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Adsorption studies of acetaldehyde on TiO₂ nanosurface

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ABSTRACT

The present work deals with the adsorption of acetaldehyde, one of the most harmful volatile organic compounds (VOCs), on the TiO₂ anatase nanosurface. The research was undertaken due to environmental concerns, as the TiO₂ nanosurface serves as an excellent catalyst for the adsorption and decomposition of VOCs. The chemistry of aldehydes on metal oxides is complex and elaborate, as it can result in a variety of reactions, such as selective oxidation, alcohols disproportionation, etherification and reductive coupling to higher olefins. The structural properties of the various nanosurfaces were first examined and finally adsorption studies were made on the $(TiO_2)_{17}$ cluster, as it shows least reconstruction and offers all kinds of coordination sites for the study. It is found that a myriad of different adsorption products are formed on the TiO_2 nanosurface, depending upon the coordination site. The low coordination (3c) sites are highly reactive and form stronger bonds with the acetaldehyde molecule, whereas adsorption at the four coordination site leads to the reconstruction of the nanosurface. Acetaldehyde chemisorbs onto the surface producing zwitterionic four-membered rings, in which the carbonyl C=O bond is considerably weakened, or it adsorbs on the TiO_2 surface in a H-bridge bonded form. The most feasible mode of adsorption on the TiO_2 nanosurface is found to be methyl hydrogen migration resulting in the formation of [CH₂-C(H)O] species, which may further undergo transformation by β -aldolization to yield crotonaldehyde and butane. Other products investigated in this work include oxidation to acetate and reduction to ethoxy species. The results obtained in this work can be of significant help in deciding the fate of reaction of acetaldehyde on the TiO_2 nanosurface, and using it for decomposition of acetaldehyde to benign products. Copyright © 2013 VBRI press.

Keywords: TiO₂ anatase nanosurface; adsorption on nanocrystals; acetaldehyde; density functional theory.



Rita Kakkar, after obtaining a PhD degree in Physical Chemistry from the University of Delhi, undertook research on various topics. She has been teaching physical chemistry at the University of Delhi for the past 28 years. Prior to that, she taught at Miranda House, University of Delhi. In the field of chemistry education, she is actively involved in designing syllabi of various universities and conducting teacher-training workshops, and for popularizing the use of Molecular Modelling in teaching chemistry. Her

main research interests are in Computational Chemistry and related fields. She heads a large research group, which is carrying out computational and experimental studies on catalysis by nanomaterials and by enzymes. The focus of the research on nanomaterials is to understand the growth, morphologies and stabilities of nanocrystalline forms of metals and metal oxides, their reactivities, and their catalytic role in various reactions, particularly those involving degradation of organic pollutants. Her research on nanoscale materials also includes theoretical and experimental studies on quantum dots and their size-dependent properties for use as semiconductor devices and sensors. The other area of research is the use of in silico techniques to understand enzyme catalysis and to design enzyme inhibitors. Her group is presently engaged in understanding the action of PDHK, PDF and urease inhibitors in order to design better inhibitors by use of docking studies and structure-activity relationships. In addition, her research group investigates potential energy surfaces and reaction paths of important organic reactions, and studies the role of catalysts on these reactions.

Professor Rita Kakkar has over 75 research publications in international journals. She has successfully supervised the work of 27 PhD and 7 MPhil students. She has delivered invited several talks at scientific conferences. She acted as an International Advisory Member, First, Second, Third, Fourth, Fifth, Sixth and Seventh Workshops on Computational Chemistry and its Applications, part of the International Conference on Computational Science, ICCS: 2006, ICCS: 2007, ICCS: 2008, ICCS: 2009, ICCS: 2010, ICCS: 2011 and ICCS: 2012. She is also an International Advisory Member for the Eighth Workshop (8th CCA), part of ICCS 2013 to be held at Barcelona, Spain. She is a member, Task Force, IUPAC Project on "Assessment of theoretical methods for the study of reactions involving global warming gas species degradation and by-product formation". She also regularly reviews manuscripts for many international journals, including those published by the American Chemical Society, Royal Society of Chemistry and Elsevier.

Introduction

The adsorption of aldehydes on metal oxide surfaces has gained importance because of both fundamental and practical perspectives. The chemistry of aldehydes on metal oxides is complex and elaborate, as it can result in a variety of reactions such as selective oxidation [1], alcohol synthesis [2], condensation to higher aldehydes and alcohols [3], disproportionation [4, 5], etherification [6] and reductive coupling to higher olefins [7]. The reactivity of these processes depends to a large extent on the characteristics of oxide catalysts: their surface structures, acid-base properties and surface defects [8-10]. Another very important aspect of the investigation of aldehyde adsorption on metal oxide surfaces is due to environmental concerns, as aldehydes are often used as fuels and fuel additives, and may also be formed as a result of incomplete combustion of fuel in the engine. However, aldehydes are particularly undesirable in the exhaust because of their potential carcinogenic effects [11]. Thus, in an effort to reduce these exhaust products, it would be helpful to have a fundamental understanding of their adsorption mechanism.

Among the large number of metal oxides, TiO_2 has been the most extensively used in technological applications [12] as it is highly stable, inexpensive, and nontoxic and also has a suitable band-gap energy; these properties in turn are dictated to a large extent by its crystal phase, morphology, and particle size. Titanium dioxide has a wide variety of industrial applications, including photocatalysis, heterogeneous catalysis, gas sensors, pigments and ceramics. The discovery of the photocatalytic splitting of water on TiO₂ electrodes [13] has motivated an increasing interest in understanding of the fundamental physical and chemical aspects of molecular adsorption at the surface of this material. The anatase form of TiO₂ is widely used in commercial catalysts and as a gas sensor for CO, CH₄, H₂ or O₂ [12]. Despite the interest generated, little is known about the mechanisms occurring during such processes. Thus we have undertaken a systematic investigation in order to study the TiO₂ anatase surface reactivity.

The reactions of acetaldehyde on the TiO₂ surface are also of considerable interest since acetaldehyde is an intermediate during the photocatalytic oxidation of ethanol on TiO_2 at room temperature [14, 15], and when acetaldehyde oxidizes on TiO₂ at elevated temperature, the catalyst rapidly deactivates, and the deactivation occurs even in absence of UV irradiation [16]. It has also been found that acetaldehyde is also produced as a surface and gas-phase product in the catalytic steam reforming of ethanol [17]. Its appearance either in the adsorbed layer or in the gas phase has been regarded as an indication of H₂ production. H₂ produced by steam reforming of ethanol can be used in fuel cells or in electric vehicles, ensuring the cleanest source of energy with practically zero emission of polluting gases. If, however, H₂ were produced catalytically from ethanol in vehicles, the presence of acetaldehyde in the exhaust would represent high danger to the environment. Thus, its catalytic transformation to less dangerous materials would play a vital role. In addition, the TiO₂ surface exhibits activity for C-C bond formation by reductive coupling of aldehydes [18, 19] and ketones [4, 7].

Although the adsorption of aldehydes on metal oxide surfaces has been investigated by various spectroscopic [20-23] and temperature programmed [9, 24] studies, theoretical studies on this system are comparatively scarce. Thus, motivated both by the general interest of molecular adsorption at metal-oxide surfaces and by the crucial role of anatase films in applications such as dye-sensitized solar cells [25, 26], heterogeneous catalysis, and gas sensors, we have considered the adsorption of acetaldehyde on the anatase nanosurface, which is the most stable surface for this material [3, 9, 27, 28].

In the present work, we have carried out a study of the structure and stability of TiO_2 nanocrystals derived from the bulk. We have made a comprehensive study of the stability and structural properties of neutral, stoichiometric $(TiO_2)_n$ nanocrystals of increasing size with n = 3, 5, 8, 10, 12, 16, 17, 21 using density functional theory. We have also calculated the surface properties of these nanoclusters, as a detailed evaluation of the surface structures is required if we have to properly understand the properties of the oxide surface. On the basis of conclusions made on the above parameters, $(TiO_2)_{17}$ was found to be the most suitable surface, and finally several possible adsorption conformations of acetaldehyde on the TiO₂-anatase nanosurface were studied on this surface.

Computational methods

First principles density functional calculations were performed using the DMol³ code [29-34] available from Accelrys Inc. in the Material Studio 4.4 package. In our calculations, we employed numerical basis sets of double- ζ quality plus polarization functions (DNP) to describe the valence orbitals and the DFT semilocal psuedopotential (DSPP) to describe the cores. The exchange-correlation contribution to the total electronic energy was treated in a spin polarized generalized-gradient corrected (GGA) form of the local density approximation (LDA) [35], with the Perdew-Burke-Ernzerhof (PBE) correlation [36]. The selection of the functional was made on the basis of a comparison of the performance of various functionals with respect to experimental quantities for TiO and TiO₂. DFT calculations at the GGA level are expected to give good prediction for the bonding energies of the carbonyl systems on the oxide surface [37-40].

As was already shown in our earlier work [**37**], the relaxation of the nanosurface is an essential requirement for chemisorption to take place, as keeping the nanosurface fixed at the bulk geometry does not lead to any interaction between the adsorbate and the nanosurface. Thus complete geometry optimizations, without restrictions, of the adsorbate as well as the nanosurface were carried out using delocalized internal coordinates [**41**]. No saturation of the dangling bonds was applied. The energy was converged upto 1×10^{-5} hartree. The binding energy values were corrected for zero point energies. The charge distributions were estimated using the Mulliken approach [**42**] and bond orders calculated using Mayer's procedure [**43**].

Results and discussions

Performance of the method

To select the best possible method that can be applied to predict the properties of $(TiO_2)_n$ clusters, we calculated

some properties of the TiO and TiO_2 molecules using various functionals and compared the results with the available experimental data [44, 45] and other theoretical calculations [46, 47], as shown in Table 1 (a, b).

 Table 1a. Predicted properties for TiO molecule using various methods.

		This		B3LYP/		
Properties	LDA		GGA		Expt.	LANL2DZ
	PWC	VWN	PW91	PBE		d
Ti-O (Å)	1.609	1.609	1.628	1.628	1.620 ^a	1.634
Vibrational						
frequency	1047	1031	1050	1014	1009 ^a	1046
(cm ⁻¹)						
					6.819±0.00	
$IP_a(eV)$	6.72	7.09	6.31	6.31	6 ^b	9.75
EA _a (eV)	0.53	0.14	0.63	0.44	1.30±0.03 ^c	1.69

Table 1b. Predicted properties for TiO₂ molecule using various methods.

		This		B3LYP/		
Properties	LDA		GGA		Expt.	LANL2DZ
	PWC	VWN	PW91	PBE		d
Ti-O (Å)	1.646	1.646	1.665	1.666	-	1.658
O-Ti-O (°)	109.9	109.4	110.7	110.7	110±15 ^a	110.8
Vibrational frequencies (cm ⁻¹)	1003, 326, 987	999, 339, 958	959, 306, 932	957, 305, 930	965, NA, 944 ^b	1026, 341, 1007
IP _a (eV)	9.90	9.75	9.47	9.40	9.5±0.1 ^c	9.75
EA _b (eV)	1.04	1.22	1.15	1.08	1.59±0.03 ^c	1.69

Quoted in a from ref 51; b from ref 52; c from ref 44; dfrom ref 47.

We first compared the computed properties of titanium oxide (TiO) with the experimentally determined ones. This molecule is of astrophysical interest [49, 53-56], and has therefore been a subject of extensive spectroscopic investigations. Indeed, it is the main opacity source in the atmospheres of cool M-type stars in the visible and near infrared. In addition, owing to its importance in model atmosphere investigations and in quantum chemistry, a number of theoretical studies have been devoted to this species [57-60]. Its electronic structure is therefore well understood. In view of the high cosmic abundance of Ti and O [61], larger clusters of titanium oxides are believed to play an important role in dust formation processes from the gas-phase in circumstellar shells of oxygen-rich stars [62].

As can be seen from **Table 1a**, all the functionals give very good agreement for the computed bond lengths of TiO with experimental results. The GGA functionals slightly underestimate the bond strength, while the LDA functionals overestimate the binding energy. The hybrid functional, however, grossly underestimates the bond strength [47]. The GGA-PBE vibrational frequency is in best agreement with the experimental value.

For TiO₂, however, there is very little experimental information [51, 63 & 64]. Table 1b shows that the agreement between experimental and theoretical results is excellent for the GGA-PBE functional, except the electron affinity, which is underestimated. However, the calculated GGA-PBE vibrational frequencies are almost exactly reproduced. In view of the excellent agreement with

experimental data, and our observation that GGA-PBE gives best agreement with experimental geometries for aminophenylhydroxy Cu(II) complexes [65], we report the rest of the calculations based on GGA-PBE.

Anatase TiO₂ nanocrystals: Structural properties

Since TiO₂ is a highly ionic semiconductor, the Ti(IV) atom prefers a large number of O neighbours, but strongly repels its Ti next nearest neighbors. In the anatase crystal structure, each Ti atom is surrounded by six oxygen atoms, but has only four Ti nearest neighbors. This is why it is one of the stable crystal structures for TiO₂. Because of the smaller oxidation number of oxygen, it has a fewer number (only three) of Ti neighbors. This crystal structure can be thought of as obtained from a distorted NaCl structure of TiO by removing half of the Ti atoms. The slight distortion from the ideal NaCl structure results in shorter Ti-O and longer Ti-Ti distances, leading to further reduction of the Madelung energy.



Fig. 1. The $(TiO_2)_n$ clusters taken for the calculation (initial and optimized structures). Here n = 3, 8, 12, 16, 21 clusters are shown. The 17 unit cluster is shown in the subsequent figures. Color codes Ti, grey; O, red.

The surfaces of the nanocrystals examined are shown in Fig. 1. These nanocrystals were derived from bulk anatase structure. The nanocrystals expose under-coordinated Ti and O atoms. The titanium atoms are present in the threefold Ti_c, fourfold Ti_d and fivefold-coordinated Ti_b states, and oxygen is present in twofold-coordinated Oa and O_b, and threefold-coordinated O_c states (Fig. 2). In addition to the above, the surface of bigger nanocrystals (n = 12 -21) contains sixfold-coordinated Ti_a titanium atoms as well. While the smaller nanocrystals expose three and four coordinated Ti atoms, five and six coordinated Ti atoms prevail in the larger nanocrystals. As in the anatase bulk, the twofold coordinated oxygens are present in two nonequivalent forms, O_a and O_b (Fig. 2): O_a (bridging oxygen) is bonded to two under-coordinated Ti atoms, forming a Ti-O-Ti angle, $\theta = 156.2^{\circ}$ between the two equatorial bonds [66], while O_b (in-plane oxygen) binds two under-coordinated Ti atoms forming a Ti-O-Ti angle, $\delta =$ 101.9° between an apical bond and an equatorial bond. The threefold-coordinated oxygen (O_c) atoms form a planar T shaped structure with their neighboring Ti atoms with a Ti-O-Ti angle, $\varphi = 101.9^{\circ}$ between an apical bond and an equatorial bond. The apical and equatorial Ti-O bond lengths for the unrelaxed nanoclusters are 1.973 and 1.930 Å, respectively. Furthermore, the bulk truncated structures of larger nanocrystals also consist of chains of O-Ti-O-Ti four membered rings which are parallel to each other and to the surface as well (Fig. 2).



Fig. 2. The structure of unrelaxed $(TiO_2)_{17}$ (two different views) cluster illustrating the various atom labels and bond parameters.

The optimized structures of the various nanoclusters are depicted in **Fig. 1**. Visual inspection of these optimized structures shows that the nanoclusters undergo substantial relaxation as compared to the unrelaxed truncated bulk crystal structure. A common feature of all these clusters is that the Ti-O bond length decreases upon relaxation. However, the decrease in bond length is more pronounced in case of smaller nanoclusters as compared to the bigger ones. The terminal Ti-O bonds are of almost constant bond length of ~1.63 Å with bond orders ranging from 2.067 for n = 3 to 2.181 for n = 21. However, the rest of the Ti-O bond lengths for the (TiO₂)₁₇ cluster vary between ~1.68 and ~2.57 Å depending upon the nature of the coordination. These results are in accord with B3LYP studies [67], which reported Ti-O bond lengths in the range 1.7-2.3 Å.

In case of larger nanocrystals, n = 12 - 21, the central bonds are found to be longer compared to the outer ones.

This increase in central bond lengths can be understood in terms of the increased coordination of the central ions. The external field produced by the larger number of surrounding ions increases the ionic character of the central bond lengths reaching the TiO₂ lattice limit (2.573 Å), while the surface bond lengths are shorter (ranging from ~1.68 Å to ~2.08 Å). The bond orders range from 0.395 to 1.657 for surface Ti-O bonds and from 0.074 to 0.655 for the central ones, indicating that some of these are purely ionic bonds. The interplanar distances, too, exhibit a similar pattern, the terminal Ti-O distances (~1.73 Å) being smaller than the central ones (~2.00 Å).

According to Burdett et al. [68], the bulk structure of anatase is controlled by a balance between two forces: the O-O repulsions, which determine the Ti-O bond distances and Ti-O-Ti bond angles, and the attractive Ti-O π interactions that determine the planarity of the O-Ti units. Our calculations indicate that upon relaxation the fourmembered ring structures undergo distortion to adopt hexagonal ring based structures, thus increasing the O-O distance from 2.458 Å in the four membered ring to ~2.989 Å in the hexagonal ring. This result is a general feature of the smaller nanocrystals; however, this effect is found to diminish as the cluster size increases and completely vanishes in case of (TiO₂)₂₁, indicating that the smaller clusters are more susceptible to reconstruction on geometry optimization, i.e. for n = 3, 5 all the rhombus structures are converted to six membered rings, for n = 8 - 17 only half of the four membered structures convert to the hexagonal structure, whereas for n = 21 this feature is not observed at all. This can be attributed to the fact that the smaller clusters have greater number of exposed surface atoms, and these surface atoms tend to acquire minimum coordination in order to fulfill the condition of maximum unsaturation. Moreover, for n = 8 - 17 clusters, the four-membered ring structures that are not converted to the hexagonal rings undergo significant Ti-O apical bond elongation (from 1.973 Å to 2.573 Å). We have also observed that the Ti-O bond distances are reduced when going from the rhombic to the hexagonal structure, from 1.892 ± 0.1 Å in the former to 1.832 ± 0.1 Å in the latter. Furthermore, the O-Ti-O-Ti rings, perpendicular to the surface, that were initially parallel to each other, become twisted upon relaxation; however, no particular pattern was observed for the dihedral angles. Thus, our results indicate that the O-O repulsions are the more important factor in deciding the structure, as they even destabilize the planar configuration of the surface oxygens preferred on the basis of π interactions.

As reported earlier, the bridging oxygens O_a bind two under-coordinated Ti atoms via two equatorial bonds, forming an angle, $\theta = 156^{\circ}$. In the optimized structures, this symmetry is broken and the two Ti-O bonds become strongly nonequivalent, with bond lengths of 2.01 ± 0.02 Å and 1.76 ± 0.02 Å, while the Ti-O-Ti angle is also reduced to $144 \pm 10^{\circ}$, which is in agreement with the results from *ab initio* studies on bulk anatase [66]. However, for n = 17, the θ angle is found to increase by 8°. In addition to this, each bridging oxygen O_b, bonded to two Ti via an apical and an equatorial bond, undergoes relaxation, leading to substantial shortening of the apical bond (1.973 Å to 1.797

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 \pm 0.06 Å) and the equatorial bond (1.930 Å to 1.983 \pm 0.04 Å), with the Ti-O-Ti δ angle decreasing from 101.9° to 99.7 \pm 3°.

The threefold-coordinated O_c, bonded to three Ti atoms via two equatorial bonds and one apical bond, shows a contraction of the equatorial Ti-O bond for n = 3 - 8. However, from n = 10 onwards, the symmetry is broken, again resulting in elongation of one of the bonds and shortening of the other, resulting in bond orders of ~0.67 and ~1.25, respectively. The apical bond, on the other hand, is lengthened from 1.973 Å to 2.321 ± 0.3 Å with bond order of ~0.07, indicating that this bond is broken.

Ladd [69] calculated the crystal energies of TiO_2 by the Born-Haber cycle and Born-Mayer equations, and suggested strongly ionic character in the Ti-O bonds. For the six-coordinated bulk Ti atoms, the calculated partial charges on the outer six-coordinated Ti atoms range from 1.385 to 1.518, compared to 1.365 to 1.429 for the undercoordinated Ti atoms present on the surface. The Mulliken partial charge on the titanium ions is found to decrease with decreasing coordination, indicating an increased covalency and thus reactivity for the under-coordinated atoms. The binding energies per TiO₂ unit for the relaxed and unrelaxed nanoclusters are compared in **Table 2**.

Table 2 Binding energy of unrelaxed (BE_{unrel}), relaxed nanoclusters (BE_{rel}), relaxation energy (E_r) for the TiO₂ surface normalized to the number of TiO₂ units and stabilization energy per TiO₂ unit (E_s) relative to the energy of a free TiO₂ molecule (in kJ/mol).

n	BE _{unrel}	BE _{rel}	E_r	E_s
3	-1894.1	-1876.1	18.0	-255.4
5	-1651.3	-1844.7	20.1	-313.2
8	-1831.7	-1956.9	148.6	-404.4
10	-1820.0	-1967.4	147.4	-421.2
12	-1830.9	-1956.9	126.0	-411.1
16	-1866.1	-1984.1	118.1	-438.4
17	-1800.7	-1939.7	139.0	-391.1
21	-1826.3	-1987.9	161.6	-442.1

As expected, the binding energies of relaxed nanoclusters are more negative than their corresponding unrelaxed structures, indicating that the nanoclusters acquire stability upon relaxation. The binding energy for a single TiO₂ molecule is -1523.6 kJ/mol, which is quite low in comparison to the other clusters. As the cluster size increases, the binding energy per TiO₂ molecule increases significantly in an oscillatory manner (**Table 2**). We have also calculated the stabilization energy per TiO₂ unit, which is given as the total energy per TiO₂ unit relative to that of a single TiO₂ molecule. We have observed that the stabilization energy increases very fast in magnitude for the smaller clusters (by ~54 kJ/mol), but decreases again for

 $(TiO_2)_{17}$ units, and again increases for n = 21 to approach a value of about 442.1 kJ/mol.

Electronic properties

The nature and magnitude of the highest occupied molecular orbital HOMO and lowest unoccupied molecular orbital LUMO levels is one of the crucial factors that helps in determining the chemical reactivity of a molecule. The isosurfaces of the HOMO and LUMO of (TiO₂)₁₇, shown in **Fig. 3**, reveal that the HOMO is mainly composed of the 2poxygen orbitals, while the LUMO comprises the 3d orbitals of titanium and has a very small oxygen 3s component as well. A very important observation from the isosurfaces is the location of the frontier orbitals; the HOMO and LUMO are centered on the under-coordinated surface atoms (Fig. 3). The reason is that an increased coordination contributes to increasing the bonding character of occupied orbitals centered on oxygen shifting their energy down, and as a consequence, the HOMO is centered on Ti=O groups, whereas in the case of titanium, increased coordination leads to increasing the antibonding character of the vacant orbitals, thus lifting the energy level of these orbitals, and as a result the LUMO is centered on the 3d orbitals of Ti. As stated previously, the bulk structure of anatase is controlled by the O-O repulsions, which determine the Ti-O bond distances and Ti-O-Ti bond angles [68]. Our results for the electronic structures of the clusters confirm this view. The HOMO for the anatase clusters is found to be anion centered which means that its energy depends upon the O-O distances. The smaller anion-anion repulsion in the nanostructure stabilizes the HOMO, increasing the HOMO-LUMO gap. As the HOMO depicts the electron rich region and the LUMO depicts the electron deficient region, in acid/base terms we can say that the oxygen sites are basic and the titanium sites are acidic in nature.



Fig. 3. Pictorial representation of the (a) HOMO (b) LUMO of (TiO₂)₁₇.

Adsorption of acetaldehyde on the TiO₂ surface

We observed that, while the smaller $(TiO_2)_n$ nanocrystals, i.e. n = 3 - 16, prefer hexagonal ring based structures, $(TiO_2)_{17}$ undergoes partial reconstruction of surface, whereas complete anatase conformation is sustained for $(TiO_2)_{21}$. Though the smallest cluster that accurately represents the anatase TiO_2 nanocrystal surface is $(TiO_2)_{21}$, we have employed $(TiO_2)_{17}$ nanocrystals for carrying out the adsorption studies in the present work because of computational time constraints.

Orientation of acetaldehyde on the oxide surface

Molecules having carbonyl groups, such as aldehydes, may adsorb on the surface of TiO2 nanoparticles by molecular adsorption or by dissociative adsorption. In the former process, a complex of the aldehyde and TiO₂ is formed, whereas in dissociative adsorption, a hydrogen atom dissociates from the aldehyde molecule and attaches to a bridging oxygen on the surface and the remaining aldehyde hydrogen bonds to the surface titanium atom. For studying the adsorption of acetaldehyde on the TiO2 surface, we considered several possible geometries of the aldehyde adsorbed on the (TiO₂)₁₇ nanocluster, as shown in Fig. 4. The first is Mode A, in which the carbonyl oxygen is aligned over a titanium ion, and the carbonyl carbon is not involved in interaction with any surface oxide ion. Mode B involves the interaction of the carbonyl group of the acetaldehyde molecule, where the carbonyl bond is almost parallel to the TiO₂ surface in such a way that the carbonyl carbon forms close contact with the surface oxide ion and the carbonyl oxygen with the surface titanium atom. Mode C involves the interaction of a methyl hydrogen of acetaldehyde with the titanium and oxygen atoms of the cluster, and Mode D involves the interaction of the aldehyde hydrogen with the TiO₂ surface.



Fig. 4 Geometry optimized structures of acetaldehyde adsorbed on $(TiO_2)_{17}$ surface (A) singly bonded, (B) carbonyl interaction, (C) methyl interaction, (D) aldehyde hydrogen.

Complete geometry optimization was performed for each of the binding modes and the corresponding adsorption energy was calculated according to the following expression:

$E_{ads} = E_{ac} + E_{TiO2} - E_{complex}$

where E_{ac} is the binding energy of isolated acetaldehyde in its equilibrium configuration (-2818.9 kJ/mol), E_{TiO2} is the binding energy of the (TiO₂)₁₇ cluster (-32902.4 kJ/mol) and $E_{complex}$ is the total binding energy of the adsorbed acetaldehyde- TiO_2 system. Positive values of the adsorption energy indicate that the adsorption process is exothermic. **Table 3** shows the adsorption energies for various binding modes of acetaldehyde adsorption on the TiO_2 surface, from which it is clear that Modes **B** and **C** are certainly preferred over the other binding modes.

Table 3. Adsorption energies, E_{ads} (kJ/mol), distortion energies, E_{dis} (kJ/mol) and interaction energies, E_{int} (kJ/mol), obtained for the adsorption of acetaldehyde for various binding modes.

Binding mode	E^a_{ads}	E^{b}_{ads}	$E_{dis}^{a}(TiO_{2})$	E_{int}^{a}
Mode A	-453.0		-33.4	52.3
Mode B	100.5	54.4	4.6	323.6
Mode C	120.2	404.9	-38.9	136.5
Mode D	65.7		50.7	558.9

^a adsorption at 3c site. ^b adsorption at 4c site.

The geometrical parameters of isolated acetaldehyde are compared to those of the adsorbed acetaldehyde for the various binding modes in **Table 4**.

Table 4. Geometrical parameters of adsorbed and isolated acetaldehyde.

	Isolated Adsorbed acetaldehyde						
	acetaldehyde	Mode A	Mode B	Mode C	Mode D		
	bond lengths (Å)						
Cc-Oc	1.216	1.216	1.396	1.238	1.242		
C _c -H _c	1.118	1.091	1.082	1.087			
C _c -C _m	1.505	1.474	1.496	1.446	1.466		
C _m -H _m	1.096	1.081	1.080	1.079	1.082		
Ti-O _c		2.381	1.880	2.071	2.043		
Cc-OTiO2			1.464				
H _m -O _{TiO2}				2.086			
$H_m^*-C_m$				1.105			
Ti-H _c							
bond angles (°)							
H _c -C _c -O _c	120.2	119.6	115.8	115.8			
C_m - C_c - O_c	123.8	123.5	112.2	125.2	121.8		
H_m - C_m - C_c	110.0	109.1	109.4	111.4	109.8		
$H_c-C_c-C_m$	116.0	116.9	114.3	118.9			
H _m -C _m -H _m	108.1	109.7	109.2	107.7	110.4		

*refers to the migrating methyl hydrogen.

In the first case (Mode A), it was found that the nearest Ti-O distance is 2.38 Å, which is less than the sum of the van der Waals radii of oxygen and titanium (3.52 Å), indicating that some covalent interaction is occurring. However, the adsorption energy is negative, indicating that this is an unfavorable mode of adsorption, as it is endothermic.

In the case of Mode **B**, acetaldehyde binds with its carbonyl oxygen coordinated to a surface Ti (1.88 Å, bond order 0.888) and the carbonyl carbon with the adjacent surface O atom (1.46 Å, bond order 0.739) to form a four membered ring structure. As a result of this coordination, it is found that the carbonyl bond weakens to almost a single

bond (bond order = 0.964) and the bond length increases from 1.216 Å to 1.396 Å (Table 4), indicating considerable weakening of the C=O bond upon adsorption. Further, it can be seen from **Table 4** that in Mode **B**, the C_m-C_C-O_C bond angle of adsorbed acetaldehyde decreases by ~11⁰ with respect to free acetaldehyde. Another important observation for this mode is that the methyl group assumes a conformation where one of the hydrogen atoms is synperiplanar with respect to the carbonyl oxygen. The stability of this conformation is due to more favorable $\pi(CH_3) \rightarrow \pi^*(C=O)$ group orbital interactions and hyperconjugation through the σ bonds [**38**].

Since the methyl hydrogen and aldehyde hydrogen are in close proximity to a surface oxide ion, there is a possibility that the acetaldehyde adsorbs on the surface, the lattice oxygen acts as a base to abstract a proton from the α position of the aldehyde or the aldehydic proton to yield a surface hydroxyl ion and adsorbed [CH₂--C(H)OTi]³⁺ or [CH₃-C⁻-OTi]³⁺ species, respectively.

In Mode C, it is found that the methyl hydrogen interacts with the surface oxygen with an O-H distance of 2.086 Å, which is much smaller than the sum of the van der Waals radii of oxygen and hydrogen 2.72 Å [70], and the surface Ti with the carbonyl oxygen with a Ti-O distance 2.071 Å (Fig. 4). For adsorption in this mode at the 3c site, it is found that, not only does the methyl group tilt to bring a methyl hydrogen close to a 3c oxygen, but spontaneous dissociation of the C-H bond also occurs, leading to the formation of surface HO⁻ and [CH₂⁻-C(H)OTi]³⁺ moieties. The product is depicted in Fig. 5(A). In this heterolytic cleavage of the C-H bond of the methyl group of acetaldehyde, the proton migrates to an edge surface oxide ion, giving rise to a OH⁻ ion. The remaining [CH₂=CHO]⁻ moiety combines with a surface Ti⁴⁺, producing [CH₂⁻-C(H)OTi³⁺. The reaction is exothermic. In the product, the O-H distance reduces to 0.989 Å from 2.086 Å in the reactant (Mode C of Fig. 4).

For the adsorption of acetaldehyde in Mode **D**, which involves the interaction of the aldehyde hydrogen with the TiO₂ surface, the adsorption energy is found to be 65.7 kJ/mol. It is observed that the aldehyde C-H bond dissociates spontaneously and a new C-O bond involving the carbonyl carbon and a surface oxygen is formed, yielding acetate like species. The product for the reaction is shown in **Fig. 5(B)**.



Fig. 5 Optimized structures of the product of (A) methyl C-H dissociation; (B) dissociation of aldehyde C-H dissociation on the Lewis basic site.

It is evident from **Fig. 4** that considerable distortion of the cluster occurs on adsorption of acetaldehyde on its surface. Therefore, we also calculated the distortion energy for the nanocluster (**Table 3**), calculated from the difference of the single point energy at the distorted geometry in the complex and the optimized energy of the nanocluster.

Thus,

$$E_{dis}(TiO_2) = E_{TiO2}(complex) - E(TiO_2)$$

The interaction energy between the nanocluster and acetaldehyde for the various adsorption modes was also computed (reported in **Table 3**), and is given as-

$$E_{int} = E_{ac}(complex) + E_{TiO2}(complex) - E_{complex}$$

The distortion energy was found to be highest for Mode **D**, as expected from Figure 4, which shows that the aldehyde C-H bond elongates considerably and even dissociates spontaneously on adsorption. For Mode **B** also the interaction energy was found to be quite high, as a result of polarization of C=O bond to C⁺-O⁻.

Table 5. Mulliken charges of isolated and adsorbed acetaldehyde.

Atom	Isolated acetaldehyde	Mode A	Mode B	Mode C	Mode D
C _m	-0.373	-0.269	-0.616	-0.305	-0.256
C _c	0.236	0.337	0.360	0.357	0.244
O _c	-0.358	-0.357	-0.636	-0.454	-0.367
H_m^{-1}	0.147	0.117	0.201	0.100	0.097
H_m^2	0.124	0.120	0.252	0.146	0.116
H_m^{3}	0.148	0.124	0.219	0.225	0.102
H _c	0.076	0.062	0.190	0.082	0.286
Ti		1.305	1.483	1.403	1.241
0			-0.771	-0.745	-0.740

Charge distribution

The calculated Mulliken charges on the atoms of acetaldehyde are given in **Table 5**. It can be seen that a considerable polarization of charge occurs upon adsorption. The polarization of the C=O bond is observed for both Modes **B** and **C**, as can be seen from the increase in the partial charges on carbon and oxygen (**Table 5**). For Mode **D**, the negative charge on the surface oxygen (-0.740) and positive charge on the aldehyde hydrogen (0.286) indicate the formation of OH on the surface. The partial charges of - 0.648 and -0.498 on the two oxygens for the product of Mode **D** (**Fig. 5**), indicate the formation of acetate-like species.

Effect of coordination

We next considered the relative adsorption energies for various low-coordinated sites. **Table 3** gives the calculated

adsorption energies for acetaldehyde at the 3c and 4c sites on the TiO₂ surface. The results for the calculated adsorption energies agree with the general trend that $E_{ads}(3c) > E_{ads}(4c)$; that is, lower coordination sites offer stronger adsorption for carbonyl interaction. This is to be expected since the low-coordinated titanium atoms have smaller positive charges, facilitating easy charge transfer to the oxygen of the carbonyl group. No surface reconstruction occurs for binding at 3c sites, but this occurs in case of 4c sites.

However, for adsorption in Mode C at the 4c site, considerable increase in the adsorption energy in comparison to that at the 3c site is observed. This can be explained on the basis of the very high distortion energies for the cluster as well as for acetaldehyde, because of the fact that the cluster changes shape completely, and also the C-H bond of acetaldehyde breaks spontaneously. However, the interaction energy is found to be 81.2 kJ/mol, which is much lower than that for the 3c site.

Effect of cluster size

We also examined the effect of cluster size on the adsorption energies. Since 3c sites offer the strongest coordination, we determined the adsorption energies for adsorption of acetaldehyde at this site for 6, 12 and 17 unit clusters (**Fig. 6**). The adsorption energies remain fairly constant with increase in cluster size, as the calculated adsorption energies are 98.4, 96.2, and 100.5 kJ/mol, respectively for the 6, 12 and 17 TiO₂ unit clusters, and no particular trend is observed.



Fig. 6 Optimized structures of acetaldehyde adsorbed on the 3c site on (A) (TiO₂)₆ and (B) (TiO₂)₁₂ surface.

The coordinating bond lengths also remain almost the same, the Ti-O bond length varying between 1.87 and 1.90 Å and the O-C bond length between 1.46 and 1.52 Å. Hence our calculations are representative of all cluster sizes.

Vibrational spectra of adsorbed species

The adsorption of acetaldehyde on TiO_2 has been earlier investigated using FT-IR spectroscopy [9, 21]. These studies deduced that acetaldehyde adsorbs molecularly in two forms on the surface: in an H-bridge bonded form and in an adsorbed form on the Lewis acid sites through one of the oxygen lone pairs. For coordination of acetaldehyde to the oxide surface, Raskó and Kiss **[21]** found that a red shift in the acetaldehyde C=O stretching from 1756 to 1729-1686 cm⁻¹ occurs due to acetaldehyde adsorbed by Hbridge bonding. They also reported some spectroscopic features above 3711 and 3665 cm⁻¹ and broad absorptions centered at 3440 cm⁻¹ which again were allocated to the adsorption of acetaldehyde through H-bridge bonding on the TiO₂ surface. The disappearance of the band at 1729-1686 cm⁻¹ in certain cases has also been reported suggesting that part of acetaldehyde is coordinated on Lewis acid sites through one of the oxygen lone pairs.

In the present work, we have calculated the vibrational spectra of the species produced, and have compared them with the experimental spectra. For free acetaldehyde, the prominent peaks are expected to be the ones due to the carbonyl stretching and the aldehyde C-H stretch. These were observed at 1750 and 2730 cm⁻¹, respectively. The calculated values are 1756 and 2830 cm⁻¹, respectively, and these are the most intense bands, having calculated intensities of 164 and 137 km/mol, respectively. Less intense bands at 1455, 1416, 1084 and 1340 cm⁻¹ (intensity $= \sim 30$ km/mol) are also expected. For adsorption on the TiO₂ surface, our calculations indicate that the carbonyl band gradually shifts to lower frequency from 1756 to 1701 and 1605 cm⁻¹ for Modes C and D, respectively, while for Mode **B** this band disappears. This is because the carbonyl bond weakens so much due to interaction with the surface that its vibration mode shifts to 1133 cm⁻¹ (52 km/mol), which is in agreement with the experimental and earlier theoretical studies [9, 21, 65].

For Mode **B**, only three important peaks were observed, 1133 cm⁻¹ (C-O stretch, 89 km/mol), 1035 cm⁻¹ (C_C-O_{TiO2} stretch, 81 km/mol) and a band at 797-741 cm⁻¹ (O_C-Ti stretch, 189 km/mol). It was further observed that for Mode **C**, a band appears at high frequency (2845 cm⁻¹, aldehyde C-H stretch, 452 km/mol) and other important peaks were observed in the 1000-1500 cm⁻¹ region (1363 cm⁻¹, C-O stretch + HCO bend, 155 km/mol; 1174 cm⁻¹, C=C stretch, 41 km/mol). The spectrum of acetaldehyde adsorbed in Mode **D** was found to be dominated by a very intense band at 957 cm⁻¹ (594 km/mol), which is a mixture of the C-O stretch and HCO bend, but it is found to lack the aldehyde C-H stretch band (centered around 2900 cm⁻¹). Other peaks were observed at 3844 cm⁻¹ (O_{TiO2}-H stretch, 52 km/mol) and 894 cm⁻¹ (O_{TiO2}-H bend, 165 km/mol).

Besides the bands of molecularly adsorbed acetaldehyde, Raskó and Kiss [21] also reported several absorptions showing transformations of acetaldehyde on the oxide surface. Among these absorptions, the bands at 1663-1638 cm⁻¹ (v (C=O)), at 1596-1586 cm⁻¹ (v (C=C)), at 1260-1280 cm⁻¹ (δ (C-H)), at 1173-1160 cm⁻¹ (ν (CC)), and at 936-981cm⁻¹ (δ (CH₃)) were attributed to adsorbed crotonaldehyde, which is produced by β -aldolization occurring between two acetaldehyde molecules on the surface. When acetaldehyde adsorbs on the surface of TiO₂, a lattice oxygen acts as a base to abstract a proton from the α position of the aldehyde to form [CH₂-C(H)O] species, which can attack the electrophilic carbonyl group of another aldehyde to form an adsorbed aldol, which then dehydrates to give crotonaldehyde or butene. It has been observed that the oxidized TiO₂ surface supports the aldol condensation to give crotonaldehyde, whereas the reduced TiO_2 surface prefers butene as the product [24].

The band at 1546-1542 cm⁻¹ (v_{as} (COO)) was assigned to surface acetate which is the result of acetaldehyde oxidation on surface oxygen sites. The corresponding band was observed in the spectrum of Mode **B** of adsorbed aldehyde at 1396 cm⁻¹ (47 km/mol), indicating that adsorbed acetaldehyde undergoes oxidation on the surface to form carboxylate species. The bands at 2868-2843 cm⁻¹ (v (CH)) and at 1079-1037 cm⁻¹ (v (C=O)) were assigned to adsorbed ethoxy (CH₃CH₂O) species which is the product of reduction of acetaldehyde on the oxide surface.²¹ This was not observed in our case as we have considered oxidized TiO₂ surface and formation of ethanol is only feasible on the reduced surface.

Conclusion

We have observed that the smaller $(TiO_2)_n$, for n = 3 - 16nanocrystals, show slightly erratic behavior, which indicates that some different conformation might be important for the smaller nanocrystals, while this fact becomes less and less important with increasing cluster size, where bulk atoms dominate successively more. The hexagonal ring based structures are preferred for smaller $(TiO_2)_n$, n = 3 - 16 clusters. The nanocluster $(TiO_2)_{17}$ shows partial reconstruction of the surface and for $(TiO_2)_{21}$ complete anatase conformation is sustained. The similar values of Mulliken charges on the titanium ions in various coordination states indicate that it is difficult to assign an electronic cause for the formation of the hexagonal ring structures in the smaller clusters, and confirms the fact that it is a packing effect rather than an electronic one. The electronic structure studies show the HOMO to be anion based, and the LUMO to be centered on the 3d orbitals of under-coordinated metal ions. The frontier orbitals are found to be centered on the unsaturated surface atoms.

A myriad of different adsorption products are formed on the TiO_2 nanosurface depending upon the coordination. The low coordination sites (3c) are highly reactive and form stronger bonds with the acetaldehyde molecule, whereas adsorption at the four coordination site leads to severe reconstruction of the nanosurface. Acetaldehyde chemisorbs onto the surface producing zwitterionic fourmembered rings, in which the carbonyl C=O bond is considerably weakened; secondly it adsorbs on the TiO_2 surface in a H-bridge bonded form, either through the aldehyde hydrogen or methyl hydrogen.

The most feasible mode of adsorption on the TiO₂ nanosurface is found to be methyl hydrogen migration (Mode C), resulting in the formation of $[CH_2^{-}-C(H)O]$ species and the second most probable mode is the interaction of the carbonyl bond. The adsorbed acetaldehyde can undergo various transformations (i) β -aldolization ($[CH_2^{-}-C(H)O]$ species may undergo aldol condensation) to yield crotonaldehyde and butene, (ii) oxidation into acetate (interaction of aldehyde hydrogen with the surface yields carboxylate like species) and (iii) reduction into ethoxy species. The results obtained in this work can be of significant help in deciding the fate of reaction of acetaldehyde on the nanosurface.

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