

Adsorption characteristics of CO and N₂ on RuO₂(110)

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Low-energy electron diffraction and density-functional theory calculations are used to examine the adsorption properties of CO and N₂ on RuO₂(110). Both molecules adsorb over the coordinatively unsaturated Ru sites (cus-Ru atoms) with their molecular axes normal to the surface plane. The chemisorption mechanism is well described within a donor-acceptor model, i.e., the Blyholder model. Since N₂ is not reacting with lattice oxygen of RuO₂, quite in contrast to CO, N₂ may serve as a chemical, nondestructive probe to titrate but also to selectively block the cus-Ru atoms; recently, the cus-Ru atoms were shown to be the active centers for the chemisorption of molecules.

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I. INTRODUCTION

Over the past few years, ruthenium dioxide RuO₂ has evolved into one of the best characterized transition-metal oxides in surface science.¹ The recent interest in RuO₂ was triggered by its surprisingly high activity towards CO oxidation^{2,3} and the prospect of RuO₂ to become a promising catalyst for the partial oxidation of organic molecules. To gain a deeper insight into the activity of RuO₂(110), a detailed knowledge of the adsorption geometries of simple molecules on this surface is mandatory. In particular, the CO adsorption site is of importance, as the chemisorption of CO is the first step in the CO oxidation reaction, assuming the Langmuir-Hinshelwood⁴ mechanism to be operative, i.e., the reaction occurs only between the species accommodated on the surface. It was demonstrated that the actual CO oxidation process proceeds via the recombination of adsorbed CO with lattice O of RuO₂, thereby reducing the RuO₂ catalyst. Under steady-state reaction conditions, however, the removed lattice oxygen is replenished with oxygen from the gas phase. This kind of redox mechanism was proposed by Mars and van Krevelen⁵ in the mid-1950s and verified on atomic scale only recently.¹

In this paper we report on the atomic geometries of adsorbed CO and the isoelectronic N₂ on RuO₂(110), employing the techniques of low-energy electron diffraction (LEED) and density-functional theory DFT calculations. The binding mechanism is shown to be similar to that on transition-metal surfaces, which is described within the Blyholder model.⁶ The CO binding energy on RuO₂(110) is 1.2 eV (DFT), e.g., much higher than on typical oxide surfaces,⁷ but smaller than on the bare Ru(0001) surface (DFT: 1.8 eV).

II. TECHNICAL DETAILS ABOUT THE EXPERIMENT AND THE CALCULATIONS

The measurements were conducted in a UHV chamber⁸ that is equipped with a four-grid back-view LEED optics, Auger electron spectroscopy, thermal desorption spectroscopy (TDS) and facilities to clean and prepare the Ru(0001) surface. The sample temperature could be varied from 100 K (by cooling with liquid N₂) to 1530 K (by direct resistive heating). The LEED intensities as a function of the incident

electron energy or as a function of time were collected at normal incidence of the primary beam and a sample temperature of 100 K. A computer-controlled high-sensitive charge-coupled device (CCD) camera was used to record spot intensities from the LEED fluorescence screen. The evaluation of the LEED data was performed after the measurements, thereby minimizing the exposure time of the oxide surface to electron irradiation. LEED *I-V* curves were computed by using the program code by Moritz⁹ and compared with the experimental LEED *I-V* curves by applying a least-squares optimization algorithm,¹⁰ based on Pendry's *r* factor R_p .¹¹

The RuO₂(110) phase was produced by exposing a well-prepared single crystal Ru(0001) to high doses of oxygen at an elevated sample temperature of 600 K. In order to reduce the oxygen background pressure in the UHV chamber, oxygen was dosed through a glass capillary array doser (with channels 3 mm long and 10 μm wide, total transparency of 50%) about 1 mm away from the sample. In this way, the local oxygen pressure at the sample was enhanced by a factor of about 100, thus allowing us to keep the oxygen partial pressure in the UHV chamber below 10⁻⁵ mbar during dosing. Typical oxygen exposures (local pressure×time) for the preparation were several 10⁺⁶ Langmuirs. After the background pressure in the UHV chamber has reached a value below 10⁻⁹ mbar, the sample was briefly annealed to 600 K in order to remove contamination by residual gas adsorption. For the measurements, the sample was cooled to 100 K. The total amount of oxygen in the oxygen-rich Ru(0001) surface was estimated by a thermal desorption experiment to be about 6 ML. The so prepared oxygen-rich phase on Ru(0001) exposes both RuO₂(110) areas and (1×1) O areas.¹ We already showed that CO adsorption on the (1×1) O is restricted to temperatures below 50 K.¹² While dosing CO (the sample temperature was 100 K), we monitored the LEED spot intensities that are related to RuO₂(110) and the (1×1) O as a function of time (which is equivalent to the CO exposure); for more details, the reader is referred to Ref. 13. The variations in LEED intensity were restricted to the RuO₂ derived LEED spots. This finding indicates that the CO molecules adsorb exclusively on the oxide domains. Similar experiments were performed with N₂ exposure. Again, the LEED measurements clearly indicate that N₂ adsorption at 100 K takes place solely on RuO₂(110) and not

on (1×1) O. In order to prepare the CO-RuO₂(110) surface, we exposed 100 L of CO at a sample temperature of 100 K, while the N₂-RuO₂(110) surface was prepared by dosing 30 L of N₂ at 100 K. In both cases, the LEED pattern remained unchanged, i.e., neither CO nor N₂ is able to form an ordered superstructure on RuO₂(110).

For the density-functional theory (DFT) calculations we employed the generalized gradient approximation (GGA) of Perdew, Burke, and Enzerhof¹⁴ for the exchange correlation functional. We used *ab initio* pseudopotentials created by the scheme of Troullier and Martins¹⁵ in the fully separable form. The Ru core is taken to consist of all orbitals up to and including $4p$ states. The O, C, and N cores consist of the $1s$ state. The electronic wave functions were expanded in a plane-wave basis set with an energy cutoff of 60 Ry. The surface was modeled by five double layers of RuO₂(110) in a symmetric slab (supercell approach).¹⁶ CO and N₂ molecules were put on both sides of the RuO₂ slab in order to preserve the mirror plane symmetry. Consecutive RuO₂(110) slabs were separated by a vacuum region of about 16 Å, which was checked to be sufficient to avoid interaction between the CO (N₂) covered RuO₂(110) slabs. Calculations were performed using a (1×1) surface unit cell. The integral over the Brillouin zone was performed using a special k point set,¹⁷ with eight k points in the irreducible part of the (1×1) Brillouin zone. Test calculations with a (2×1) unit cell show that the binding energies of CO and N₂ vary only by 0.1 eV to higher values, i.e., the mutual interaction among the CO and N₂ molecules is weakly repulsive. The (2×1) unit cell was also used for the determination of the CO diffusion barrier. To accelerate the electronic relaxation, Fermi broadening of the occupation numbers was used with a width of 0.1 eV, and the energies were extrapolated to zero temperature. The calculation scheme allows for the relaxation of the electrons and the atoms' positions. We relaxed all O, C, N, and Ru coordinates, which maintain the planar $2mm$ symmetry. Only the O and Ru positions of the central Ru+O layer lying on the mirror plane normal to the $[110]$ direction of the symmetric RuO₂(110) slab were frozen in. The lattice parameters ($\sqrt{2}a = 6.58$ Å and $c = 3.23$ Å) of RuO₂(110) were determined via DFT optimization of the corresponding bulk RuO₂, which values compare favorably with experimental values of $\sqrt{2}a = 6.38$ Å and $c = 3.11$ Å, exhibiting overestimations of lattice parameters as typical for GGA.

III. RESULTS AND DISCUSSION

In a recent paper, we presented the atomic structure of the bare RuO₂(110) surface (cf. Fig. 1).¹³ RuO₂ crystallizes in the rutile structure such as TiO₂. The Ru atoms in bulk RuO₂ are octahedrally coordinated to six O atoms, and the O atoms are bonded through sp^2 hybrids to three Ru atoms. The surface of clean RuO₂(110) is characterized by terminating bridging oxygen atoms and the appearance of coordinatively unsaturated Ru sites (so-called cus-Ru atoms, serving as acidic centers). Although RuO₂(110) is metallic¹⁸ and a very good conductor, the cus-Ru atoms expose a kind of dangling bond,¹ which may explain the high activity of this oxide

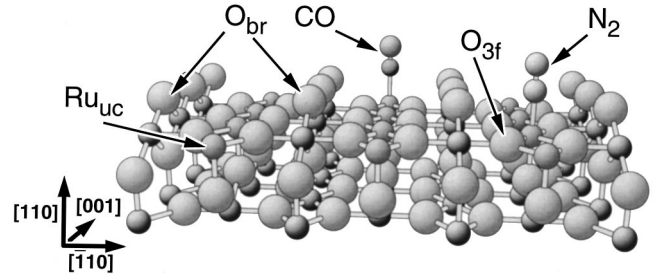


FIG. 1. Stick and ball model of the bridging oxygen terminated RuO₂(110) surface. Large balls represent oxygen, and small balls represent ruthenium atoms of RuO₂(110). A highly active coordinatively unsaturated Ru atom (cus) as well as bridge bonded and threefold coordinated O atoms are indicated by arrows. The adsorption sites of CO and N₂ are indicated.

surface. Obviously, the once imposed hybridization of Ru in the bulk RuO₂ is retained at the surface. The bridging O atoms are also undercoordinated (twofold instead of threefold) and may therefore also be important for the adsorption properties of RuO₂(110) (keyword: basic center). The metallic character of RuO₂ is related to the high density of occupied and empty d states at the Fermi level.¹⁸

Exposing the RuO₂(110) surface to 100 L CO at 100 K does not change the LEED pattern, but it does significantly alter the experimental LEED I - V curves of RuO₂(110), as quantified by a R_p factor of 0.54 between the clean and CO covered RuO₂(110) surface (cf. Fig. 2); the cumulative energy of the eight symmetry-non-equivalent LEED I - V curves was 890 eV. From the variation of the LEED I - V curves together with preserving the (1×1) LEED pattern, we imply that CO adsorption takes place in specific sites without establishing a superlattice. Model structures that were tested in the LEED analysis are CO adsorption on top of cus-Ru at-

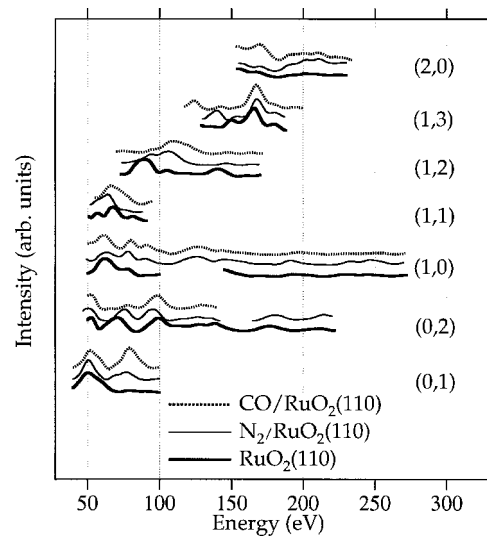


FIG. 2. Comparison of experimental LEED I - V data of the CO-RuO₂(110) and N₂-RuO₂(110) with those of the clean RuO₂(110) surface. The R_p factors between CO-RuO₂(110) and RuO₂(110) is 0.54, while that between N₂-RuO₂(110) and CO-RuO₂(110) is 0.31.

TABLE I. The optimum R_p factors obtained after automated LEED refinements of four essentially different structural models for the adsorption geometry of CO on RuO₂(110).

Model	R_p factor
1: CO on top of cus Ru	0.30
2: CO bridging cus Ru	0.51
3: CO on top of O _{br}	0.64
4: CO bridging O _{br}	0.70

oms (model 1; cf. Fig. 1), CO molecules bridging two cus-Ru atoms (model 2). Model 2 may also be regarded as a kind of carbonate CO₃ species, since the CO molecules also bridge the two threefold coordinated O atoms in the topmost (Ru+O) plane of RuO₂(110). The third model (model 3) assumes CO adsorption on top of the undercoordinated O_{br} atoms in an upright position, and the fourth model places the CO molecules in bridge position over the O_{br} atoms of the RuO₂(110) substrate. The optimum R_p factors reached after structure refinement are gathered in Table I for these four models; a large region in the multidimensional parameter space was explored.

Model 1 with CO adsorption above the cus-Ru atoms is clearly preferred over the other models. The CO molecule is sitting upright with the C end attached to the cus-Ru atom since the frontier orbitals of CO have a larger weight on the C than on the O end. The internal C-O bond length is 1.12 Å and the Ru-C bond length is 2.00 Å. Both values are similar to those found for CO on Ru(0001): The internal C-O and the C-Ru bond lengths are 1.15 ± 0.05 Å and 1.93 ± 0.04 Å, respectively.¹⁹ The slightly larger C-Ru bond length and the slightly shorter C-O bond length on RuO₂(110) is in line with the weaker CO bonding on RuO₂(110) than on Ru(0001). Detailed parameter values for the underlying RuO₂(110) surface are summarized in Fig. 3. The experimental LEED I - V curves are compared to those calculated for the optimum structure in Fig. 4; the overall agreement is quantified by $R_p = 0.30$. The agreement between experimental and calculated LEED I - V data for CO-RuO₂(110) is as good as for the clean RuO₂(110) surface.¹³ CO adsorption induces the cus-Ru atom to move upwards by 0.08 Å in comparison with the clean RuO₂(110) surface. Other structural parameters of the clean RuO₂(110) are not changed upon CO adsorption (within the quoted error bars).

For model 1, we performed DFT calculations by minimizing the total energy with respect to the geometrical and electronic structure. The optimum structural parameters are included in Fig. 3. The agreement between the structural parameters determined by LEED and DFT calculations is better than 0.05 Å, giving additional confidence in the present structure analysis. The CO adsorption geometry on Ru(0001) is characterized by a C-O bond length of 1.16 Å and a C-Ru bond length of 1.93.²⁰ In comparison with the values found on RuO₂(110), i.e., C-O: 1.13 Å and C-Ru: 1.95 Å, these results are consistent with a weaker CO bonding on RuO₂(110) than on Ru(0001); the $2\pi^*$ back donation is reduced on RuO₂(110). Indeed, the CO adsorption energy

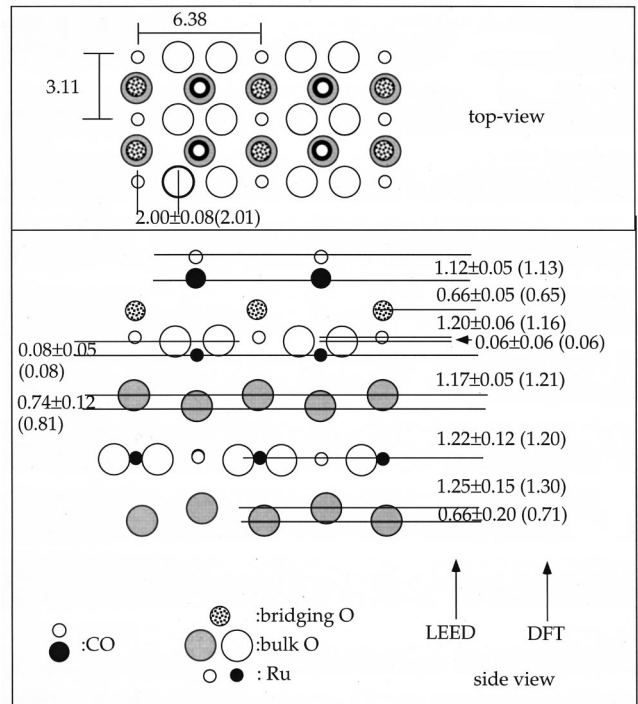


FIG. 3. The optimum surface geometry of the CO-RuO₂(110) as determined by LEED and DFT calculations (parameter values are in parentheses). All values are in Å. The corresponding layer spacings in bulk RuO₂ are 1.27 and 0.635 Å.

was determined by DFT calculations to be 1.20 eV, which is 0.6 eV smaller than on Ru(0001) (DFT: 1.80 eV);²⁰ using a 2×1 unit cell on RuO₂(110) the CO binding energy turned out to be 70 meV higher. The CO adsorption energy of 1.2 eV is also consistent the observed CO desorption temperature of 350 K.^{2,21} In addition, we calculated the diffusion barrier of CO on RuO₂(110) along the densely packed rows

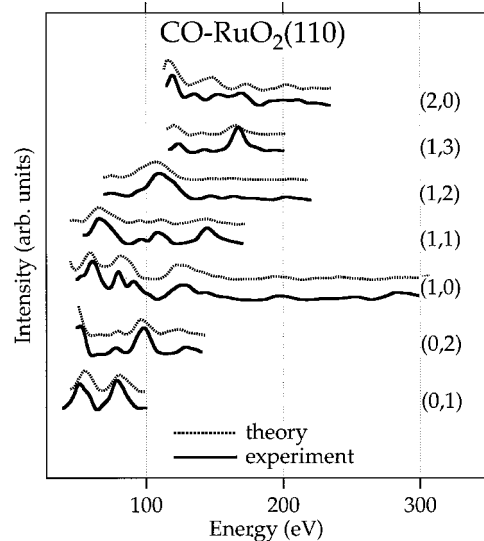


FIG. 4. Comparison of experimental and calculated LEED I - V data for the best-fit model of the CO-RuO₂(110) surface (cf. Fig. 3). The overall R_p factor is 0.30.

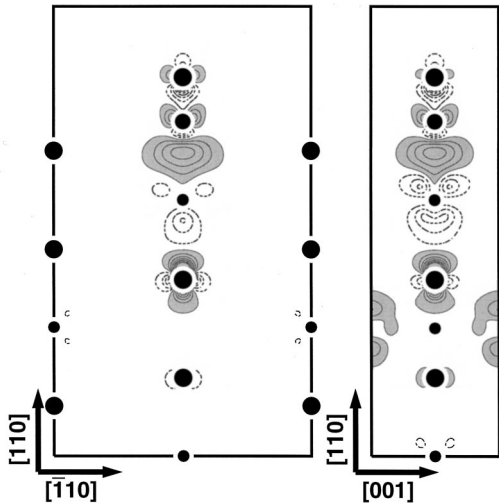


FIG. 5. Charge difference plot of CO-RuO₂(110) and RuO₂(110); left: cut along the $[\bar{1}10]$ direction through the cus-Ru atom, right: cut along the $[001]$ direction through the cus-Ru atom. Charge depletion is marked by shadowed regions. Solid and dashed contour lines indicate charge accumulation and depletion, respectively. Small, medium, and large balls indicate Ru, C, and O atoms, respectively. The symmetry of charge depletion and accumulation around the CO molecule is consistent with the Blyholder model.

in $[001]$ direction to be 1.0 eV; for these calculations we used a (2×1) unit cell. The diffusion barrier is almost as high as the binding energy of CO to the RuO₂(110) surface so that diffusion and desorption of CO are competing processes at the surface while heating it. The high diffusion barrier also explains that CO cannot form an ordered overlayer on RuO₂(110) for kinetic reasons.

On the basis of our DFT calculations, we infer that the CO binding mechanism is similar to that described for transition metal surfaces by the so-called Blyholder model.⁶ The CO 5σ orbital couples to metal states with σ symmetry, which is accompanied by a charge transfer from the CO molecule to the surface. This charge donation is counter balanced by a back donation of d electrons from the substrate with π symmetry to the $2\pi^*$ -derived level of CO. In Fig. 5, the charge-density difference between the CO-RuO₂(110) and the RuO₂(110) is shown. The gray shadowed regions with solid contour lines indicate charge accumulation. The symmetry of the gray regions around the CO molecules is consistent with the shape of the CO $2\pi^*$ orbital. On the other hand, the shape of the dashed contour lines (indicative of charge depletion) around the CO molecule reveals 5σ symmetry. Both findings are supportive for the Blyholder model, as it was nicely demonstrated with the CO adsorption on Ni(100).²²

We should emphasize that CO adsorption on RuO₂(110) may be considered as a chemical probe to count or titrate the number of cus-Ru at the RuO₂ surface. This may be very helpful information when studying other faces of RuO₂, such as the (100) or the (101) surface of RuO₂. In order to count the cus-Ru atoms, one has to count the number of adsorbed CO molecules. Tracy and Palmberg²³ demonstrated that the

adsorbed CO molecules can be considered as particles that need at least a circular area with about 3 Å diameter. Since the Ru-Ru distance is 3.11 Å in RuO₂(110), it is reasonable to suppose that the saturation coverage of CO equals the number of cus-Ru atoms. Supported is the view by the present LEED analysis that revealed the best agreement between calculated and experimental LEED data, assuming a CO coverage of 1.0 ± 0.2 ML, i.e., every cus-Ru atom is capped by a CO molecule. The counting of CO molecules is then simply accomplished by a thermal desorption experiment of CO. The big drawback of this method is, however, that during CO desorption, the RuO₂(110) surface is partially reduced by the recombination of CO with bridging oxygen to form CO₂.¹ Therefore, we were looking for a more appropriate (i.e., gentle) molecule that is able to probe the number of cus-Ru atoms on the surface without attacking the oxide surface. The molecule of choice is nitrogen N₂, which is iso-electronic to CO and therefore binds to the transition metal surface with the same (Blyholder) mechanism as CO. Since the activation of the N-N bonding is extraordinarily demanding, we can safely assume that N₂ practically does not react with oxygen or other reactants on RuO₂(110) under UHV conditions.

The LEED I - V curves were measured after exposure of 30 L of N₂ to the RuO₂(110) surface at 100 K; the total energy range amounts to 960 eV. In Fig. 2, the experimental LEED I - V curves of the clean RuO₂(110) surface are compared with those of the CO and the N₂ saturated RuO₂(110) surface. The CO and N₂ related data sets are quite similar as quantified by a R_p factor of 0.31. This observation already implies that the adsorption sites of N₂ and CO are identical. The very same conclusion was previously drawn for the systems N₂-Ru(0001) and CO-Ru(0001).²⁴ Structure determination by inspecting and comparing experimental LEED I - V data is termed the LEED fingerprinting technique, whose strength and broad applicability have been illustrated by a multitude of instructing examples.²⁵

In order to determine the detailed atomic geometry of N₂ on RuO₂(110), we performed a complete LEED analysis and DFT calculations, assuming, as suggested by LEED fingerprinting, on-top adsorption of N₂ over the cus-Ru atoms. The refined structural parameters are summarized in Fig. 6. The internal bond length of N₂ is 1.11 ± 0.06 Å, similar to that found on the clean Ru(0001) surface (1.10 ± 0.06 Å) and the (2×2) O precovered Ru(0001) surface (1.12 ± 0.06 Å),²⁶ for comparison, the gas phase value of N₂ is 1.095 Å. The N-Ru bond length for N₂-RuO₂(110) is 2.06 ± 0.06 Å. This value is slightly larger than the corresponding values of N₂ on Ru(0001) (2.00 ± 0.04 Å)²⁵ and N₂ on Ru(0001)- (2×2) O (2.00 ± 0.05 Å).²⁶ In comparison with the bare RuO₂(110) surface, the surface structure of the underlying RuO₂(110) substrate is only marginally altered by N₂ adsorption. This finding is consistent with the low adsorption energy of N₂ on RuO₂(110), which is inferred from a desorption temperature of 120–180 K depending on the N₂ coverage. The agreement between the structural parameters obtained by LEED and DFT is as excellent as with CO-RuO₂(110) (cf. Fig. 6), giving additional confidence to

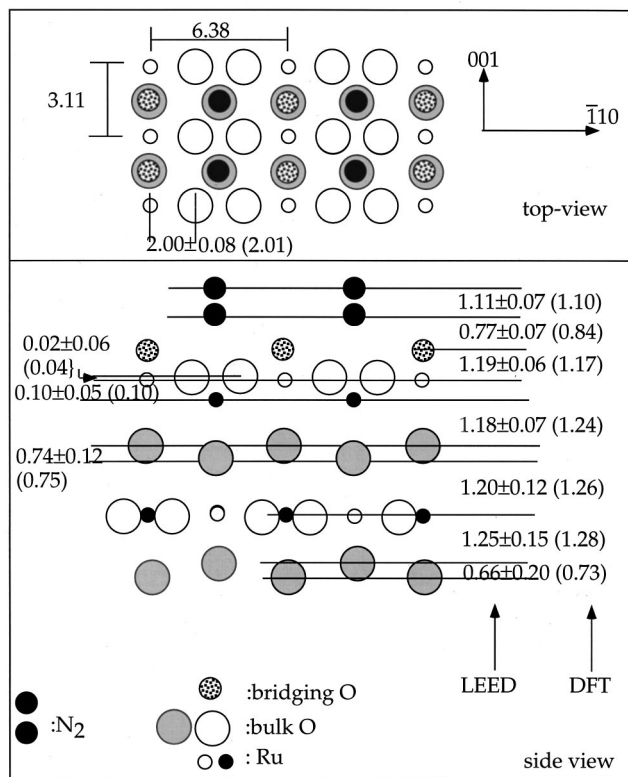


FIG. 6. The optimum surface geometry of the N₂-RuO₂(110) as determined by LEED and DFT calculations (parameter values are in parentheses). All values are in Å. The corresponding layer spacings in bulk RuO₂ are 1.27 and 0.635 Å.

the structural parameters. DFT calculations determined a N-cus-Ru bond length of 2.04 Å, which is identical to that determined for N₂ on Ru(0001). Therefore, we consider the experimentally found modification of the N-Ru bond length for N₂-RuO₂(110) and N₂-Ru(0001) as not being significant. The calculated LEED *I-V* curves for the optimum structure of N₂-RuO₂(110) are compared to the experimental data in Fig. 7; the resulting *R_p* factor was 0.34.

TDS suggests an even higher binding energy of N₂ on RuO₂(110) than on the (2×2) O precovered Ru(0001) surface, indicating that the presence of excessive oxygen stabilizes the N₂ adsorption, while it destabilizes the CO adsorption. The adsorption energy of N₂ on RuO₂(110) is 0.59 eV [DFT: using a (2×1) unit cell], while on Ru(0001)N₂ is bonded by 0.55 eV (DFT). The adsorption of N₂ on RuO₂(110) may be useful not only for titrating cus-Ru atoms but also to selectively block these active sites for the adsorption of other molecules, coming from the gas phase. N₂ preadsorption should “poison” the RuO₂(110) surface.

This kind of experiment was carried out to titrate the adsorption site of the weakly held oxygen (O_γ) on RuO₂(110); the weakly held oxygen desorbs at 450–500 K.²⁷ The basic property that allows this kind of titration experiment is that N₂ adsorbs above the cus-Ru atoms. Therefore, O_γ and N₂ will compete for the same adsorption sites, if O_γ adsorbs also over cus-Ru atoms. In the N₂ titration experiments, the RuO₂(110) surface is precovered with various coverages of

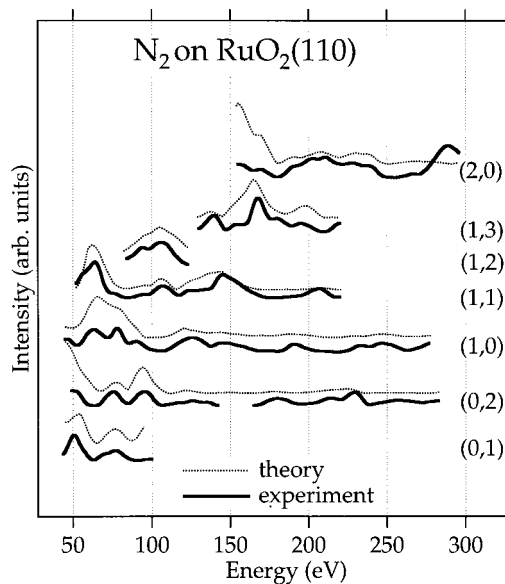


FIG. 7. Comparison of experimental and calculated LEED *I-V* data for the best-fit model of the N₂-RuO₂(110) surface (cf. Fig. 6). The overall *R_p* factor is 0.34.

O_γ and subsequently, the surface is saturated by N₂. In the saturated N₂-RuO₂(110) overlayer, all cus-Ru atoms are capped. With TDS, both the relative coverages of O_γ and N₂ were measured. The results of the titration experiments are summarized in Fig. 8. Obviously, with increasing O_γ coverage, the N₂ coverage decreases in a way that the total coverage of N₂ and O_γ is preserved, thus providing evidence for the on-top adsorption of O_γ. At saturation of O_γ, still some

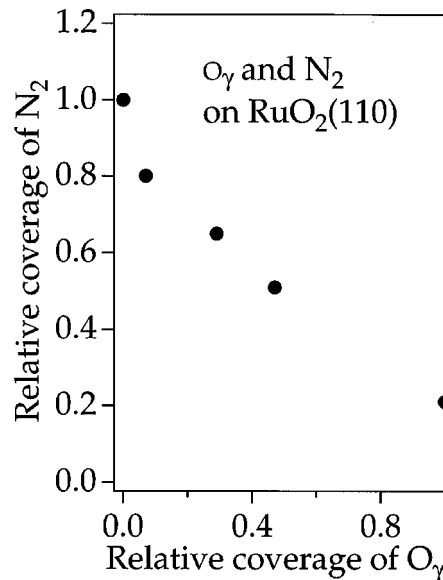


FIG. 8. The RuO₂(110) surface was precovered by various coverages of O_γ and subsequently saturated by N₂. N₂ is known to occupy directly above the cus-Ru atoms. If O_γ occupy the same adsorption site as N₂, then the coverages of O_γ and N₂ are related by $\theta(O_\gamma) = \theta(\text{cus-Ru}) - \theta(N_2)$. $\theta(\text{cus-Ru})$ is the number of cus atoms on RuO₂(110).

N₂ (20% of its saturation coverage) can adsorb on RuO₂(110). In a forthcoming paper, these suggestions will be confirmed by a combined LEED/DFT analysis.²⁸

IV. SUMMARY

The adsorption geometries of CO and N₂ on RuO₂(110) were determined by using quantitative LEED and DFT calculations. Both molecules are sitting above the cus-Ru atoms, which are known to dominate the activity of the RuO₂(110) surface. The molecular axes of N₂ and CO are

normal to the surface with intramolecular bond lengths of 1.11 and 1.13 Å, respectively. N₂ adsorption can be used to titrate the cus-Ru atoms and also to impede adsorption of other molecules over the cus-Ru atoms.

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