

When the electron density was observed (amount of charge transfer) around NO, it could be say that the charge transfer is occurred between the  $5\sigma$  and  $\pi^*$  molecular orbitals on NO and the  $s$  and  $p$  orbitals (or  $sp$  band) of aluminum cluster. Commonly accepted idea of the NO bonding in metal systems is  $\sigma$  donation and  $\pi$  back donation. In the case of NO adsorption, electron density is significantly increased in three-fold site adsorption compared to the NO electron density of 11.00 for free NO and there is a very small difference observed in other two adsorption sites.

According to the classical Blyholder model<sup>12</sup>, the orbital interactions NO adsorbed on metal surfaces consist mainly of the  $5\sigma$  donation and  $2\pi^*$  back-donation contributions, as illustrated in

Figure 9. Both the  $5\sigma$  donation and  $2\pi^*$  levels split up into bonding and antibonding resonance due to their interaction with localized  $sp$ -band states. Since the  $5\sigma$  state is low lying in energy, binding in low-coordination sites can minimize its antibonding contribution. For the  $2\pi^*$  level, on the other hand, the bonding resonance has a significant density-of-states near the Fermi level, whereas its antibonding resonance is usually of high energy so that it does not play a role. On this basis, the back-donation interaction should favor chemisorbate binding at high-coordination sites. Conversely, the donation term is more favorable for atop and bridge coordination. When the direction of adsorption was considered, the NO molecule is placed in  $z$ -axis, and N atom pointed towards the aluminum atoms. Therefore the  $p_z$  orbital of aluminum is involved in interaction with  $5\sigma$  and  $\pi^*$  molecular orbitals of NO in on top, and  $p_x$  and  $p_y$  orbitals are involved in bridge and three-fold site adsorption.



**Figure 9: Orbital energy-level diagram for metal- chemisorbate systems<sup>12</sup>**

## CONCLUSION

Based on our result, the more negative value of binding energy obtained for the small clusters in all on top, bridge and three- fold site adsorptions. And the same time the most negative value of binding energy obtained for bridge in some cases three-fold site adsorption in all clusters. Therefore it is concluded that the NO adsorbs preferentially on bridge and also three-fold site in all cluster models. And also the geometry optimization of on top converged to bridge, close to bridge and the three-fold site geometry in their final geometry; the on top adsorptions are unstable.

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