Quantum Chemical Study of the NO Adsorption on the WO_3 Nano-clusters

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Abstract: Ab initio calculations, using the density functional theory with the B3LYP functional, have been applied to study the NO adsorption on the $(WO_3)_n$ nano-clusters. For this study some general clusters with n=2, 3, 4, 6 have been chosen and fully optimized. The results show that the adsorption energy is not strongly dependent on the cluster size. The mean value of 25.4 kcal.mol^{-1} for adsorption energy confirmed the chemical nature of the NO and surface interaction which confirmed by AIM and NBO analysis.

Keywords: WO3, DFT, Adsorption, AIM, NBO analysis.

1.Introduction

A new class of nano-catalysts includes Tungsten oxide clusters in the form of $(wo_3)_n$ (n= 2, 3, 4, 6) supported on the metal oxides such as TiO_2, Sno_2 and Al_2O_3. Since these transition metal oxides have high catalytic activity, they can be used as gas sensor for determining and measuring the air pollutant chemicals and also are used in other industrial chemical processes such as isomerization and condensation of some organic compounds [1-3].

These catalytic behaviors can be interpreted by some chemical concepts such as Bronsted-Acid sites and chemical structure of the band gap in these materials. Air pollutant chemicals which possess oxygen and nitrogen atoms act as a Bronsted base at the surface of nano-cluster, thus the adsorption process can be interpreted as acid-base reaction.

In order to obtain a comprehensive understanding of the intermolecular interaction at the surface of nano-clusters and investigation of the size effects of these catalysts on the adsorption parameters, a theoretical study was done on the clusters of $(wo_3)_n$(n=2, 3, 4, 6), using the density functional theory (DFT) [4].

2. Theoretical procedure

$(wo_3)_n$(n=2, 3, 4, 6) structures were generated in the vacuum and fully optimized. To mimic the site of the $(wo_3)_n$ surfaces, some general clusters which experimentally confirmed [5] and contain 2, 3, 4, 6 W atoms were used (figure 1). For these types of nano-clusters, B3LYP level of the theory with the LANL2DZ basis set [6] was used as implemented in the gau

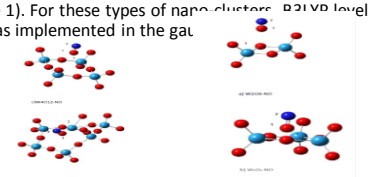

Figure 1. Optimized Structures of Nano-clusters

These models are electro neutral; the adsorption of NO molecule on these cluster models is investigated to reactivity of nano-crystality. On the other hand NO molecule has two atoms which, each of them can be considered as a Boronsted Base. Based on the adsorption site of the adsorbent, intermolecular interaction between the surface and NO molecule will be different from the energy point of view. Therefor different orientations of NO toward these nano-clusters were examined. Devaluate the uring these calculation for the geometry optimization NO molecule is taken relaxed but optimized structures of $(wo_3)_n$ were kept frozen. Atomic charges, intermolecular interactions and their characters are determined applying the NBO analysis (Natural Bond Orbital) [8] and Atoms in molecules (AIM) theory of Bader [9]. Computed interaction energies were corrected by the basis set supper position error (BSSE).

3. Result and discussion

Optimized structures of the NO adsorbed on the $(wo_3)_n$ (n=2, 3, 4, 6) clusters are illustrated in the figure1. This figure includes the main geometrical parameters, too. It can be seen from the figure 1 that the O_1 atom of the NO molecule is directly oriented toward the w_3 atoms of the clusters. Computed adsorption energies for all the possible orientations shows that the direct interaction between O_1 and W_3 atoms is the most probable interaction between the surface and adsorbent.

Computed energies for these interactions indicate that the most stable orientation is the direct orientation and other situations such as bridge and N_2-W_1conjuction are less important from the energy point of view. According to this, we focus on the direct orientation of $O_1 \rightarrow W_3$ in all of clusters and these orientations were fully investigated.

Adsorption energies for four clusters of wo_3 with different size and hence different surfaces confirmed that the cluster size is an important factor in the solid-gas interface interaction. Comparison between the computed values of adsorption energy shows that the cluster model with n=6 is a better representation of the cluster surface on which a chemical interaction was occurred.

The interaction energy corrected by BSSE of the adsorption system computed at the B3LYP/LANL2DZ level. The mean value of BSSE is about 5*10^{-2} percent of total energies of adsorption and may be ignored.

Atomic Charges for the atoms were calculated using the natural population analysis of adsorbed and isolated molecules. These charges on all of models show that O1 and W3 atomic charges are decreased since the positive characters of W3 atoms and negative characters of O1 atoms during the adsorption processes are decreased. This induces a good interaction at the atomic level between NO molecule and $(WO3)_n$ clusters, confirming the Bronsted acid-base reaction at the surface.

AIM analysis shows the formation of ion-dipole interaction through which O_1-W_3 new bond formation take places. A value of ρ and its laplacian for this bond is larger than other probabilities (mean value of laplacian is about 0.15), confirming the distance reduction between the surface W3 atoms and adsorbent (O1).

4. Conclusion

The DFT/B3LYP calculations of the adsorption of NO on the model (WO3)n n=(2, 3, 4, 6) indicates that NO is strongly bonded to these nano-clusters through the O1-W3 bond. AIM studies and NBO analysis also support this fact. The strong interaction of the O1-N2 bond with the W3 atom of the clusters was observed for n=6, confirming the positive effect of cluster size on the chemisorption.

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