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Catalytic CO oxidation over
ruthenium—bridging the pressure gap

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Abstract

The CO oxidation over Ru under UHV conditions reveals by far the lowest catalytic activity among the late transition metals, while under strongly oxidizing reaction conditions the catalytic activity of Ru turns out to be superior to Pt, Rh and Pd. This observation was taken as manifestation of the so-called pressure gap. Recent experiments have shown that this transformation from an inactive catalyst towards an active catalyst is attributed to a structural transformation of Ru to RuO₂. The autocatalytic oxidation of the Ru(0001) surface leads to the formation of an epitaxially grown RuO₂(110) film whose catalytically active sites are identified with the onefold under coordinated Ru atoms (1f-cus-Ru). On the 1f-cus-Ru atoms the CO molecules adsorb strongly (120 kJ/mol), ensuring a high CO concentration on the oxide surface under reaction conditions. Experiments together with density functional theory (DFT) calculations indicate that the most important elementary reaction step during the CO oxidation is the recombination of adsorbed CO molecules with bridging O atoms from the oxide surface. Equally important for being a good oxidation catalyst is the facile replenishment of bridging O atoms on RuO₂ by oxygen exposure. This process is mediated by on-top O atoms above the 1f-cus-Ru atoms. The on-top O atoms are by 1.4 eV less strongly bound than bridging O atoms. However, the activation barriers for CO recombination with on-top O and bridging O are nearly degenerated as determined by DFT calculations. Entropy effects make the oxidation von on-top CO less efficient with on-top O than with bridging O. Recent experiments provide evidence that the pressure gap for the CO oxidation reaction on RuO₂ is successfully closed.

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1. Introduction

In general, processes on realistic catalysts are far too complex to allow the identification of the microscopic reaction steps. This problem calls for idealization of the experimental conditions such as the use of single crystalline surfaces and the investigations under well-controlled vacuum conditions (UHV conditions) [1]. The price to pay for this so-called surface science approach is the introduction of a pressure and material gap by which catalytic properties (elementary reaction steps, reaction intermediates, etc.) determined under well-defined conditions may not be transferable to realistic reaction conditions. The relevance of surface science studies to realistic catalytic systems is therefore still debated, although for some reactions, such as the CO oxidation reaction over transition metal catalysts and the ammonia synthesis over Fe and Ru catalysts, the pressure (and material) gap has successfully been bridged [2].

The CO oxidation reaction over late transition metals has been the most widely studied surface catalyzed reaction. The CO oxidation reaction is of practical importance for the control of the environmental pollution that results from combustion processes. In general, the catalytic activity for the CO oxidation over transition metal surfaces is determined by the propensity of the metal surface to dissociate oxygen molecules and counter balanced by the bond strength of the active oxygen species on the metal surface [3]. This behaviour is reflected in the well-known volcano curve for

transition metals. The transition metals with half-filled d-bands reveal the highest activity, where the dissociation probability is not too low and the adsorption energy is not too high. Accordingly, Pt, Pd, and Rh are efficient metal catalysts, while Ru—due to its very high binding energy of oxygen—is a poor catalyst for the CO oxidation reaction under UHV conditions.

A prominent example for the manifestation of an apparent pressure gap was previously reported for the CO oxidation reaction over the ruthenium surface [4]. While under UHV conditions the Ru surface is by far the poorest catalysts among the late transition metals, this ranking in catalytic activity reverses when the CO oxidation reaction proceeds under high pressure and oxidizing conditions. Here Ru turns out to be much more active than the other late transition metal surface.

2. CO oxidation over ruthenium under oxidizing conditions: brief review

Under UHV conditions, the low activity of Ru(0001) is traced to the strong O–Ru bonding. Peden and Goodman [4] assigned therefore the high activity of Ru(0001) under oxidizing conditions to the presence of a weakly bound oxygen species that cannot be populated under normal UHV conditions. Peden and Goodman demonstrated that the activity of the Ru(0001) surface is practically identical to that of a supported Ru catalyst, i.e. the CO oxidation reaction over Ru is structure insensitive. With Auger electron spectroscopy the O coverage of the active O/Ru(0001) surface was estimated to be 1 ML.

In fact, it is possible to prepare a well-ordered (1×1) -O overlayer on Ru(0001) (with an O coverage of 1 ML) under UHV conditions by using NO_2 as a kind of atomic oxygen source [5]. Density functional theory (DFT) calculations determined the binding energy of oxygen in the (1×1) -O overlayer to be 0.5 eV lower than for low O-coverages [6]. This observation was first considered to rationalize the high activity of Ru(0001) under oxidizing conditions. However, the (1×1) -O overlayer impedes the adsorption of CO above 40 K which in turn results in a low activity of the (1×1) -O pre-covered Ru(0001) surface. With infrared spectroscopy (FTIR) Hofmann and coworkers [7] did not detect any CO adsorption on the Ru(0001)- (1×1) O surface during CO oxidation under oxidizing conditions. This observation was taken as evidence that CO molecules do not adsorb on the oxygen saturated Ru(0001) surface, albeit CO_2 is produced. Therefore, Hofmann et al. proposed that the Eley–Rideal mechanism is operative under these experimental conditions, i.e. the incoming CO molecule reacts directly from the gas phase with the adsorbed oxygen atoms on the Ru(0001) surface. However, this conclusion was challenged by a careful DFT study. Stampfl and Scheffler [8] found that the activation barrier for such an Eley–Rideal mechanism is far too high to explain the high turnover frequencies observed in the experiments of Peden and Goodman.

An alternative explanation of the experiments of Peden and Goodman is that the Ru(0001) surface is covered with a defected (1×1) -O overlayer and CO may adsorb into these vacancies. We are then left with a Langmuir–Hinshelwood type reaction. The corresponding activation barrier was calculated to be 1.5 eV [9]. In addition, the

CO adsorption on such a defected (1×1)-O surface is activated by 0.35 eV [9]. Both effects end in a far too low reaction rate. Experiments verified the activated adsorption of CO on the Ru(0001)-(2 \times 2)-3O overlayer that is considered as an ordered vacancy structure of the (1×1)-O overlayer [10].

3. CO oxidation over ruthenium dioxide RuO₂

3.1. A brief retrospective

In recent studies Böttcher et al. [11] succeeded in the preparation of an oxygen-rich Ru(0001) surface that revealed an extraordinarily high activity for the CO oxidation reaction. The catalytically active oxygen rich phase develops beyond an oxygen load of 3 ML at the Ru(0001) surface. Therefore, this oxygen rich phase may not be related to the activity measurements of Peden and Goodman, since in those experiments the total oxygen coverage was about 1 ML.

The nature of Böttcher's oxygen-rich Ru(0001) surface was first controversially discussed. Böttcher and coworkers discussed the high activity of the oxygen rich Ru(0001) surface in terms of subsurface oxygen [12], while Over et al. attributed the oxygen rich phase to a RuO₂(110) film epitaxially grown on Ru(0001) that is responsible for the high activity [13]. In the meanwhile the latter interpretation is generally accepted.

In the following we focus our discussion on the CO oxidation reaction over RuO₂ and how the pressure gap can be successfully closed for this system. A comprehensive understanding of the elementary reaction steps in this reaction has been achieved by the DFT calculations of Ari Seitsonen [14]. We should recall that in general oxide surfaces are less suitable for bridging the pressure and material gap than metal surfaces since the activity of the oxide catalyst is mostly controlled by the concentration of defects on the catalysts surface and not by the stoichiometric oxide surface.

3.2. Oxidation of ruthenium

Exposing of the Ru(0001) surface to molecular oxygen under UHV conditions is able to form a (2 \times 2)-O and a (2 \times 1)-O overlayer [15]. The dissociative sticking coefficient drops from almost one to less than 10^{-3} so that under normal UHV conditions the (2 \times 1)-O phase was considered as the saturation phase. Dosing much more oxygen, say more than 1000 L, the Ru(0001) surface stabilizes two additional phases of chemisorbed O, namely the (2 \times 2)-3O and the (1×1)-O [16]. The stability of both phases was predicted by DFT calculation [6].

The dissociative sticking coefficient of oxygen over the Ru(0001)-(1 \times 1)O surface is estimated to be less than 10^{-6} [17]. Consequently, oxygen uptake beyond a coverage of 1 ML becomes the rate determining step for the initial oxidation of Ru(0001). However, as soon as an oxide nucleus is formed on the Ru(0001)-(1 \times 1)O surface, the progressing oxide formation proceeds in an autocatalytic way

[18], since the sticking coefficient on the oxide surface is as high as 0.7 [17]. Auto-catalytic reaction means that the surface produces its own ‘catalyst’ (i.e. the oxide nucleus) to dissociate readily the oxygen molecules, resulting in a self-acceleration of the oxidation process. Autocatalytic oxidation was first reported for ultra-pure Pb microcrystallites [19].

The role of subsurface oxygen in the O/Ru(0001) system has not been settled. DFT calculations favor the formation of subsurface islands directly below the surface [20] that is not reconciled with the experiments. Medium energy ion scattering by Quinn et al. [21] showed some evidence for subsurface oxygen, but the Ru subsurface layer spacings increased only very little so that the formation of subsurface oxygen islands can clearly be excluded. Note that the subsurface oxygen is to expand the Ru layer spacing by about 60% [22]. DFT studies suggested a so-called tri-layer model that should serve as a ‘transition state’ between chemisorbed oxygen and the oxide phase [23] for which, however, only little or no experimental evidence exists [24,25].

The transition from oxygen adsorption to oxide formation on Ru(0001) becomes structurally even more complex by the coexistence of various oxygen phases on the surface [24] (see the Fig. 1) that results in a complex pattern formation on the micrometer scale [26].

If not molecular oxygen but NO_2 is used as the oxidant, then many monolayers of oxygen can be accommodated at the Ru(0001) surface without forming an oxide on the surface. Activity experiments indicate that this kind of oxygen rich phase is catalytically inactive [27]. Since the solubility of oxygen in the late transition metals

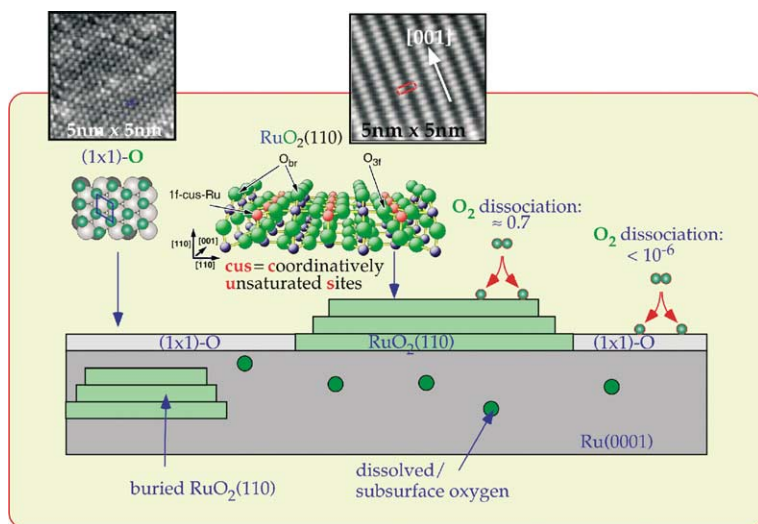


Fig. 1. The rich oxygen–ruthenium surface chemistry. Chemisorbed oxygen, surface oxide, buried oxides and subsurface oxygen may coexist in the near surface region of Ru(0001). This complexity is characteristic of oxygen chemistry of many transition metal surfaces [18]. High resolution STM images (5 nm × 5 nm) of the Ru(0001)-(1 × 1)O phase (left) and the RuO₂(110) phase (right) are included.

(and in particular in Ru) is very small, the presence of so much dissolved oxygen in the near Ru(0001) surface region is not very likely. Instead, we favor the development of a buried RuO₂ layer as suggested by measurements of the chemical reduction of RuO₂(110) by CO: STM in combination with high resolution core level spectroscopy demonstrate that a heavily reduced RuO₂(110) surface consists of an ultra-thin metallic Ru film that caps the RuO₂ surface [24]. Similar results were reported for single crystalline RuO₂ surfaces [28]. Fig. 1 illustrates and summarizes the rich oxygen–ruthenium surface chemistry.

3.3. CO oxidation on RuO₂(110)

In the bulk rutile structure of RuO₂ the Ru atoms are sixfold coordinated to oxygen atoms, while the O atoms are coordinated to three Ru atoms in a planar sp² hybridization. On the stoichiometric RuO₂(110) surface two kinds of under-coordinated surface atoms are encountered (cf. Fig. 2A) [29]. These are the bridging oxygen atoms O_{br}, which are coordinated only to two Ru atoms underneath, and the so-called 1f-cus-Ru atoms, i.e. onefold coordinatively unsaturated Ru atoms.

The high catalytic activity of stoichiometric RuO₂(110) towards CO oxidation was demonstrated (on the atomic scale) to be controlled by the presence of 1f-cus-Ru atoms [27]. We emphasize this point since not defects (as generally encountered with oxide surfaces) but rather the regular, under-coordinated surface atoms govern the activity of RuO₂. On the stoichiometric RuO₂(110) surface, CO molecules adsorb strongly (adsorption energy exceeds 1.2 eV [30]) on-top of the 1f-cus-Ru atoms (cf. Fig. 2B) from where the actual oxidation reaction takes place via recombination with the bridging oxygen atoms to form CO₂. The strong CO adsorption on RuO₂(110) ensures a high CO concentration on the surface under reaction conditions. Recent high resolution energy electron loss spectroscopy (HREELS) measurements [31] have confirmed this view, and DFT calculations characterized the transition state of this reaction pathway [32,33]. Ari Seitsonen provides illustrative movies about the recombination of on-top CO with bridging O and on-top O over RuO₂(110) on his WEB site [34]. If several neighboring bridging oxygen atoms have been removed, twofold coordinatively unsaturated Ru sites (2f-cus-Ru) are exposed (cf. Fig. 2C) offering two dangling bonds for the bonding with molecules from the gas phase. The adsorption energy of a single CO molecule substituting a bridging O atom is 1.73 eV [35]. If all O_{br} atoms have been removed, CO molecules bridging two neighboring 2f-cus-Ru atoms are bound by even 1.85 eV [35].

An equally important process is the facile re-oxidation of a (partially) reduced RuO₂(110) surface by oxygen supply from the gas phase. A weakly held oxygen species was found to adsorb on-top of the 1f-cus-Ru atoms of the stoichiometric RuO₂(110) surface [36] (cf. Fig. 2B) with a sticking probability of 0.7 at room temperature [17], and it was argued that this species actuates the restoration of the reduced RuO₂(110) surface [36]. The latter process is mandatory to keep the oxide catalyst active under reaction conditions.

The RuO₂(110) surface supplies the CO oxidation reaction with two potentially catalytically active oxygen species. Besides the bridging O atoms, the RuO₂(110)

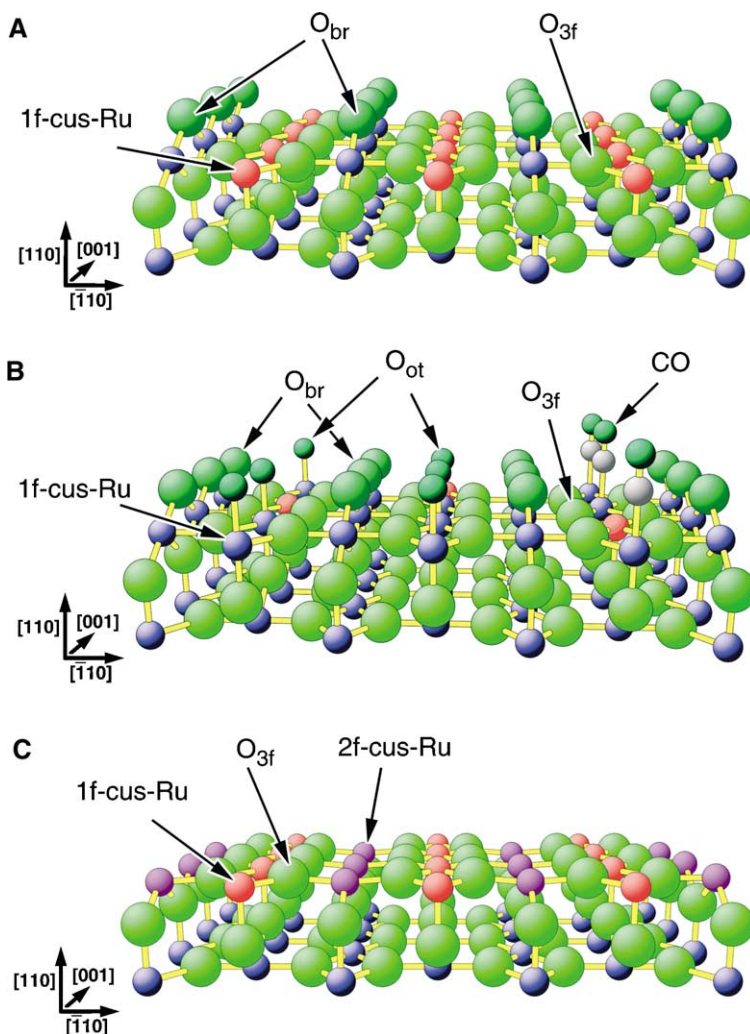


Fig. 2. (A) Stick and ball model of the clean RuO₂(1 1 0) surface. Large balls represent oxygen, and small balls represent ruthenium atoms of RuO₂(1 1 0). The bridge-bonded O_{br} and 1f-cus-Ru atoms are indicated. Both surface species are onefold undercoordinated with respect to bulk-coordination [13]. (B) The adsorption of CO and oxygen onto the stoichiometric RuO₂(1 1 0) surface. Both adsorbants occupy the on-top positions above the 1f-cus-Ru atoms [30,37]. (C) The mildly reduced RuO₂(1 1 0) surface is characterized by missing bridging O atoms in the O_{br} rows. CO adsorbs above the 2f-cus-Ru atoms thereby replacing the bridging O atoms [35].

surface stabilizes an on-top oxygen species (see Fig. 2B) which is 1.4 eV more weakly bound than the bridging O atoms [37]. Following the Hammond postulate [38] the on-top O species is anticipated to dominate the activity of RuO₂(1 1 0), a conclusion that was supported by HREELS measurements [39]. However, there is now experimental evidence that the on-top O species is significantly less active in oxidizing CO

than the bridging O species. Careful isotope labeling experiments with ^{18}O disentangle contributions coming from the recombination of CO with bridging O and on-top O. DFT calculations attribute this counter intuitive finding to the important role of the activation entropy together with an activation energy that is almost degenerate for the CO recombination with on-top O and bridging O [40].

3.4. Reaction mechanism for the CO oxidation on $\text{RuO}_2(110)$

In order to understand the reaction mechanism, we will consider the following scenarios: (a) Let the CO/oxygen ratio in the gas feed be 2:1 and the sample temperature be between 350 and 400 K. This surface temperature is high enough to ensure facile CO oxidation, but also low enough to prevent the surface from restructuring (see Ref. [33] for further details). This temperature window was also explored in recent steady state reaction experiments by Wang et al. [39]. Under these conditions both reactants initially adsorb over the 1f-cus-Ru atoms. CO adsorbs molecularly in an upright position above the 1f-cus-Ru atoms. Molecular oxygen adsorbs dissociatively above the 1f-cus-Ru atoms, requiring two neighboring vacant 1f-cus-Ru sites. At temperatures in the range of 350–400 K, adsorbed CO molecules easily recombine with bridging O atoms (O_{br}) to form CO_2 . Thereby vacancies are formed in the bridging O rows. The diffusion barriers for on-top O and on-top CO along the 1f-cus-Ru rows are quite high with 1.0 eV, while diffusion perpendicular to the 1f-cus-Ru rows into O-bridge vacancies is only 0.7 eV [14]. Therefore, both CO molecules and on-top O atoms can easily hop from the 1f-cus-Ru atoms into the O_{br} vacancies above room temperature, thereby increasing their binding energies to the surface by 0.5 and 1.4 eV, respectively.

The main point to note is that CO do not efficiently recombine directly with on-top O atoms, as suggested by recent isotope labeling experiments and DFT calculations [40]. Instead the on-top O atoms migrate to the O_{br} vacancies, where they recombine with on-top CO molecules. If, on the other hand, CO moves into such vacancies, then the CO molecule can either recombine with a neighboring bridging O atom or with an on-top O atom on the 1f-cus-Ru atom. DFT calculated activation energies for these reaction pathways clearly exclude the recombination of bridging CO with bridging O at 350–400 K since the activation barrier is with 1.3 eV far too high [14]. In contrast, the recombination of bridging CO with on-top O is only 0.6 eV so that this reaction channel is efficient, preventing the $\text{RuO}_2(110)$ surface from self-poisoning by strongly adsorbed CO molecules above the 2f-cus-Ru atoms [14,33].

In summary, CO molecules recombine predominantly with bridging O atoms from the $\text{RuO}_2(110)$ surface, while the on-top oxygen atoms are predominantly used to replenish the vacancies in the bridging O rows or to remove bridging CO molecules.

Preliminary experiments with a gas shower (local pressures at the sample: $P(\text{CO}) = 10^{-2}$ mbar, $P(\text{O}_2) = 5 \times 10^{-3}$ mbar; sample temperature: below 400 K) indicate that under such conditions the $\text{RuO}_2(110)$ surface is stable over the long-term [41].

Changing the CO/O₂ ratio in the gas feed to higher values than 2:1 will deteriorate the overall activity due to blocking of the surface by CO molecules. The rate determining step is then the dissociation of oxygen. Lower values of CO/O₂ are less critical for the overall activity of the surface [41].

Considering now (b) Sample temperatures below 250 K: CO₂ is not formed due to an apparent activation energy of about 0.9 eV [33].

(c) Sample temperatures above 500 K: This temperature is high enough to allow bridging CO molecules to recombine with bridging O atoms thus opening an alternative reaction channel. In addition, the reduced RuO₂(1 1 0) is not stable any more. The initially flat surface reconstructs readily into a rough surface [24] so that the overall reaction mechanism becomes quite complex.

3.5. Bridging the pressure and material gap for the case of RuO₂

In contrast to commonly used oxide surfaces, the under-coordinated surface atoms (1f-cus-Ru and bridging O) of the stoichiometric RuO₂(1 1 0) surface are already the

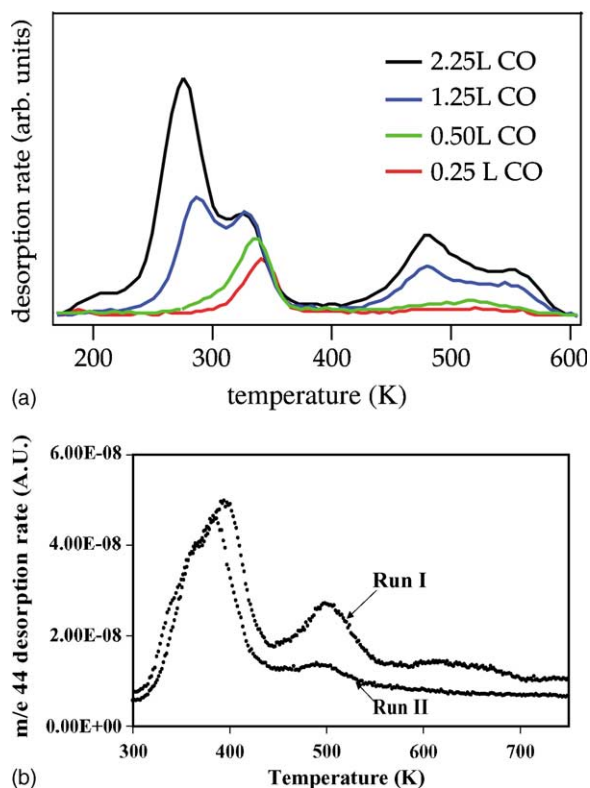


Fig. 3. CO₂ production during CO TDS over RuO₂ of single crystalline RuO₂(1 1 0) films [33] (a) in comparison with polycrystalline RuO₂ powder (b) [42]. In panel (b) means Run I: fresh sample and Run II: means used sample that has been regenerated with O₂ at 573 K for 2 h at 1 bar.

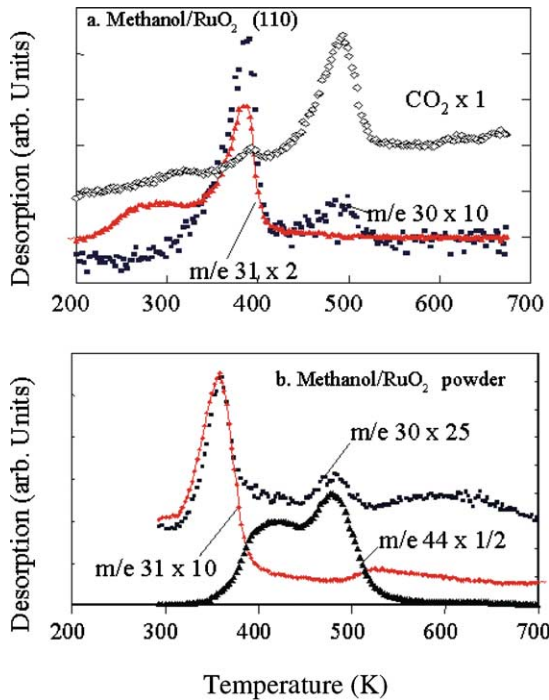


Fig. 4. Formaldehyde (partial oxidation) and CO_2 (total oxidation) formation during methanol TDS over RuO_2 surfaces of single crystalline films (a) in comparison with polycrystalline RuO_2 powder (b) [43].

active centers, without invoking active defect sites. In addition, we know that the efficiency for CO oxidation is almost independent of the orientation of RuO_2 (at least for the (110), (100), and the (101) orientations) and is governed by the concentration of 1f-cus-Ru atoms [27]. Since the (110), (100) and (101) surfaces of RuO_2 are low energy surfaces, these orientations are also the prevailing orientations on polycrystalline RuO_2 . Altogether, we therefore expect that the activity of polycrystalline RuO_2 is equally determined by the presence of 1f-cus-Ru atoms. Corresponding CO oxidation measurements support this view as indicated in Fig. 3 [33,42].

To further support this view, we conducted experiments with methanol over $\text{RuO}_2(110)$ and polycrystalline RuO_2 [43]. Indeed, both the partial oxidation of methanol to formaldehyde proceeds very similar for single crystalline $\text{RuO}_2(110)$ under UHV conditions and polycrystalline RuO_2 in the high pressure regime (cf. Fig. 4). Together with the CO oxidation experiments these results support the view that the catalytic activity of RuO_2 is not determined by defects on the oxide surface but rather by the 1f-cus-Ru atoms on the RuO_2 surfaces. Otherwise, if defects were controlling the activity, one would expect large differences between polycrystalline RuO_2 (with many defects) and single crystalline RuO_2 (with a low defect concentration).

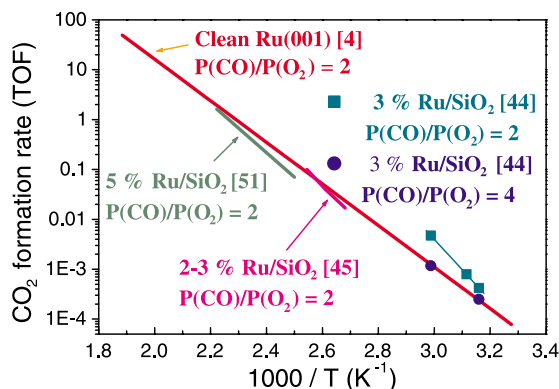


Fig. 5. Arrhenius plot of rates of CO₂ formation (TOF = turnover frequency, number of CO₂ molecules formed per active metal site per second) over the Ru/SiO₂ catalyst for various CO/O₂ reactant feed ratios [44]. The measurements were conducted in a TAP reactor at partial pressure of about 10 mbar. Also data are included that are obtained on a Ru(0001) catalyst [4] and two silica-supported ruthenium catalysts prepared by impregnation [45,51].

Experiments on SiO₂ and MgO supported Ru catalysts have shown that RuO_x is identified with the catalytically active phase [44], where the exact number of x waits to be determined. If x turns out to be 2 the material gap is closed. The activity in the oxidation of CO over the supported oxidized Ru catalysts is nearly independent of the support [44].

In Fig. 5, the turnover frequencies (TOF = number of CO₂ molecules produced per metal surface site per second) in the form of Arrhenius plots are shown for a Ru(0001) single crystal surface and silica-supported ruthenium catalysts prepared by impregnation as well as by chemical vapour deposition of Ru₃(CO)₁₂. The applied pressures are in the 10 mbar range. There is very good agreement regarding the slope (activation energy of 82 kJ/mol) and the absolute scale. This activation energy is close to the value of 0.9 eV found in our UHV studies of RuO₂(110) [33]. The activation energy depends on the CO/O₂ reactant feed ratio. The reaction rate for the oxidation of CO with a CO/O₂ reactant feed ratio of 2 at 321 K is of the order of about 10¹² molecules cm⁻² × s⁻¹. Similar reaction rates were reported by Wang et al. [39] for the steady state oxidation of CO on a RuO₂(110) single crystal surface under UHV conditions, indicating that the pressure gap has indeed been closed. It is important to note that the proposed reaction mechanism by Wang et al. is questionable, since it is based on the tacit assumption that the on-top oxygen species prevails the activity of RuO₂(110) in the CO oxidation reaction. As discussed above the on-top O species is less important than intuitively expected [40].

3.6. Deactivation of RuO₂

Kiss and Gonzalez [45] observed an irreversible deactivation for Ru/SiO₂ at atmospheric pressure. Is there any observation that points to an irreversible

deactivation of RuO₂ under UHV condition? For the RuO₂(1 1 0) surface a deactivation of the surface has not been observed, but on the RuO₂(1 0 0) surface a deactivation has been documented [46]. The RuO₂(1 0 0) surface is stable in two essentially different configurations which do coexist on the surface, a (1 × 1) phase and a c(2 × 2) phase. While the (1 × 1) phase is catalytically as active as the RuO₂(1 1 0) surface, the c(2 × 2) phase is catalytically inactive [46]. CO molecules are not able to adsorb on the c(2 × 2) phase. CO exposure at room temperature and elevated temperature is therefore not able to reduce the c(2 × 2) phase. This is clear from LEED measurements as well as from STM investigations [46,47]. The c(2 × 2) phase may therefore be considered as a promising candidate to explain the irreversible deactivation of Ru/SiO₂ catalysts at mbar pressures. So far, no structural information is available on the catalytically inactive c(2 × 2) phase. We should add that the heavy oxidation of Ru(0 0 1) leads partly to the growth of RuO₂(1 0 0) domains on the surfaces that consists of (1 × 1) and c(2 × 2) phases [46]. Therefore, it might be that this c(2 × 2) phase is of more general importance than hitherto expected.

The irreversible deactivation of the oxidized Ru/SiO₂ catalyst at higher partial pressures has not yet been confirmed by related experiments in Bochum [48]. It might be that the Ru/SiO₂ catalyst of Kiss and Gonzales consists of larger Ru clusters than the catalysts in Bochum (typical cluster size dimension: 1 nm). This speculation will be checked by corresponding measurements on polycrystalline RuO₂ powders. However, a reversible deactivation of the Ru/SiO₂ catalyst is observed in Bochum under oxidizing conditions [44]. Going to more reducing conditions reactivates the catalyst.

4. Outlook

There is ample experimental evidence (under UHV and atmospheric conditions) that the pressure gap is bridged for the CO oxidation over RuO₂. Yet, it would be more convincing to directly close the pressure gap from the UHV regime to the mbar range with one particular sample, using a single technique such as infrared spectroscopy (RAIRS). Such experiments are in progress in the laboratory at the JLU in Giessen. These RAIRS measurements can be compared with corresponding FTIR measurements (DRIFTS) on supported catalysts from Bochum [48], thus definitely bridging the pressure and materials gaps. Microkinetic modeling of the CO oxidation should be the ultimate goal of such experiments which may serve as a benchmark for theoretical modeling.

On the theory side, the binding energies of CO and O in various configurations, the barriers for diffusion of these species on the surface and the activation energies for particular reaction pathways have already been calculated [14]. The main points missing are the calculated sticking probabilities for oxygen and CO adsorption. Altogether these quantities may serve as input in Monte Carlo simulations to mimic integrally the CO oxidation reaction over RuO₂ and to compare them with related experiments [49]. In this context, it is important to pay attention to the important role of entropy contributions in the elementary reaction steps to the overall reaction rate, such as encountered with the recombination of on-top CO with on-top O [40].

Of course the atomic geometry of the inactive $c(2 \times 2)$ phase on the $\text{RuO}_2(1\ 0\ 0)$ surface is of central importance to understand the deactivation of a catalyst. Further effort has to be put in this direction, applying alternative techniques such as high resolution core level spectroscopy and surface X-ray diffraction possibly, the reversible deactivation of the supported Ru/SiO_2 catalyst under oxidizing conditions is related to this inactive $c(2 \times 2)$ phase.

The original experiments of Peden and Goodman [4] about the CO oxidation over single crystalline $\text{Ru}(0\ 0\ 0\ 1)$ surface and the high activity under oxidizing conditions are still not well understood. It is still not clear whether the $\text{Ru}(0\ 0\ 0\ 1)$ surface transforms (at least partially) into an oxide surface under the experimental conditions of Peden and Goodman. The main obstacle is that these authors determined the total oxygen content on the $\text{Ru}(0\ 0\ 0\ 1)$ surface to be 1 ML which is not compatible with the onset of oxide formation beyond 3 ML as determined by Böttcher. This unsatisfying situation calls for further UHV experiments. We will study the oxidation of $\text{Ru}(0\ 0\ 0\ 1)$ by using a mixture of oxygen and CO (with ratio 2:1) in order to mimic more closely Peden and Goodman's measurements. The activity of these surfaces should be followed with in situ RAIRS measurements.

Last but not least, we will expand on the type of reaction studied on RuO_2 . Here in particular the partial dehydrogenation of methanol or ethanol to aldehydes both under well-defined (surface science approach) and more realistic conditions (supported Ru catalysts, high pressure) is in the focus point. Preliminary experiments [50] indicate that this reaction is much more involved than the CO oxidation reaction. This is due to a variety of reaction intermediates that are stabilized on the surface and the abstraction of hydrogen that has to be stabilized on RuO_2 and which further reacts to water.

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