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First Principles Calculations of the Chemisorption Properties of Nitro-Containing Molecules on the Al₂O₃(0001) Surface

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Abstract

First-principles calculations based on density functional theory (DFT) and the generalized gradient approximation (GGA) have been used to study the adsorption of nitromethane (NM) and 1,1-diamino-2,2-dinitroethylene (FOX7) molecules on the basal plane of α -Al₂O₃ crystal. The calculations employ a (2x2) supercell slab model and 3D periodic boundary conditions. Based on these calculations we have determined that both NM and FOX7 molecules can adsorb nondissociatively on the surface, with the most stable adsorption configurations parallel to the surface. The corresponding binding energies are found in the range 25.3–26.0 kcal/mol for NM and 35.6–48.3 kcal/mol for FOX-7 depending on the relative molecular orientation and the corresponding surface sites. The minimum energy pathways for NM dissociation have been determined and a low energy pathway leading to H elimination with formation of adsorbed CH₂NO₂ and hydroxyl species has been identified. Additional calculations have focused on adsorption properties of aci-nitromethane tautomers and on description of the energetic pathways connecting adsorbed nitromethane molecule with these tautomers.

1. Introduction

Powderized aluminum has long been used as an energetic ingredient in rocket propellant formulations, comprising approximately 15–20% of conventional ammonium perchlorate solid propellant.^[1] Its primary roles are to increase the combustion exothermicity and the regression rate of solid propellant grains and to enhance the blasting effect of explosives. Moreover, aluminum particles have been found to have beneficial effects by

reducing the combustion instabilities in rocket motors.^[2,3] The efficiency of such processes has been found, however, to depend on the size of the Al particles. For example, in the case of Al nanopowders significant improvements in the performance of some energetic materials over the common micron-size Al powders have been reported.^[4,5]

2. Computational Method

The calculations performed in this study were done using the Vienna *ab initio* simulation package (VASP).^[6–8] This program evaluates the total energy of periodically repeating geometries based on density-functional theory and the pseudopotential approximation. In this case the electron-ion interaction is described by fully non-local optimized ultrasoft pseudopotentials similar to those introduced by Vanderbilt.^[9,10] Periodic boundary conditions are used, with the one-electron pseudo-orbitals expanded over a plane-wave basis set:

$$\Psi_i(\mathbf{r}) = \sum_G c_{iG} \exp(iG\mathbf{r}) \quad (1)$$

The expansion includes all plane waves whose kinetic energy, $\hbar^2\mathbf{k}^2/2m < E_{\text{cut}}$, where \mathbf{k} is the wave vector, m the electronic mass and E_{cut} is the chosen cutoff energy. In this study a cutoff energy of 495 eV is chosen which ensures the convergence with respect to the basis set. Calculations were performed using the generalized gradient approximation (GGA) density functional theory with PW91 exchange-correlation functional.^[11] The sampling of the Brillouin zone was performed using a Monkhorst-Pack scheme.^[12]

The minimum energy path between different minima was optimized by use of the nudged elastic band (NEB) method of Jónsson and co-workers.^[13] In this approach,

the reaction path is “discretized,” with the discrete configurations, or images, between minima being connected by elastic springs to prevent the images from sliding to the minima in the optimization.

3. Results and Discussion

NM Adsorption. The adsorption studies of NM on the α -Al₂O₃(0001) surface were done using a 2x2 supercell. Adsorptions at several surface sites and for distinct orientations of NM molecule relative to the surface were first examined. The corresponding adsorption energies calculated throughout this work were obtained based on the expression

$$E_{\text{ads}} = E_{\text{molec}} + E_{\text{slab}} - E_{(\text{molec}+\text{slab})} \quad (2)$$

where E_{molec} is the energy of the isolated NM molecule in its equilibrium position, E_{slab} is the total energy of the slab and $E_{(\text{molec}+\text{slab})}$ is the total energy of the adsorbate/slab system. A positive E_{ads} corresponds to a stable adsorbate/slab system. The energy of the isolated NM molecule was determined from calculations performed on a single NM molecule in a cubic cell of length 12 Å. The same Brillouin-zone sampling has been used to calculate the energies of the bare slab and of the molecule-slab systems

The first set of adsorption configurations investigated corresponds to the case where the NM molecule is adsorbed with the C-N bond perpendicular to the surface and the nitro group oriented towards the surface. Panels a1-d1 in Figure 1 present the initial configurations while panels a2-d2 present the corresponding final optimized configuration, subsequently denoted as NM(I), NM(II), NM(III) and NM(IV), respectively. In the optimization process, all the other atoms of the slab model and of the NM molecule were allowed to relax, with the exception of the bottom Al and O layers of the slab. Panels a1-c1 of Figure 1 illustrate the cases in which the NM molecule was placed initially directly on top of a surface O or Al atom or above an fcc hollow site. As indicated in panels a2-c2 of Figure 1, independent of the initial configuration of NM molecule, adsorption on the surface takes place by an initial bonding of one of the oxygen atoms of the nitro group to an Al atom of the surface. For all these upward configurations the binding energies have similar values in the range 19.3–19.7 kcal/mol. The lengths of the Al-O bonds formed upon adsorption range between 1.939–1.942 Å. Relative to the isolated molecule, the N-O1 bond involved in bonding to the surface is stretched by about 0.34–0.38 Å while the other N-O2 bond is slightly compressed by 0.02 Å. The existence of a strong interaction between NM and the oxide surface is also reflected by an upward shift of 0.63–0.71 Å of the Al

atom involved in bonding relative to the relaxed surface structure.

We have also investigated the case when the NM molecule was initially oriented perpendicular to the surface with the methyl group directed toward the surface (not shown). However this configuration was found not to lead to a stable minimum.

Another set of optimizations has been done in which the initial configuration of the NM molecule had both the C-N bond and the NO₂ group parallel to the surface. Several cases were tested in which the initial position of the N atom was placed either above Al or O atoms of the surface or above the hollow sites. The final results were similar, and we present a representative case (denoted hereafter as NM(IV)) in Figure 1d. As indicated in this figure, during the optimization process the nitro group, initially parallel to the surface (see Figure 1, panel d1), rotates to minimize the repulsive interactions with O atoms of the surface. In the final configuration (see Figure 1, panel d2), the nitro group is practically perpendicular to the surface plane leading to an eclipsed conformation of the NM molecule. In this state the major binding of the molecule to the surface takes place through the Al1-O1 bond. In this parallel adsorption configuration, the binding energy of the NM molecule increases to 26 kcal/mol. This value is about 7 kcal/mol higher than for the vertical adsorption configuration, indicating a more stable adsorption configuration.

Minimum Energy Path for NM Dissociation. Starting from the parallel adsorption configuration of NM on Al₂O₃(0001) surface (NM(IV)), two minimum energy pathways for molecular dissociation have been investigated. The first corresponds to CH bond scission with formation of a surface OH bond. The second pathway corresponds to the C-N bond dissociation with formation of adsorbed CH₃ and NO₂ species. As can be seen from plot a) in Figure 2, the activation energy for the CH bond rupture reaction is about 13.8 kcal/mol. The other process, corresponding to C-N bond breaking (see plot b in Figure 2), has a higher activation energy of about 37 kcal/mol. Both of these two activation energies are significantly smaller than the corresponding energies for gas phase molecules.

Acid-Nitromethane Adsorption on Al₂O₃(0001) Surface. In this study we have investigated the adsorption properties of both the cis and trans acid-nitromethane (a-NM) species on α -Al₂O₃(0001). A pictorial view of these configurations is given in Figure 3. When the OH group is on the side of the NM molecule toward the surface (configuration a-NM(I) in Figure 3a), the adsorption takes place with a binding energy slightly smaller than the one found for NM molecule, namely 24.2 kcal/mol. This energy is evaluated with respect to the energies of isolated slab and isolated a-NM molecule in a

cis configuration. However, when the binding energy is calculated with respect to the total energy of the isolated slab and of the isolated NM molecule in the gas phase, the corresponding value is only 12.3 kcal/mol. Beside the cis a-NM(I) configuration, we have also attempted to optimize a trans a-NM configuration in which the OH is close to the surface. The final configuration a-NM(II) is represented in Figure 3b. In this case the O1H1 bond is rotated outward relative to C-N-O1 plan with a torsional angle $\tau(\text{C-N-O1-H1}) = -100.04^\circ$. The total binding energy of this configuration is 1.8 kcal/mol smaller than the one determined for a-NM(I) structure.

Finally, the other two configurations we have analyzed correspond to cis and trans forms for the case when the OH bond is oriented away from the surface. These configurations, denoted as a-NM(III) and a-NM(IV) are represented in Figures 3c and 3d. In these cases the binding energies relative to isolated NM molecule and isolated surface are 19.7 kcal/mol and 13.7 kcal/mol, respectively. These results indicate that among all four a-NM configurations, the a-NM(III) state corresponding to a cis tautomer with OH group far from the surface is the most stable followed by the trans a-NM(IV) tautomer.

Minimum Energy Potential Path Dissociation of a-NM(I). In this section we investigate the energetic requirements of a dissociation reaction of a-NM(I). The corresponding potential energy pathway for this process is represented in Figure 4. In this process, the H1 atom of a-NM(I) migrates from molecule to the surface and a new OH group (denoted as Os-H1) is formed. The remaining CH_2NO_2 radical also remains adsorbed on the surface. Upon dissociation, the hydroxyl group has a bond length $r(\text{Os-H1})=0.984 \text{ \AA}$ while the separation between H1 and the oxygen O1 of the CH_2NO_2 radical is $r(\text{O1...H1})=2.544 \text{ \AA}$.

FOX-7 Adsorption on $\text{Al}_2\text{O}_3(0001)$ Surface. Panel a1 of Figure 5 depicts the initial configuration of FOX-7 in which the C=C bond of FOX-7 is perpendicular to the surface and one of the O atoms from each of the nitro groups of the molecule are pointing towards the surface. Similarly, panel b1 of Figure 5 illustrates an initial configuration in which the FOX-7 molecule has been rotated such that C=C bond is oriented at about 55° from the surface normal and only one nitro group of the molecule points towards the surface. The molecular configurations corresponding to adsorption on the surface, starting from the initial structures given in panels a1 and b1 of Figure 5, are represented in panels a2 and b2 of the same figure. The corresponding adsorption energies for the two configurations are 19.7 kcal/mol and 22.8 kcal/mol, respectively.

Panels c1 and c2 of Figure 5 present initial and final configurations for the case in which the FOX-7 molecule

is adsorbed parallel to the surface such that lateral bonding of both nitro groups to the Al surface atoms can take place. In this case one O atom from each nitro group is bonded to one of the Al atoms while the other O atom of each nitro group is rotated away from the surface, due to repulsive interactions with surface O atoms. For this configuration, not only do both nitro groups participate in surface bonding but also do both amino groups. Particularly, each amino group has one of its hydrogen atoms participating in hydrogen bonding to O surface atoms. The binding energy for this configuration is significantly larger than that obtained for the vertical adsorption configurations with a value of 45.9 kcal/mol. We have also identified a parallel adsorption configuration in which binding can take place through both the N atom of an amine group and the O atom of a nitro group, but in this case the adsorption energy is somewhat smaller with a value of 35.6 kcal/mol

The results presented in this work indicate, as in the case of the NM system, the most stable adsorption configurations of FOX-7 molecule correspond to a parallel configuration. In both these cases multiple bonding can take place. We have identified configurations in which both nitro and amino groups can be involved in bonding to the surface. The main bonding seems to take place through formation of Al-O or Al-N bonds. Additionally, the H atoms of FOX-7 molecule can form hydrogen bonds to surface O atoms.

4. Conclusions

The interaction of NM and FOX-7 molecular systems with the $\text{Al}_2\text{O}_3(0001)$ surface has been investigated based on optimizations performed using plane-wave density functional theory calculations with PW91 exchange-correlation functional. Our calculations indicate that initial binding takes place through formation of Al-O bonds to the nitro group of NM or one of the nitro groups of FOX-7. The corresponding binding energies for such vertical configurations are similar, with values in the range 19.1–19.8 kcal/mol for NM and 19.7–22.8 kcal/mol in the case of FOX-7. However, for both these molecular species the most stable adsorption configurations correspond to the case when the molecules are laying parallel to the surface. For such geometries the binding energies increase to 26 kcal/mol for NM and 35.6–45.9 for FOX-7.

The second objective of this work was to analyze possible decomposition pathways of NM on the oxide surface and to evaluate the corresponding activation energies. We have determined that as a result of adsorption on the surface there are significant variations in the bond dissociation energies of NM. Our

calculations have indicated that H scission reaction to a nearby surface O atom can take place with a small activation energy of about 14 kcal/mol, while in the case of C-N bond dissociation reaction leading to adsorbed CH_3 and NO_2 fragments, the activation energy is about 38 kcal/mol. Both these values are significantly smaller than the corresponding activation energies for gas phase molecule.

The final objective of this study was to investigate the adsorption properties of various tautomeric forms of NM. Particularly we have analyzed four aci-NM tautomers and have determined that relative to isolated NM molecule and isolated slab surface the corresponding adsorption energies are 12.3, 10.5, 19.6 and, 13.7 kcal/mol for aci-NM(I), aci-NM(II), aci-NM(III) and aci-NM(IV), respectively.

Future work will extend this set of investigations to include the role played by oxygen surface defects upon chemisorption properties of nitro containing compounds.

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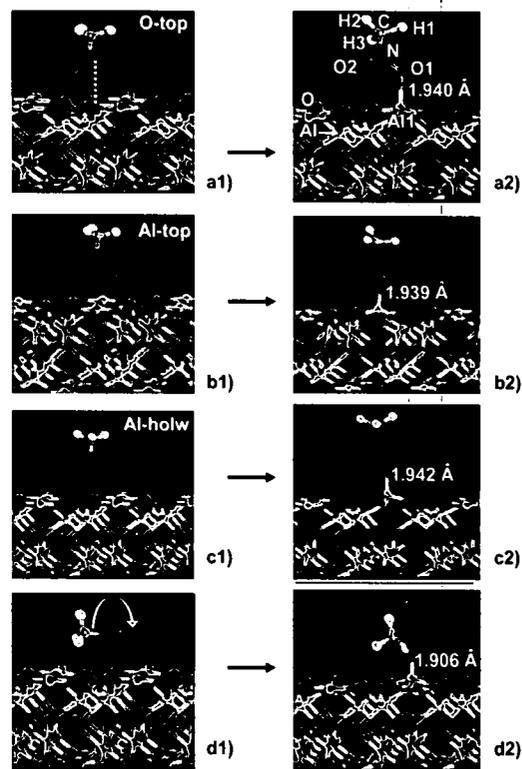


Figure 1. Initial and optimized structures of nitromethane interacting with $\text{Al}_2\text{O}_3(0001)$ surface

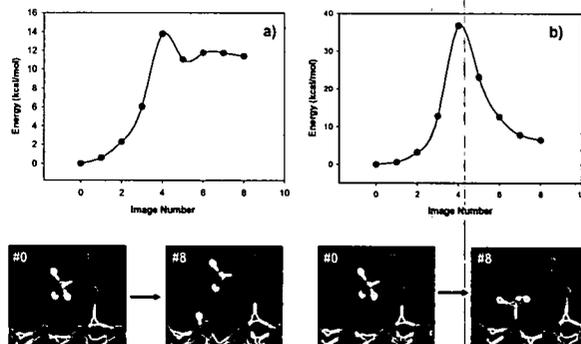


Figure 2. Minimum energy potential pathways for dissociation of NM molecule starting from the parallel adsorbed configuration: (a) H scission from methyl group with formation of CH_2NO_2 and OH species and (b) C-N bond dissociation with formation of adsorbed CH_3 and NO_2

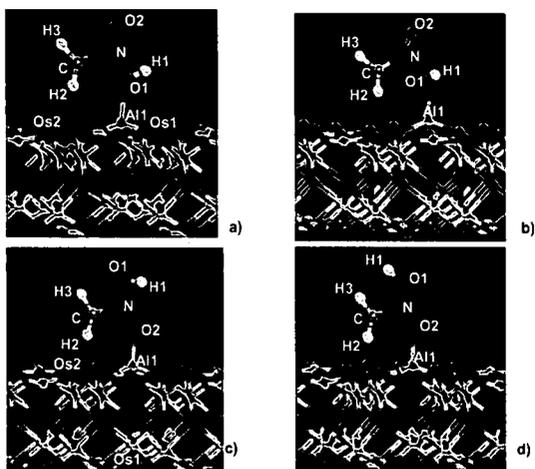


Figure 3. Adsorption configurations of cis and trans aci-nitromethane on Al_2O_3 (0001) surface

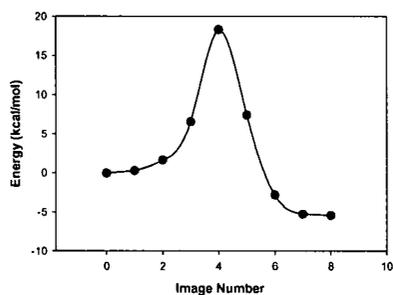


Figure 4. Minimum energy reaction pathway for dissociation reaction of a-NM(l) leading to adsorbed OH. The atomic configurations corresponding to the initial, transition states and final states are represented at the bottom of the figure.

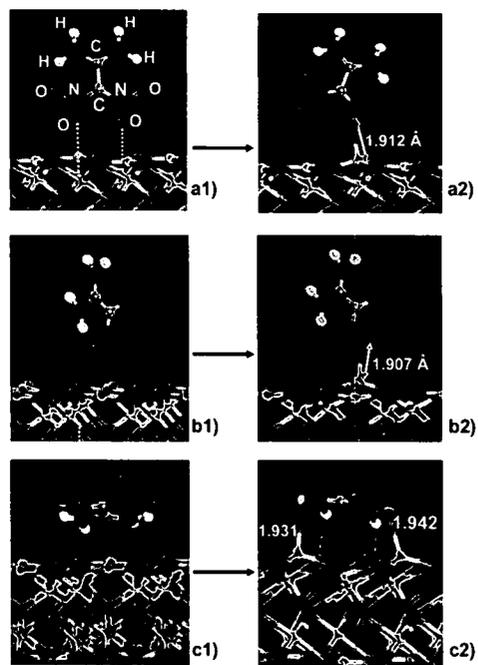


Figure 5. Initial and optimized structures of FOX-7 molecule adsorbed on Al_2O_3 (0001) surface