

What Are the Adsorption Sites for CO on the Reduced TiO₂(110)-1 × 1 Surface?

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A knowledge of CO adsorption behavior on reduced TiO₂ surfaces is of great importance for a wide variety of applications,¹ such as CO oxidation at low temperature,² CO hydrogenation, and the water-gas shift reaction.³ Many efforts to obtain a detailed atomic-scale understanding of the principles governing catalyzed reactions on oxide-supported metal-based catalysts have been made using scanning tunneling microscopy (STM).⁴ Surprisingly, adsorption and diffusion of CO molecules even on the widely studied rutile TiO₂(110)-1 × 1 surface are not well-understood,^{5–8} though they are fundamentally important. To date, the detailed adsorption information for CO on TiO₂(110)-1 × 1 is highly controversial. For instance, an early study by Göpel and co-workers suggested bridge-bonded oxygen vacancies (BBO_v's) to be the adsorption sites for CO,⁵ and this conclusion was supported by some theoretical work.⁹ However, the results from temperature-programmed desorption (TPD) experiments suggested that at low coverages, CO adsorption occurs at nonadjacent five-coordinate Ti⁴⁺ (Ti_{5c}) sites on the reduced TiO₂(110) surface,^{7,8} as supported by a different set of theoretical calculations.¹⁰ It was recently found that the clean TiO₂(110) surface and the inverse catalysts of TiO₂ and CeO₂ particles on bulk gold can perform the oxidation of CO,¹¹ where the CO adsorption behavior at oxygen vacancies plays a key role.^{4a,12} There is thus an urgent need to clearly understand the performance of CO on reduced oxide surfaces. This communication reports our experimental study of the adsorption of CO on a reduced clean TiO₂(110)-1 × 1 surface at an atom-resolved scale using in situ STM, combined with density functional theory (DFT) calculations. Our STM results reveal that the next-nearest-neighbor Ti_{5c} sites close to a BBO_v are the most preferred adsorption sites, and our DFT calculations show that this can be well-understood energetically.

To conduct our experiment, the reduced rutile TiO₂(110)-1 × 1 samples were prepared in an ultrahigh vacuum chamber with a base pressure of <3 × 10⁻¹¹ Torr that had been baked for a long time to minimize the background water in the chamber.¹³ All of the STM measurements were performed at 80 K. We allowed an in situ CO (99.999%) dosing of 0.1 L at 80 K, where 1 L = 1 × 10⁻⁶ Torr s. Figure 1 shows STM images before and after CO dosing in the same areas of the hydroxyl-free TiO₂(110)-1 × 1 surface; these images show that after the CO dosing, CO molecules adsorb predominantly at Ti_{5c} sites close to BBO_v's (Figure 1b) and are separated from each other by at least one lattice distance in a given Ti_{5c} row. No CO adsorption at the bridge-bonded oxygen (BBO) site was observed.

In the magnified STM images superposed with the structure of TiO₂(110)-1 × 1, the CO adsorption sites can be determined (Figure 1d). Statistically, we counted the adsorbed CO at different Ti_{5c} sites with respect to the BBO_v (the sites are defined in Figure 2a). The events of CO adsorption at site 0 and the BBO_v are extremely low. The probability distributions for CO adsorption at different sites for three TiO₂(110)-1 × 1 samples with BBO_v concentrations of 22, 11, and 5% are plotted in Figure 2b. It is noteworthy that in each case the probability at sites 1 and 2 was over 60% and the probability at site 1 was ~2 times that at site 2, indicating that these two sites are the most

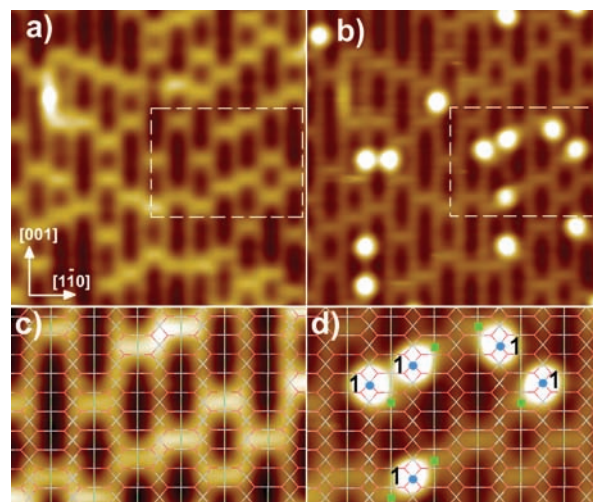


Figure 1. STM images acquired in the same area (8.2 × 8.2 nm²) of a hydroxyl-free TiO₂(110)-1 × 1 surface (a) before and (b) after CO dosing. (c, d) Corresponding magnified images with superposed structure (4.4 × 3.0 nm²). Green squares denote BBO_v's and blue dots the CO adsorption sites on a Ti_{5c} row. Conditions: $V_{\text{bias}} = 1.4$ V, $I_{\text{set}} = 10$ pA, $T = 80$ K.

preferred adsorption sites for CO, in contrast to the suggestion by Sorescu et al.,^{10f} without an obvious dependence on the BBO_v concentration. This result is coincident with our recent result that the excess charge of a BBO_v defect is delocalized over multiple surrounding titanium atoms, mainly at sites 1 and 2.^{13b} The CO molecules adsorbed at these sites may thus be negatively charged through back-donation of the charge from the surface.^{9b}

For a better understanding of the adsorption behavior, we used DFT to calculate the adsorption energy of CO on TiO₂(110)-1 × 1, employing a (6 × 2) unit cell with one oxygen atom removed from the BBO row in the uppermost layer; this unit cell is larger than that in previous calculations.^{9,10} It was found that the CO adsorption at site 1 has the lowest adsorption energy, 8.8 kcal/mol. The calculated energy differences, δE , for other sites with respect to site 1 are plotted in Figure 2c. The adsorption energies at the BBO_v and site 0 are higher than that at site 1 by 5.0 and 1.4 kcal/mol, respectively. In comparison, the adsorption energies at sites 2 and 3 are higher than that of site 1 by only 0.1 and 0.3 kcal/mol, respectively. These values are in good agreement to the experimental value of 9.9 kcal/mol⁷ and on the same order of magnitude as obtained in previous calculations.^{9,10} Qualitatively, it is thus easy to understand that the BBO_v and site 0 are not energetically favorable. More interestingly, these values make it possible to analyze the adsorption behavior quantitatively. With the calculated adsorption energy differences, the equilibrium distribution of CO adsorption at different sites can be estimated with the Boltzmann relation $\exp(-\delta E/kT)$ (where k is Boltzmann's constant), as shown in Figure 2d. The calculated distribution largely reproduces the experimental observations in Figure 2b. Thus, it can be suggested that the

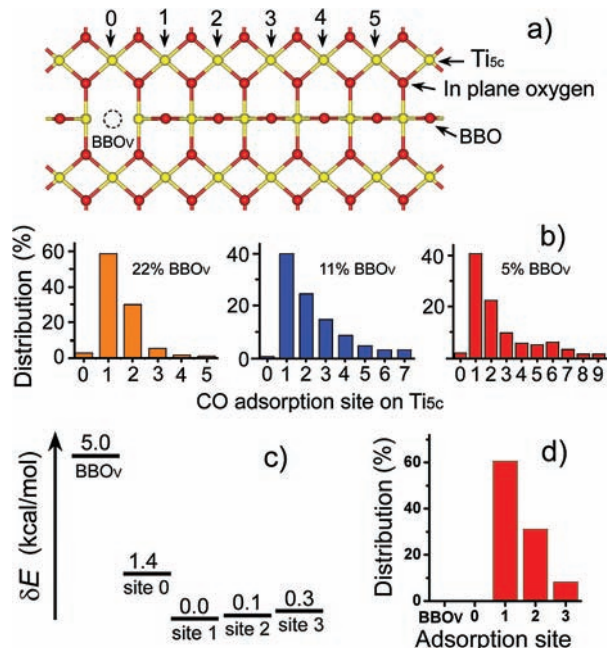


Figure 2. (a) Schematic drawing of TiO₂(110)-1 × 1 with a BBO_v; the Ti_{5c} sites are labeled according to the lattice distance with respect to the BBO_v. (b) Plots of distributions of CO adsorption on Ti_{5c} with BBO_v concentrations of (left to right) 22, 11, and 5%. (c) Calculated adsorption energy difference, δE , for CO adsorption at different sites with respect to the lowest energy (at site 1). (d) Simulated distribution of CO adsorption at different sites obtained using the Boltzmann distribution.

CO adsorption follows the Boltzmann distribution, which reflects thermally driven behavior. This may be attributed to “hot” CO molecules from the gas initially landing on the different sites of the surface and eventually reaching equilibrium through thermal diffusion. Significantly, our finding here reveals that CO adsorbs preferentially at site 1, namely, the next-nearest-neighbor Ti_{5c} site close to the BBO_v, and not at the BBO_v itself.^{1b} A similar site dependence for the adsorption of O₂ has been predicted.¹⁴

In addition, we obtained CO diffusion barriers (in kcal/mol) of 5.3 (BBO_v to site 0) and 9.0 (site 0 to BBO_v), 7.6 (site 0 to site 1) and 8.0 (site 1 to site 0), 8.1 (site 1 to site 2) and 8.0 (site 2 to site 1), and 7.6 (site 2 to site 3) and 7.4 (site 3 to site 2). Our observed diffusion events at the initial adsorption stage agree well with our calculated adsorption energies and diffusion barriers. As shown in Figure 3 by a series of consecutively acquired STM images, frames A in Figure 3a–c show CO diffusion crossing a BBO row through a BBO_v. The intermediate state of CO on the BBO_v site, which was occasionally observable (as marked by frame A in Figure 3c and frame C in Figure 3d), always diffuses to site 0 and then to site 1. Frames B in Figure 3c,d demonstrate CO diffusion from site 2 to site 1.

In conclusion, we have studied in situ the low-coverage adsorption of CO molecules on TiO₂(110)-1 × 1 surfaces using STM at 80 K. Our results show that CO molecules preferentially adsorb at the next-nearest-neighbor Ti_{5c} atoms close to the BBO_v at equilibrium, which disagrees with the idea that the BBO_v itself acts as an adsorption site for CO. Adsorbed CO molecules diffuse along Ti_{5c} rows and across the BBO row through the BBO_v. Although CO adsorption on the BBO_v can be observed occasionally, the BBO_v is not a stable adsorption site but rather an intermediate state during CO diffusion across a BBO row, even at 80 K.

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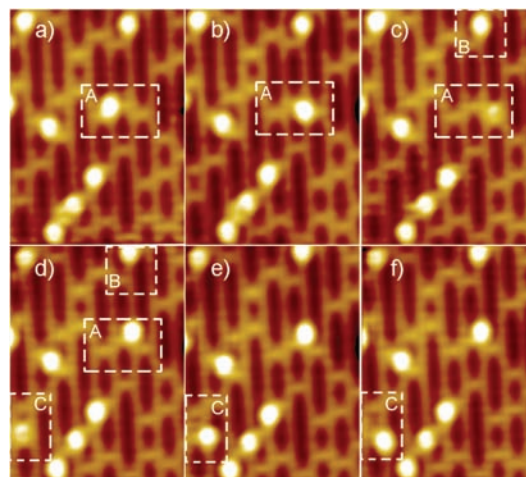


Figure 3. (a–f) Consecutively acquired STM images ($5.4 \times 7.3 \text{ nm}^2$). The frames labeled by A show the CO diffusion across the BBO row through a BBO_v, frames B the CO diffusion from site 2 to site 1, and frames C the CO diffusion from the BBO_v to site 0 and then to site 1.

Supporting Information Available: Computational details and consecutively acquired STM images showing the CO adsorption and diffusion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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