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J. Phys. Chem. C, Just Accepted Manuscript • Publication Date (Web): 03 May 2017
Downloaded from http://pubs.acs.org on May 7, 2017

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The Adsorption Mechanisms of Typical Carbonyl-Containing Volatile Organic Compounds on Anatase TiO$_2$ (001) Surface: A DFT Investigation

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ABSTRACT: The carbonyl-containing compounds (CCs) are typical volatile organic compounds (VOCs) and ubiquitously present in the environment. Therefore, the adsorption structures and properties of typical CCs on anatase TiO$_2$ (001) surface were investigated systematically with density functional theory (DFT) to understand their further catalytic degradation mechanisms. The adsorption mechanisms show that three selected typical CCs, acetaldehyde, acetone and methylacetate, can easily be trapped on the anatase TiO$_2$ (001) surface via the interaction between carbonyl group with Ti$_{5c}$ sites of catalyst surface. Especially for acetaldehyde with the bare carbonyl group and the strongest adsorption energy, it is the most stable on the surface, because the bare carbonyl group can interact with not only Ti$_{5c}$ atom but also O$_{2c}$ atom of the surface. The substituent effect of different CCs has less impact on its adsorption models in this studied systems and the bare carbonyl group is the key functional group within studied CCs. The Ti$_{5c}$ atoms of anatase TiO$_2$ (001) surface are active sites to trap CCs. Our theoretical results are expected to provide insight into the adsorption mechanisms of these carbonyl-containing VOCs on TiO$_2$ catalyst and also to help understand the further catalytic degradation mechanisms of air pollutants at the molecular level.

Key words: Carbonyl-containing compounds; Adsorption mechanism; Anatase TiO$_2$; (001) surface; Density function theory
1. INTRODUCTION

The carbonyl-containing compounds (CCs) are major component of the volatile organic compounds (VOCs), which have rich natural and anthropogenic sources. CCs can be directly emitted into atmosphere from vegetation and secondary production of other VOCs.\(^1\)-\(^2\) Therefore, they are ubiquitously present in the urban atmosphere.\(^2\)-\(^5\) Meanwhile, they are also closely related to the photochemical air pollution due to an important role in the formation of photochemical smog and secondary organic aerosol (SOA).\(^4\), \(^6\)-\(^7\) Furthermore, CCs, particularly with low molecular weight such as formaldehyde and acetaldehyde, are toxic and carcinogenic, which can irritate the eyes, skin and nasopharyngeal membranes.\(^7\)-\(^9\) Therefore, the removal of CCs from the atmosphere has been receiving growing scientific attention due to their profound impacts on air quality and human health.

At present, photocatalytic technology is considered as a green cleaning method with excellent purification capability. It has received enormous attention for the pollution control of VOCs in air.\(^10\)-\(^11\) For example, TiO\(_2\) used for the photocatalytic air purification is inexpensive and can completely oxidize organic pollutants into CO\(_2\) and H\(_2\)O.\(^12\)-\(^13\) Previous researches reported that the varied forms of TiO\(_2\) exhibit different photocatalytic activity on the degradation of CCs.\(^14\)-\(^18\) For instance, the TiO\(_2\) film shows much higher photoactivity than Degussa P-25 TiO\(_2\) powder for acetaldehyde degradation.\(^16\) Sano et al. utilized Pt loading TiO\(_2\) to modify the catalyst to oxidate acetaldehyde into CO\(_2\) effectively.\(^17\) Our previous studies showed that low molecule weight gaseous CCs such as formaldehyde, acetaldehyde, propionaldehyde and acetone can also be degraded efficiently by TiO\(_2\)/SiO\(_2\) photocatalyst.\(^18\)
Although there are number of reports on the photocatalytic degradation of CCs, the adsorption and degradation mechanisms are still not sufficient. Nevertheless, the adsorption and desorption models of atoms or molecules on the catalyst surface are an initial and prerequisite step for various catalytic reactions, and studying the adsorption mechanisms of the different CCs on the catalyst surface can help us to better understand the further photocatalytic mechanisms.

In this study, therefore, the adsorption mechanisms of three typical CCs on the anatase TiO$_2$ (001) surface are investigated systematically using density functional theory (DFT) calculations. Anatase is the common natural TiO$_2$ polymorphs, and the (001) surface has more unsaturated coordinated Ti and O atoms than the (101) and (100) surfaces. Some previous studies have proven that it has higher catalytic activity than other surfaces due to the effect of surface dangling bonds.$^{13,19,22}$ Acetaldehyde, acetone, and methylacetate are the typical CCs molecules, and they have same carbonyl functional group and can ubiquitously present in urban atmosphere. For example, acetaldehyde is a key component of photochemically generated air pollution with a large concentration in the troposphere; photolysis of acetone in the troposphere is a major source of hydrogen oxide radicals with important implications for global tropospheric chemistry; methylacetate is one of typical esters, with profound impacts on air quality and human health.$^{7-9}$ Hence, the adsorption configurations and characteristics of three investigated CCs on anatase TiO$_2$ (001) surface is investigated using DFT calculations in this work. Accurate electronic calculation including local density of states (LDOS) and charge density difference (CDD) at anatase TiO$_2$ (001) surface is fundamental to understand
their local physical and chemical properties, and in particular the condition of surface states
play a crucial role in the adsorption and catalytic performance. Therefore, the LDOS and
CDD are further performed to identify the adsorption properties and mechanisms.
Furthermore, acetaldehyde has a simplest carbonyl group, aldehyde group, which do not
affected by other groups, and the carbonyl group in this case is called the bare group in this
study. For acetone and methylacetate, the carbonyl groups are surrounded by other groups
methyl and methoxyl groups. Hence, the substituent group effect is also considered to
understand the nature of the adsorption mechanisms of CCs on anatase TiO$_2$ (001) catalyst
surface. The current results can provide a theoretical basis for the photocatalytic degradation
of organic pollutants in air.

2. COMPUTATIONAL METHODS

The calculations were carried out at the DFT plane-wave level utilizing the Vienna ab initio
simulation package (VASP).$^{23-24}$ For the treatment of the exchange and correlation, the
gradient-corrected Perdew-Burke-Ernzerhof (PBE) functional of the generalized gradient
approximation (GGA) was used.$^{25}$ Valence electrons included the Ti 3s/3p/3d, O 2s/2p, C
2s/2p, and H 1s shells, and the one-electron wave function was expanded using a plane-wave
basis set with an energy cutoff of 400 eV. Ion–electron interactions were described by the
projector augmented wave (PAW) method.$^{26-27}$ The calculated bulk lattice parameters of
anatase TiO$_2$ are $a = 3.776$ Å, $c = 9.486$ Å and $c/a = 2.512$, with a k-point grid of $(3\times2\times1)$,
which are consistent with the previously reported theoretical data ($a=3.776$ Å, $c=9.486$ Å,
$c/a=2.512$)$^{13}$ and experimental results ($a=3.785$ Å, $c=9.514$ Å, $c/a=2.514$)$^{28}$.
To balance the calculated accuracy and efficiency, the (2×3) supercell of anatase TiO$_2$ (001) surface is selected, because it provide an enough big surface to simulate all the adsorption patterns of acetaldehyde, acetone, and methylacetate on anatase TiO$_2$ (001) surface. In anatase TiO$_2$ (001) surface, the periodic slab model are composed of four O-Ti-O layers with (2×3) supercell comprising 24 Ti atoms and 48 O atoms on the basis of the optimized lattice parameters. All slabs were separated by a vacuum spacing of approximately 17 Å, which guaranteed no interactions between the slabs. The Brillouin zones were sampled with the chosen (3×2×1) k-points for surface calculations to balance the accuracy and the computing time. A unit cell of 3.776 × 3.776 × 9.486 Å$^3$ was used for the calculations on the isolated molecule. The convergence of total energy during electronic self-consistent iteration process was considered to be achieved until two iterated steps with energy difference less than 1.0×10$^{-5}$ eV. In this slab models, the atoms in the bottom two layers of the slab were kept frozen at the optimized bulk positions, while the remaining layers and adsorbates were fully relaxed during the calculations. For the sake of discussion, the adsorption energy $\Delta E_{\text{ads}}$ was calculated according to the following equation:

$$\Delta E_{\text{ads}} = (E_{\text{mol}} + E_{\text{surf}}) - E_{\text{mol/surf}}$$

(1)

where $E_{\text{mol/surf}}$, $E_{\text{surf}}$, and $E_{\text{mol}}$ are the calculated individual energies of the adsorbed species on the surface, a clean surface, and a gas-phase molecule, respectively. From the above equation, a positive $\Delta E_{\text{ads}}$ indicates an exothermal process; otherwise it indicates an endothermic process which suggests an unstable adsorption structure. The LDOS and CDD were also calculated to investigate the charge distribution and the bonding situation between the
gas-phase molecules and the catalyst surface.

3. RESULTS AND DISCUSSION

3.1. Anatase TiO$_2$ (001) Surface. The structure of anatase TiO$_2$ (001) surface is optimized and presented in Figure 1. It is corrugated with coordinated and uncoordinated O atoms as well as uncoordinated Ti atoms: three-fold coordinated O atom (denoted as O$_{3c}$, the same hereinafter), two-fold coordinated bridge site O atom (O$_{2c}$), and five-fold coordinated Ti atom (Ti$_{5c}$), respectively. The structures in Figure 1 show that the current results agree well with the published computational values (1.93 Å of Ti$_{5c}$–O$_{3c}$ and 1.96 Å of Ti$_{5c}$–O$_{2c}$). 30 This indicates that the optimized anatase TiO$_2$ (001) surface structure at the current method is reliable. One O$_{2c}$ atom bonds with two adjacent Ti$_{5c}$ atoms to form the Ti$_{5c}$–O$_{2c}$–Ti$_{5c}$ chain along the [010] direction (Figure 1). An obvious surface tension is found due to the big bond angle of the Ti$_{5c}$–O$_{2c}$–Ti$_{5c}$ of 148.7°. The distance between Ti$_{5c}$ and O$_{2c}$ atoms is 1.961 Å, which is approximately 0.3 Å longer than Ti$_{5c}$–O$_{3c}$ bond, implying that the site in Ti$_{5c}$–O$_{2c}$ bond should more easily to be broken. Thus, O$_{2c}$ and Ti$_{5c}$ atoms are expected to be the active sites during the adsorption process rather than O$_{3c}$ atoms. According to the above optimized surface structures, all possible adsorption mechanisms of three investigated CCs on anatase TiO$_2$ (001) surface are considered, and the results are illustrated in Figures 2 and S1-S3. The corresponding adsorption energies are listed in Tables 1 and S1-S3.

3.2. Adsorption Mechanisms. 3.2.1. Acetaldehyde (ACH). According to the different adsorption sites, there are three types of adsorption modes: O$_{C=O}$–Ti$_{5c}$ mode, O atom in
carbonyl group of acetaldehyde (O\(_{\text{C}=\text{O}}\)) adsorbed on surface Ti\(_{5\text{c}}\) atom; H\(_{\text{C}=\text{O}}\)−O\(_{2\text{c}}\) and H\(_{\text{CH}_3}\)−O\(_{2\text{c}}\) modes, H atom of carbonyl and methyl group of acetaldehyde (H\(_{\text{C}=\text{O}}\) and H\(_{\text{CH}_3}\)) adsorbed on surface O\(_{2\text{c}}\) atom. As Figure S1 shows, the O−H distance is 2.278 Å in H\(_{\text{C}=\text{O}}\)−O\(_{2\text{c}}\) mode, which is approximately 0.2 Å shorter than that in H\(_{\text{CH}_3}\)−O\(_{2\text{c}}\) mode. Thus, H\(_{\text{C}=\text{O}}\)−O\(_{2\text{c}}\) mode is expected to be higher adsorption energy than the H\(_{\text{CH}_3}\)−O\(_{2\text{c}}\) mode. The adsorption energies listed in Table S1 show that the Δ\(E_{\text{ads}}\) of the former is calculated to be 0.44 eV, which is 0.1 eV larger than the latter. Thus, H\(_{\text{C}=\text{O}}\)−O\(_{2\text{c}}\) mode is slightly stable than H\(_{\text{CH}_3}\)−O\(_{2\text{c}}\) mode.

For O\(_{\text{C}=\text{O}}\)−Ti\(_{5\text{c}}\) mode, four adsorption patterns are found, denoted as Type A_ACH, Type B_ACH, Type C_ACH and Type D_ACH, respectively. The lowest adsorption energy among the four kinds of O\(_{\text{C}=\text{O}}\)−Ti\(_{5\text{c}}\) adsorption modes is 0.81 eV (Table 1), which is still two times higher than H\(_{\text{C}=\text{O}}\)−O\(_{2\text{c}}\) mode. This indicates that O\(_{\text{C}=\text{O}}\)−Ti\(_{5\text{c}}\) mode is the most stable among three types of adsorption modes, and acetaldehyde preferred to be adsorbed on Ti\(_{5\text{c}}\) site of anatase TiO\(_2\) (001) surface rather than O\(_{2\text{c}}\) site. The interactions in H\(_{\text{C}=\text{O}}\)−O\(_{2\text{c}}\) and H\(_{\text{CH}_3}\)−O\(_{2\text{c}}\) modes are not stronger than those in O\(_{\text{C}=\text{O}}\)−Ti\(_{5\text{c}}\) modes. Therefore, the following discussion will focus on the four kinds of O\(_{\text{C}=\text{O}}\)−Ti\(_{5\text{c}}\) modes.

In the Type A_ACH, O\(_{2\text{c}}\) atom is completely pulled out from the surface to form the new C\(_{\text{C}=\text{O}}\)−O\(_{2\text{c}}\) bond with the length of 1.408 Å (Figure 2a). This behavior also makes the Ti\(_{5\text{c}}\)−O\(_{2\text{c}}\) bond broken, and the distance becomes to 3.647 Å. The O\(_{\text{C}=\text{O}}\)−Ti\(_{5\text{c}}\) bond is calculated to be 1.830 Å, which is almost the same with the old Ti\(_{5\text{c}}\)−O\(_{2\text{c}}\) bond (1.807 Å). The double bond length of C=O in acetaldehyde is elongated by 15% and becomes to 1.401 Å (1.219 Å in the gas phase). The case in the Type B_ACH (Figure 2a) is a forming new bond process between
O\textsubscript{C=O} atom and adjacent Ti\textsubscript{5c} atom, and the distance of new bond is 2.194 Å. And there is not a big deformation in acetaldehyde. For example, the C=O bond length of acetaldehyde slightly elongates to 1.231 Å, only 1% elongation compared to the gas-phase. As Figure 2a shows, acetaldehyde in the Type C_ACH and the Type D_ACH is not obvious distorted as it is adsorbed on anatase TiO\textsubscript{2} (001) surface. However, the lattice structures of catalyst surface in three configurations are all somewhat distorted. For example, in the Type C_ACH, the surface O\textsubscript{2c}–Ti\textsubscript{5c} bond breaks and extends from 1.961 to 3.426 Å, and the new forming bonds are calculated to be 2.046 Å for O\textsubscript{C=O}–Ti\textsubscript{5c} and 2.178 Å for H\textsubscript{C=O}–O\textsubscript{2c}, respectively. As discussed above, among the four O\textsubscript{C=O}–Ti\textsubscript{5c} adsorption modes, only the Type A_ACH has an obvious saddle-like structure due to the large distortion in adsorption sites. The previous studies have also reported similar results, such as in the case of formaldehyde and formic acid on anatase TiO\textsubscript{2} (001) surface.\textsuperscript{21,31} The adsorption energies listed in Table 1 show that the Type A_ACH has the largest adsorption energy, which is approximately 2.5 times larger than other configurations. It implies that the saddle-like structure should make the adsorption of acetaldehyde on the catalyst surface stable. Previous experimental studied have proven that the most stable adsorption configuration of other CCs shows the similar saddle-like structure just like the Type A_ACH with the highest adsorption energy. The Type A_ACH has an obvious saddle-like structure due to the large distortion in adsorption sites, which is in agreement with the experimental observation. For example, the previous studies have also reported similar results that the most stable adsorption configuration characterizes the saddle-like structure, such as in the case of formaldehyde and formic acid on anatase TiO\textsubscript{2}. 
The formation of the Type A_ACH is a large exothermic process, and some new bonds such as O=C=O_Ti5c, C=C=O_O2c and H=C=O_O2c are formed, indicating that anatase TiO2 (001) surface can effectively adsorb and capture acetaldehyde on the surfaces.

3.2.2. Acetone (ACE). For the case of acetone, there are also three types of adsorption modes observed: O=C=O_Ti5c, O=C=O_O2c and H=CH3_O2c. For the O=C=O_O2c and H=CH3_O2c modes. No obvious structural deformation are observed between acetone and anatase TiO2 (001) surface. The acetone is vertical to the surface and forms bonds via O=C or H/O atom with O2c atom. As shown in Figure S2, the length of O=C=O_O2c is 2.788 Å, which is 0.3 Å longer than that of H=CH3_O2c, implying the slight interaction of O=C=O with O2c atoms. This is also agree with the energies listed in Table S2, where the ΔE_ads = 0.27 eV of O=C=O_O2c mode is lower by 0.08 eV than that of H=CH3_O2c mode. For the three kinds of O=C=O_Ti5c modes, the ΔE_ads of them are at least twice than those of O=C=O_O2c and OD_CH3=O2c modes (Table 1). Thus, similar results can be drawn from the case of acetone, i.e., acetone is readily trapped by the catalyst surface via C=O group interaction with Ti5c site. Therefore, we will focus on the most possible adsorption mode of O=C=O_Ti5c in this section.

In three O=C=O_Ti5c modes, acetone adsorbs on anatase TiO2 (001) surface from different directions. As shown in Figure 2b, there are still not obvious distortion and also not formation of the saddle-like structure for the three O=C=O_Ti5c modes. The largest change is found in the Type A_ACE configuration, whose O2c atom is pulled out from the surface and the distance of Ti5c=O2c elongate from 1.961 to 3.429 Å. However, for other two O=C=O_Ti5c modes, the Type B_ACE and Type C_ACE, the length of two Ti5c=O2c bonds are also extended (2.455 and
2.313 Å), which are 25% and 18% longer than the initial distance, respectively. As discussed above, the adsorption energies of three O\(_{\text{C}=\text{O}}\)–Ti\(_{5c}\) modes are expected to be little difference. Table 1 shows that the computed adsorption energies of three modes are 0.81, 0.86 and 0.71 eV, respectively, with small adsorption energies difference. Compared with the structure of acetaldehyde, the carbonyl group in acetone is in the middle of two terminal methyl group, and thereby there is not the bare C=O group. Hence, the bare C=O group play an important role in adsorption mechanism of CCs.

3.2.3. Methylacetate (MAC). Due to with ester group in MAC, there are four possible types of adsorption modes: O\(_{\text{C}=\text{O}}\)–Ti\(_{5c}\), O\(_{\text{ester}}\)–Ti\(_{5c}\), O\(_{\text{ester}}\)–O\(_{2c}\) and H\(_{\text{CH}_3}\)–O\(_{2c}\). Similar with the cases of acetaldehyde and acetone, it is difficult for methylacetate interaction with O\(_{2c}\) site to form O\(_{\text{ester}}\)–O\(_{2c}\) and H\(_{\text{CH}_3}\)–O\(_{2c}\) modes, with the \(\Delta E_{\text{ads}}\) of 0.34 and 0.16 eV (Figure S3 and Table S3). However, the binding energy of O\(_{\text{ester}}\) atom with Ti\(_{5c}\) atom (O\(_{\text{ester}}\)–Ti\(_{5c}\) mode) is 0.32 eV, which is even smaller than that of O\(_{\text{ester}}\) atom with O\(_{2c}\) atom (O\(_{\text{ester}}\)–O\(_{2c}\) mode). This further confirms that CCs should be trapped by the TiO\(_2\) surface predominantly via C=O group interaction with Ti\(_{5c}\) site rather than O\(_{\text{ester}}\) atom. For the O\(_{\text{C}=\text{O}}\)–Ti\(_{5c}\) mode, there are only two possible adsorption modes for methylacetate, labeled as Type A_MAC and Type B_MAC. It can be found that for the three investigated CCs, the number of kinds for O\(_{\text{C}=\text{O}}\)–Ti\(_{5c}\) mode decreases as the size of substituent group numbers increases, from four kinds of acetaldehyde to two kinds of methylacetate.

As shown in Figure 2c, the C=O lengths are 1.243 Å for the Type A_MAC and 1.232 Å for the Type B_MAC, respectively, which are somewhat longer than the corresponding
gas-phase structure (1.220 Å). The Ti\textsubscript{5c}–O\textsubscript{2c} distances stretch to 2.930 Å for the Type A\_MAC and 2.456 Å for the Type B\_MAC, implying that the little change in structure of methylacetate and the catalyst surface in two O\textsubscript{C–O}–Ti\textsubscript{5c} adsorption modes. Therefore, the adsorption energies of two adsorption modes are also little different. The Table 1 shows the $\Delta E_{\text{ads}}$ being 0.78 eV for the Type A\_MAC mode and 0.82 eV for the Type B\_MAC mode.

As discussed in mechanism above, three investigated CCs are readily trapped by the Ti\textsubscript{5c} site of anatase (001) surface, indicating that Ti\textsubscript{5c} atom is the activity site on the TiO\textsubscript{2} (001) surface, in agreement with our previous study that VOCs are readily trapped by Ti atom in TiO\textsubscript{2} catalyst.\textsuperscript{29} In addition, the three CCs are all easily adsorbed on anatase TiO\textsubscript{2} (001) surface via C=O group interaction with Ti\textsubscript{5c} atoms. Compared to the results of three investigated CCs, the bare carbonyl group is the key functional group. If H atom in aldehydic group is substituted by other group, the adsorption energy rapidly declines. However, the size of substituent group only affects the number of adsorption mode but do not the adsorption energy. The CCs with the bare C=O group will be more active to be adsorbed on the anatase (001) surface, and their adsorption modes are more distortion.

3.3. Electronic Structures of Adsorption Configurations. To further understand adsorption properties and mechanisms, the LDOS and CDD induced by adsorption are analysed. Here, we considered the energetically most favourable adsorption mechanisms for three investigated CCs. For the LDOS, the overlap peaks of adjacent atoms can directly show the interactions between the adjacent atoms. The area of overlap peaks between the LDOS of two atoms represents the strength of the interaction. As discussed above, this section mainly
focused on the interaction of Ti$_{5c}$ and O$_{2c}$ atoms of anatase TiO$_2$ (001) surface with C$_{C=O}$ and O$_{C=O}$ atoms of three investigated CCs. The LDOS shown in Figure 3 is taken for the top layer interaction surface O$_{2c}$ and Ti$_{5c}$ atoms as well as C and O atoms of C=O group in CCs. The LDOS of three investigated CCs are also listed in Figure 3b-d as background. The CCs gas-phase peaks are all very sharp, typical for a molecule. From total DOS of (001) surface and LDOS of surface interaction O$_{2c}$ species of the slab, the high-energy edge of valence band is mainly constituted by states from O$_{2c}$ atoms on the surfaces and the conduction band is mainly occupied by Ti$_{5c}$ atoms. It indicates that the reactive activity of the catalyst surface is actually formed mainly by the surface O$_{2c}$ and Ti$_{5c}$ atoms. It is consistent with the analysis from the structure of optimized catalysts discussion where the surface O$_{2c}$ and Ti$_{5c}$ sites are most active and have the strongest adsorption energy.

The LDOS for the adsorption modes of acetaldehyde, acetone and methylacetate are shown in Figures 4 and S4. Compared with Figure 3a, the adsorption of acetaldehyde on anatase TiO$_2$ (001) surface induces the state perturbation of O$_{2c}$, Ti$_{5c}$, O$_{C=O}$ and C$_{C=O}$, implying that there are the formation of the new bonds or the deformation of the original bonds. For example, as shown in Figure 4b-c of the O$_{2c}$ and C$_{C=O}$ states and Figure 4a and d of the Ti$_{5c}$ and O$_{C=O}$ states, the strong overlap peak appears in the valence band of -5.5 – -4.8 eV, and the weak overlap peak lies in conduction band of 2 – 4 eV. It indicates that the strong interaction between C$_{C=O}$ atom with surface O$_{2c}$ atom and the weak interaction between O$_{C=O}$ atom and surface Ti$_{5c}$ atom. In addition, the states of O$_{C=O}$ is broadened (-5.4 to 0 eV); and the peaks of surface Ti$_{5c}$ in the conduction band part becomes lower (from -4 to -5.4 eV),
indicating a certain degree of electron transfer between the two atoms. The LDOS of O$_{2c}$ and O$_{C=O}$ atoms are almost the same upon the adsorption, indicating that the newly formed Ti$_{5c}$−O$_{C=O}$ bond is identical to the old deformative Ti$_{5c}$−O$_{2c}$ bond. The current results of LDOS agree with the above discussion in mechanism section. According to the geometric structures of the Type B_ACE of acetone and the Type B_MAC of methylacetate (Figure S4a-d), the newly formed hybrid peaks in the range of -6 to 0 eV indicates that the interaction between two CCs with the catalyst surface is a little strong, consistent with the newly formed O$_{C=O}$−Ti$_{5c}$ bond of two structures.

The CDD plots shown in Figure 5 indicate the charge redistribution upon adsorption. The CDD is defined as the charge density difference between the clean surface, gas-phase CCs, and the surface with adsorbed CCs. Thus, the effect the adsorbed CCs’ interaction with anatase TiO$_2$ (001) surface on charge distribution can be seen from CDD plots analysis. The yellow part means the area gaining electrons, and the blue one represents the area losing electrons. The charge transfer mainly occurs between C$_{C=O}$ with surface O$_{2c}$ atoms and O$_{C=O}$ with Ti$_{5c}$ atoms, which is in agreement with the results of LDOS. From Figure 5a, acetaldehyde mainly bonds with the surface Ti$_{5c}$ and O$_{2c}$ atoms by covalent interactions, and the interactions between O$_{C=O}$ with surface Ti$_{5c}$ atom as well as C$_{C=O}$ with surface O$_{2c}$ atoms are relatively strong, indicating the formation of O$_{C=O}$−Ti$_{5c}$ and C$_{C=O}$−O$_{2c}$ bonds. The enhancement of the charge density between O$_{C=O}$ and surface Ti$_{5c}$ atoms indicates their interaction strengthen. Vice versa, the interaction between surface O$_{2c}$ with surface Ti$_{5c}$ becomes weak. As a result, the surface O$_{2c}$ atom prefer to form a bond with C$_{C=O}$ atom. This
is consistent with the results of the optimized adsorption mechanism of the Type A_ACH. Similar results are drawn from the CDD data of the Type B_ACE and Type B_MAC shown in Figure 5b-c. The charge density between O\(_{C=O}\) with surface Ti\(_{5c}\) atoms increases, indicating that their interaction is strong. In summary, the LDOS and CDD calculations also show that CCs prefer to adsorb on anatase TiO\(_2\) (001) surface through the interaction between Ti\(_{5c}\) atoms and C=O groups.

4. CONCLUSION

In this work, the adsorption mechanisms of three typical carbonyl-containing VOCs, acetaldehyde, acetone and methylacetate, on anatase TiO\(_2\) (001) catalyst surface have been studied using the first principles calculations. All possible adsorption structures of acetaldehyde, acetone and methylacetate are considered and calculated. From these adsorption structures, it is can be found that anatase TiO\(_2\) (001) surface readily traps CCs mainly via the interaction between carbonyl group of CCs with Ti\(_{5c}\) sites of TiO\(_2\) catalyst surface. There are four O\(_{C=O}\)−Ti\(_{5c}\) adsorption modes for acetaldehyde, three for acetone, and two for methylacetate, respectively. The adsorption energy rapidly decreases when the H atom of aldehyde group is substituted by other groups. However, the sizes of substituent group have less impact on the adsorption energy. The bare carbonyl group is more easily adsorbed on anatase TiO\(_2\) (001) surface. For example, acetaldehyde with the bare C=O group is calculated to be easily adsorbed on anatase TiO\(_2\) (001) surface via the interaction of C\(_{C=O}\) with O\(_{2c}\), and O\(_{C=O}\) with Ti\(_{5c}\) to form a saddle-like adsorption structure. The structure of the Type A_ACH has the largest adsorption energy, implying that it is the most stable mode. For acetone and
methylacetate, only O\textsubscript{C=O}–Ti\textsubscript{5c} bonds are formed. The results from LDOS and CDD further confirm the results of adsorption structures and mechanisms from the view of electronic aspects. All these results indicate that anatase TiO\textsubscript{2} (001) surface can effectively trap CCs and is expected to have a good catalytic activity to CCs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Details of simulations results (PDF)

ACKNOWLEDGMENTS

This work was financially supported by National Natural Science Foundation of China (41425015, 41373102 and 41675122), Team Project from the Natural Science Foundation of Guangdong Province, China (S2012030006604), and the Special Program for Applied Research on Super Computation of the NSFC-Guangdong Joint Fund (the second phase), and the National Supercomputing Centre in Guangzhou (NSCC-GZ), and Science and Technology Program of Guangzhou city (201707010188).

References


Table 1 Calculated adsorption energies of CCs on anatase TiO$_2$ (001) surface. (unit: eV)

<table>
<thead>
<tr>
<th>Modes</th>
<th>$E_{\text{ads}}$ (Acetaldehyde)</th>
<th>$E_{\text{ads}}$ (Acetone)</th>
<th>$E_{\text{ads}}$ (Methylacetate)</th>
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<td>Type A</td>
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<td>0.78</td>
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<tr>
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<td>0.86</td>
<td>0.82</td>
</tr>
<tr>
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<td>0.71</td>
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<td>Type D</td>
<td>0.94</td>
<td>—</td>
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</tbody>
</table>
Figure captions:

**Figure 1.** Optimized structures of (a) side view and (b) top view of anatase TiO$_2$ (001) surface. Ti and O atoms are labeled as shallow grey and red spheres, respectively. The bond length is Å and the angle is °.

**Figure 2.** Optimized geometries of (a) acetaldehyde, (b) acetone and (c) methylacetate on anatase TiO$_2$ (001) surface. C and H atoms of CCs are labeled as dark grey and blue spheres, respectively. The number in parentheses is the original bond length (unit: Å).

**Figure 3.** Local density of states (LDOS) for (a) clean anatase TiO$_2$ (001) surface, (b) gas-phase acetaldehyde, (c) gas-phase acetone and (d) gas-phase methylacetate. The Fermi energies are set as 0 eV.

**Figure 4.** Local density of states (LDOS) of Type A_ACH. (a) adjacent Ti$_{5c}$ atom of anatase TiO$_2$ (001) surface; (b) adjacent O$_{2c}$ atom of anatase TiO$_2$ (001) surface; (c) C$_{C=O}$ atom of acetaldehyde; (d) O$_{C=O}$ atom of acetaldehyde.

**Figure 5.** Charge density difference (CDD) of (a) Type A_ACH, (b) the Type B_ACE and (c) Type B_MAC.
Figure 1
Figure 2

(a) Type A_ACH

(b) Type A_ACE

(c) Type A_MAC

Type B_ACH

Type B_ACE

Type B_MAC
Figure 3

(a) Clean surface
(b) Acetaldehyde
(c) Acetone
(d) Methylacetate
Figure 4

![Graph showing Local Density of State (electron/eV) with Type A_ACH, Ti, O, and C=O]
Figure 5

(a) Type A_ACH  (b) Type B_ACE  (c) Type B_MAC
Table of Contents (TOC) Image
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