Interaction of CO and O\textsubscript{2} with Supported Pt Single-Atoms on TiO\textsubscript{2}(110)

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In view of the high activity of Pt single atoms in the low-temperature oxidation of CO, we investigate the adsorption behavior of Pt single atoms on reduced rutile TiO\textsubscript{2}(110) surface and their interaction with CO and O\textsubscript{2} molecules using scanning tunneling microscopy and density function theory calculations. Pt single atoms were prepared on the TiO\textsubscript{2}(110) surface at 80 K, showing their preferred adsorption sites at the oxygen vacancies. We characterized the adsorption configurations of CO and O\textsubscript{2} molecules separately to the TiO\textsubscript{2}-supported Pt single atom samples at 80 K. It is found that the Pt single atoms tend to capture one CO to form Pt-CO complexes, with the CO molecule bonding to the fivefold coordinated Ti (Ti\textsubscript{5c}) atom at the next nearest neighbor site. After annealing the sample from 80 K to 100 K, CO molecules may diffuse, forming another type of complexes, Pt-(CO)\textsubscript{2}. For O\textsubscript{2} adsorption, each Pt single atom may also capture one O\textsubscript{2} molecule, forming Pt-O\textsubscript{2} complexes with O\textsubscript{2} molecule bonding to either the nearest or the next nearest neighboring Ti\textsubscript{5c} sites. Our study provides the single-molecule-level knowledge of the interaction of CO and O\textsubscript{2} with Pt single atoms, which represent the important initial states of the reaction between CO and O\textsubscript{2}.

Key words: Rutile TiO\textsubscript{2}, Single atom catalysis, CO oxidation, Scanning tunneling microscope

I. INTRODUCTION

Low temperature CO oxidation is an important reaction in energy conversion, environmental pollution control and industrial application [1, 2], which has attracted considerable research interests in recent years. Numerous conventional catalysts have been studied for this purpose, such as the various metal oxides of TiO\textsubscript{2}, CeO\textsubscript{2}, MgO, Fe\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} [3–16], and the metal nanoparticles of platinum (Pt), gold (Au) and etc. [17–20]. The activity has been recognized to be related to the defects, step edges on oxide surfaces, as well as the size, shape of nanoparticle [20–24]. Many investigations indicate that Pt is of great activity for CO oxidation on TiO\textsubscript{2} surface [21–26]. By reducing the particle size, the catalytic activity of CO on Pt deposited TiO\textsubscript{2} surface can be significantly improved from nano-scale to atomic scale [20, 25]. At the single atoms (SAs) limit, Pt SAs have been realized to have excellent stability and high activity for CO oxidation [26]. Unlike the metal clusters, supported SAs can provide the maximum utilization of atoms, low coordination environments and abundant active sites [8, 27–29], which make the SA catalysis a new frontier in heterogeneous catalysis [30–33].

The interaction of molecules with the active sites of a catalyst surface is the premise to initiate the catalytic reactions, which requires a systematic knowledge of the structure, adsorption energy, thermal stability and charge transfer [10, 34–37]. Surface science approaches, such as scanning tunneling microscope (STM), have been applied to study the interaction between the CO, O\textsubscript{2} molecules and the catalyst surfaces at the single-molecule-level. Our previous studies had revealed the adsorption properties of CO and O\textsubscript{2} on the rutile TiO\textsubscript{2}(110) surfaces at low temperature of 80 K [38–40]. It is found the CO molecules prefer to adsorb at the five-coordinated Ti sites (Ti\textsubscript{5c}) which can diffuse across the bridging O row through an oxygen vacancy (O\textsubscript{V}) [38]. The molecular O\textsubscript{2} can adsorb at O\textsubscript{V} sites which can dissociate with one O atom healing the O\textsubscript{V} defect and the other O atom adsorbing as an adatom (O\textsubscript{ad}) at adjacent Ti\textsubscript{5c} [40]. We found the dissociated O\textsubscript{ad} can bond with 1 or 2 CO molecules to form stable CO-O and CO-O-CO complexes, however, the oxidation reaction to form CO\textsubscript{2} was not observed at the TiO\textsubscript{2} surface at 80 K [39]. Therefore, it is highly desired to introduce SAs to TiO\textsubscript{2} surface, which may provide sufficient activity for low temperature CO oxidation [41]. For example, Zhou et al. has directly observed the CO oxidation by Au SAs on CuO monolayer and found the charge state of the Au SAs plays a key role in the activity [42].

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In view of the great advantages of SA catalysis, we investigate the adsorption of Pt SAs at TiO$_2$ surface, as well as the interaction of CO and O$_2$ with the presence of Pt SAs on TiO$_2$ surface. By using the high-resolution STM method joint with the density functional theory (DFT), we investigate the prior adsorption sites and configurations of Pt SAs on the reduced rutile TiO$_2$(110) surface. By dosing the CO and O$_2$ molecules to the Pt SAs pre-loaded TiO$_2$ surface in situ, we have directly observed the Pt-CO can form a skew configuration with CO pointing to the nearest neighboring Ti$_{5c}$ site, and the Pt-O$_2$ can form two kinds of configurations with O$_2$ pointing to either the nearest or the next nearest neighboring Ti$_{5c}$ sites. The adsorption behaviors of CO and O$_2$ on Pt/TiO$_2$ provide an important reference for the future study of low temperature CO oxidation at the metal/oxide co-catalytic surface.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

The STM experiments were conducted in a low temperature STM (Omicron, Matrix) with a base pressure $<6 \times 10^{-11}$ mbar. The STM tip is an electrochemically etched polycrystalline tungsten tip. All the images were obtained with constant current mode and the bias is denoted as sample bias. The reduced rutile TiO$_2$(110) (Princeton Scientific Corp.) was prepared by Ar$^+$ ion sputtering (2000 eV) and vacuum annealing at 900 K for more than 30 cycles. The temperature dependent measurements were conducted from 80 K to 100 K with an in-situ heater (LakeShore model 311 Temperature Controller) at the STM stage. Pt (Goodfellow, rod, 99.95%) was evaporated with an electron beam heated evaporator (Focus, EFM 3T) and the evaporation rate was controlled by monitoring the flux. The beams of Pt atoms, CO (99.999%), and O$_2$ (99.999%) were aligned straightly to the TiO$_2$ surface at the STM stage in situ, where the tip was retracted from the surface by about 20 μm and the surface temperature was kept at 80 K during the dosing procedure [40, 43, 44].

Our density functional theory (DFT) calculations are performed using a Vienna ab initio simulation package (VASP) [45–47]. The electron-nuclear interactions are described using the projector-augmented wave (PAW) method [48]. We use the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional in all calculations [49]. vdW interactions are included in the simulations using the D2 approach [50]. A 2×2 supercell with four layers of TiO$_2$ describes the Pt/TiO$_2$ system. The bottom layer Ti and O dangling bonds are saturated with pseudo-hydrogens with nuclear charges of +1.33 and +0.66. A 15 Å of the vacuum region along the z-direction is used to avoid interaction between two adjacent periodic images. The structures are relaxed using a conjugate gradient scheme until the maximum force on each atom is less than 0.02 eV/Å. And plane-wave basis sets with energy cutoff of 400 eV. The Hubbard model is used to treat strong on-site Coulomb interaction within the DFT+$U$ method in the Dudarev formalism [51]. An effective $U$ ($U_{eff}=U-J$, the difference between the Coulomb $U$ and exchange $J$ parameters, hereafter referred to as $U$) value of 4.5 eV is selected for Ti 3d electrons.

III. RESULTS AND DISCUSSION

A. The interaction of CO with Pt SAs.

FIG. 1 (a) shows an empty state STM image of the pristine TiO$_2$(110) surface obtained at 1.0 V, 10 pA. The TiO$_2$ surface consists of alternating rows of Ti$_{5c}$ and bridge-bonded oxygen (O$_{br}$) atoms, which is characterized as bright and dark rows, respectively [52–55]. The spots distributing at the dark rows are the defects of O$_{br}$’s. By using the e-beam evaporator, the Pt atoms can be gradually loaded onto the TiO$_2$ surface with keeping TiO$_2$ substrate at 80 K in situ. The same area images after Pt adsorption reveal the Pt SAs can stably adsorb at the O$_V$ defects as the bright protrusions in FIG. 1 (b), while the adsorption of Pt at Ti$_{5c}$ sites is not observed. This is in good agreement with previous theoretical predictions that the adsorption energy of Pt SA at O$_V$ is considerably larger than that at stoichiometric Ti$_{5c}$ site [56, 57]. By using the aberration-corrected scanning transmission electron microscopy, Chang et al. observed five different adsorption sites for Pt SAs at room temperature, where the most favorite adsorption sites are the three-fold coordinated basal oxygen vacancies and the bridging oxygen vacancies at the air-annealed TiO$_2$(110) surface [58]. In our case, at the reduced TiO$_2$(110) surface we find the Pt SAs solely adsorb at the bridging O$_V$ sites with the coverage of 0.01 ML (1 ML=5.2×10$^{14}$ cm$^{-2}$) at 80 K, and the stability of Pt SAs at O$_V$ is not affected by increasing the temperature from 80 K to 100 K.

Next, we study the interaction of CO with the pre-loaded Pt SAs at TiO$_2$ surface. Our previous study has revealed the adsorption and diffusion of CO at pristine TiO$_2$ surface at 80 K [39]. We find the adsorption of CO leads to a site-dependent distribution at specific Ti$_{5c}$ sites, that the most preferred site for CO adsorption is the next nearest Ti$_{5c}$ site with respect to an O$_V$. Furthermore, it is found the CO cannot stably adsorb at the O$_V$ sites and the CO can diffuse across the surface through an O$_V$ site [39]. Here, after dosing CO molecules to the Pt/TiO$_2$ surface, it can be seen not only the adsorption of CO at Ti$_{5c}$ sites is reproduced, but also some new protruded geometry features appear at the Pt SAs (FIG. 1 (c)). The areas in the dashed rectangles in FIG. 1 (b) and (c) are enlarged in FIG. 1 (d) and (e), respectively. The yellow arrows indicate the CO adsorption at Ti$_{5c}$ sites. It can be seen two Pt SAs in the middle have changed to more...
FIG. 1 (a–c) Sequential STM images obtained at the same area of a clean TiO$_2$(110) surface, after Pt SA deposition and after CO dosing. The images are obtained at 1.0 V, 10 pA, 80 K. (d) and (e) the magnified regions marked by white rectangles in (b) and (c), respectively. Yellow arrows indicate CO adsorption at Ti$_{5c}$ sites. Red and white dashed crosses indicate the center of the original O$_V$ positions before Pt atom and CO adsorption. (f) The difference image obtained by subtracting (d) from (e), where the contrast and curved arrows show the change after CO adsorption. (g) Line profiles obtained at the “cross” positions labeled by the number in (d) and (e), indicating the changes after Pt (orange line) and CO (blue lines) adsorption, respectively. The green lines are obtained at the same positions before Pt and CO adsorption in (a).

protruded geometry. Meanwhile, the center of the two has left away from the original positions forming an asymmetric shape as indicated by the dashed crosses. To see more clearly, we obtain the difference image in FIG. 1(f) by subtracting FIG. 1(d) from FIG. 1(e). As indicated by the curved arrows, the contrast changes in blue and red show the geometric change to the upper left and lower left for the two Pt SAs after CO adsorption, respectively. The height and position differences can be distinguished clearly from the corresponding line profiles (FIG. 1(g)) obtained at the labeled lines in FIG. 1(d, e).

The much-protruded geometries appearing after CO adsorption at Pt SAs reveal certain configurations of Pt-CO. The height histogram obtained at 80 K indicates the Pt SAs at O$_V$’s have an average height of 0.17 nm, while the complexes of Pt-CO have an average height of 0.23 nm (FIG. 2(a1–a3)). After dosing ~0.1 Langmuir CO to the surface with 0.025 monolayer (ML) Pt SAs, we find only 10% CO molecules adsorb at Pt SAs while 90% CO adsorb at the surface Ti$_{5c}$ sites. The stable adsorption of CO at Ti$_{5c}$ sites and the Pt SAs at O$_V$’s at 80 K have restricted the direct interaction between CO and Pt SAs. Therefore, we gradually increase the sample temperature from 80 K to 100 K to stimulate the diffusion of CO across the surface [38, 39], which can effectively enhance the chance for CO molecules to interact with Pt SAs. When the moving CO encounters a stably adsorbed Pt SA, the strong interaction forms new configurations of Pt-(CO)$_x$ complex. In FIG. 2(a1–e1), the sample has been kept at each temperature for 3 h and the images were obtained at the end to see the changes. It can be seen, except the Pt-CO with the average height of 0.23 nm, a third adsorption geometry with much larger and brighter contrast and a specific height of 0.31 nm appears at elevated tem-
FIG. 2 Pt-CO interaction and the configuration change at elevated temperature from 80 K to 100 K. (a1) Large scale STM image (26.5 nm × 26.5 nm) obtained at different temperature (upper panels), and the corresponding magnified regions (8.7 nm × 8.7 nm) marked by the yellow rectangles (lower panels). (a2) Line profiles of Pt SAs at O_V’s (green), Pt-CO (orange) and the Pt-(CO)_2 (blue), obtained at the corresponding position marked by the dashed color lines in the lower panels of (a1). (a3) Plot of the height distribution of the configurations of Pt SA, Pt-CO and Pt-(CO)_2 at each temperature.

perature (FIG. 2(b1−e3)), which is possibly a configuration of 2 CO molecules attaching to a Pt SA, that is, Pt-(CO)_2. With the continuous CO diffusion at elevated temperature, the percentage of Pt-(CO)_2 gradually increases and becomes the dominant configuration (FIG. 2(e1−e3)). Even though, we note the coverage of CO at Ti_{5c} sites does not decrease during temperature rising, which is probably due to the releasing of CO from the STM stage to surface at elevated temperature.

B. Interaction of O_2 with Pt SAs

In our previous study, we have systematically studied the O_2 adsorption and dissociation at pristine TiO_2(110) surface [40]. At low coverage, the molecular O_2 can adsorb at O_V sites and dissociate with one O atom healing the O_V and the other O sitting at Ti_{5c} to form an O adatom (O_{ad}). At high coverage after all the O_V sites being full filled, the O_2 start to dissociate at Ti_{5c} sites directly to form a pair of O_{ad}. In this context, we next investigate the interaction O_2 with Pt SAs (FIG. 3). The same area images before and after a small amount of O_2 (0.05 Langmuir) was exposed to the Pt SAs pre-loaded TiO_2 surface are shown in FIG. 3(b, c). The prior adsorption sites are O_V’s with either the molecular or dissociated state adsorption. It can be seen the molecular state adsorption of O_2 makes a dim contrast at O_V and the dissociated state forms O_{ad} as small bright spots at Ti_{5c}, however, no changes were made to the Pt SAs (FIG. 3(c)). Then, a large amount of O_2 (0.2 Langmuir) was exposed to the surface, which fills most of the O_V sites. Meanwhile, it is found the morphology of some Pt SA becomes less protruded after the O_2 dosing, as indicated by the yellow arrows in FIG. 3(d). To see the morphologic change more clearly, the enlarged areas as marked by the dashed rectangles in FIG. 3(b, d), as well as the difference map between them, are shown in FIG. 3(e−g), respectively. It can be seen not only the contrast becomes less protruded,
but also the geometry changes to asymmetric shapes as indicated by the crosses, respectively. The geometry of the left one inclined to the upper left as shown in FIG. 3(e–g), while the geometry of the right one just shifts to the left, but not tilted to the upper or lower site. Such asymmetric shapes are more clearly shown in the difference map in FIG. 3(e) and the height changes can be seen in the corresponding line profiles in FIG. 3(h, i). Obviously, these morphology changes are the results of the O$_2$ interaction with Pt SAs. Since there is no dissociated O$_{ad}$ appearing at the sites nearby, we suggest the configuration is the molecular state O$_2$ interacting with Pt SA, that is Pt-O$_2$. The STM observations reveal the O$_V$ sites are prior for O$_2$ adsorption, while the interaction between O$_2$ and Pt may happen after the reduced surface is fully oxidized. Also, the contrast changes for Pt-O$_2$ and Pt-CO are completely opposite, which indicate different charger transfer processes between the molecules and Pt SAs.

**C. Optimized structures of Pt SAs, Pt-CO and Pt-O$_2$ and charge transfer between Pt SA and the adsorbed molecules**

To better understand the configurations of Pt SA at O$_V$ site, the Pt-CO, and Pt-O$_2$ as observed in STM measurements, we conducted the DFT calculations to obtain the optimized structures of those species. The optimized structure for Pt SA at the O$_V$ site is shown in FIG. 4 (a, b). The Pt SA stands up much higher than the O$_{br}$ atoms and bonds with two six-fold coordinated Ti atoms forming a symmetric Ti-Pt-Ti configuration along the [001] direction (FIG. 4(b)), which is similar to the Au SAs at O$_V$ site observed in our previous study [43]. The Pt–Ti distance is 2.421 Å, which is 0.534 Å longer than O–Ti bond in stoichiometric surface and 0.226 Å shorter than Au–Ti distance for Au SA at O$_V$. This makes a stable Pt SA adsorption configuration at O$_V$ with the adsorption energy of $-4.471$ eV, which is 1.51 eV higher than that of Au at O$_V$.

FIG. 3 (a–d) Sequential STM images obtained at the same area of a clean TiO$_2$(110) surface, after Pt SAs adsorption, after exposure to 0.05 L O$_2$ and after exposure to 0.2 L O$_2$, respectively. The O$_2$ was dosed successively in situ with the substrate at 80 K, and the images were obtained at 1.0 V and 10 pA. The white arrows in (b)–(d) indicate Pt single atom with no O$_2$ adsorption, and yellow arrows indicate O$_2$ adsorption on Pt atoms. The dashed rectangles in (c) mark the molecular O$_2$ at O$_V$ sites and the red arrows mark the dissociated O adatoms. (e) and (f) The magnified regions as marked by dashed rectangles in (b) and (d) respectively. (g) The difference image obtained by subtracting (e) from (f). Crosses in red, yellow and black indicate the center of O$_V$’s before Pt SAs and O$_2$ adsorption. (h) Line profiles of Pt SAs and Pt-O$_2$ configurations obtained at the corresponding position as marked by the lines with the numbers in (a–d).
After putting a CO molecule to a Pt SA, we obtain two stable configurations as marked by α-Pt-CO and β-Pt-CO in FIG. 4(c, d), respectively. For the α-Pt-CO, the Pt SA shifts to one side in the [110] direction and bonds with the C atom forming a skew Pt-C-O configuration pointing to the next nearest Ti$_{5c}$ site (denoted as Ti$_{5c}$-1) (FIG. 4(c)). In this configuration, the bond length of two Pt-Ti are 2.756 Å and 2.646 Å, that is, the one near CO is shorter. The distance of C–O is 1.172 Å, which is a little bit longer than that in gaseous CO of 1.144 Å. Meanwhile, the surface lattice is distorted slightly that the Ti$_{5c}$-0 atom moves closely to the Pt SA (FIG. 4(e)). In contrast, the β-Pt-CO shows a symmetric configuration with respect to the [110] direction with Pt-C-O pointing to the Ti$_{5c}$-0 site (FIG. 4(d)). Clearly, the shift of the Pt SA and the lattice distortion are much less than those in the α-Pt-CO configuration. The calculated adsorption energies are −1.146 eV for α-Pt-CO and −1.448 eV for β-Pt-CO, indicating the β-Pt-CO should be more stable. However, we note the α-Pt-CO may have four equivalent asymmetric configurations which can better satisfy with the STM observations in FIG. 1(e, f), while the β-Pt-CO configuration is not observed in STM images. The reason is possibly that the interaction between the Pt and CO is initiated by the moving of CO along the Ti$_{5c}$ rows towards a Pt SA, whereas, the Ti$_{5c}$-1 is the most stable adsorption site during CO moving as revealed in our previous study [38].

For the O$_2$ interaction with Pt SA, we have also obtained two stable configurations, as marked by α-Pt-O$_2$ and β-Pt-O$_2$ in FIG. 4(e, f), respectively. Similarly, in the α-Pt-O$_2$ configuration, the Pt SA shifts along the [110] direction and forms the Pt-O-O-Ti bonding with the Ti$_{5c}$-1 atom (FIG. 4(e)), while in the β-Pt-O$_2$ configuration, the Pt-O-O-Ti bonds with the Ti$_{5c}$-0 atom (FIG. 4(f)). According to the apparent symmetry, these two configurations can be well associated with the STM observations in FIG. 3(e–g), that the left Pt-O$_2$ complex in FIG. 3(f) can be assigned to the α-Pt-O$_2$ configuration and the right one can be assigned to the β-Pt-O$_2$ configuration.

To understand the charge transfer between the Pt SAs and the adsorbed molecules, we plot the differential charge density maps for those configurations in FIG. 5. When the Pt SA is adsorbed at an O$_2$ site, the excess electrons from the O$_2$ defect will accumulate to Pt SA and partially occupy the Pt-5d and Pt-6s orbitals (FIG. 5(a)) and the electron transfer with 0.906 e$^-$ is estimated from the Bader charge analysis. When a CO molecule is adsorbed to a Pt SA with the α-Pt-CO or β-Pt-CO configurations (FIG. 5(b, c)), the O-2p state in CO and Ti-3d state in Ti$_{5c}$ atom are of bonding character and the presence of CO weakens the interaction of Pt SA and TiO$_2$. The charge redistribution can be clearly seen in FIG. 5(b, c) showing the electrons transfer from Pt SA to CO. The Bader charge analysis indicates the electron quantity at Pt SA and CO, that is 0.656 e$^-$ (Pt) and 0.225 e$^-$ (CO) for α-Pt-CO configuration, and 0.538 e$^-$ (Pt) and 0.405 e$^-$ (CO) for β-Pt-CO configuration, respectively. As an O$_2$ molecule is adsorbed at Pt SA, because the electronegativity of O is high, electrons transfer to O$_2$ both from Pt SA and Ti$_{5c}$ atom, which form Pt–O and Ti–O bond, respectively. The Bader charge analysis shows electron quantity at the Pt SA and O$_2$, that is 0.492 e$^-$ (Pt) and 0.559 e$^-$ (O$_2$) for α-Pt-O$_2$ configuration, and 0.173 e$^-$ (Pt) and 0.863 e$^-$ (O$_2$) for β-Pt-O$_2$ configuration, respectively (FIG. 5(d, e)). These results indicate much more electron accumulation at O$_2$ as compared with CO. Due

![FIG. 4](https://example.com/figure4.png)

**FIG. 4** Top view (left) and side view (right) of the ball-and-stick model of reduced TiO$_2$(110) surface with Pt, CO and O$_2$ adsorption. (a) Clean TiO$_2$(110) surface. The dashed green sphere represents O$_V$. (b) Pt SA adsorption. (c) α-Pt-CO configuration. (d) β-Pt-CO configuration. (e) α-Pt-O$_2$ configuration. (f) β-Pt-O$_2$ configuration. The blue, yellow and gray spheres indicate the Ti, Pt, and C atoms, respectively. The red spheres represent O atoms of the substrate, and the green spheres are O atoms from CO or O$_2$. The black arrows mark the Ti$_{5c}$-0 site and the equivalent Ti$_{5c}$-1 sites.
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FIG. 5 The differential charge density map of (a) Pt SA, (b) α-Pt-CO configuration, (c) β-Pt-CO configuration, (d) α-Pt-O$_2$ configuration, and (e) β-Pt-O$_2$ configuration. Blue (red) color denotes diminishing (accumulation) of electrons. The numbers of electron are obtained from Bader analysis.

to the much complicated situations for co-adsorption of CO and O$_2$ with the Pt SAs, we believe that our understanding on the separate adsorption of CO and O$_2$ could be a key step for atomistic understanding of low-temperature CO oxidation using Pt SAs [41].

IV. CONCLUSION

In summary, we have studied the adsorption behavior of Pt SA on the reduced rutile TiO$_2$(110) surface, as well as its interactions with CO and O$_2$ molecules by STM measurement and DFT calculation. It is found the Pt SAs can stably adsorb at the defect of O$_V$ site, however, the adsorption at Ti$_{5c}$ site is not observed even at the low temperature of 80 K. After CO deposited on Pt/TiO$_2$ system, CO preferentially points to the next nearest neighboring Ti$_{5c}$-1 site, forming the skew α-Pt-CO configuration. In contrast, the molecular O$_2$ can point to both the next nearest Ti$_{5c}$-1 site and the nearest Ti$_{5c}$-0 site, leading to the formation of both the α-Pt-O$_2$ and β-Pt-O$_2$ configurations. Dissociated O adatom is not observed during the O$_2$ interacting with Pt SAs. The charge redistribution among the TiO$_2$ surface, Pt SAs and the CO, O$_2$ molecules are studied by the differential charge density maps and the Bader charge analysis. It reveals the electron can transfer from the O$_V$ defect to the Pt SA, and further to the adsorbed CO and O$_2$ molecules. These results lay the foundation for the subsequent study on the low temperature CO oxidation by the Pt/TiO$_2$ co-catalyst at the molecular level.

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