

# A disordered oxide as an active phase during CO catalytic oxidation on Ru(0001)

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## ABSTRACT

The identification of the active phase of a catalyst under operando conditions is probably the most relevant task in basic catalysis research. In this respect, the Ru (0001) surface during CO oxidation is a traditional studied model, for both its importance in applied catalysis and for its peculiar behavior. In this work, we study the CO catalytic oxidation reaction on flat and defective Ru(0001) surfaces, concluding that the highest activity is achieved in oxidizing conditions when a disordered and thin Ru oxide is formed at the surface. Also, we find that in defective surfaces, with a high density of surface steps, this reaction is enhanced, related to the facile sub-surface incorporation of atomic oxygen and to the easier formation of the oxide. Thus, the CO catalytic oxidation on Ru(0001) is a structure-sensitive reaction, being active on the surface of the oxide formed in reaction conditions.

## 1. Introduction

The catalytic oxidation of carbon monoxide is a model chemical reaction, very often studied on transition metals [1]. Among these, a metal displaying a most singular behavior is Ru. The particular response of the Ru(0001) surface consists in a quite low catalytic activity for CO oxidation in UHV conditions (as compared to Pt, Pd, Ir or Rh), but a rather high activity in oxidizing conditions when close to atmospheric pressure [2,3]. Hence, the system quite clearly illustrates the problem of the pressure gap and is of considerable interest, regarding the active phase driving this particular behavior [2,4–6].

The study of the active phase during CO oxidation has been extensively studied in different transition metals [7–12]. Specifically, the debate on the catalytically active phase of Ru during CO oxidation is well known and has generated much discussion (see, for instance, the discussion between the groups of Goodman and Over [13–15]). The three considered scenarios describing the active phase during the catalytic activity of Ru in reaction conditions are a) a dense oxygen layer covering the metallic Ru(0001) surface, b) the formation of rutile stoichiometric RuO<sub>2</sub>(110) thin film, and c) the formation of a pre-oxide disordered phase, where the structure and stoichiometry of rutile RuO<sub>2</sub> are not completely defined. The first hypothesis is supported by studies (for instance, those from Goodman's group [6]) which state that the active catalyst for this reaction is metallic Ru(0001), covered by a dense monolayer of oxygen. This idea is backed by the fact that Ru (0001) can support unusually high oxygen concentrations at the surface [16]. Other authors, on the contrary, state that RuO<sub>2</sub>(110) is the most

active phase, whose formation is promoted when the substrate is exposed to thermal oxidizing [17] or to reaction conditions (see, for instance, the works by Over and collaborators [4,18]). Specific reaction mechanisms have been proposed, involving, for example, CO adsorption on under-coordinated Ru atoms, its recombination with bridging O atoms from the oxide, and replenishment of the oxygen vacancies [4]. Finally, other studies also discard metallic Ru(0001) as the active phase [5] but propose instead the formation of a pre-oxide phase, which serves as a catalytic support for the oxidation reaction when it occurs at a temperature lower than the formation temperature of RuO<sub>2</sub>(110). The formation of disordered or non-stoichiometric oxides through oxygen sub-surface incorporation is a most relevant issue in catalysis [19–21]. These kind of phases, somehow lying in between the metal and the ordered oxide, have been described in Ru as a trilayer formed by an O layer, a Ru layer and another O layer, keeping the hexagonal symmetry of the surface plane, while its stoichiometry is close to that of RuO<sub>2</sub> [5]. The formation of trilayer structures under oxidative conditions has been proposed for Rh [10] and Pt [11] surfaces as well. Finally, the probable active coexistence and cooperation of all three phases in certain conditions has been proposed as well [22].

An interesting issue, in this context, is related to the presence of surface defects as active sites, either in metallic or oxide surfaces. There are studies stating that Ru step edges are the sites where CO is dissociated [23,24], oxidized [25,26] or where the ruthenium oxide preferentially nucleates and grows [27]. We have observed in our group, for instance, that Ru steps are the sites where formate is preferentially formed during catalytic methanol oxidation [28]. In this respect, it has

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been reported [6] that the Ru oxide is reduced when exposed to CO, being the reduced areas the places where the oxidation reaction takes place. The fact that these surface patches seem to be more active than the original metallic Ru surface (prior to the chemical reduction) is justified by the authors because chemical reduction roughens the surface, so that more under-coordinated (defective) surface atoms are exposed and the reaction is more facile. Other surface oxides have been also reported to roughen when reduced [10]. These examples illustrate another preeminent role of surface defects, and it is that they do not only influence the catalytic activity but also determine the evolution of the morphology and chemical composition of the catalysts in reaction conditions. One additional consideration is that surface defects may also be unimportant [29] or even have negative effects for certain catalytic reactions. For instance, by increasing the ignition temperature for CO oxidation [30], or by poisoning the surface with dissociation products preferentially occurring at the steps [31].

In this work we have performed a study of the catalytic oxidation of CO on Ru(0001) where we have considered the oxygen partial pressure, the temperature and the controlled presence of surface defects as an additional parameter whose influence is studied. Surface defects are created with Low Energy Ion Bombardment (LEIB). LEIB is a very common tool to create surface defects and modify surfaces [32]. Defects may not only act as new active sites for a reaction, playing an important role on its efficiency, but also play a role in the surface restructuring under reaction conditions and thus they may considerably affect the catalytic processes. In this work we will study how the presence of surface defects affects the catalytic activity and the formation of Ru oxide under reaction conditions, with a CO partial pressure of  $5 \cdot 10^{-2}$  mbar, far from UHV conditions. The introduction of defects can be also deemed as an attempt or approach to bridge the materials gap, since most real surfaces are indeed defective. Nanoparticles, even with flat facets, display corners and edges with under-coordinated atoms, where reactions may preferentially take place [33].

## 2. Experimental methods

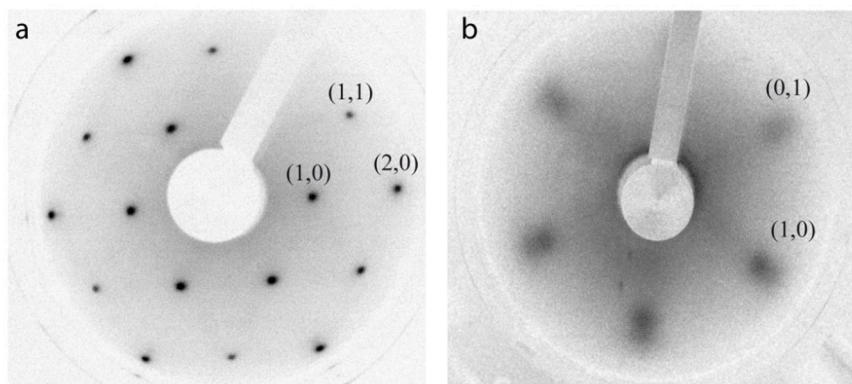
The studies have been carried out on a Ru(0001) sample with a diameter of 9 mm, from Surface Preparation Laboratories. To achieve a clean flat surface,  $\text{Ar}^+$  bombardment ( $E = 1 \text{ keV}$ ,  $t = 1 \text{ hour}$ ) and several vacuum annealings up to  $1250 \text{ }^\circ\text{C}$  ( $1523 \text{ K}$ ) are carried out, first in the presence of oxygen ( $1 \cdot 10^{-6}$  mbar for a few seconds) to remove surface carbon (most of which segregates from the bulk) and then in UHV to desorb the remaining adsorbed oxygen.

The surface crystalline quality and cleanness are checked with Low Energy Electron Diffraction (LEED) and Auger Electron Spectroscopy (AES). The process is repeated until the diffraction pattern has sharp spots and the Auger spectra presents no signs of oxygen or other

adsorbates. When the process is complete, the LEED shows the diffraction pattern from Ru(0001) (Fig. 1a). The modification of the surface with LEIB is carried out with an  $\text{Ar}^+$  beam with an energy of 1 keV, which is scanned across the surface to ensure a uniform dose for 45 min. The dose to produce a defective surface is of the order of  $10^{15}$  ions/cm<sup>2</sup>. After this process, the diffraction pattern shows a brighter background and broadened spots, the later having a characteristic energy-dependent splitting which reveal the existence of multiple surface steps (Fig. 1b) [34].

The experiments have been carried out in a UHV system with two chambers: a main chamber, where the preparation, modification and characterization of the samples is carried out, and a homemade reaction cell, where IRRAS measurements are performed. These chambers are interconnected with a gate valve, thus allowing the pressures to be independent, in order to be able to reach high pressures in the infrared chamber without affecting the main UHV chamber. The chamber where the IRRAS measurements are made is provided with two independent gas lines. The IRRAS spectrometer is an evacuated Vertex 80 V interferometer with an external MCT detector in reflection mode with an incidence angle of  $7^\circ$ . The resolution of the spectra shown in this work is  $4 \text{ cm}^{-1}$ . The catalytic reaction is performed in a closed reactor conditions, filling the chamber with the reactants. The pressure of the gasses involved in the catalytic process is not high enough to completely obscure the IR absorption bands of CO adsorbed on the surface. In the quantifications presented in this work, the evolution of the gasses involved in the reaction (CO and CO<sub>2</sub>, in our case, since O<sub>2</sub> is not IR-active) is measured by integrating the area of the absorption bands in the spectra. In this way, using IRRAS to quantify the gas phase with these working pressures we get, in a single spectrum, simultaneous information about both surface and gas species. Also, we obtain a direct signal of the gas phase (CO and CO<sub>2</sub>), avoiding the presence and interference of molecular species in the cracking pattern if we used, instead, mass spectrometry.

The catalytic oxidation of CO on Ru(0001) has been carried out on two different surface morphologies (flat and defective surfaces), with two different proportions of reactant gasses (reducing and oxidizing conditions) and at four temperatures ( $110 \text{ }^\circ\text{C}$ ,  $150 \text{ }^\circ\text{C}$ ,  $180 \text{ }^\circ\text{C}$  and  $240 \text{ }^\circ\text{C}$ ). The temperatures have been measured with a pyrometer, previously calibrated at the same sample with a thermocouple which was later removed. The CO conversion into CO<sub>2</sub> has been tracked by taking consecutive IRRAS spectra. In order to get oxidizing conditions, we introduce a CO pressure of  $5 \times 10^{-2}$  mbar and an O<sub>2</sub> pressure of  $1 \times 10^{-1}$  mbar. Thus, the O<sub>2</sub>/CO relation in oxidizing conditions is about 4 times the stoichiometric ratio for the reaction. In order to get reducing conditions, we introduce a CO pressure of  $5 \times 10^{-2}$  mbar (the same partial pressure as for the case of oxidizing conditions) and an O<sub>2</sub> pressure of  $6 \times 10^{-3}$  mbar. Thus, in reducing conditions, the O<sub>2</sub>/CO



**Fig. 1.** a) Low energy diffraction patterns of a) a flat Ru(0001) surface after the cleaning procedure (electron energy  $E = 206 \text{ eV}$ ), and b) the same surface after low energy ion-bombardment (electron energy  $E = 106 \text{ eV}$ ). The diffraction pattern of the defective surface shows split and broad spots due to the interference of the atomic periodicity with the surface steps created by LEIB [28].

relation is about 1/4 of the stoichiometric ratio for the reaction. To measure the pressure of the reactants we have used a dual Pirani-capacitive gage, which doesn't need a correction factor for O<sub>2</sub> and CO (which is 1 for both gasses). The purity of CO is 99.998%, while that of O<sub>2</sub> is 99.999%. We have checked that, at the working temperatures used, the order in which the gasses are introduced is critical for the efficiency of the catalytic process. The activity is lower if the first gas introduced is O<sub>2</sub> since it strongly adsorbs on the surface with a high coverage, thus impeding further CO adsorption. In order to optimize the reaction process, we have systematically introduced CO prior to oxygen. Carbonyl or cold traps in the gas line are not needed under the conditions of our experiments. We have not detected, in post-reaction Auger spectra, any signal apart from those of Ru<sub>MNN</sub>, O<sub>KLL</sub> and C<sub>KLL</sub> (the later overlapping with the Ru<sub>MNN</sub> peak). So, we discard the adsorption of Ni or other elements derived from carbonyls.

To evaluate and subtract the spurious catalytic activity of some parts of the reaction chamber (such as the heating W filaments or the side and back parts of the sample) we have carried out preliminary conversion tests for i) Ru(0001) clean single crystals (both flat and defective), ii) a Ru(0001) single crystal with the front surface capped with a continuous Au thin film grown by thermal evaporation and iii) a Au(111) single crystal. Au, both in the form of a continuous film or as a Au(111) single crystal is, of course, inert towards CO oxidation. Besides, the contribution of the elements in the chamber providing a spurious catalytic activity is part of a constant background activity for the two types of surfaces we are testing (flat and defective), because the ion-bombardment modification only affects the front side of the sample. In brief, these preliminary conversion tests show that the spurious contributions exist, but are much lower than the main contribution from the front of the sample.

We have carried out observations of the surface structure and composition with LEED and Auger spectroscopy before and after the conversion. To determine the oxygen coverage at the surface after one complete catalytic reaction, we have previously taken as references some well-known oxygen coverages observed by LEED. By exposing the sample to 10<sup>-4</sup> and 10<sup>-1</sup> mbar of O<sub>2</sub>, we obtain the (2 × 1) and (1 × 1) reconstructions, respectively (see Fig. 2). Although the (2 × 1) and (2 × 2) O/Ru(0001) structures show the same overall diffraction pattern, we know this is (2 × 1) because the oxygen exposure has been sufficiently high and the Auger spectra show the corresponding ratio in the intensity of the peaks. The (1 × 1) reconstruction is equivalent (in terms of the geometry of its diffraction pattern) to the clean flat surface as observed

by LEED, although its spots are broader, caused by disorder induced by the adlayer of oxygen atoms. Once the reconstructions are identified, we carry out the chemical quantification with Auger spectroscopy, by calculating the O/Ru ratio of the integrals of the peaks. This ratio, as measured from our Auger spectra, is 0.133 for the (2 × 1) structure and 0.267 for the (1 × 1) adsorption. So, their proportion (1/2) is exactly as expected from the oxygen population in both cases (0.5 ML and 1 ML). Quantitative analysis after each reaction test is done by integrating the main oxygen peak and the Ru peak at 140 eV and calculating the ratio between them afterwards. Both integration values are normalized to the background intensity.

### 3. Experimental results

We have observed the surface diffraction pattern with LEED after each reaction (Fig. 3). In some cases, the diffraction spots were almost imperceptible. The spots are more diffuse after the reaction on the modified surface than over the flat surface, which is consistent with the fact that the modified surface is initially rough at the atomic level. Also, the reducing conditions favor a more intense LEED pattern. At the same time, increasing the reaction temperature yields an even more diffuse LEED pattern.

We have also measured the post-reaction chemical composition of the surface with AES. The quantification of the oxygen present on the

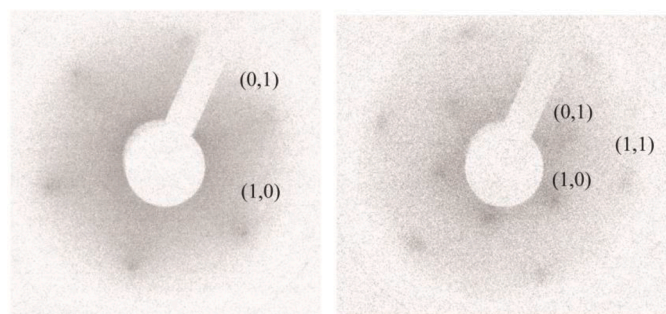


Fig. 3. Example of post-reaction LEED diffraction patterns after a catalytic conversion in reducing conditions on the flat surface, for electron energies of 65 eV (left) and 156 eV (right). Although the spots are diffuse and the background is bright, the (1 × 1) symmetry is still clearly seen.

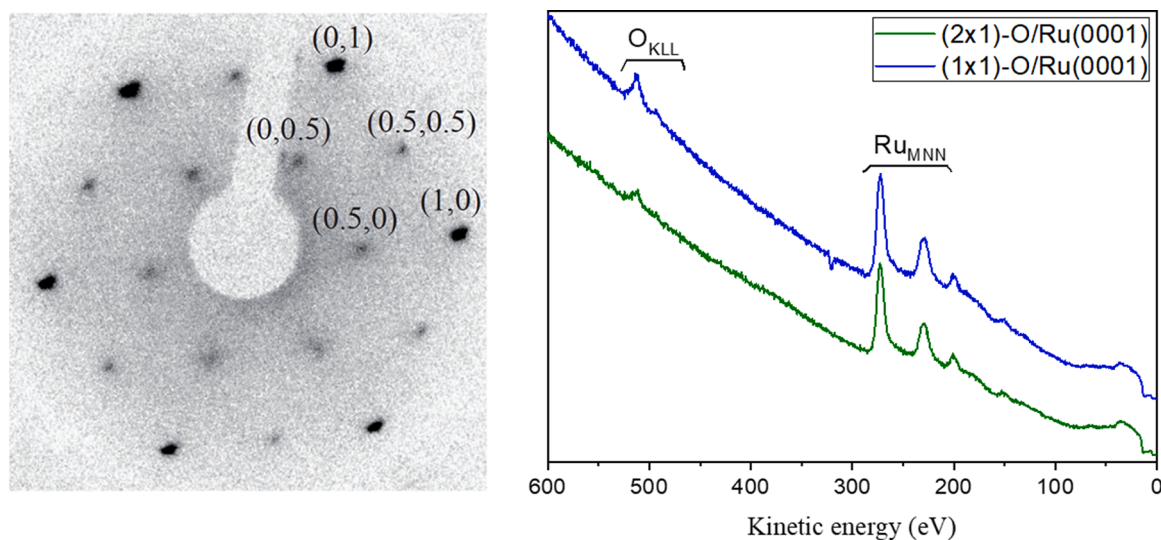


Fig. 2. Left) (2 × 1) O/Ru(0001) LEED diffraction pattern of a Ru surface with adsorbed oxygen. Right) Auger spectra for the (2 × 1) and (1 × 1) adsorption layers. The O<sub>KLL</sub> peak in the (1 × 1) blue spectrum (normalized to the corresponding Ru<sub>MNN</sub> peak of the same spectrum) is twice times higher than that in the (2 × 1) green spectrum, as expected.

surface is obtained by comparison with the reference spectra acquired for the (2 × 1) and (1 × 1) oxygen layers. The (1 × 1) reconstruction is equivalent to 1 Monolayer (ML); the observed results are expressed in ML by referring to the O/Ru ratio measured in that later case. This study has been systematically done for the oxidizing conditions. For the reducing conditions, as we have checked, the remaining post-reaction adsorbed oxygen mostly belongs to adsorbed CO molecules. Thus, Auger spectra do not yield, in this case, useful information about the coverage of atomic oxygen, which is quite low.

The quantitative Auger results for the oxidizing conditions are presented in Fig. 5, beside each conversion curve. We can see that the results obtained for the oxidizing conditions show, in general, an increase of the oxygen coverage with reaction temperature. For reducing conditions, the amount of oxygen is much lower, as previously stated. For the highest temperature and for the modified surface the final oxygen coverage is only 0.5 ML. This oxygen most probably belongs, as already mentioned, to post-reaction adsorbed CO.

We show in Fig. 4, as a descriptive example of consecutive IRRAS spectra, the evolution, at three different times, of CO<sub>gas</sub>, CO<sub>ads</sub> and CO<sub>2, gas</sub> spectra in the case of reducing conditions at  $T = 180\text{ }^{\circ}\text{C}$  on the modified surface. The first spectrum is obtained after the introduction of the reactive gasses and just after the reaction starts, and shows the gas band of CO, as well as the band of CO adsorbed on the surface. CO<sub>2</sub> does not adsorb at the temperatures used in this work, and no adsorption bands are expected. This Figure presents a reaction where part of the CO<sub>gas</sub> which participates in the reaction is partially consumed due to the relative concentration of reactants. On the contrary, the evolution of the IRRAS spectra in oxidizing conditions (see Supplementary Material), CO<sub>gas</sub> is fully consumed in most of the cases. A second relevant difference between the two different reaction conditions is the absence of the CO<sub>ads</sub> adsorption band in oxidizing conditions. The concentration of adsorbed oxygen is sufficiently high as for to immediately react with adsorbed CO, reducing the CO time of residence at the surface to very low values. In the case of reducing conditions, an initial slight declining in adsorbed CO concentration is sometimes observed, followed by an

increase when oxygen is consumed. Also, a shift to lower wavenumbers in reducing conditions is detected during the reaction, which probably indicates a lower CO concentration at the surface.

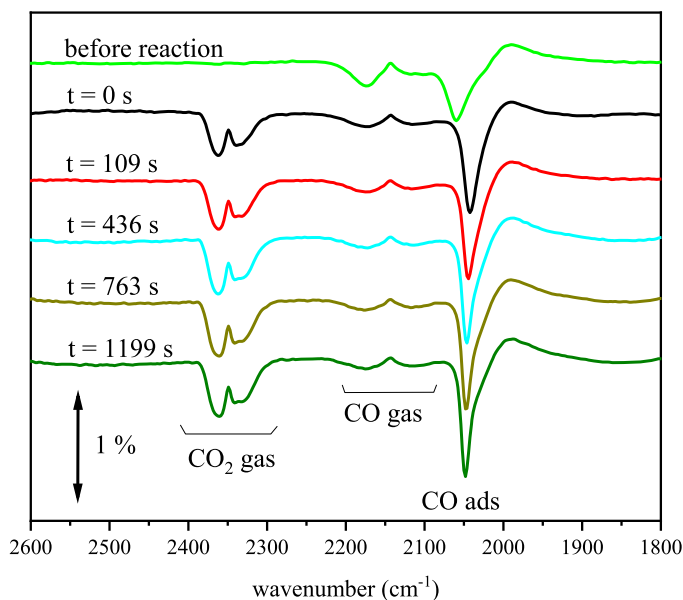
To monitor the evolution of the catalytic reaction, we calculate the area of the CO<sub>2, gas</sub> band from every obtained IRRAS spectrum. This integral, which represents the amount of CO<sub>2</sub> produced during the reaction at a given time, is represented as a function of time for the reaction conditions considered in this work (Fig. 5). At  $t = 0$  we represent the integral of the CO<sub>2</sub> band after the reaction is ignited (i.e. once the sample temperature is stationary and both reactants have been introduced in the reaction chamber) and all the scans are completed. Each spectrum takes 109 s to be completed. So, each spectrum (and each point in Fig. 5) represents the average state of the surface during the last 109 s.

Under oxidizing conditions, the flat surface (Fig. 5a) presents an almost negligible catalytic activity at the lowest temperature (110 °C), but for higher temperatures the catalytic activity is relevant and increases with temperature. On the contrary, under reducing conditions (Fig. 5c) the process does not seem to depend on temperature. In general, under reducing conditions, the process does not depend too much either on temperature or on the morphology of the surface (Figs. 5c and 5d). For the case of the modified surface under oxidizing conditions (Fig. 5b), the interpretation of the process is less straightforward. The activity increases with temperature, being highest for  $T = 180\text{ }^{\circ}\text{C}$  and then decreases for  $T = 240\text{ }^{\circ}\text{C}$ .

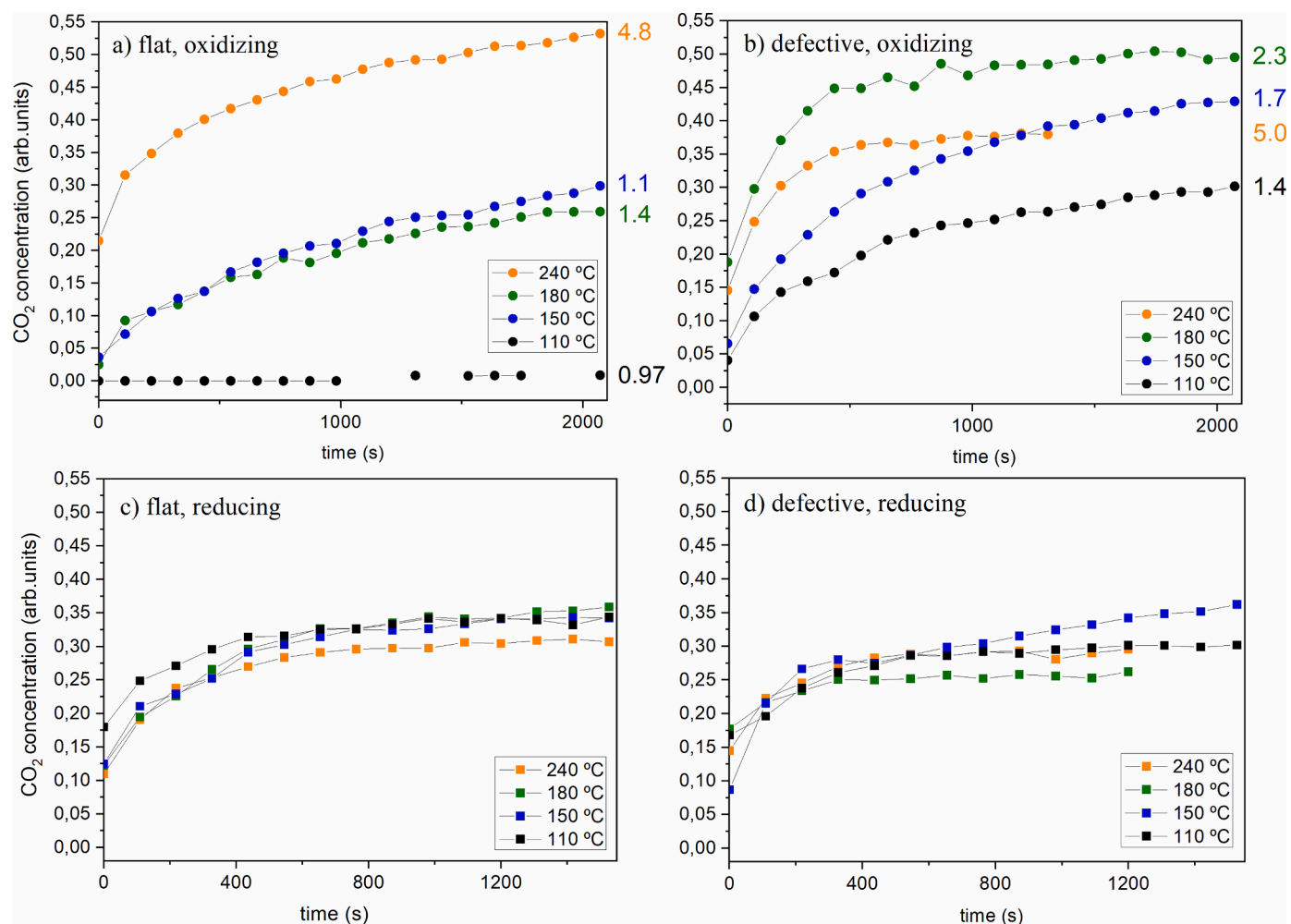
#### 4. Discussion

Under reducing conditions, the catalytic activity is barely dependent on the temperature or on the morphological state of the surface, showing only small variations among the different cases. The observed oxygen coverage at the end of each reaction is comparatively rather low (always well below the monolayer) and mostly originates from the adsorbed CO, so that the concentration of adsorbed atomic oxygen is expected to be very low. The activity seems to be mostly dependent on the impinging rate of O<sub>2</sub> molecules. So, in absence (or deficit) of oxygen on the surface, the evolution of the reaction does not depend drastically on the dynamics of adsorbed species nor on the existence of active sites, which makes the reaction also less dependent on temperature and on the morphological state of the surface. The reaction is limited by the dissociative adsorption of oxygen on the available free sites at the surface. Also, there is no oxide formation in reducing conditions. We do not observe, either, signs of formation of carbonaceous species due to CO cracking, as we have observed for methanol exposure [35].

In the case of oxidizing conditions, the situation is different and more complex. In this case, we observe that not only pressure and temperature, but also the initial density of surface defects in Ru(0001), prior to reaction, are parameters which clearly modify the catalytic activity during CO oxidation. In general, the activity is larger for higher temperatures and it is correlated to the subsurface incorporation of oxygen to the Ru lattice. In fact, the only case with no significant activity is that of the flat surface at the lowest temperature explored (110 °C). In that case, the surface after the reaction seems to be completely covered by oxygen (about 1 ML), but the temperature has not been high enough as to incorporate the O to the Ru lattice and to significantly promote any reaction. This situation may be considered similar to that described by the literature for the Ru surface in UHV conditions, when the catalytic activity is despicable, and supports the idea that metallic Ru is inactive at this temperature. For intermediate temperatures (150 °C and 180 °C) on flat surfaces the situation changes and the activity is, comparatively, much higher. The incorporation of oxygen increases as well, albeit not substantially. However, the fact that the oxygen coverage is above 1 ML strongly suggests the formation of a pre-oxide, formed by a O-Ru-O trilayer and with a total oxygen coverage in the range of 1–2 ML. A qualitatively different behavior seems to occur for the highest temperature (240 °C), where the incorporation of oxygen reaches a value of about 5 ML and the catalytic activity is the largest. In this case the



**Fig. 4.** Example of set of IRRAS spectra during the reaction in reducing conditions for the defective surface at  $T = 180\text{ }^{\circ}\text{C}$ . Three IR absorption bands are observed in this spectra: adsorbed CO<sub>ads</sub> (here as a single band) and both CO<sub>gas</sub> and CO<sub>2, gas</sub> in the gas phase (both as double rotational-vibrational bands). For this particular example, the CO<sub>2</sub> band grows and saturates relatively fast, and that of CO<sub>gas</sub> decreases. The band of adsorbed CO shows a first shift from 2060  $\text{cm}^{-1}$  (before reaction) to 2042  $\text{cm}^{-1}$  (0 s) and then a gradual shift to 2049  $\text{cm}^{-1}$  (1199s).



**Fig. 5.** CO<sub>2</sub> gas evolution shown for every temperature during the catalytic reaction, for the flat (left graphs) and defective (right graphs) surfaces and for the oxidizing (top) and reducing (bottom) conditions. It can be observed that the kinetics of the reaction, under oxidizing conditions, is more dependent on temperature and on the state of the surface than under reducing conditions. For the case of oxidizing conditions, the post-reaction surface concentrations of oxygen after the catalytic conversions (expressed in Monolayers (ML)) are shown beside the curve for each condition, based on the O/Ru ratio of the Auger spectra.

surface oxide is much thicker. These results are compatible with the idea, proposed by some authors [5], of subsurface oxygen incorporation into a disordered or poorly-defined oxide above 130 °C and the formation of a stoichiometric rutile-type oxide above 230 °C.

Regarding the reaction mechanism, the absence of adsorbed CO during CO<sub>2</sub> production, as seen with our IRRAS experiments, and the expected low O adsorption energy of a (1 × 1)-O overlayer [16] suggest an Eley-Rideal (ER) mechanism, as other authors have suggested in the past [36]. DFT studies have claimed, however, that an ER mechanism is not able to explain the observed high turnover rates, so that a Langmuir-Hinshelwood (LH) mechanism, taking place at the O vacancies of a defective (1 × 1)-O overlayer, could be the operative mechanism [37]. Other studies suggest a Mars-van-Krevelen (MvK) process [4]. However, our results do not allow us to propose which is the most probable active mechanism.

For the case of the defective surface in oxidizing conditions, the situation differs from the case of the flat counterpart. Below 240 °C, the activity of the defective surface is higher than that of the flat surface. First, at 110 °C, the surface is already active (differently to the flat counterpart), and this activity increases with temperature for the first three temperatures (110 °C, 150 °C and 180 °C). Second, the incorporation of oxygen is also higher for the defective surface, and increases continuously for the four temperatures explored. And third, the activity slows down at the highest temperature (240 °C) where the total amount

of CO<sub>2</sub> conversion saturates soon and does not reach the values obtained for the two lower temperatures. This moderate reduction of the activity is, in some way, peculiar, since it amends the observed tendency at lower temperatures. The catalytic activity of Ru oxide depends on the availability and configuration of the active sites, and these may change for the temperatures considered. These active sites are, as considered by some authors, under-coordinated Ru atoms to bind CO and bridge O atoms to contribute to the oxidation mechanism. If any of these sites have been modified at 240 °C, due to a partial reduction or to a morphological restructuring of the surface, a change in the catalytic activity is expected. This reduction of the catalytic activity at 240 °C may be also related to the formation of a thick oxide. As we discuss in the Supplementary Material, due to the high surface sensitivity of the Auger spectroscopy, the maximum concentration of detectable oxygen is around 5 ML [38]. So, for the highest temperature tested, we probably have a thick oxide (thicker than the 5 ML limit). And it has been repeatedly reported that the catalytic activity of Ru oxide may be reduced or even extinguished in the bulk oxide or in thick films [2]. Other transition metal bulk oxides, such as Rh [7] or Pd [9], also show a low or null activity for CO oxidation.

In both types of surfaces (flat and defective), the incorporation of oxygen increases with the reaction temperature, reaching a value equivalent to about 5 ML for the highest temperatures. This can be interpreted as the formation of an oxide, which is more easily formed at

the modified surface. When studying the oxidizing conditions, the modified surface shows a higher efficiency related to the presence of defects which act as preferential sites for both oxygen incorporation, oxide formation and CO oxidation. However, the exact nature of this oxide is more difficult to determine under the information obtained with our experiments. The LEED pattern does not support the formation of crystalline RuO<sub>2</sub>(110): no post-reaction pattern compatible with the (110) rutile structure has been observed. On the contrary, when the LEED pattern has been visible, it has been that of a very defective Ru(0001). It is possible, however, that the local stoichiometry corresponds to the oxide, which is supported by the assertion of Gao *et al.* [6], affirming that this oxide can be formed with a coverage above 4 monolayers.

Comparing our results with those found in the literature, we can say that the formation of an oxide does not seem to be an essential condition to achieve a moderate catalytic activity under oxidizing conditions (curves for the flat surface at 150 °C and 180 °C and for the defective surface at 110 °C illustrate this affirmation) where the oxygen concentration is just around 1–1.5 ML. Our results point to the fact that metallic Ru (with a high oxygen coverage) and Ru oxide are both active phases under the conditions studied in this work. However, the highest activities are attained when the surface oxide is formed. An anomaly in this sense is the case of the defective surface at the highest temperature, where the activity is lowered. One reason to explain the decrease in the catalytic activity may be the formation of a thick oxide film. Another reason may be that we are facing a type of oxide different to those oxides formed at lower temperature. The configuration of the defects and their catalytic activity has probably changed, transitioning from being the preferential sites for the adsorption and dissociation of O<sub>2</sub> to present a lower residence time, being thus the reason why the efficiency of the reaction is decreased. This fact is coherent with the observations by Gao *et al.* [6].

## 5. Conclusions

The catalytic activity of Ru(0001) during CO oxidation is a relatively complex process. It obviously depends on the total and relative O<sub>2</sub>/CO pressures and on the working temperature, but also on the initial density of surface defects. This dependency on the surface morphology, which is only relevant in oxidizing conditions, is related to the formation of a disordered surface oxide, which is in turn favored by the presence of an initially defective surface. Under reducing conditions there is a much smaller sensitivity to temperature or to the presence of surface defects. It is interesting to note, however, that the catalytic activity in reducing conditions is not negligible, but is mostly limited by a high CO coverage and low O<sub>2</sub> adsorption and dissociation. The activity in reducing conditions is probably determined by the impinging rate of oxygen molecules at the surface, which is mainly covered by CO.

The formation of a surface sub-oxide layer in oxidizing conditions is promoted by moderately increasing the temperature. This oxide is in a disordered or quasi-amorphous state, formed by the incorporation of oxygen into the Ru lattice, but lacking the ideal crystalline structure of RuO<sub>2</sub>. A significant catalytic activity is observed under oxygen concentrations above 1 ML. So, a disordered pre-oxide, probably non-stoichiometric and lacking the rutile structure, is necessary to obtain a relatively moderate activity under the conditions studied in this work, and this oxide is more easily formed in the presence of surface defects. However, at a temperature of 240 °C the oxide formed on a defective surface has a lower catalytic response. This is probably associated to qualitative changes in the stoichiometry and structure of the oxide at this temperature (a more stoichiometric and ordered RuO<sub>2</sub>) or to the formation of a thick Ru oxide.

The defective surface shows, in oxidizing conditions, a higher incorporation of oxygen and a higher conversion than the flat surface (as long as the temperature is below 240 °C). Thus, we can conclude that the pre-oxide is an active phase during the catalytic oxidation of CO on Ru

(0001) and that it is a structure-sensitive reaction. The presence of a preliminary defective surface morphology determines a higher oxygen incorporation, a more facile way to form a disordered oxide, and a higher catalytic activity.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.surf.2023.103028](https://doi.org/10.1016/j.surf.2023.103028).

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