

# Oxidative Reactivity of Neutral and Anionic $(\text{TiO}_2)_3$ Oxide Clusters towards Nitric Oxide: A DFT Study

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**Abstract**— The structural properties of neutral and anionic  $(\text{TiO}_2)_n$  clusters with size  $n=1-4$  and further oxidation reaction of  $(\text{TiO}_2)_3^{0/-1}$  clusters with hazardous environmental pollutant nitric oxide (NO) have been investigated under the formalism of density functional B3LYP/6-31+G(d) method. The stability of clusters increases with increase in the size. For the purpose of oxidation reaction, NO has preferably different possible active sites to react i.e., bridging and terminal oxygen atoms in the global minimum geometries of  $(\text{TiO}_2)_3^{0/-1}$  clusters. However, the reaction of NO at every possible site with varying orientations have been tried but in each case, either NO molecule did not react with the given clusters or nitrogen atom of NO makes bond with the terminal oxygen of both clusters but fails to detach it from the clusters. Therefore, the observed results revealed that both neutral and anionic  $\text{Ti}_3\text{O}_6$  clusters are already such stable cyclic geometries that they did not show reaction with NO molecule and hence, cannot provide its oxygen for the oxidative reactions.

**Keywords**— Neutral and Anionic  $(\text{TiO}_2)_n$  Clusters, Toxic Nitric oxide (NO)

## I. INTRODUCTION

In the last few decades, transition metal oxide (TMO) clusters has attracted continuous interest of research groups due to the tremendous amount of technological and scientific applications. Among the TMO clusters, the predominant use of titanium oxide clusters in numerous industrial applications makes them very important models in the diverse areas of physics, chemistry and material science. They have been also used as both catalysis supports or heterogeneous catalysts in the chemical industry.

Titanium dioxide ( $\text{TiO}_2$ ) being cheaper, chemically and biologically inert finds application in the field of energy storage, photovoltaics, gas-sensors and photocatalysis. For instance,  $\text{TiO}_2$  particles can be used in photooxidation of water on  $\text{TiO}_2$  surfaces [1].  $\text{TiO}_2$  is widely used in bacterial inactivation and as a white pigment in paints [2]. Small  $(\text{TiO}_2)_n$  clusters are involved in dust formation processes of oxygen-rich stars [3]. Under ambient conditions, out of rutile, anatase and brookite crystals of  $\text{TiO}_2$ , rutile is found as the thermodynamically most stable structure. However, the anatase phase becomes more stable than the rutile phase if particle diameters of  $\text{TiO}_2$  are smaller than about 14nm.

Calculations provide evidence that the neutral TMO clusters are more difficult to study as they cannot be size selected and a valid method is required to ionize neutral species without fragmentation. Despite of this, numerous experimental work [4-7] together with theoretical calculations [8-11] have been carried out for isolated, neutral as well as charged titanium oxide clusters, e.g., Matsuda and Bernstein [12] studied single-photon ionization mass spectra of  $\text{Ti}_m\text{O}_n$  neutral clusters. The electronic structure and band evolution of  $(\text{TiO}_2)_n^-$  ( $n=1-10$ ) clusters were investigated by Zhai and Wang [13]. The lowest geometries of  $(\text{TiO}_2)_n$  clusters were also obtained by Qu and Kroes [11] using density functional calculations. Li and Dixon [14] have studied the molecular structure and energies of neutral and anionic  $(\text{TiO}_2)_n$  clusters using DFT and CCSD(T) calculations. Very recently, Neogi and Chaudhary [15] employed SA/GA-DFT technique to evaluate the global and local minimum structures of  $(\text{TiO}_2)_n$ ,  $n=1-12$ .

Nitric oxide (NO) is one of the major hazardous pollutant present in the environment. Apart of its importance in biological and technical systems, it is popularly known for its harmful effects on human life as well as on environment. NO is found as a main cause for air pollution problem and hence, extensive methods are available for its removal from the atmosphere such as, absorption, reduction, etc [16, 17]. Since,  $\text{NO}_2$  (Nitrogen dioxide) can be easily removed than NO by absorption and also for  $\text{NO}_x$  reduction,  $\text{NO}_2$  is always more favoured than NO thus, efforts has been taken to develop catalysts for oxidizing NO to  $\text{NO}_2$  [18-19]. Various metal oxide clusters with supported catalysts has been used for NO oxidation [16, 17] but to the best of our knowledge, no study is available for the oxidation of NO using titanium oxide clusters in the absence of supported catalyst.

Keeping this in mind, the current paper employs both neutral and anionic  $(\text{TiO}_2)_3$  clusters for the removal of NO via oxidation process in the gas phase without using any supported catalyst. For this, we first present the optimization of neutral and anionic  $(\text{TiO}_2)_n$ ;  $n=1-4$  clusters. Once the geometries are obtained, the reaction of both neutral and anionic  $(\text{TiO}_2)_3$  clusters with toxic NO molecule have been performed to explore their oxidative capabilities. The current calculations are carried out within the formalism of density functional theory (DFT) which is established as a benchmark for the theoretical investigations of transition metal oxide clusters [20-22].

## II. COMPUTATIONAL METHOD

Several properties such as charge, bonding and spin distribution in TMO clusters often cannot be explained by the experimental studies, the theoretical calculations is important in predicting those properties. Thus, the present calculations including the structural parameters of neutral and anionic  $(\text{TiO}_2)_n$  clusters and their oxidation reaction with NO are investigated using hybrid density functional theory (DFT). DFT calculations provide appreciable results on the geometries and harmonic frequencies for numerous transition metal complexes [20-22]. Under the DFT framework, the electron exchange-correlation interaction plays an essential role in understanding the cluster properties and for this, we chose the popular Becke's three-parameter exchange functional [23] along with the Lee-Yang-Parr's correlation functional [23] i.e., B3LYP functional and all-electron basis set 6-31+G(d) [24] for the atomic orbitals (Ti, O and N atoms) using the Gaussian 09 program package [25]. The reliability of our method has been tested by comparing the different parameters of small  $\text{TiO}_2$  cluster with the available experimental data. All  $(\text{TiO}_2)_n$  clusters are fully optimized and characterized by harmonic vibrational frequency analysis. The optimized stationary geometries are verified as real local minima (without any imaginary frequencies). Geometry optimizations were performed without any symmetry constrains and zero point correction factor is included in all calculations. The ionization potential ( $\text{IP}_v$ ) and electron affinity ( $\text{EA}_v$ ) are calculated for the test calculations (by single point calculations) are defined as follows:

$$\text{IP}_v = E[(\text{TiO}_2)_n^+] - E[(\text{TiO}_2)_n]$$

$$\text{EA}_v = E[(\text{TiO}_2)_n] - E[(\text{TiO}_2)_n^-]$$

Where,  $E[(\text{TiO}_2)_n]$ ,  $E[(\text{TiO}_2)_n^-]$  and  $E[(\text{TiO}_2)_n^+]$  are the total energies of neutral, negatively charged and positively charged titanium oxide clusters, respectively, without any zero point correction.

## III. RESULTS AND DISCUSSION

### A. Test calculations

In order to check the reliability of our calculations, the different parameter values of small  $\text{TiO}_2$  cluster have been cross-checked with the available experimental and reference values (Table.1) and the excellent reliability of the B3LYP/6-31+G(d) level of theory for  $\text{TiO}_2$  clusters suggests its applicability to larger  $(\text{TiO}_2)_n$  clusters.

### B. Equilibrium geometries of Neutral and Anionic $(\text{TiO}_2)_n$ ; $n=1-4$ clusters

The global minimum geometries of neutral and anionic  $(\text{TiO}_2)_n$  clusters with size ranges from  $n=1-4$  are fully optimized by the current computational scheme. The cluster stability increases with increase in the cluster size which is in good agreement with previous literature [15]. Fig.1 represents the equilibrium geometries of neutral as well as anionic  $(\text{TiO}_2)_n$  clusters with  $n=1-4$  with their energy and bond length values.

TABLE I. Calculated and experimental values of geometry and properties of  $\text{TiO}_2$  cluster

$\text{TiO}_2$	Present work	Experimental [26]	Neogi and Chaudhary [15]
$d_{\text{Ti-O}} (\text{\AA})$	1.64	1.62	1.64
$\theta$ (deg)	111.8	110	111.8
$\text{IP}_v$	9.67	9.54	9.68
$\text{EA}_v$	1.69	1.59	1.68
Symmetry	$\text{C}_{2v}$	-	$\text{C}_{2v}$

### C. Reaction of neutral and anionic $(\text{TiO}_2)_3$ clusters with NO

Since, the cluster structure gets start converges towards the less strained cyclic structure from  $(\text{TiO}_2)_n$ ;  $n=3$  size, thus closely packed  $\text{Ti}_3\text{O}_6$  cluster and its anion are considered for further reaction with NO. Fig.1 (c, g) illustrates the global minimum six-member ring of  $\text{Ti}_3\text{O}_6^{0/-1}$  clusters which consists of a triple-bridge oxygen atom at the centre, and two terminal oxygen atoms with three  $-(\text{Ti-O})-$  units in excellent agreement with the earlier predictions [15]. The equilibrium structure of neutral and anion  $\text{Ti}_3\text{O}_6$  clusters are almost similar with negligible difference in their bond lengths [Fig.1 (c, g)].

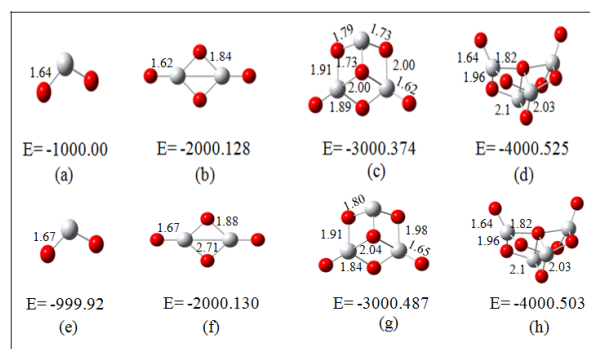


FIGURE 1. Equilibrium geometries of neutral (a-d) and anionic (e-h)  $(\text{TiO}_2)_n$ ;  $n=1-4$  clusters. Bond lengths are in angstroms and energies are in hartrees. The red spheres and grey spheres representing the oxygen atoms and the titanium atoms, respectively.

After optimization of both neutral and anionic  $(\text{TiO}_2)_n$  clusters, NO molecule was made to interact with the oxygen atoms of  $\text{Ti}_3\text{O}_6^{0/-1}$  clusters to explore their oxidative capability. The initial inputs conceived for the reaction between NO and  $\text{Ti}_3\text{O}_6^{0/-1}$  clusters and the resulting optimized structures are depicted in Fig.2 and 3. For the reaction, NO has four different possible active sites to react: O1, O2, O3 and O4 in both clusters (Fig. 2(a) and 3(a)). In order to ascertain the most favourable active site for the reaction, NO was placed at different non-equivalent active sites; near the terminal as well as bridging oxygen atoms at varying distances from the  $\text{Ti}_3\text{O}_6^{0/-1}$  clusters. However, the results depicts that the NO molecule did not show affinity towards the bridging oxygen atoms present in both neutral and anionic clusters while it show interaction with the terminal undercoordinated oxygens (Fig.2 and 3). The results obtained for  $\text{Ti}_3\text{O}_6^{0/-1}$  clusters shows that the distance between the terminal oxygens and nitrogen atom of NO gets increased in most of the cases (Fig.2c and 3b)

## IV. CONCLUSIONS

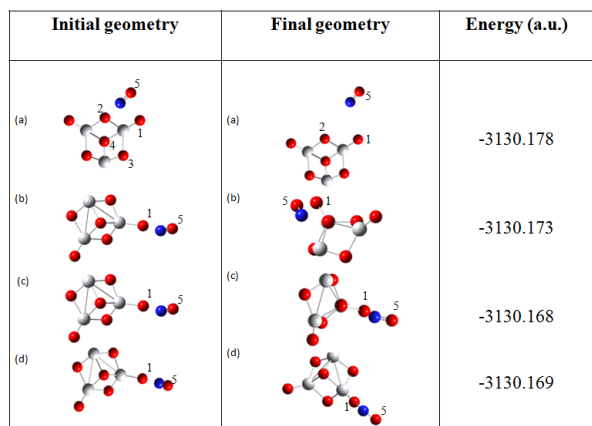


FIGURE II. Initial and final optimized geometries for the reaction of neutral  $Ti_3O_6$  cluster with NO, where (a) shows the reaction with bridging oxygen [O2] while (b), (c) and (d) shows the reaction with terminal oxygen [O1] of neutral  $Ti_3O_6$  cluster at different orientations. The energy values for the reactions are in hartrees.

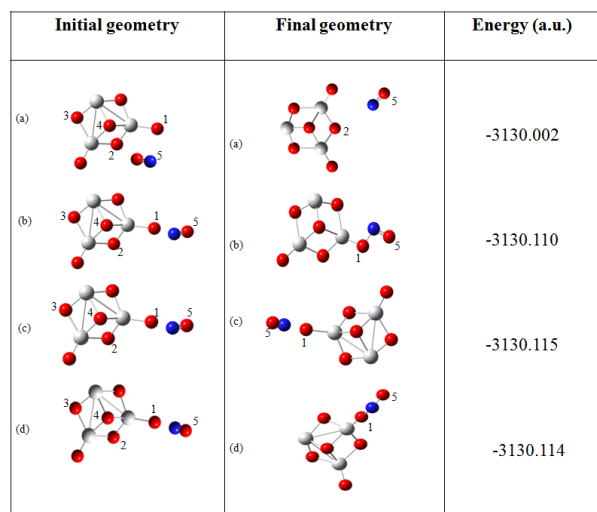


FIGURE III. Initial and final optimized geometries for the reaction of anionic  $Ti_3O_6$  cluster with NO, where (a) shows the reaction with bridging oxygen [O2] while (b), (c) and (d) shows the reaction with terminal oxygen [O1] of anionic  $Ti_3O_6$  cluster at different orientations. The energy values for the reactions are in hartrees. The red, grey and blue spheres represent the oxygen, titanium and nitrogen atoms respectively.

but, on changing the orientation of NO towards the terminal oxygen of both clusters, it is found that the nitrogen of NO molecule makes bond with the O1 but fails to detach it from the clusters [(Fig. 2 (b, d) and 3 (c, d)]. Table.2 lists the change in bond distances and their relative energies for the reaction of  $Ti_3O_6^{0/-1}$  clusters with NO. Thus, our calculations in the current work indicates that both neutral and anionic  $Ti_3O_6$  clusters are already such stable cyclic geometries that they did not show reaction with NO molecule and therefore, cannot provide its oxygen for the oxidative reactions.

The current report concentrates on the optimization of global minimum geometries of  $(TiO_2)_n$  clusters with size ranges from  $n=1-4$  and further oxidation reaction of  $Ti_3O_6^{0/-1}$  clusters with hazardous pollutant NO molecule have been carried out using the density functional B3LYP/6-31+G(d) method. The predicted bond lengths and energies obtained for the optimized geometries of  $(TiO_2)_n$  clusters agree well with the available literature. The geometries of global minimum structures of  $Ti_3O_6^{0/-1}$  clusters are found to be very similar with only slight difference in their bond lengths. To explore the oxidative properties of  $Ti_3O_6^{0/-1}$  clusters, NO has different possible active sites to interact i.e. terminal and bridging oxygens. The reaction of NO at every possible site with varying distances was tried but in each case, either distance between the oxygen atoms of given clusters and NO molecule increased or nitrogen atom of NO makes bond with the terminal oxygen of both clusters but fails to detach it from the clusters. The results predicted in the current work indicates that both neutral and anionic  $Ti_3O_6$  clusters are already such stable geometries that they did not show reaction with NO molecule and hence, did not provide its oxygen for the oxidative reactions.

TABLE II. Energy values for the reaction between terminal oxygen of both  $Ti_3O_6^{0/-1}$  clusters with NO at varying distances. Units of energy and Gibbs free energy values are atomic units. Bond distances are in angstroms.

$Ti_3O_6$	Initial geometry			Final geometry			Energy
	Ti-O1	O1-N	N-O5	Ti-O1	O1-N	N-O5	
Neutral	1.62	1.29	1.14	1.97	1.31	1.19	-3130.31
	1.62	1.30	1.14	2.04	1.32	1.22	-3130.29
	1.62	1.23	1.14	1.98	1.33	1.19	-3130.70
Anionic	1.65	1.14	1.14	1.85	1.33	1.19	-3130.95
	1.65	1.23	1.14	1.92	1.26	1.16	-3130.21
	1.65	1.35	1.14	2.03	1.37	1.19	-3130.31

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