Orientation-Dependent Interaction between CO$_2$ Molecules Adsorbed on Ru(0001)

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ABSTRACT: Determining the molecular structure of CO$_2$ adsorbed on metal surfaces and its mutual interactions is important to understand its catalytic conversion reactions. Here, we study CO$_2$ adsorption on Ru(0001) using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations. Adsorbed at 77 K, the CO$_2$ molecules form mainly disordered structures at submonolayer coverage, except for small ($2 \times 2$) domains. The adsorbed molecules are no longer linear as in the gas phase, but instead, they adopt a "V"-shape geometry with the carbon atom occupying three-fold hcp hollow sites and possess three symmetry-equivalent orientations. Annealing to 250 K causes partial desorption of the molecules, while the remaining molecules form trimers of three different configurations with different interaction energies determined by their relative orientations. The "strong"-interacting trimer shows a cyclic structure, about 40 meV more stable than the "weak"-interacting trimer that is composed of three parallel molecules.

Chemical conversion of carbon dioxide (CO$_2$) has recently attracted intense scientific interest due to the environmental concerns of global warming caused by CO$_2$ a greenhouse gas. However, CO$_2$ has rather low energy content as compared with carbon monoxide (CO), and transition-metal catalysts are utilized to facilitate CO$_2$ conversions. Catalytic processes, such as the Sabatier reaction, have been developed to transform CO$_2$ into useful chemical compounds using metal catalysts. These processes, which involve the adsorption and reactions of CO$_2$ molecules on the catalyst surface, have led to several fundamental studies to understand their adsorption and interactions. Ni and Ru are two active catalysts for CO$_2$ hydrogenation or methanation that have been extensively studied. Chemisorbed CO$_2$ on Ni surfaces was found to be partially negatively charged, with a bent and carbon-bonded "V" shape configuration. The charge transfer from the Ni substrate to CO$_2$ results in an activated state that plays a crucial role in the hydrogenation process. In contrast, few surface science studies have been reported on Ru, even though Ru catalysts have been actively explored for CO$_2$ hydrogenation.

The interactions between adsorbed species typically play a relevant role in the adsorbate structures and their chemical reactions. The interaction between CO$_2$ molecules is very weak due to their linear and centrosymmetric configuration with no electrical dipole. For chemisorbed CO$_2$ on a Ni surface, there is no significant lateral interaction between CO$_2$ molecules at 1/4 monolayer coverage, but strong repulsive interaction is found at 1/2 monolayer. Nevertheless, CO$_2$ dimers, trimers, and other clusters were found in supersonic jets. In these clusters, the molecules interact weakly through van der Waals forces. The intermolecular interactions, however, may change when adsorbed on a metal surface due to the charge transfer resulting from bonding. The study of these fundamental processes should benefit our understanding of the CO$_2$ reaction mechanism on metal catalyst surfaces. Here, we combine scanning tunneling microscopy (STM) and density functional theory (DFT) to study CO$_2$ adsorption and interactions on the Ru(0001) surface at the molecular level.

Figure 1a shows a STM image of the Ru(0001) surface after the adsorption of CO$_2$ at submonolayer coverage at 77 K. The molecules appear as bright protrusions with an apparent height of about 20 pm. The nearest distance between CO$_2$ molecules is about $\sqrt{3}$ the Ru lattice parameter ($\sim 4.68 \text{ Å}$). No long-range ordered structure was observed upon adsorption at this temperature except for some small ($2 \times 2$) domains, such as those enclosed by circles in the image. The molecules started to desorb after annealing to temperatures above 200 K and remained disordered. As shown in Figure 1b, these molecules partially desorbed after annealing to 250 K for 20 min. The coverage further decreased after a total annealing to 250 K for 40 min, with the remaining molecules forming trimers, such as those indicated by arrows in Figure 1c. These observations are different from an earlier study, which reported physisorption of CO$_2$ on clean Ru(0001) at 85 K and undissociated desorption at 100 K. In contrast, a recent study reported an adsorption energy of 0.52 eV for CO$_2$ on the Ru(0001) surface, which indicates chemisorbed CO$_2$ on Ru and supports our observation. It is likely that both physisorption and chemisorption occur, similar to the case of CO$_2$ on a Ni...
surface, while our study dealt with chemisorbed CO2 at low coverage here.

The adsorption site of the CO2 molecules was determined by a close inspection of the STM images. Figure 2a shows an image covering two adjacent terraces separated by a monatomic step. Expanded images on each terrace are shown in Figure 2b and c, with both the atomic lattice of Ru and adsorbed CO2 molecules clearly resolved. A grid of lines drawn along the Ru lattice is used to determine the site of the adsorbed molecules. From these, we can conclude that the molecules occupy three-fold hollow sites. Comparison of the grid orientation on the neighboring terrace images indicates that the site is the same (Figure 2c) on both, either fcc or hcp, because the grid triangles surrounding each molecule rotate $120^\circ$ orientation between terraces.

DFT calculations were performed to determine the adsorption geometry of the monomer, which indicated that CO2 occupies the three-fold hcp hollow site (Figure 2d) with the carbon atom making one short and two long bonds ($2.1$ and $2.4$ Å) with the Ru atoms below while the oxygens tilt upward and lean toward top sites ($O$–Ru distance is $2.2$ Å), leading to a $124^\circ$ "$V$"-shaped configuration similar to that of chemisorbed CO2 on Ni(110). This calculated geometry is consistent with previous study. The local pm adsorption geometry leads to three equivalent molecular adsorptions on the Ru(0001) surface, which, as we show next, is crucial for the relative stability of small CO2 clusters.

Figure 3a−c shows STM images of CO2 trimers on neighboring Ru terraces formed after annealing to $250$ K. Interestingly, the CO2 trimers show alternating orientations on neighboring Ru terraces, as indicated by the superimposed triangles in Figure 3b and c. They have the same orientation within each terrace but rotate by $60^\circ$ across neighboring terraces. Three different structures are observed that have different contrast, such as those in the area enclosed by a rectangle in Figure 3c. A color contrast enhanced image on the right side shows the difference more clearly. We label them with numbers 1, 2, and 3. The statistical abundance for the three structures was obtained on samples that were annealed to $250$ K for $40$ min. We assume that the annealing is long enough to reach the equilibrium distribution, which was preserved after quickly cooling down to $77$ K for imaging. As shown in Figure 3d, structure 1, 2, and 3 have a statistical weight of $9.2$, $31.5$, and $59.3\%$, respectively. The probability distribution $P_i$ for state $i$ ($i = 1, 2, 3$) is then expected to follow the Boltzmann distribution, $P_i \propto e^{-\frac{E_i}{kT}}$, where $E_i$ is the energy of state $i$, $k$ is the Boltzmann constant, and $T = 250$ K is the annealing
CO2 clusters formed in supersonic jet expansions. Shown in Figure 3g. Such a cyclic trimer has been conformed for CO2, which is essentially preserved in all trimer structures, the relative arrangement of the molecules becomes markedly different between the two orientations. Whereas for the trimers centered at a top site (Figure 4a) one of the oxygen atoms points toward the C atom of a neighboring molecule, in those centered at a fcc site (Figure 4b), each oxygen atom points to an oxygen of another molecule instead. The maps of the charge density difference (total isolated atoms) are shown in Figure 4c,d, which reveals the charge transfer from the carbon to the oxygen atoms, leaving the latter negatively charged. Following simple electrostatic arguments, it thus becomes clear that the trimers centered at a top site will be more stable than those centered at a fcc site, as indeed corroborated by the DFT, which yields an energy difference of 33 meV between them. The alternating orientation of CO2 trimers on neighboring Ru terraces is therefore a result of the hcp bulk Ru lattice, which inverses the orientation of each hollow site with respect to the top site above among neighboring terraces. This substrate-dependent effect has also been observed during formation of triangular hydrogen vacancy patterns on Ru(0001).30

Therefore, the relative energy difference between two states $i$ and $j$ may be estimated as $\Delta E_{ij} = E_i - E_j = kT \cdot \ln[F_i/F_j]$. From the experimental distribution, we thus find that the energies of structures 2 and 3 are about 26.5 and 40 meV more stable than that of structure 1, respectively (Figure 3e).

Assuming that the strength of the intermolecular interactions is associated with an increased electron density between them, the three molecules in structure 1 would correspond to a relatively “weak” interacting configuration as they appear “isolated” in the STM image. In contrast, there is certain bridging charge between two molecules in structure 2 and an even stronger interaction between all three molecules in structure 3. The same hierarchy in interaction strengths follows from the intermolecular distances within the trimer, with smaller values corresponding to stronger interactions. As shown in Figure 3f, in structure 1, the distance between the CO2 maxima is close to twice the Ru interatomic distance (∼5.4 Å), while a smaller distance is found for structure 2 (∼5.2 Å) and structure 3 (∼4.9 Å). The three structures of the CO2 trimers may be explained by considering three different relative orientations of the molecules. In one, all molecules align parallel to each other, in another, one molecule is rotated by 60°, and in the third, the molecules form a cyclic structure, as shown in Figure 3g. Such a cyclic trimer has been confirmed for CO2 clusters formed in supersonic jet expansions.5

The proposed models have been confirmed by DFT total energy calculations, which give rise to the optimized geometries shown in Figure 3g. The cyclic trimer has the lowest energy, being more stable than structures 2 and 1 by 19 and 27 meV, respectively. The experimental energetic hierarchy is thus correctly reproduced by the calculations, although the theoretical energy differences are somewhat smaller most probably due the choice of the van der Waals functional employed (see the Experimental and Computational Methods section). It may also indicate that perfect thermodynamic equilibrium was not reached by annealing to 250 K due to the proximity to the desorption temperature. Nevertheless, discrepancies on the order of 10 meV are at the edge of the overall accuracy of DFT.

The prevalence of one single orientation of the trimers within each terrace is also explained by the calculations. As shown in Figure 4a,b, inverting the orientation of a trimer is equivalent to positioning its center either at a top site or at a fcc site. Due to the reduced pm local symmetry of the adsorbed CO2, which is essentially preserved in all trimer structures, the relative arrangement of the molecules becomes markedly different between the two orientations. Whereas for the trimers centered at a top site (Figure 4a) one of the oxygen atoms points toward the C atom of a neighboring molecule, in those centered at a fcc site (Figure 4b), each oxygen atom points to an oxygen of another molecule instead. The maps of the charge density difference (total isolated atoms) are shown in Figure 4c,d, which reveals the charge transfer from the carbon to the oxygen atoms, leaving the latter negatively charged. Following simple electrostatic arguments, it thus becomes clear that the trimers centered at a top site will be more stable than those centered at a fcc site, as indeed corroborated by the DFT, which yields an energy difference of 33 meV between them. The alternating orientation of CO2 trimers on neighboring Ru terraces is therefore a result of the hcp bulk Ru lattice, which inverts the orientation of each hollow site with respect to the top site above among neighboring terraces. This substrate-dependent effect has also been observed during formation of triangular hydrogen vacancy patterns on Ru(0001).30
In summary, we have studied the adsorption and interactions of CO$_2$ on the Ru(0001) surface using STM imaging and DFT calculations. CO$_2$ adsorbed on Ru(0001) at 77 K with submonolayer coverage shows no long-range ordering but small (2 × 2) arrangements. The adsorbed molecules distort into a “V”-shaped geometry with the carbon atom close to a hcp hollow site, with three possible but equivalent orientations. The molecules partially desorb after annealing to 250 K, while the remaining form trimers exhibiting different configurations depending on the relative orientations of its constituent molecules. The most stable trimer has a cyclic structure with an energy about 40 meV lower than that with three parallel molecules. The trimers follow the same orientation within a single Ru terrace with the triangle centered at a top site so that they appear rotated by 60° among neighboring terrace, indicating that the interaction between CO$_2$ molecules is affected by the Ru substrate. This study contributes to a better understanding of the binding and intermolecular interactions of CO$_2$ on metals, which is helpful for the study of the CO$_2$ reaction mechanism on metal surfaces.

**EXPERIMENTAL AND COMPUTATIONAL METHODS**

The experiments were performed using a home-built, low-temperature ultrahigh vacuum (UHV) STM at a base pressure below 5 × 10$^{-11}$ Torr.$^{31}$ The Ru(0001) surface was cleaned first by argon ion sputtering at 1 kV, followed by annealing and cooling cycles between 773 and 1773 K in an oxygen atmosphere to remove carbon impurities from the surface. The remaining oxygen on the Ru surface was removed by a final annealing to 1673 K in UHV. The cleanliness of the surface was confirmed by both Auger electron spectroscopy (AES) and STM. CO$_2$ (Airgas, 99.999%) was dosed through a leak valve and a dosing tube pointing toward the sample at 77 K. The sample was annealed to higher temperature to enhance surface mobility and activity. After annealing, the sample was quickly cooled down to 77 K for STM imaging. All STM images presented in this Letter were acquired at 77 K.

All DFT calculations have been performed with the GREEN package$^{32}$ and its interface to the SIESTA formalism.$^{33}$ In a first stage, we relaxed the slabs described below under the Generalized Gradient Approximation (GGA)$^{34}$ for the exchange–correlation, while in a second refinement step, we included the van der Waals (vdW) functional of Klimes et al.$^{35}$ We chose this particular scheme, among others implemented in SIESTA, because it yielded the smallest deviation in the Ru lattice parameter (2.73 Å) with respect to the 2.706 Å experimental value. Nevertheless, differences in the quoted energies between the GGA and GGA+vdW schemes were always smaller than 10 meV, while the geometries differed by less than 0.05 Å in the atomic coordinates. All considered 2D slabs were six Ru layers thick, while we employed a (4 × 4) supercell to study the adsorption of isolated CO$_2$ and a larger (6 × 6) for the trimer structures. The Ru lattice parameter was fixed to the bulk experimental value. A double-$\zeta$-polarized scheme was used to construct the atomic orbital basis set for all elements, with highly extended orbitals for the C, O, and the two surfacemost Ru atoms (energy shift set to 10 versus 100 meV used for the rest of the bulk-like Ru atoms). A 0.006 Å$^3$ resolution (Mesh cutoff set to 700 Ry) and k-supercells around (30 × 30) relative to the Ru(0001)-(1 × 1) lattice were employed for the real space meshes and Brillouin Zone integration, respectively. Symmetries, when present (e.g., p3 for the cyclic trimer or pm for the isolated molecules), were exploited both in k-space and during the atomic relaxations.

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**Notes**

The authors declare no competing financial interest.

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