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STM evidence for the dissociation of carbon monoxide on ruthenium steps

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Abstract

In heterogeneous catalysis, identifying the active site for key reaction steps is an important contribution for the optimization of industrial synthesis. The structure sensitivity of CO dissociation on a metal catalyst, which is the rate-limiting step for the methanation and the Fischer-Tropsch processes under certain conditions, has been debated for years. Here, scanning tunnelling microscopy (STM) and density functional theory (DFT) are used in order to clarify the role of monoatomic steps in the splitting of CO on a stepped Ru(0 1 54) crystal, which displays alternating steps with either 4-fold or 3-fold symmetry. After CO doses at elevated temperatures, the STM images reveal step decorations characteristic of atomic oxygen resulting from CO dissociation on every second step. The comparison of the STM images with the results of DFT calculations shows that the step decoration occurs on the steps displaying the 4-fold symmetry. We conclude that the active sites for CO dissociation on ruthenium are located on the 4-fold symmetry monoatomic steps.

1. keywords

Catalysis, CO dissociation, Ruthenium, Scanning Tunnelling Microscopy, STM, Density Functional Theory, DFT.

2. Introduction

CO dissociation plays an important role in industrially relevant reactions such as the methanation reaction and the Fischer-Tropsch process, which are involved in the preparation of synthetic fuels.1–3 Various metal catalysts such as iron, cobalt, nickel and ruthenium can be used in these processes, usually in the form of nanoparticles supported on a carbon or metal oxide substrate.1 Despite the scarcity of ruthenium,4 it is of interest to elucidate the mechanism of these
chemical reactions on a ruthenium surface since this metal is known for being a better catalyst than the more widely used cobalt or nickel for both the Fischer-Tropsch$^1$ and the methanation reactions. In early studies, Goodman and co-workers measured the rate of methane formation for various facets of nickel and ruthenium, as well as for supported catalysts.$^5,6$ For both metals, these authors did not find any significant change between the activation energies obtained for the different facets and the supported particles. This observation led them to suggest that the methanation reaction is not structure sensitive. However, later studies based on catalytic tests, scanning tunnelling microscopy (STM) and density functional theory (DFT) calculations have highlighted the importance of monoatomic steps for CO dissociation on Ni(1 1 1) under ultra high vacuum conditions (UHV).$^3$ For the case of ruthenium, isotopic scrambling experiments on stepped surfaces clearly showed that step sites are more efficient for splitting CO than terraces.$^7,8$ Recently, in our group, Vendelbo et al. highlighted the role of steps and the accumulation of carbon on the surface. This was accomplished by combining temperature programmed desorption (TPD) and carbon uptake measurements on a Ru(0 1 54) single crystal, with DFT calculations.$^9$ These results were further confirmed by high pressure methanation and step blocking experiments.$^{10}$

It is worth mentioning that ruthenium is also a good catalyst for other processes such as ammonia synthesis. For instance, Dahl et al. used thermal rate measurements combined with step blocking experiments to demonstrate that the active site for N₂ dissociation, which is the rate-limiting step for ammonia synthesis, is located at the monoatomic steps on a Ru(0 0 1) surface.$^{11}$ Furthermore, in the same work, DFT calculations allowed the identification of particular sites, the so-called B5 sites located at the steps with 4-fold symmetry, as the sites responsible for the activation of N₂ on the surface of a ruthenium single crystal. Later studies also revealed the importance of steps for supported Ru catalysts. These suggest - based on geometrical considerations - an optimum activity for 2 nm Ru nanoparticles, for which the abundance of step-like sites was proposed to be the highest.$^{12}$ After including the effect of temperature in the DFT calculations, it was later proposed that the optimal size is around 3 nm.$^{13}$

The aforementioned studies are based on averaging techniques and do not bring a localized experimental insight into individual catalytic processes. This crucial information can nevertheless be provided by microscopy techniques. The use of scanning probe microscopies, and in particular STM, has been extremely fruitful at bringing insight into catalytic processes.$^{14,15}$ Diverse types of samples have been considered, such as low Miller index surfaces on single-crystals, nanoparticles on various atomically flat substrates and thin films of oxides. High pressure STM measurements have been used to show the effect of reactive gases on the catalyst surface. For example, Tao et al. evidenced the reconstruction of the Pt(5 5 7) and Pt(3 3 2) surfaces into clusters as an effect of the exposure to high pressures of CO (above 0.1 bars). These observations were supported by high-pressure X-ray photoelectron spectroscopy (XPS) and DFT calculations.$^{16}$ Another success of STM in reference to catalysis has been the demonstration that, for MoS₂ nanoclusters, the catalytic sites for the hydodesulfurization process$^{17}$ and for the hydrogen evolution reaction are located on the edges of the particles.$^{18,19}$

In the case of ruthenium, STM was used by Neddermeyer’s group in order to investigate the different structures adopted by an oxygen overlayer as a function of coverage. This study showed that a p(2×2) structure dominates for coverages below 0.35 monolayers (ML), with a perfect ordering at 0.25 ML. For higher coverages, p(2×1) domains appear until the saturation coverage of 0.58 ML, for which these domains cover the entire surface.$^{20}$ Menzel and co-workers showed the effect of lattice strain on the adsorption of oxygen atoms at room temperature showing in particular that the p(2×2) structure is favored if the lattice spacing is slightly expanded.$^{21,22}$ Ertl and co-workers studied the behavior of nitrogen and oxygen atoms after NO dissociation on a Ru(0 0 1) surface.$^{23–25}$ Their work gave evidence of the high mobility of adsorbed oxygen at low coverages, compared to nitrogen, unless an oxygen atom is
either located in the vicinity of a monoatomic step or included within a cluster of oxygen atoms adopting a p(2 × 2) periodicity with respect to the ruthenium lattice. It also allowed for the identification of the monoatomic steps as the active site for NO dissociation under UHV conditions. During this study, the authors also observed a different behavior depending on whether the step presents a 4-fold or a 3-fold symmetry. Although both types of steps seem to be active, a rim of oxygen atoms is accumulated at the top of the steps with a 4-fold symmetry and progressively deactivates these steps, whereas the steps with a 3-fold symmetry remain active. More recently, in a series of low temperature STM experiments, Shimizu et al. observed the formation of C-H species after the dissociative adsorption of either H₂ or H₂O on a Ru(001) surface containing up to 0.03 ML of carbon impurities. It is also of interest to note that defect-free graphene layers can grow over a large area of a Ru(001) single crystal. Previously, STM has been used to study the structural and electron modifications induced by the lattice mismatch between the graphene layer and the ruthenium substrate. An interesting aspect is the possible use of the moiré pattern observed for graphene overlayers on Ru(001) as a template for the deposition of transition metal nanoparticles.

Regarding CO adsorption, early low energy electron diffraction (LEED) studies provided evidence that CO molecules adsorb preferably on atop sites on the Ru(001) terraces. Furthermore, several periodical structures have been observed at low temperature (110 K), including a \( \sqrt{3} \times \sqrt{3} R30^\circ \) lattice for coverages up to one third of a monolayer and a \( 2 \sqrt{3} \times 2 \sqrt{3} R30^\circ \) structure for coverages varying between 0.33 ML and 0.58 ML. At room temperature, only the \( \sqrt{3} \times \sqrt{3} R30^\circ \) structure is observed and the CO overlayer is believed to be disordered for coverages higher than 0.33 ML. The \( \sqrt{3} \times \sqrt{3} R30^\circ \) CO structure has also been identified in two independent STM studies. Moreover, it is found that the images of dense CO layers (with a coverage higher than 0.33 ML) do not exhibit any discernable feature because of a weak corrugation. In (CO + O) coadsorption experiments, also in ref. 22, the \( \sqrt{3} \times \sqrt{3} R30^\circ \) CO lattice is observed in the vicinity of monoatomic steps, on the top terrace. At the same time a p(2 × 2) periodicity corresponding to oxygen atoms with CO impurities is present further away from the step edges. This behavior was assigned to modifications of the adsorbates’ binding energies as a function of the compressive or extensive lattice strain induced by the presence of steps.

The aim of the work presented here is to directly observe the results of CO dissociation on a ruthenium catalyst under UHV conditions. Since monoatomic steps are suggested to be the active sites according to several studies, special attention was devoted to these low coordination sites. In particular, we investigate whether the different step geometries (i.e. 3-fold versus 4-fold geometry) affect the reactivity towards CO splitting. For this purpose, we performed STM studies of CO dissociation on a Ru(01 54) stepped surface. Simulated STM images, adsorption energies and transition state energies calculated using DFT were used to support our interpretation.

3. Methods

The sample is a vicinal Ru(01 54) single crystal from Mateck, GmbH. Its surface presents (001) terraces with an average width of approximately 7 nm, corresponding to 27 atomic rows, separated by monoatomic steps. The geometry is depicted schematically in Figure 1. According to the hexagonal close-packed structure of ruthenium, one can observe alternating structures for the monoatomic steps, namely the A-type and B-type steps. As evidenced by the model close-ups in Figure 1, the A steps present a 3-fold symmetry whereas a 4-fold symmetry is observed for the B steps.

All experiments were performed in a UHV chamber equipped with a STM, together with facilities for XPS, ion scattering spectroscopy (ISS) and TPD. The background pressure was 7×10⁻¹¹ torr. The sample was cleaned via repeated cycles involving Ar⁺ sputtering at 800 K (30 min., 1.5×10⁻⁷ torr), surface oxidation (O₂,
10^{-7} \text{ torr}, 1100 \text{ K}, 10 \text{ min.}), surface reduction (H_2, 2\times10^{-6} \text{ torr}, 500 \text{ K}, 20 \text{ min.}) and annealing to 1400 K for 2 min. Sample heating is provided by an electron beam heater implemented within the manipulator. The sample cleanliness was regularly controlled with XPS and CO-TPD. All STM measurements were performed at room temperature in an Århus-type STM\textsuperscript{35} working in constant current mode. STM images were typically recorded at a bias voltage of 1 V or lower and tunnelling currents of 0.4-1 nA. The software package SPIP\textsuperscript{36} was used to process the images. Typical image treatments include plane correction, noise removal using a median filter and derivation of the height along the fast-scan axis in order to emphasize small features in the image. Atomic resolution on either HOPG(0 0 1) or Au(1 1 1) were used as references to calibrate the STM images in the horizontal plane while the height measurements were calibrated against the height obtained for steps on Au(1 1 1).

The DFT calculations were performed with the plane wave code DACAP\textsuperscript{37} using the RPBE exchange-correlation functional\textsuperscript{38} a converged plane wave cutoff of 340 eV and a density cutoff of 400 eV. DACAP\textsuperscript{3} uses ultrasoft pseudopotentials to represent the ion-electron interaction.\textsuperscript{39} We used the Ru(1 0 9) system, with a four-layers thick 2x1 supercell to model the surfaces, as described in ref. 9. The Brillouin zone of all slabs was sampled with 4x1x1 Monkhorst-Pack grids, which ensures that the product of the supercell dimensions and the k-points was more than 20 Å in all directions. The vertical separation between consecutive slabs was in all cases more than 12 Å and dipole corrections were applied. Only atoms in the topmost layer were free to move and the atomic relaxations were done with the quasi-Newton minimization scheme, until the maximum force was below 0.05 eV/Å. The self-consistent RPBE density was determined by iterative diagonalization of the Kohn-Sham Hamiltonian at an electronic temperature of $k_B T = 0.1$ eV, using Pulay mixing of densities, with all total energies extrapolated to $T = 0$ K. All adsorption and transition state energies were calculated following the procedure described therein. The simulated STM images were made within the Tersoff-Hamann approach as implemented in the Atomic Simulation Environment (ASE) package.\textsuperscript{40,41} The coupling channel between the surface and STM tip was modeled using an s orbital. The tomograph was generated with a density of states of 10\textsuperscript{-3} at the Fermi level. A grid spacing of 0.2 Å was used to produce the STM image, with a bicubic interpolation.

4. Results and discussion

4.1. Experimental results. Figure 2 displays STM images of the freshly cleaned Ru(0 1 54) surface, with line profiles as inserts, as a reference for the images after CO exposure. The surface in Figure 2a exhibits straight, parallel monoatomic steps. Kinks can be observed along the steps. The height of the monoatomic steps is measured at 0.21 \pm 0.01 nm (Figure 2a), which is consistent with the value extracted from the crystallographic structure of ruthenium (0.214 nm). In general, the terrace width varies between 4 and 10 nm, in agreement with the expected average value of 7 nm. On some occasions, we also observed regions displaying some step bunching, characterized by 5 to 8 monoatomic steps separated by narrow terraces (1 to 2 nm wide). Next to these areas with step bunching, we usually find relatively broad terraces, with a typical width of 15 to 25 nm. It is of interest to note that none of our STM experiments show the presence of double
steps on the freshly cleaned Ru(0 1 54) surface, unlike the observations made by Yates’ group on the Ru(1 0 9) surface. Furthermore, we occasionally observed the presence of locally strained areas (2-3 nm wide) which have previously been assigned to subsurface argon bubbles trapped a few atomic layers below the surface. Although the lattice stress induced by those bubbles has been shown to locally modify adsorption energies, we estimate that, due to a very low density, it does not significantly influence the results from averaging experiments such as TPD. Furthermore, during STM measurements, we ensured that the areas we studied after CO exposures did not contain such local areas of lattice strain. Figure 2b presents an image of the ruthenium surface with atomic resolution. The hexagonal pattern and the interatomic distance of 0.27 ± 0.02 nm are consistent with the crystal structure of ruthenium.

If the ruthenium surface is exposed to CO while cooling down (typically 5×10⁻⁸ torr, 1000 seconds, at a cooling rate of ca. 0.4 Ks⁻¹) from 700 K to 400 K or after a CO TPD, we observe a partial decoration of the monoatomic steps. On the STM image presented in Figure 3, one can distinguish periodic features on every other step. Furthermore, a faint hexagonal lattice is observed on the terraces which can be seen more easily on Figure 3b where we show a derivative image of the image presented on Figure 3a.

Figure 4 exhibits STM images recorded on two different areas of the same sample. In order to emphasize the periodic features, a cyclic color scale, which distributes the full color scale over the height of a single step and then starts over on the next step, has been applied. On both pictures, the hexagonal lattice on the terraces is highlighted by a series of blue dots. It is rotated by 30° with respect to the ruthenium lattice (see Figure 2b) and we measure a spacing of 0.47 ± 0.03 nm, much larger than the interatomic distance between Ru atoms (0.27 nm). We assign this structure to the (√3 x √3)R30° superlattice (√3 x 0.27 nm = 0.47 nm) adopted by CO molecules for coverages lower than 0.33 ML, and previously observed using LEED and STM. The partial step decoration is highlighted by green dots. It is ob-

Figure 2. a- 50×50 nm² STM image of the clean Ru(0 1 54) surface, b- 5×5 nm² atomically resolved STM image of the ruthenium lattice, the red dots on the image are highlighting the hexagonal array. For both images, height profiles extracted along the red markers are presented as inserts.
Figure 3. a- 20×20 nm² STM image of the Ru(0 1 54) surface after a CO-TPD, b- gradient image of figure 3a, further highlighting the step decoration.

served on every other step edge and can be described as "fingers" separated by 0.55 ± 0.05 nm. On a few occasions, we observe that this structure is extended into a hexagonal lattice with a 0.55 nm spacing. This is the case, for instance, on the terrace on the left-hand side of Figure 4b. This periodicity corresponds to twice the interatomic distance on the ruthenium (0 0 1) terrace. Previous STM studies have shown that adsorbed oxygen atoms adopt a p(2×2) superstructure at coverages lower than 0.35 ML. The adsorbed oxygen atoms are located in hcp 3-fold hollow sites. They are observed as dark spots on the STM image since their presence leads to a decrease of the density of states at the Fermi level for the neighboring ruthenium atoms. Furthermore, Ertl and co-workers have shown that, for coverages of the order of 0.01 to 0.02 ML, isolated oxygen atoms adsorbed on the Ru(0 0 1) surface are extremely mobile and only appear as "dashes" when imaged using typical STM parameters. However, these authors also demonstrated that the adsorbed oxygen atoms included in a cluster of oxygen atoms (with a p(2×2) periodicity with reference to the ruthenium lattice) or located in a 3-fold hollow site next to a monoatomic step, are far less mobile and they are also observed as dark spots on the ruthenium surface. As a consequence, we attribute the presence of the "fingers" decorating every other step to oxygen atoms located in 3-fold hollow sites next to the top of a step edge. Since no oxygen is present on the surface before the CO exposure, we suggest that these oxygen atoms are provided by CO splitting occurring on step sites. The fate of the carbon atoms is less clear. CO-TPDs and oxygen titration measurements of the amount of carbon have been performed after dosing CO at high temperatures. The results of the titration experiments are shown in the supplementary information. The CO-TPD spectra usually exhibit the presence of a peak with a maximum at 480-500 K corresponding to molecularly adsorbed CO, and a shoulder appearing at 550-600 K which has been assigned to desorption of CO dissociated at step sites. Furthermore, the carbon content measured using oxygen titration is approximately 0.02 ML, in agreement with the observations made by Vendelbo and co-workers. These experiments confirm the presence of carbon at the step edges of our Ru crystal after dosing CO.
while the sample cools down from 700 K to 400 K. In STM, the presence of isolated carbon atoms has been observed at low temperatures (6 K) on the terraces of a Ru(001) crystal. As in the case of oxygen atoms, carbon atoms are characterized by dark spots due to a lowering of the density of states for the neighboring Ru atoms, as compared to unmodified Ru atoms. Their presence is not observed in our STM experiments, probably because the carbon atoms resulting from CO dissociation are located at the bottom of the steps, in areas which are screened by tip convolution effects.

Figure 4. a- 10×5 nm$^2$ STM image of the Ru(0154) surface after a CO-TPD, b- 20×10 nm$^2$ STM image of another area of the Ru(0154) surface after a CO-TPD. For both images, a cyclic color scale is optimised in order to further highlight the periodical lattices, especially at the step edge. The blue dots correspond to the periodicity observed on the terraces and the green dots are used to evidence more clearly the periodical features observed at the steps and their vicinity.

4.2. Theoretical Modeling. In order to confirm our interpretation, a theoretical study based on DFT calculations has been undertaken. The Ru(109) surface, exhibiting the same succession of A and B monoatomic steps but narrower terraces (~1 nm wide) was chosen to model the Ru(0154) surface. We find that this model provides a good description of our experimental data at a reasonable computational cost. The geometry of the clean Ru(109), and that of the same system with different adsorbates (molecular CO, dissociated CO and adsorbed atomic oxygen) on both types of steps was optimized. We present theoretical STM images calculated for each optimized structure using a method derived from the Tersoff-Hamann model in Figure 5.

Figure 5a exhibits the atomic configuration and the corresponding simulated STM image of the clean Ru(109) surface. It shows no significant difference between the two types of monoatomic steps, aside from the registry between the (001) terraces. Furthermore, the small variations in apparent height between ruthenium atoms and the interatomic space is consistent with the low corrugations observed experimentally.

The case of CO molecules adsorbed on the B-type steps is presented on Figure 5b. We find that CO molecules adsorb preferentially on bridge sites at the step edge, with the carbon atom binding to the surface, and are tilted away from the step. A similar calculation has been performed for molecular CO adsorbed on the A step. In this case, the CO molecule is also located on a bridge site at the step edge and tilted towards the lowest part of the step. This orientation is in good agreement with the observations made by Shincho et al. during an investigation of CO adsorption on a stepped Ru(1110) using angle resolved ultra-violet photoemission spectroscopy. These authors find that the CO molecules adsorbed at the step edge are tilted by approximately 30° with respect to the direction normal to the (001) plane. The adsorption on a bridge site at the steps might seem in contradiction with the adsorption on atop sites on the terraces. In fact, we find that a bridge site is a more favorable adsorption site than a step atom by a very small margin of approximately 30 meV. For both the A and the B steps, the theoretical STM images display very prominent CO molecules at the step edge, contrary to the experimental data. As a consequence, the step edges would appear as bright rims on the STM images of a ruthenium surface with CO adsorbed at the step edges and clean terraces. One also needs to consider the case of CO adsorbed on both steps and ter-
Figure 5. Simulated STM images of the Ru(109) surface with various adsorbates: a- clean surface; b- with molecular CO adsorbed on B steps; c- with CO dissociated on A steps; d- with CO dissociated on B steps; e- with atomic oxygen adsorbed at the top of A steps; f- with atomic oxygen adsorbed at the top of B steps. On the ball models, ruthenium atoms are represented in gray, carbon atoms in black and oxygen atoms in red. On the model images, the orange color scale corresponds to apparent height (in Å with respect to the bottom of the cell) in the simulated STM image and the black dots indicate the position of the surface atoms.
races. Previous STM experiments, performed on ruthenium covered with 0.33 ML of CO, did not show a significant height difference between the CO molecules adsorbed on either the step edges or the terraces.\textsuperscript{22,24} Therefore, we conclude that the molecular adsorption of CO on the ruthenium steps does not explain the step decoration presented in Figure 3 and Figure 4.

In Figure 5c and Figure 5d, we consider the case of CO dissociated on the A and B steps, respectively. For the A steps (Figure 5c), the most stable structure corresponds to the oxygen atom located in a fcc 3-fold hollow site next to the step edge, on the top terrace, with the carbon atom also sitting in a fcc 3-fold hollow site located in the vicinity of the bottom of the step. On the theoretical STM image, the oxygen atom appears slightly higher than the neighboring ruthenium atoms. A lower density of states, and hence a lower apparent height, is observed at the step edge, in the area located between the adsorption sites of the carbon and oxygen atoms. In the case of CO dissociation on the B step, we first considered the case where the carbon atom is found in the 4-fold sites at the bottom of the step and the oxygen atom located in the hcp 3-fold hollow site closest to the carbon adsorption site. This structure was found to be less stable than the structure with CO adsorbed at the step edge, which will be discussed later. Another structure was then considered in which the oxygen atom is found in a hcp 3-fold hollow site displaced one position along the step with respect to the carbon atom, see Figure 5d. This so-called "cross structure" is more favorable than both the initial adsorbed state and the dissociated state. Furthermore, it is energetically more favorable than having the carbon and oxygen atoms far from each other at the step, as can be calculated from the individual adsorption of the species. It most probably results from a migration of the oxygen atoms immediately after the dissociation, thanks to the low diffusion barrier for oxygen atoms, estimated at 0.7 eV by Wintterlin et al.\textsuperscript{23} The model STM image, in a similar fashion to that obtained for CO dissociated at the A step, displays a lower density of states in the areas located next to the oxygen atoms. The oxygen atom, however, is not as prominent as it is in the case of the A step.

The presence of the carbon atoms also seems to induce a small decrease of the density of states, probably negligible compared to that induced by the oxygen atoms. On the basis of our calculations, both these configurations could explain our STM images, with a small preference for the case of the dissociation on the B step, since the oxygen atoms do not appear higher than their neighboring ruthenium atoms on the experimental data.

As we mentioned earlier, similar step decoration has been observed in previous work for low coverages of oxygen after dissociation of NO or O\textsubscript{2}.\textsuperscript{23–25} This suggests that the presence of oxygen atoms at the top of the step edge is the main factor contributing to the formation of the "fingers" at the step edges as observed in our STM investigation. As a verification, we performed calculations with oxygen atoms adsorbed in the same sites as in the case of the dissociated CO. Namely, we consider the fcc 3-fold hollow site closest to the top of the step edge for the A step (Figure 5e) and the hcp 3-fold hollow site closest to the top of the step edge for the B step (Figure 5f), in the absence of carbon. The model STM images are very similar to those obtained for dissociated CO, hence confirming that the oxygen atoms have a larger influence than the carbon atoms on the STM images. As a further verification, simulated STM images with carbon atoms at the bottom of the steps have been calculated (see supplementary information) and these clearly show that these carbon atoms have little influence on the STM images.

In order to help identify the type of step on which the decoration occurs, we present an energy diagram comparing the role of the (0 0 1) terraces, the A steps and the B steps for the dissociation of CO (Figure 6). For these three types of structures, all energies have been calculated with respect to a cell containing the Ru slab as described in the methods section and one CO molecule in the gas phase (i.e not interacting with the surface).

First, these calculations show that the adsorption energies of molecular CO are approximately 1.5 eV for the three types of adsorption sites we consider. We find CO adsorbed on the B step is slightly more stable than CO on the A step or on
Figure 6. Energy diagram for CO dissociation on the Ru(109) surface, the dissociation on the A step is represented by the blue dashed line and the solid red line corresponds to dissociation on the B step. For comparison, the black dotted line illustrates CO dissociation on the Ru(001) terraces. From left to right, the thumbnails show a CO molecule in the gas phase and in various consecutive configurations on a B step: adsorbed, in the transition state, dissociated and in the cross structure obtained after migration.
the terrace, by approximately 0.1 eV. Moreover, if one focuses on the transition states, one will notice that the energy barrier is significantly lower for CO dissociation on the B step, as compared to the A step (by 0.4 eV) or to the terraces (by 1.2 eV). This suggests that the dissociation is most likely to occur on the B step. In addition, for the A step and the terraces, the transition states are found to be less stable than the ruthenium surface with a CO molecule in the gas phase. This means that CO desorption is more probable than CO dissociation on these sites. As a consequence, the step decoration resulting from CO dissociation should only be observed on B steps.

After dissociation, we find that the configuration with a carbon atom sitting at the bottom of the step and an oxygen atom in the first available 3-fold hollow site at the top of the step is more stable for the B step than the equivalent structure for the A step (by approximately 0.45 eV). Furthermore, the "cross structure", obtained after migration of the oxygen atoms at the top of steps, is 0.55 eV more favorable than the dissociated state. It appears to be slightly lower in energy than the surface with a CO molecule adsorbed at the B step. On the other hand, for both the A step and the (0 0 1) terraces the dissociated state is less favored than the molecularly adsorbed state. This further confirms that the step decoration resulting from CO dissociation is more likely to be observed on the B steps.

Another interesting aspect is the discrepancy between the preferred site for oxygen atoms next to the monoatomic steps. For the case of the A-type steps, our calculations show that the oxygen atoms sit preferentially in the fcc 3-fold hollow site in the immediate vicinity of the step edge. On the other hand, for B steps, the most favorable adsorption site for oxygen is the hcp 3-fold hollow site, also located in the immediate vicinity of the step edge. Previous works show that the adsorption site for oxygen atoms on the (0 0 1) terraces is the hcp 3-fold hollow site and that, for low oxygen coverages, the adsorbed oxygen atoms are organized according to a p(2×2) superstructure with reference to the ruthenium lattice. As a consequence, if the CO molecules were dissociated on the A steps, there would be a lattice mismatch between the adsorption sites of oxygen atoms at the A step and the preferred p(2×2) oxygen overlayer on the terraces, while there would be a lattice match in the case of a dissociation on the B steps. Experimentally (Figure 4b), we observe that the p(2×2) overlayer and the step decoration are well aligned which again suggests that the CO molecules dissociate on the B steps under our experimental conditions.

Finally, on the right-hand side of the diagram on Figure 6, we consider the migration of carbon and oxygen atoms away from the step sites to the terraces. For the A steps, we find that, if CO dissociation were to occur on these steps, the carbon atom would preferably migrate to the neighboring terrace whereas the oxygen atoms would tend to remain at the step. The behavior of CO dissociated on the B step is quite different; it is energetically favorable for the oxygen atoms to move away from the dissociation site in order to form the "cross structure". The structure corresponding to the carbon atom remaining at the B step and the oxygen atom located on the terraces (respectively the configuration with the oxygen atom at the B step and the carbon atom on the terraces) is approximately 0.4 eV (respectively 0.9 eV) less stable than the "cross structure". The latter case is consistent with the observation of carbon poisoning at the ruthenium steps after exposure to CO at 550 K. It also accounts for the formation of a rim of oxygen atoms at the top of the steps for CO dissociation on ruthenium. Moreover, a similar behavior has also been observed for isolated oxygen atoms after NO dissociation on Ru(0 0 1).

To summarize, the simulation of STM images confirms that our experimental data can be explained by the dissociation of CO on step edges with a main contribution coming from oxygen dissociation on the A steps, and a lattice mismatch between the adsorption sites of oxygen atoms at the A step and the preferred p(2×2) oxygen overlayer on the terraces, while there would be a lattice match in the case of a dissociation on the B steps. Experimentally (Figure 4b), we observe that the p(2×2) overlayer and the step decoration are well aligned which again suggests that the CO molecules dissociate on the B steps under our experimental conditions.
atoms located in 3-fold hollow sites in the immediate vicinity of the step. Furthermore, when considering the total energies for the transition states and for the system after dissociation, we conclude that CO dissociation occurs preferentially on the B-type steps, which is further confirmed by registry between the p(2x2) oxygen overlayers and the step decoration. Furthermore, our calculations are also consistent with both the high mobility of oxygen atoms on the surface of ruthenium and the accumulation of carbon on step sites observed earlier in our group.

4.3. Discussion. To summarize, our STM experiments exhibit a step decoration on every other step and the comparison with simulated images allowed us to assign this step decoration to CO dissociated at the step edge. Furthermore, the calculation of an energy diagram showed that the dissociation occurs preferably on the steps with a 4-fold symmetry on which a "cross-structure" is stable for the carbon and the oxygen atoms.

As mentioned in the introduction, the identification of the active site for CO dissociation has been an open question for decades. While early measurements suggested that the reaction rate for methanation was independent of the nature of the ruthenium surface (Ru(001) compared with Ru(110) and with supported particles), several experimental studies based on stepped crystals lead to the conclusion that the active site for CO activation is located on steps. For instance, Shincho et al. used time domain spectroscopy (TDS), Auger electron spectroscopy (AES), ultraviolet photoelectron spectroscopy (UPS) and XPS to investigate the adsorption of CO on Ru(1110) and Ru(001). The comparison between the results obtained for the stepped (1110) surface and those gathered for the basal plane demonstrated that CO is adsorbed in the molecular state on the (001) terraces and that the CO molecules dissociate on step sites, provided that the adsorption temperature is high enough (approx. 500 K). Later, Yates’ group used another route, involving infrared (IR) spectroscopy and isotopic exchange experiments, to demonstrate that the steps, which appear to be two atomic rows thick after reconstruction, are responsible for the dissociation of CO on a Ru(109) surface. More recently, Vendelbo et al. also showed the importance of steps for the dissociation of CO, together with carbon accumulation at the steps, by means of TPD and carbon uptake measurements performed on a Ru(0154) surface. The step decoration we observed using STM, after exposing ruthenium to CO at temperatures varying from 700 K down to 400 K or after a CO-TPD, provides further evidence that CO adsorbs dissociatively on monoatomic steps at elevated temperature. Moreover, our STM data shows that CO is dissociated on every other step under our experimental conditions (Figure 3 and Figure 4), demonstrating that either the A steps or the B steps are more effective at activating CO. DFT calculations were performed in order to rationalize this observation (Figure 5 and Figure 6) and, based on the comparison between the results of this theoretical modeling and the experimental data, we suggest that the active sites are located at the B steps. This is also in agreement with the predictions, based upon DFT calculations, that CO dissociation would preferably occur on the so-called B5 site in the case of ruthenium, nickel, and rhodium. It is worth mentioning that the B5 site is considered as the active site for several structure sensitive reactions such as N2 dissociation.

In terms of reactivity, the stability of the "cross structure" (see Figure 5 and Figure 6) is of importance. Firstly, because of the migration of the oxygen atoms in order to form this configuration, these atoms are at equal distance from two equivalent carbon atoms. Thus, during TPD experiments, the recombination can occur either between C and O atoms resulting from a single CO molecule or between atoms arising from two different molecules, with equal probability. This observation is in very good agreement with the results of isotopic exchange measurements reported by Yates and co-workers and Shincho et al. Both found random mixing of the different isotopes in the peak corresponding to the dissociative adsorption at steps. Secondly, for the "cross structure" the adsorption sites located just above the carbon atoms, namely the step bridge site, the closest hcp 3-fold hollow site and several atop sites are still available for other reactants. As a conse-
In a study of the interaction of adsorbates on a ruthenium surface presenting local strain induced by Ar "bubbles" trapped a few atomic layers below the surface, Jakob and coworkers used STM and IR spectroscopy to describe the behavior of co-adsorbed CO molecules and oxygen atoms, with a deposition performed at room temperature. Their results showed that a pure \( (\sqrt{3} \times \sqrt{3}) \) \( R30^\circ \) CO phase is prevalent in the vicinity of the steps, on the upper terrace, while a \( p(2\times2) \) superstructure characteristic of adsorbed oxygen, probably with CO impurities, is observed further away from the step edge. This results from a local lattice compression in the proximity of a step (upper terrace) which leads to a more favorable adsorption for the \( (\sqrt{3} \times \sqrt{3}) \) \( R30^\circ \) CO overlayer in this area. On the other hand, the \( p(2\times2)-(O + CO) \) phase is more favorable for an unstrained or an expanded ruthenium lattice. Furthermore, their interpretation is consistent with previous theoretical studies. The behavior we observe after CO deposition at high temperature (Figure 3 and Figure 4), with a \( p(2\times2) \) oxygen overlayer next to a step on the upper terrace and \( (\sqrt{3} \times \sqrt{3}) \) \( R30^\circ \) CO phase in the unstrained areas further from the step edge is opposite to that reported by Jakob et al.\(^{22} \) In our opinion, this discrepancy can only be explained if, in our experiment, the oxygen atoms are generated at the steps while the \( (\sqrt{3} \times \sqrt{3}) \) \( R30^\circ \) CO overlayer is forming (or is already formed). Thus, it confirms the hypothesis that CO molecules adsorb dissociatively at step sites on the ruthenium surface, provided the temperature is sufficiently high.

Recent studies demonstrated that the surface of metal catalysts could be strongly modified in the presence of reactive gases at the relatively high temperatures necessary for the catalysed reactions to take place. As an example, Somorjai’s group has demonstrated that stepped platinum surfaces (Pt(5 5 7) and Pt (3 3 2)) undergo drastic restructuring leading to the formation of triangular or parallelogram-shaped nanoclusters when exposed to CO at a high pressure (1 torr).\(^{16} \) For the case of ruthenium, STM measurements performed in a CO rich environment at high temperatures by Frenken and coworkers exhibited the formation of "clusters" on the Ru(001) surface.\(^{48} \) Since the density and the shape of these clusters evolve with the gas composition, they were assigned to carbonaceous species able to react with \( \text{H}_2 \) or \( \text{O}_2 \) in the gas phase. Furthermore, these authors also observed a step roughening during CO oxidation. Such a phenomenon could be involved in the modified reactivity of the Ru(0 1 54) surface after exposure to CO (\( 10^{-5} \) torr).\(^9 \) We are currently performing STM experiments in order to clarify this behavior.

As opposed to our experiments performed in UHV on model crystals, industrial catalysis is usually performed using supported metal particles at high pressures and temperatures.\(^1 \) As a consequence, one compares the behavior of a well characterized crystalline surface in the model experiments to a juxtaposition of various facets, steps and kinks in the case of nanoparticles. Despite this so-called structure gap, our observations, especially the fact that the B steps are more active at dissociating CO, are relevant to the industry. In particular, this could lead to developing new strategies aiming at optimising the density of active sites at the surface of supported particles.

Furthermore, recent work suggests that the role of the substrate in the catalytic process is not negligible.\(^{49} \) In our opinion, two approaches could aid in addressing this question. The first concerns the surface science study of nanoparticles on a crystalline substrate such as HOPG\(^{50} \) or metal oxides.\(^{14} \) The second approach is based on the concept of reverse catalysts: nanoparticles of substrate material grown at the surface of a catalytically active species.\(^{14} \) We believe both these approaches may bring relevant insight into phenomena such as charge transfer or spill over effects.

### 5. Conclusion

STM results obtained after exposing a stepped Ru(0 1 54) surface to carbon monoxide under UHV conditions exhibit step decoration. We assign this decoration to CO dissociated at step sites...
and more particularly to the presence of oxygen atoms in 3-fold hollow sites in the immediate vicinity of the step, on the upper terrace. DFT calculations have been performed in order to rationalize our observation and the comparison between the experimental data and the theoretical results lead us to confirm our interpretation. Moreover, we observe that the step decoration occurs on every other step, which demonstrates that CO dissociation is structure sensitive since the hcp structure of ruthenium results in alternating A (3-fold symmetry) and B (4-fold symmetry) steps. An energy diagram calculated for CO dissociation, together with some considerations about the organization of the adsorbates, suggest that the active site is located on the B steps, in agreement with theoretical predictions concerning CO activation on ruthenium and other metal catalysts. Finally, we propose the extension of this work to determine the influence of CO exposure on the reactivity, via both nanoparticle studies and a reverse catalyst approach.

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Supporting Information Available

Supplementary informations include the results of temperature programmed desorption experiments in various conditions and carbon uptakes measurements through oxygen titration. Simulated images for carbon adsorbed at the bottom of the A and B steps as well as that of CO absorbed at the A step are also presented. This material is available free of charge via the internet at http://pubs.acs.org.

■ REFERENCES


(36) SPIP software, Image metrology A/S, Denmark.


