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14. ABSTRACT

First-principles density functional theory (DFT) calculations using the generalized gradient approximation (GGA) have been used to expand the analysis of the adsorption properties of polynitrogen and high nitrogen compounds on Al(111) and AlN(0001) surfaces. The electron-ion interaction has been described using ultrasoft (PAW) pseudopotentials in the case of Al (AlN). All calculations have been done using the PW91 generalized gradient approximation. Specifically, we have considered representative six-membered P-N-C heterocycles containing azide ligands on the C and P atoms such as $C_2N_{15}P$, $CN_{18}P_2$ and $N_{21}P_3$ systems. Additionally, we extended our analysis by including compounds containing the nitrogen rich CN_7^- anion (i.e., the energetic salts $NH_4^+CN_7^-$, $N_2H_5^+CN_7^-$, and $CN_4H_7^+CN_7^-$) and heterocyclic-based ionic systems ($C_2N_3H_4^+$- NO_3^-) for which direct optimizations and ab initio molecular dynamics simulations have been performed. Finally, the interaction properties of atomic and molecular oxygen and of other energetic species like nitromethane (CH_3NO_2) with AlN(0001) and AlN $(000\bar{1})$ surfaces have been analyzed.

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Polynitrogen/Nanoaluminum Surface Interactions

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Abstract

First-principles density functional theory (DFT) calculations using the generalized gradient approximation (GGA) have been used to expand the analysis of the adsorption properties of polynitrogen and high nitrogen compounds on Al(111) and AlN(0001) surfaces. The electron-ion interaction has been described using ultrasoft (PAW) pseudopotentials in the case of Al (AlN). All calculations have been done using the PW91 generalized gradient approximation. In the case of Al, the calculations employ periodic slab models with 4 layers, ranging in size from (4×4) to (6×6) surface unit cells, and containing up to 144 Al atoms. For AlN, slab models with (2x2) and (3x3) unit cells and with 8 an 4dual AlN layers, respectively, have been considered. Complementary quantum chemical calculations, utilizing DFT and second-order perturbation theory methods, of the ground state potential energy surfaces of the corresponding polynitrogen/high nitrogen species in the absence of the aluminum surface also have been performed. Previous results obtained in the first two years of this challenge project, related to adsorption properties of all nitrogen N_x(x=1-6,8-12) compounds or of non-substituted and mono-substituted triazenes have been extended to the case of high nitrogen heterocycle systems. Specifically, we have considered representative six-membered P-N-C heterocycles containing azide ligands on the C and P atoms such as $C_2N_{15}P$, $CN_{18}P_2$ and $N_{21}P_3$ systems. Additionally, we extended our analysis by including compounds containing the nitrogen rich CN_7^- anion (i.e., the energetic salts $NH_4^+CN_7^-$, $N_2H_5^+CN_7^-$, and $CN_4H_7^+CN_7^-$) and heterocyclic-based ionic systems ($C_2N_3H_4^+$- NO_3^-) for which direct optimizations and ab initio molecular dynamics simulations have been performed. Finally, the interaction properties of atomic and molecular oxygen and of other energetic species like nitromethane (CH_3NO_2) with AlN(0001) and AlN$(000\bar{1})$ surfaces have been analyzed. For these systems the individual bonding mechanism involving either nondissociative (molecular) or dissociative processes has been determined, depending on both the molecular orientation and the surface sites involved. The binding energies were found to be highly sensitive to the specific adsorbed species and its local configuration. Dissociation processes were also found to be highly exothermic.

1. Introduction

Investigation of the interactions of energetic high-nitrogen compounds with ultrafine or nanophase aluminum particles is a topic of current DoD interest with potential applications in rocket and missile propulsion. One of the topics of prime importance is to determine if the thermal instability inherent in many high nitrogen compounds might be reduced by adsorption or chemisorption onto the surface of aluminum, while simultaneously forming a protective coating on the metal surface which minimizes the formation of an inert oxide surface layer.

2. Computational Methods

The calculations performed in this study were done using the Vienna *ab initio* simulation package (VASP).[1-3] This program evaluates the total energy of periodically repeating geometries based on density-functional theory and the pseudopotential approximation. For calculations on the Al surface the electron-ion interaction is described by fully non-local optimized ultrasoft pseudopotentials[4] while the projector augmented wave (PAW) method of Blöchl [5] was used for the AlN surface. This difference in treatment was due to availability of PAW pseudopotentials for partially charged H atoms used in the AlN slab calculations. Periodic boundary conditions were used, with the one-electron pseudo-orbitals expanded over a plane-wave basis set with cutoff energies of 435 eV for Al and 500 eV for AlN. These cutoff energies are consistent to the precision level required by the VASP code for the chemical species of interest. Calculations were performed using the generalized gradient approximation (GGA) density functional theory with the PW91 exchange-correlation functional.[6] The sampling of the Brillouin zone was performed using a Monkhorst-Pack scheme.[7] The minimum energy path between different minima was determined using the climbing image nudged elastic band method developed by Jónsson and co-workers.[8,9]

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The GAMESS[10] quantum chemistry code was used to predict the structures and properties of isolated polynitrogen and high-nitrogen compounds. The theoretical methods employed included second order perturbation theory[11] (MP2, also known as MBPT(2)) and density functional theory (DFT) using the hybrid B3LYP[12] functional. The 6-311G(2df,p) and 6-311++G(2df,p)[13] basis sets were used for nonionic and ionic species, respectively.

3. Results and Discussion

Extension of our comprehensive analysis of the interaction between high-nitrogen and polynitrogen compounds with aluminum surface was done by considering four new classes of nitrogen systems. The first class consists of high nitrogen heterocyclic systems. In this case we have considered the case of six-membered P-N-C heterocycles containing azide ligands on the C and P atoms such as $C_2N_{15}P$, $CN_{18}P_2$ and $N_{21}P_3$.

The second class is comprised of salts of the CN_7^- anion. As shown very recently,[14] such systems represent promising candidates for development of nitrogen-rich green energetic materials. For this set of compounds we have analyzed several high explosive salts containing the CN_7^- anion, namely the hydrazinium ($[N_2H_5][CN_7]$), ammonium ($[NH_4][CN_7]$) and aminoguanidinium ($[CN_4H_7][CN_7]$) salts.[14]

The third class of systems includes compounds which combine an oxygen-rich dinitramide anion with a nitrogen-rich cation such as 1,5-diamino-4-methyltetrazolium dinitramide ($[C_2N_6H_6][N_3O_4]$). Such systems[15] represent promising candidates for development of new tetrazole-based oxidizers. Finally, we extended our analysis to the case of heterocyclic-based ionic systems ($C_2N_3H_4^+$-NO_3^-) for which direct optimizations and ab initio molecular dynamics simulations have been performed.

The adsorption studies of the above described systems have been studied using 3D periodic slab models of different sizes. These range from (4×4) surface supercells used in the case of small systems to (6×6) surface units for the largest systems. In all cases, the slab models contained four layers of atoms. The optimizations have been performed for both the adsorbate and the Al atoms in the top two layers while the bottom two layers were frozen at the bulk optimized conditions. Adsorption at different surface sites and for different molecular orientations have been investigated and the corresponding adsorption energies have been calculated using the expression $\mathbf{E_{ads}=E_{molec}+E_{slab}-E_{(molec+slab)}}$, where E_{molec} is the energy of the isolated molecular species at its equilibrium geometry, E_{slab} is the total energy of the isolated aluminum slab, and $E_{(molec+slab)}$ is the total energy of the adsorbate/slab system. A positive E_{ads} corresponds to a thermodynamically stable adsorbate/slab system.

<u>P-N-C Heterocycles Adsorption on on Al(111)</u>. The adsorption properties of $C_2N_{15}P$, $CN_{18}P_2$ and $N_{21}P_3$ systems have been evaluated using a (6x6) slab model. Representative adsorption configurations are presented in Figure 1 and the corresponding binding energies are summarized in Table I. In the case of $C_2N_{15}P$, several distinct binding configurations were found, including non-dissociative adsorptions. A representative configuration of this type is shown in Figure 1a in which adsorption takes place with formation of multiple Al-N bonds. Additional similar configurations were found, with adsorption energies ranging from 60.1 to 65.9 kcal/mol. The presence of N_3 groups in close proximity to the surface can also lead to bond fragmentation and elimination of one (Figure 1b) or two (Figures 1c and 1d) molecules of N_2. The dissociative adsorption of $C_2N_{15}P$ was found to be highly exothermic, with dissociation enthalpies as high as 92.3 kcal/mol relative to the adsorbed, undissociated state (Figure 1a).

Similar adsorption characteristics were found for the other two heterocycle systems $CN_{18}P_2$ and $N_{21}P_3$. Specifically, molecular (undissociated) adsorption states were found to be possible for both types of species (see Figures 1e, 1i, and 1j). The non-dissociative configurations form varying number of Al-N bonds, which in turn lead to a spread in the calculated binding energies. For example, the binding energies of the non-dissociative configurations illustrated in Figures 1i and 1j are 49.5 kcal/mol and 80.9 kcal/mol, respectively, in which four and six Al-N bonds, respectively, are formed. Dissociative adsorption was also found to take place for both $CN_{18}P_2$ and $N_{21}P_3$ compounds and the overall processes are highly exothermic. Representative dissociative binding configurations are illustrated in Figure 1, corresponding to formation of $CN_{16}P+N_2$, (panel 1f), $CN_{14}P$ $+2N_2$ (panels 1g and 1h), $N_{19}P_3+N_2$ (panel 1k), and $N_{17}P_3+2N_2$ (panel 1l). In all these cases formation and desorption of N_2 molecules was found to be thermodynamically favored. The presence of several Al-N bonds in these cases contributes to the increased stability of these systems.

<u>Adsorption of CN_7 Salts Systems</u>. A primary objective of the adsorption studies of $[CN_7]^-$ salts on the Al(111) surface is to determine how ionic adsorption differs from adsorption of neutral compounds. For all three cases investigated; i.e. for hydrazinium ($[N_2H_5][CN_7]$), ammonium ($[NH_4][CN_7]$) and aminoguanidinium ($[CN_4H_7][CN_7]$) salts, the anion was found to bind directly to the Al surface. Additionally, the anion serves as an anchor center for the cation system. Such representative adsorption configurations are depicted in Figure 2.

In the case of hydrazinium 5-azidotetrazolate, the $[CN_7]^-$ anion can adsorb either non-dissociatively (see Figure 2a) or dissociatively with elimination of a N_2 molecule (see Figure 2b). In both instances, bonding to the surface is mediated by formation of several Al-N bonds. The resultant CN_7 or CN_5 fragments bonded directly to the surface also function to anchor the corresponding $[N_2H_5]^+$ cation. Furthermore, this can take place either with (Figure

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2c and 2d) or without (Figures 2a and 2b) proton transfer from the cation to the anion, with the former process being energetically favored (see Table 1.) Additionally, adsorption of the $[CN_7]^-$ anion with subsequent elimination of N_2 molecules is also more exothermic than non-dissociative adsorption.

In the case of ammonium 5-azidotetrazolate ($[NH_4]^+[CN_7]^-$; see panels 2e-2h) the primary bonding to the surface is also through the $[CN_7]^-$ anion. Not surprisingly, the corresponding adsorption energies increase with the number of Al-N bonds. The cation remains bonded to the adsorbed anion and in all instances charge neutralization takes place via proton transfer from the cation to the anion. The energetically most favorable process is dissociative absorption of the anion, leading to desorption of N_2 and chemisorption of the remaining CN_5 fragment, as illustrated in Figure 2h.

Similar behavior is observed in the case of the 1-aminoguanidinium 5-azidotetrazolate ($[CN_4H_7]^+[CN_7]^-$) salt (see Figures 2i-2l.) The adsorption energies increase with the increase in number of Al-N bonds between $[CN_7]^-$ and the Al surface. Additionally, dissociative adsorption of the anion with formation of N_2 is found to be energetically favorable. A unique feature of this system is that no proton transfer from the $[CN_4H_7]^+$ cation to the $[CN_7]^-$ anion is observed for any of the adsorption configurations investigated.

Adsorption of 1,5-diamino-4-methyltetrazolium dinitramide (DMTD) In the case of DMTD, which contains both an oxygen-rich dinitramide anion and a nitrogen-rich cation, adsorption to the surface can take place through both the anion and the cation. In the majority of cases investigated, adsorption takes place with dissociation of dinitramide anion (see Figure 3) and formation of strong Al-O bonds via isolated O atoms or NO_2 fragments. Additionally, formation and desorption of N_2 molecules is also observed. The overall reactions are highly exothermic due to the large energy release upon formation of Al-O bonds.

Adsorption of O species on AlN Surface One of the fundamental issues considered in this study is the possibility of using AlN as a coating to inhibit or prevent formation of oxide layers on the aluminum surface. For this purpose the adsorption properties of atomic and molecular oxygen on different surfaces of AlN are analyzed. Given the nature of the AlN crystal with alternating layers of Al and N atoms, both the Al terminated AlN(0001) surface and the N terminated $AlN(000\bar{1})$ surface are studied. These calculations have been done using 2x2 slab models with eight AlN layers and terminated with fractionally charged H atoms. The role of these pseudohydrogens is to saturate the dangling bonds in the bottom of the slabs and to prevent unphysical charge transfer between the top and the bottom surfaces of the slab. For the Al-terminated (0001) surface, both the regular surface and the surface model with one N atom adsorbed at the H3 hollow site are considered. This N-adatom model was shown previously to be the most stable structure under N-rich conditions.[16]

The main adsorption configurations of atomic oxygen on Al-terminated AlN(0001) surface are shown in Figure 4, panels a-c. The nomenclature used to identify these configurations is taken from ref. 16. Among the sites at hollow H3, hollow T4 and atop sites[16], the adsorption at H3 site is the most stable with a binding energy of 204.7 kcal/mol with respect to the isolated surface and an isolated O atom. The adsorption energy of the T4 site decreases to 168.6 kcal/mol due to the repulsive interaction between the adsorbed O atom and the N atom in the second surface layer. For the most stable adsorption site H3, increasing the coverage to 0.5 ML decreases the adsorption energy to 171 kcal/mol per oxygen atom. At a coverge of 1.0 ML, the adsorption energy drops further to 124.3 kcal/mol. In the case of the N-adatom model (Figures 4d and 4e), the binding energy of the O atom decreases somewhat but it remains strong with a maximum value of 108.1 kcal/mol corresponding to the H3 site (Figure 4d).

In the case of the N-terminated $AlN(000\bar{1})$ surface, adsorption on the Al-adatom H3 site, as illustrated in Figures 4f and 4g and shown before[16] to be the most stable site under N-rich conditions, has been investigated. As indicated in Table 1, the corresponding adsorption energies of atomic oxygen remain high due primarily to Al atom bonding. These results indicate that under N-rich conditions, the O atom can still interact strongly with Al atoms on the AlN surface, independent of Al or N termination of the surface.

As an extension of prior studies of the interactions of nitromethane (NM) on the α-Al_2O_3(0001) surface,[17] the adsorption properties of NM on AlN(0001) surface have been calculated. The results presented in Figure 4h and in Table 1 indicate the existence of a stable adsorption configuration with a binding energy of 133 kcal/mol. Molecular bonding in this case takes place by formation of both Al-O and Al-N bonds. From the initial adsorbed configuration (see Figure 4h) the NM molecule can easily dissociate by overcoming a barrier of about 8 kcal/mol with formation of adsorbed CH_3NO(a) + O(a) fragments. In a second reaction step, the remaining O atom of CH_3NO can be eliminated with formation of CH_3N(a)+2O(a). The overall reaction is highly exothermic by 161 kcal/mol. These results clearly indicate that the Al terminated AlN surface can also function to efficiently adsorb and dissociate the NM molecule.

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4. Conclusions

A systematic study of a series of (a) P-N-C heterocycles containing azide ligands, (b) salts consisting of the $[CN_7]^-$ anion paired with hydrazinium, ammonium and aminoguanidinium cations, and (c) compounds containing both an oxygen-rich anion (dinitramide) and a nitrogen-rich cation (1,5-diamino-4-methyltetrazolium) interacting with the aluminum (111) surface have been performed using plane-wave DFT calculations in conjunction with aluminum surface slab models. These calculations indicate that, in the majority of cases molecular adsorption takes place by formation of multiple Al-N or, in the case of O-containing compounds, Al-O bonds. For the ensemble of molecular systems considered here, significant variation in binding energies has been predicted, depending on the number of surface bonds involved as well as the surface site and the molecular orientation. Additionally, adsorption is found to lead to significant molecular deformations and upward shifts of some of the surface aluminum atoms. For the high-nitrogen species investigated, dissociative adsorption readily occurs leading to desorption of N_2 molecules. Atomic oxygen binds strongly to the AlN surface. In such cases the presence of surface Al atoms or Al-adatoms is sufficient to lead to large adsorption energies. Dissociation of NM was found to be highly exoenergetic and to take place with a small activation energy on the Al-terminated (0001) AlN surface.

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Table I. Calculated adsorbate binding energies, in kcal/mol, for various systems analyzed in this study (indicated in parentheses) together with the corresponding supercell model used in simulations.

Adsorbate	Binding Energies (kcal/mol)	Supercell Model
$C_2N_{15}P$	60.1 **(1a),** 115.8 **(1b)**, 138.7 **(1c),** 152.4 **(1d)**	6x6
$CN_{18}P_2$	55.8 **(1e)**, 139.9 **(1f),** 157.8 **(1g),** 180.4 **(1h)**	6x6
$N_{21}P_3$	49.5 **(1i),** 80.9 **(1j),** 110.3 **(1k)**, 149.3 **(1l)**	6x6
$[N_2H_5][CN_7]$	41.0 **(2a),** 63.0 **(2b),** 65.5 **(2c),** 80.9 **(2d)**	4x4
$[NH_4][CN_7]$	14.0 **(2e),** 40.9 **(2f),** 44.4 **(2g),** 93.5 **(2h)**	4x4
$[CN_4H_7][CN_7]$	24.8 **(2i),** 34.7 **(2j),** 54.5 **(2k)**, 91.6 **(2l)**	4x4
DMTD	20.4 **(3a),** 121.**9 (3b),** 127.5 **(3c),** 242.9 **(3d)**	4x4
O/AlN(0001)	204.7 **(4a)**, 168.6 **(4b),** 150.4 **(4c)**	2x2
O/N adatom H3/AlN(0001)	108.1 **(4d)**, 98.7 **(4e)**	2x2
O/Al adatom H3/AlN $(000\bar{1})$	100.5 **(4f),** 80.0 **(4g)**	2x2
NM/AlN(0001)	133.0 **(4h)**	3x3

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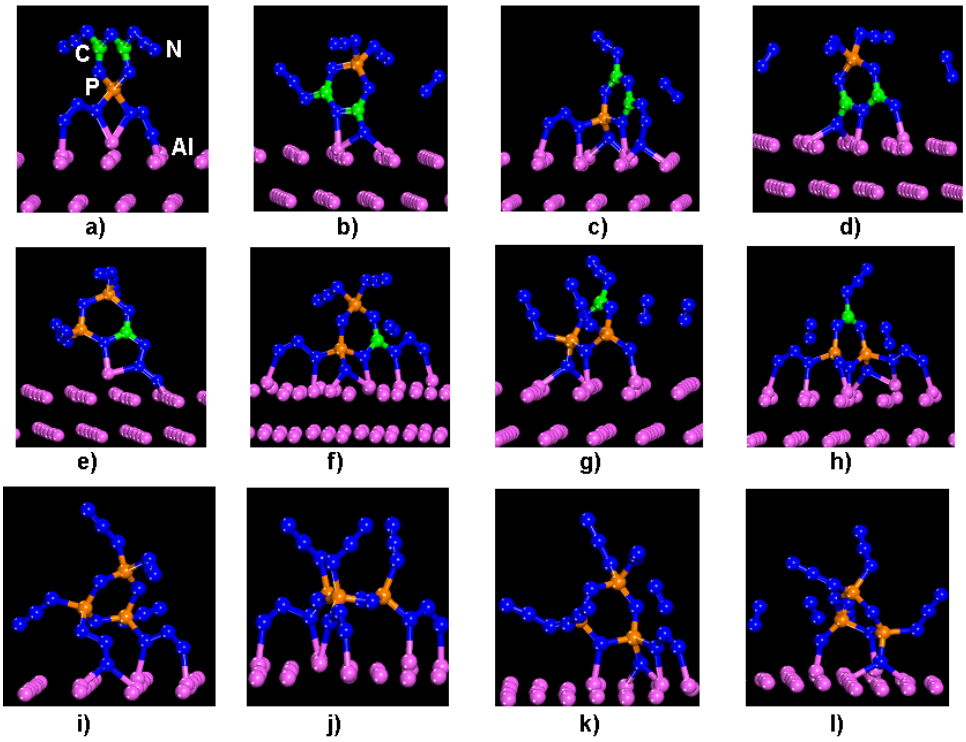

Figure 1 Side views of representative adsorption configurations of $C_2N_{15}P$ (panels a-d), $CN_{18}P_2$ (panels e-h) and $N_{21}P_3$ (panels i-l) on Al(111) surfaces.

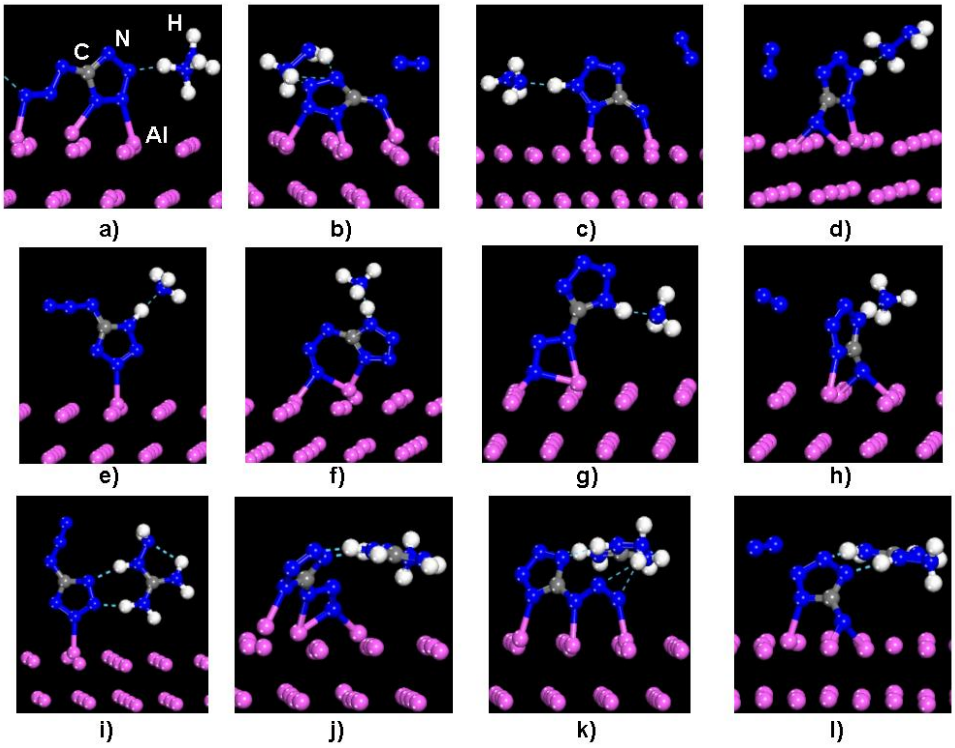

Figure 2. Side views of representative binding configurations of $[N_2H_5][CN_7]$ (a–d), $[NH_4][CN_7]$ (e-h) and $[CN_4H_7][CN_7]$ (i-l),

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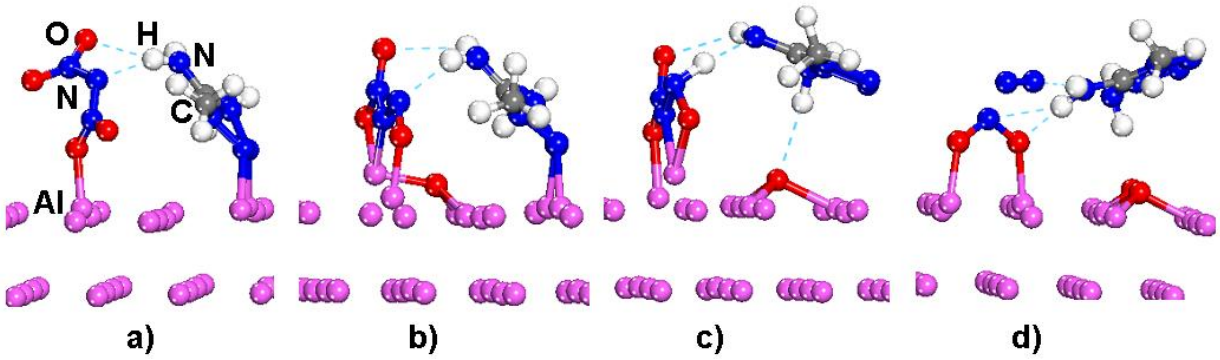

Figure 3. Pictorial views of the adsorption configurations of DMTD on Al(111) surface.

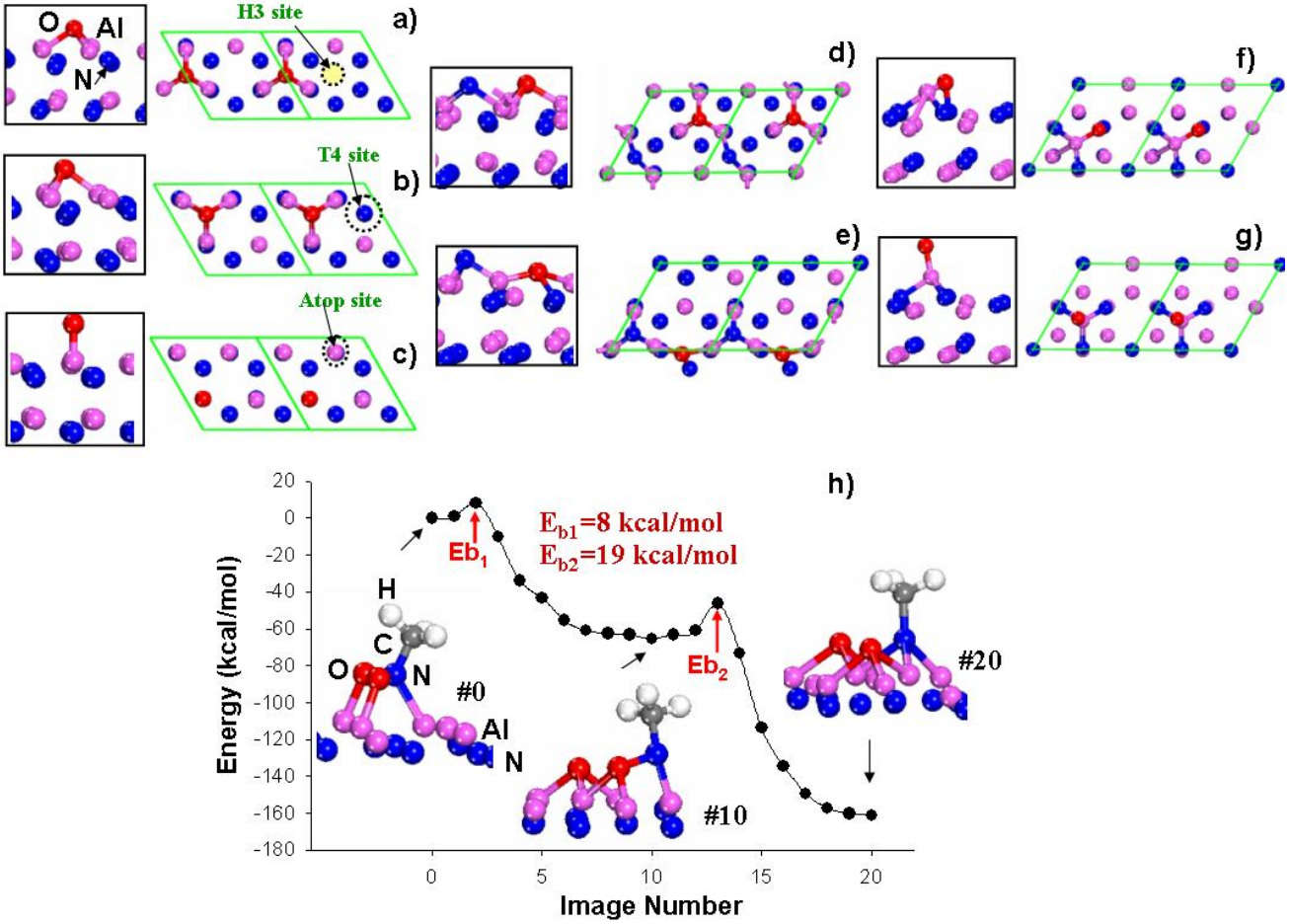

Figure 4. Side and top views of the oxygen adsorption configurations on AlN(0001) (a-c), N-adatom AlN(0001) (d-e) and Al-adatom AlN $(000\bar{1})$ (f-g). Configurations (a-c) correspond to adsorption at hollow H3, hollow T4 and on-top sites, on Al terminated AlN(0001) surface. Panels d) and e) correspond to O adsorption at H3 and T4 sites in the presence of a coadsorbed N atom at H3 site. Panels f) and g) correspond to O adsorption on N terminated Al(000-1) surface when a coadsorbed Al is presented at a H3 hollow site. Panel h) indicates the minimum energy potential pathways for dissociation of nitromethane on AlN(0001) surface leading to formation of NCH_3(a) radical and two adsorbed O atoms .

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