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Composition Dependent Reactivity of Titanium Oxide Clusters

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Based on first-principles calculations of titanium oxide clusters, Ti_nO_m*(n=1-4)*, we reveal the composition dependent reactivity of titanium oxide clusters. Our interesting results include: (1) The reactivity depends on the ratio of O atoms in the clusters, with smaller O ratios associated with higher reactivity; (2) among the different titanium oxide species investigated, the most stable structures are the Ti_nO_{2n}, but their reactivities are relatively lower than the clusters with a smaller O atom ratio; moreover, (3) when the O atom ratio is small, the reactivity required to form the Ti-Ti bond is larger than either the Ti-O or O-O bond between two interacting titanium oxide clusters. These results will be useful for designing efficient titanium oxide catalysts, or photocatalysts, in particular, for energy and environmental applications.

Introduction

Titanium dioxide is an important material with a wide range of applications due to its low cost, good stability, pigment properties, and environmental compatibility.[1-4] In recent years, it has emerged as a prototypical transition metal oxide owing to its comparatively simple structures,[5,6] and has garnered much academic interest. However, the progress of its many and various potential implementations has been hindered due to the fast electron-hole recombination rates near the surface and its wide band gap (3.0eV for rutile; 3.2eV for anatase)[1] which facilitates light absorption of only ultraviolet (<387 nm) light by bulk TiO_2.[3] In some previous publications, such prototypes including TiO_2 nanoparticles, thin films, and mesoporous materials were reported[7] and the materials in both nanoscale tubular and wire forms have been synthesized. The nanoscale materials hold promise in many important usages such as environmental purification, integral parts in gas sensors, and high-efficiency solar cells. Lately, considerable efforts have been focused on the optimization of their photocatalytic properties by doping, enabling the formation of composites with other semiconductors as components, or surface modification.[1,3]

TiO_2 might exist in nature as minerals as rutile, anatase, and brookite crystals, with rutile being the most thermodynamically stable. However, the anatase phase is even more stable than the rutile when the particle diameters are smaller than about 14 nm. At significantly smaller diameters, the TiO_2 structures may not be derived from the bulk characteristics.[8] Therefore, exploration of their structures and the corresponding novel properties are of tremendous scientific importance.

Upon losing oxygen, rutile TiO_2 can form the Magneli phase crystalline structure which is a sub-stoichiometric titanium oxide of the general formula Ti_nO_{2n-1} (n=4-10), commercially marketed as “Ebonex®”. Three compounds of composition Ti_4O_7, Ti_5O_9, and Ti_6O_{11} are known to have the highest conductivities.[9-11] The Magneli phase titanium oxide can be prepared either by heating TiO_2 with metallic titanium in an inert atmosphere, or by reducing TiO_2 at high temperatures (at greater than 1000^oC) using a reducing agent, like the H_2 gas. The Magneli phase can be used as electrochemical materials owing to their good conductivities, excellent resistance to aggressive media and wide electrochemical window in aqueous electrolyte.[9] The study of titanium oxide clusters with varied compositions would facilitate the designing of an optimal Magneli phase for commercial or industrial applications.

To acquire fundamental insights into the complex surfaces and catalysts, numerous theoretical studies on Ti_nO_m clusters have been performed.[8,12-15] However, the associated reports focus mainly on Ti_nO_{2n}. Attention has yet to be paid to all the small Ti_nO_m clusters with a range of varying oxygen ratio. In particular, systematic studies are still needed to obtain their geometric and electronic structures. Considering the importance of the investigation of the properties of titanium oxides, including the structure, stability and reactivity that are crucial for releasing their application potential, in diverse fields such as electrochemistry, energy and environment, we have conducted a systematic study to examine the geometric structures of Ti_nO_m*(n=1-4)* and reveal their reactivity in this work, in order to provide a guide of their future utilization and further development.

Theoretical Approach and Computations

In this work, we study Ti_nO_m with different combinations of n and m, with sizes ranging from a few to 15 atoms. In the initial stage, most

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of the structures of Ti_nO_m*(n=1-4)* were obtained from our rational design, which used the Monte Carlo method to generate a large number of initial structures for each size of clusters.[16] We generated about 500 initial structures for all small clusters and 800 structures for the larger Ti_4O_5, Ti_4O_6, Ti_4O_7, Ti_4O_8, and Ti_4O_9. It is unrealistic to produce all the possible initial structures, because the number of possible configurations of clusters increases dramatically with cluster size. To solve this problem, after some calculations were carried out on the structures obtained using the Monte Carlo method, we constructed new possible structures (that is, not included in the list already determined), following the structural trends we had observed in the above described searches. Hence, we believe the geometric and electronic structures predicted by the present approach are meaningful for understanding the various issues relevant to titanium oxide systems. The energetic favorability of all these models was evaluated by performing various levels of calculations using the Gaussian 09 package. To achieve a balance between accuracy and computational time in our first-principles calculations, we used the basis set of 6-311G(d) for O and the Wachters-Hay all electron basis set for Ti atoms.[17] We screened these structures by firstly performing geometric optimizations using the Hartree-Fock (HF) method[18,19] which is computationally less time consuming than other first principles methods. We then further optimized those competitive lower energy structures and calculated their electronic structures at the B3LYP level of density functional theory (DFT), which is based on the Becke-type three-parameter functional.[20] The methodology is consistent with that used for studying silicon oxide systems in our previous work.[21] We validated our calculations by comparing some of our results with those reported by Qu et al.[8] Taking Ti_1O_2 as an example, the O-Ti-O angle is 111.4° in this work, while the angle is 110.8° in the work of Qu et al. As the difference is minimal, we believe the result can be considered as acceptable.

Results and Discussion

A. Geometric Structures of Titanium Oxide Clusters.

We have conducted a thorough search for the ground-state structures of small Ti_nO_m*(n=1-4)* clusters. Since most of the predicted ground-state structures of Ti_nO_m in our work have not been reported in the literature before, our systematic study will be helpful in understanding the trends of the geometric structures of each type of clusters. We found that most of the predicted ground-state structures of Ti_nO_m contain ring-shaped or polyhedron even for different choices of n and m, as illustrated in Figures 1, 2, and 3.

The energetically-favored structures of Ti_nO_m clusters with n≤2 are shown in Figure 1. When n=2, most clusters contain a rhombus. And when n=1, the TiO_3, TiO_4, and TiO_5 are not planar. The O-Ti-O angle of TiO_2 is about 111.4°, and the Ti-O bond lengths are close to 1.6 Å. Ti_2O cluster forms a triangle, with the Ti-O-Ti and Ti-Ti-O angles being 69.4° and 55.3° respectively. The Ti-O bond lengths of Ti_2O are about 1.82 Å, while the Ti-Ti bond length is around 2.1 Å. The Ti-O bond lengths in these rings of Ti_2O_3, Ti_2O_4, and Ti_2O_5 are about 1.8 Å, and the Ti-Ti bond lengths are close to 2.7Å, while the Ti-Ti bond length of Ti_2O_2 is about 2.1Å.

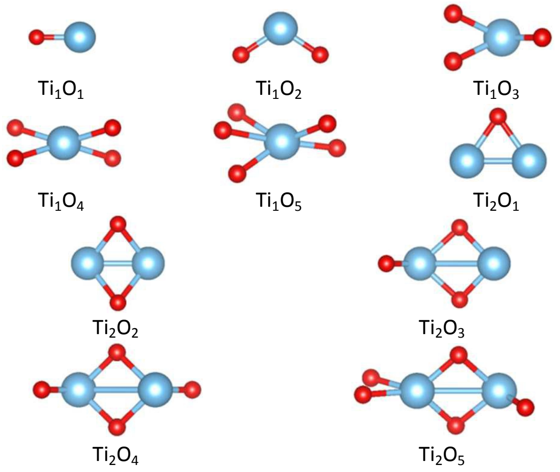

Figure 1. Optimized structures of Ti_nO_m with n≤2; the blue and red balls denote the Ti and O atoms, respectively.

Figure 2 presents the Ti_nO_m clusters with n=3. There is at least one triangle or rhombus in each of these except for Ti_3O_4 and Ti_3O_7. Ti_3O, Ti_3O_2 and Ti_3O_3 include one isosceles triangle with three Ti-Ti bonds. When the number of O atoms increases to 3, they are not all in one plane. Ti_3O_5 and Ti_3O_6 contain two rhombuses, which are almost perpendicular to each other, with each Ti-O-Ti angle close to 94°. There are two special structures: Ti_3O_4, which has a five-atom ring composed of one Ti-Ti bond (bond length is 2.29Å) and four Ti-O bonds (bonds length are 1.8Å approximately), and the structure of Ti_3O_7 which is more complicated than Ti_3O_4 and whose atoms are not in one plane.

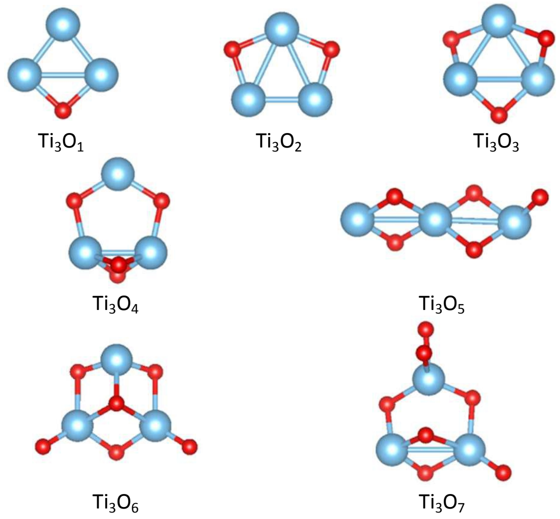

Figure 2. Optimized structures of Ti_nO_m with n=3; the blue and red balls denote the Ti and O atoms, respectively.

The geometric structures of Ti_nO_m with n=4 are illustrated in Figure 3. We found that almost every structure contains a polyhedron, such as tetrahedron or elongated triangular pyramid. Ti_4O, Ti_4O_2, Ti_4O_3, and Ti_4O_4 possess a regular tetrahedron comprising four Ti atoms or a triangular dipyramid with four Ti and one O atoms. If we consider these to be regular tetrahedrons, the Ti-Ti bond lengths are about 2.6Å. Similarly, if we consider them as triangular dipyramids, the three Ti-O bond lengths are close to 2Å, and the Ti-O-Ti angles are 82°. Ti_4O_5 and Ti_4O_6 comprise a tetrahedron consisting of four Ti atoms, and each Ti atom is connected to two or three O atoms. Both Ti_4O_7 and Ti_4O_8 include one elongated triangular pyramid, with four Ti and three O atoms. Through the comparison of Ti_nO_m with different n and m, we can see that more atoms we have, the more complicated the ring or polyhedron.

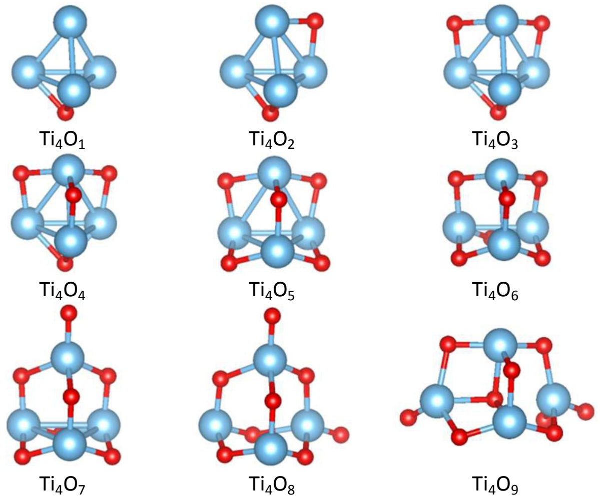

Figure 3. Optimized structures of Ti_nO_m with n=4; the blue and red balls donate the Ti and O atoms, respectively.

B. Cohesive Energy and Electronic Structures of Titanium Oxide Clusters.

The cohesive energy per atom of Ti_nO_m was calculated using the following equation:[22,23]

$$E_{cohesive} = \frac{E\ (total) - [nE(Ti)+mE(O2)/2]}{n+m},$$

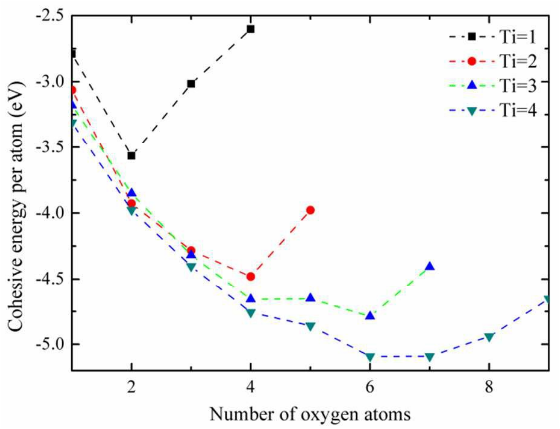

Figure 4. Cohesive energy per atom of Ti_nO_m (n=1-4) clusters as a function of the number of O atoms based on total energies calculated at the B3LYP/6-311G(d) level.

where $E_{cohesive}$ denotes the cohesive energy per atom of Ti_nO_m, E (total) denotes the total energy of Ti_nO_m, and n and m are the numbers of Ti and O atoms, respectively. The results are shown in Figure 4. Each curve has a minimum at the center, indicating that the ratio of Ti and O atoms in the most easily formed clusters is close to 1:2. The most energetically favorable small clusters are TiO_2-like, with the same stoichiometry.

Density of states (DOS) calculations[24] were also performed for each of the most energetically favorable structures described above. In solid-state and condensed matter physics, DOS denotes the number of states per interval of energy, which are available to be occupied by electrons at each energy level. The contribution of the individual atoms to the total electronic structures can be deduced from the total DOS (TDOS).[22] The projection of the DOS to individual atoms not only gives the properties of electronic states, but also provides a clear view of the differences in the reactivity and bonding contributions of each atom.[25] Such a treatment allows quantitative analysis of these properties and is particularly convenient for studying a large system, as previous study demonstrated.[24] The emphasis on this work is using such a treatment to identify the atoms in which the frontier orbitals (that is, the highest occupied and lowest unoccupied molecular orbitals, HOMO and LUMO) are found, in order to map the sites of high chemical reactivity and possible reactions within the system.[26] Early studies[27] established that the nature of the chemical reaction is determined by the overlap between the HOMO of one molecule and the LUMO of another. As the extent of electron delocalization is inversely proportional to the energy difference between these molecular orbitals, a smaller energy difference between them indicates the enhanced reactivity. Following on from this, it is essential to perform a DOS analysis to show the reactive sites and reactivity in the titanium oxide clusters. If some atoms contribute more to HOMO or LUMO, their projected DOS (PDOS) will be more intense. Therefore, the DOS analysis is a convenient way to identify the reactive sites and reactivity. In other words, the reactivity of a system (A) with another system (B) is related to $HOMO_A$ or $LUMO_B$, and the closer $HOMO_A$ (or $LUMO_A$) to $LUMO_B$ ($HOMO_B$) in B, the greater the reactivity.

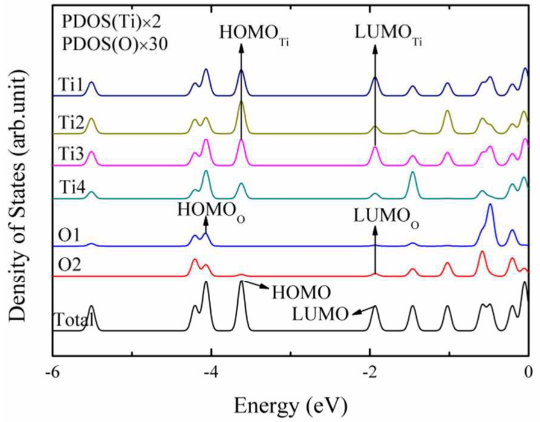

Figure 5. TDOS and PDOS of a representative titanium oxide cluster (Ti_4O_2).

The reactivity of the titanium oxide system determines the possibilities for its interaction, reaction, and/or bonding with another system, and its own internal structural reconstruction, all of which can be found from the analysis of the frontier orbitals. Accordingly, the TDOS and PDOS for all the deduced structures illustrated above were also studied. Figure 5 illustrates the TDOS and PDOS of a representative titanium oxide cluster (Ti_4O_2) obtained from B3LYP calculations. We denote the molecular orbitals closest to the gap, which contain a significant contribution from the Ti and O atoms, as $HOMO_{Ti}$, $HOMO_O$, $LUMO_{Ti}$, and $LUMO_O$, respectively, following previous practice[22].

Table 1. The molecular orbital compositions of Ti_nO_m*(n=1-4)*.

	TiO		Ti_1O_2		Ti_1O_3	
	Ti	O	Ti	O	Ti	O
HOMO	94.0%	6.0%	5.1%	94.9%	2.8%	97.2%
LUMO	100%	0%	87.9%	12.1%	82.5%	17.5%
	Ti_2O		Ti_2O_2		Ti_2O_3	
HOMO	95.6%	4.4%	84.3%	15.7%	95.3%	4.7%
LUMO	99.2%	0.8%	99.3%	0.7%	93.6%	6.4%
	Ti_2O_4		Ti_2O_5		Ti_3O	
HOMO	4.8%	95.2%	4.8%	95.2%	99.6%	0.4%
LUMO	80.4%	19.6%	88.5%	11.5%	98.9%	1.1%
	Ti_3O_2		Ti_3O_3		Ti_3O_4	
HOMO	99.2%	0.8%	89.4%	10.6%	94.4%	5.6%
LUMO	95.6%	4.4%	96.0%	4.0%	92.3%	7.7%
	Ti_3O_5		Ti_3O_6		Ti_3O_7	
HOMO	97.8%	2.2%	7.1%	92.9%	7.1%	92.9%
LUMO	89.2%	10.8%	86.3%	13.7%	86.7%	13.3%
	Ti_4O		Ti_4O_2		Ti_4O_3	
HOMO	99.7%	0.3%	99.6%	0.4%	98.1%	1.9%
LUMO	99.6%	0.4%	99.5%	0.5%	98.8%	1.2%
	Ti_4O_4		Ti_4O_5		Ti_4O_6	
HOMO	93.1%	6.9%	85.7%	14.3%	85.0%	15.0%
LUMO	97.6%	2.4%	94.5%	5.5%	91.3%	8.7%
	Ti_4O_7		Ti_4O_8		Ti_4O_9	
HOMO	81.1%	18.9%	6.5%	93.5%	7.9%	92.1%
LUMO	91.6%	8.4%	82.0%	18.0%	81.6%	18.4%

The contribution of both Ti and O atoms to the HOMO and LUMO can be summarized in Table 1. The molecular orbital compositions of Ti_nO_m were calculated using area normalization method. We observe that the Ti atoms of Ti_nO_{2n} always make the smallest contribution (from 4.8% to 7.1%) to the HOMO, which is very low compared to other structures. For example, the composition of Ti atoms of Ti_3O_6 to HOMO is 7.1%, while the contribution of Ti atoms of Ti_3O_5 to HOMO is 97.8%. It is because with an increase in the O ratio, Ti is oxidized, until the oxidation number reaches +IV (stoichiometry, two O for one Ti), and then increasing the O ratio cannot oxidized more Ti. For the LUMO, an increasing trend in the contribution of the O atoms can be obtained as their number increases with the same Ti atom number.

Figure 6(a) illustrates the $LUMO_{Ti}$ and $LUMO_O$ of Ti_nO_m clusters. The example of the PDOS in Figure 5 presents clear evidence of the differences between $LUMO_{Ti}$ and $LUMO_O$ and the localization of the LUMO at the Ti atoms for the titanium oxide clusters. These clusters may play the role of electron acceptor at both types of atom when interacting with other materials, with oxides having a moderate O atom ratio achieving slightly higher favorability on the O atom sites (electron acceptor).

Figure 6(b) shows the data points of the $HOMO_{Ti}$ and $HOMO_O$ of different Ti_nO_m systems. It can be seen that as the O atom ratio increases, the $HOMO_{Ti}$ and $HOMO_O$ show a clearly decreasing trend. Comparing these two HOMOs (electron donors) of the Ti and O atoms at the same O atom ratio, we can see that the $HOMO_{Ti}$ is higher than the $HOMO_O$ at small ratios, indicating high reactivity in a titanium-rich cluster. It is interesting that when we compare the $HOMO_{Ti}$ and $HOMO_O$ of titanium oxide in the same cluster when the O atom ratio approaches 0.5 or more, the $HOMO_{Ti}$ is roughly the same as the $HOMO_O$. This indicates a drop in reactivity of Ti atom, with the difference between them decreasing as O atom ratio increases. From the point of view of orbital interaction, this means that when the O atom ratio is lower than 0.5, the Ti atom has a higher reactivity than the O atom. With the extent of the reactivity depending on the O atom ratio, the smaller this is, the higher the reactivity. These interesting findings indicate that (1) the HOMO and LUMO are mainly located at the Ti atoms in titanium-rich clusters; and (2) from the point of view of orbital interaction, when the O atom ratio is lower than 0.5, the Ti atom has a higher reactivity than the O atom, but once the O atom ratio approaches 0.5 or larger, the reactivity of Ti atom declines.

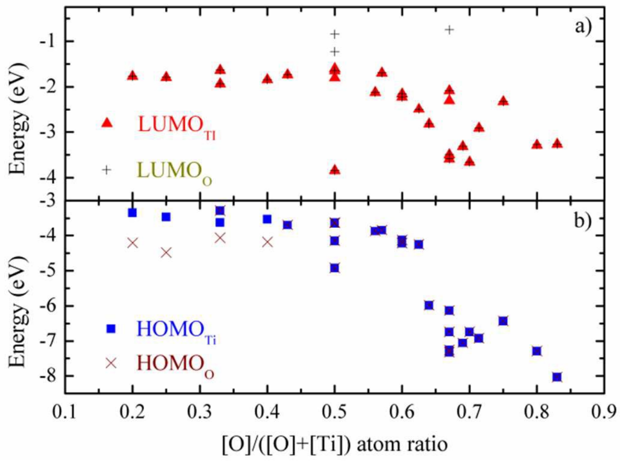

Figure 6. The energy of the $LUMO_{Ti}$, $LUMO_O$, $HOMO_{Ti}$, and $HOMO_O$ of Ti_nO_m clusters as functions of the O atom ratio obtained from B3LYP calculations.

Furthermore, the energy difference [ΔE=LUMO (electron acceptor)-HOMO (electron donor)] of the HOMO and LUMO provides an indication of catalytic activity. It is clear from Figures 6 and 7 that with the increase of the O atom ratio, the energy difference of the HOMO and LUMO also rises, indicating that titanium oxides with a large O atom ratio are relatively resistant to oxygen-etching. In other words, titanium oxides with small O atom ratios can lead to higher catalytic activity.

In addition, the reaction between the titanium oxide clusters would result in the formation of a bond between their respective Ti and O atoms. The trends of such bond formations is noticeable and can be seen in Figure 7, which depicts the inverse of the energy difference [ΔE=LUMO (electron acceptor)-HOMO (electron donor)] and thus the reactivity (proportional to the inverse of the energy difference) of Ti-Ti, Ti-O, or O-O bond between two clusters. This is expressed as a function of the O atom ratio and calculated using the $LUMO_{Ti}$, $LUMO_O$, $HOMO_{Ti}$, and $HOMO_O$ fitted by fourth-order polynomials[22] as shown in Figure 6. Thus the reactivity of Ti-Ti bond between two titanium oxide clusters is larger than that of O-O bond when the O atom ratio is less than about 0.8, and when the O atom ratio is smaller than 0.55, the reactivity of Ti-Ti bond is larger than Ti-O bond. When the O atom ratio lies in the range from 0.4 to 0.5, the Ti-Ti bonding reaches the peak.

Moreover, as illustrated in Figure 4, the cohesive energy per atom of a smaller cluster is larger, indicating that small clusters tend to form larger clusters. However, the reactivities of small and large clusters are vastly different and, in most cases, the reactivity exhibits a declining trend with the increase of the cluster size. Take $(TiO)_n$ as an example, the reactivity of TiO is the highest and Ti_4O_4 is the lowest one among them. Thus, in applications, one can tune their reactivities by controlling their structures.

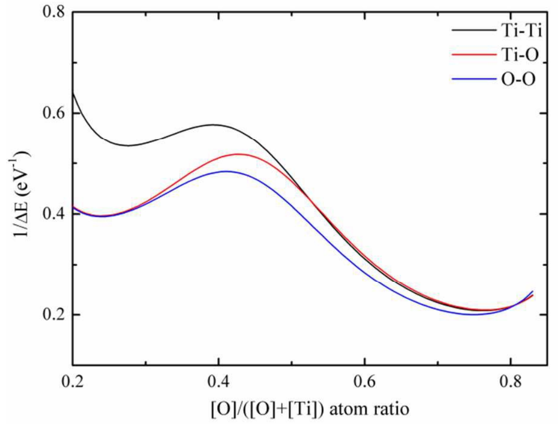

Figure 7. The inverse of the energy difference [ΔE=LUMO (electron acceptor)-HOMO (electron donor)] for the Ti-Ti, Ti-O, or O-O bond between two titanium oxide clusters.

Conclusions

A systematic study of Ti_nO_m*(n=1-4)* clusters using DFT reveals the structures and reactivity of titanium oxide clusters. It has been found that, in general, the ground-state structures of small titanium oxide clusters contain ring-shaped or polyhedron units. The calculations of the cohesive energy per atom, the PDOS, and the inverse of the energy difference have also provided a window for better understanding of the reactivity and stability of Ti_nO_m*(n=1-4)*. The most stable structure has been found to be Ti_nO_{2n}, and titanium-rich clusters possess high reactivity with the Ti atoms. The reactivity of Ti-Ti bond between two clusters is larger than that of Ti-O or O-O bond at a small O atom ratio.

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