Oxidation Reactions over RuO$_2$: A Comparative Study of the Reactivity of the (110) Single Crystal and Polycrystalline Surfaces

H. Madhavaram,* H. Idriss,* Y. D. Kim Id, M. Knappe,† H. Overy,† J. Aßmann,‡ E. Löffler,‡ and M. Mühler‡

*Centre for Surface and Materials Science, Department of Chemistry, University of Auckland, Auckland, New Zealand; †Fritz-Haber Institute der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 D-Berlin, Germany; and ‡Laboratory of Industrial Chemistry, Ruhr-Universität Bochum, D-44780 Bochum, Germany

Received January 24, 2001; revised May 13, 2001; accepted May 20, 2001

The present work is devoted to the investigation of oxidation reactions over RuO$_2$ surfaces. Two main points are addressed. First, on the fundamental level, a detailed investigation of the site requirement for CO (as well as for methanol) and O$_2$ adsorption on the surface of a well-defined RuO$_2$(110) crystal is conducted. Second, a comparison with polycrystalline RuO$_2$ toward these oxidation reactions is presented. Both results, those in UHV over RuO$_2$(110) and those at atmospheric pressure over polycrystalline RuO$_2$, agree fairly well. This indicates that the surface chemistry of the (110) single crystal is very similar to that of the polycrystalline material. Both the activity of the RuO$_2$(110) surface in the UHV regime and the activity of polycrystalline RuO$_2$ in the high-pressure regime were investigated by temperature-programmed desorption and by X-ray photoelectron spectroscopy. The reasons for the unusually high catalytic activity for oxidation reactions of RuO$_2$ are traced back to the strong bonding of the reactants over the undercoordinated Ru atoms together with the presence of weakly bound undercoordinated oxygen species, serving as the oxidizing agent.

© 2001 Academic Press

I. INTRODUCTION

RuO$_2$ is now receiving considerable attention for its extraordinarily high catalytic activity (below room temperature) toward CO oxidation. This reaction was investigated at the atomic scale by applying a whole battery of surface science techniques under ultra high vacuum (UHV) conditions (1-3). To test the potential of this surface for other reactions, the present work is devoted to the investigation of the oxidation reaction of methanol over RuO$_2$ surfaces and compares it to CO. Considering both oxidation reactions, CO to CO$_2$ and methanol to formaldehyde and CO$_2$, as a case study, the work mainly addresses the following questions. (i) On a fundamental level, what is (are) the site requirement(s) of this very efficient oxidation reaction? In that regard, a detailed investigation of the site requirement for CO (as well as for methanol—as a representative of organic pollutants) and O$_2$ adsorption on the surface of a well-defined RuO$_2$ is analyzed. (ii) With regard to application, what is the reactivity of polycrystalline RuO$_2$ toward these oxidation reactions and how does it compare with UHV experiments of RuO$_2$ single crystal? A complementary question arises from the second one. (iii) What is the behavior of a reduced (oxygen defected) Ru oxide surface toward these same reactions? This latter point is central to our understanding of oxidation reactions over oxides in general, since ideally the surface is continuously oscillating between the oxidized and reduced states. To achieve this objective, a comparative study is conducted to investigate the reactivity of rutile RuO$_2$(110) single crystal, under ultra high vacuum conditions, as well as that of polycrystalline RuO$_2$ at 1 atmosphere, toward these oxidation reactions. This work shows that both results agree fairly well.

Rutile RuO$_2$(110) surface (like rutile TiO$_2$(110) and SnO$_2$(110)) possesses alternating rows of fivefold and sixfold coordinated Ru cations (the fivefold coordinated Ru cations are designated cus-Ru, where cus stands for coordinatively unsaturated sites). The energies of the relaxed (110) surfaces of these three oxides are relatively comparable (1.78 (4), 1.78 (5), and 2.06 (6) eV per unit cell for TiO$_2$(110), RuO$_2$(110), and SnO$_2$(110), respectively).

Only very recently, has detailed work been conducted under UHV conditions of the rutile RuO$_2$(110) single crystal surface (3). The adsorption sites of RuO$_2$ for several molecules such as CO, N$_2$ (7), and methanol (8) are shown to be on the cus-Ru atoms. Two main differences are clearly observed between rutile RuO$_2$(110) and the corresponding surfaces of TiO$_2$ or SnO$_2$: (i) Thermal desorption spectroscopy (TDS) (1), as well as first principles density functional theory (DFT) calculations (7), has shown that unlike CO adsorption over cus-Ti of TiO$_2$(110) or cus-Sn of SnO$_2$(110), CO adsorption on cus-Ru is very strong (1.2 eV (7)). This is to be compared with CO-TiO$_2$(110) =...
0.3 eV (4) and CO-SnO$_2$(110) = 0.25 eV (6). (ii) Unlike TiO$_2$ and SnO$_2$, terminal bonded atomic oxygen can be stabilized on RuO$_2$(110) with a binding energy of 3.1 eV (9); for comparison the bridging oxygen on RuO$_2$(110) is bonded by 4.6 eV (values are given with respect to neutral atomic oxygen in the gas phase). These two essential differences, the strong CO adsorption and the presence of dissociative adsorption of O$_2$ molecules (with high sticking probability) (10), at moderate temperatures, explain naturally the high activity of RuO$_2$(110) for CO oxidation (11).

This high activity is unusual when compared not only to TiO$_2$(110) and SnO$_2$(110) but also, in fact, to any other known oxide single crystal to date.

The reactions of methanol and ethanol on the surfaces of oxide materials are of technological and fundamental importance (12, 13). Moreover, besides its use as a model for fundamental research, methanol is an atmospheric pollutant, with a tropospheric concentration reaching up to 5 ppbv and a relatively long lifetime (ca. 1 week) (14). It is used as a fuel additive and as such its concentration in the atmosphere is expected to rise worldwide. In addition, methanol is a good candidate, in the next decade or so, as a source for H$_2$ production for fuel cells. Since present fuel cell technology does not tolerate the presence of CO (formed by partial oxidation of methanol), it is thus important to rely on chemical processes completely selective for the oxidation of carbon-containing molecules to CO$_2$.

A detailed study of the reaction of alcohols over oxide surfaces can be found in Ref. (12). It is, however, worth mentioning a few points. Over TiO$_2$(110) methanol is unreactive (15). For example, DFT calculations have shown that dissociative adsorption of methanol over TiO$_2$(110) (nor on SnO$_2$(110)) surfaces. The adsorption energies of methanol over TiO$_2$(110), at \( \theta = 1 \) ML, is 70.4 and 74.3 kJ mol$^{-1}$ for nondissociative and dissociative modes, respectively (15). Those on SnO$_2$(110) for the same modes were 110.4 and 114.5 kJ mol$^{-1}$ (16). As will be shown in this work there is a dramatic difference between the reactivity of rutile RuO$_2$(110) and that of rutile TiO$_2$(110) toward this organic compound.

II. EXPERIMENTAL DETAILS

II.A. Polycrystalline RuO$_2$

Polycrystalline RuO$_2$ (purity > 99.99%) was obtained from Merck-Schuchardt Corp. BET analysis has shown that it has a surface area of 9.8 m$^2$/g. TPD was performed using a fixed-bed reactor containing 30 mg of RuO$_2$. More details about the TPD apparatus can be found in Ref. 50.

RuO$_2$ is heated under O$_2$ for 2 h or under hydrogen for 18 h at 573 K (\( P = 760 \) Torr). A fast cooling to room temperature (under O$_2$ or H$_2$) the reactor was pumped down to $10^{-3}$ Torr. Methanol was placed in a saturator at room temperature. It was cleaned by freeze–pump–thaw cycles. Desorption of the reactant from the oxide was conducted by allowing the vapor pressure (ca. 100 torr) to equilibrate between the reactor and methanol, typically for 3 min. The reactor was then pumped by a roughing pump for ca. 1 h at room temperature to remove traces of the reactant in the TPD line as well as weakly adsorbed molecules on the surface of the catalyst. The gas flow was introduced into the vacuum chamber through the interface (50). The ramping rate during TPD was kept fixed at 15 K/min. The fragmentation pattern of each product was checked to identify unambiguously the reaction products by following the method described in Refs. (17, 18).

XPS analyses were performed using a KRATOS X-SAM 800 model with a base pressure of $10^{-9}$ Torr. A T$_{Ka}$($h\nu = 1486.6$ eV) radiation was used at 180 W. A %-ion sputtering experiments were performed, at room temperature, using a direct-beam KRATOS ion gun at a pressure of $5 \times 10^{-7}$ Torr. An accelerating voltage of 2.7 kV was used, and the emission current was 20 mA. Unreduced RuO$_2$ was loaded into the system without further treatment. Narrow scans were obtained with a pass energy of 20 eV, which translates to an energy resolution of 1.1 eV. In the case of H$_2$-reduced RuO$_2$ the reactor valves were closed before transferring the sample to the XPS instrument. There, the powder was transferred onto the stainless steel sample stub with indium foil, under an oxygen-free nitrogen atmosphere. The sample stub was then transferred into the vacuum chamber. The whole process of transferring the sample took 30–40 s.

XRD spectra were collected using a Phillips 1130 generator and a Phillips 1050 goniometer. Radiation by X-rays was achieved using a Cu tube (broad focus) (\( K_{\alpha} \) : \( \lambda = 1.514 \) Å) at 44 kV and 20 mA. Diffraction patterns were collected from 10$^o$ to 90$^o$ (2θ).

The temperature-programmed reduction (TPR) experiments were performed in a quartz cell built according to the design by Monti and Baiker (19) using a heating rate of 2 K/min. Prior to the TPR measurement, RuO$_2$ was heated to 573 K using a heating rate of 10 K/min in synthetic air (20.5% O$_2$ in N$_2$) with a volumetric flow rate of 100 ml/min. Under these flow conditions, RuO$_2$ was calcined at 573 K for 2 h followed by cooling in synthetic air to room temperature. After flushing in diluted H$_2$ (4.2 vol% H$_2$ in Ar, supplied by Rosemount) for 30 min, the heating ramp up to 573 K was started using a flow rate of 84.1 ml/min. The effluent gas mixture was passed through a cold trap at 195 K to remove water and analyzed quantitatively by a calibrated thermal conductivity detector (Hydros 100, 0–5% H$_2$ in Ar, supplied by Rosemount).

II.B. RuO$_2$ Single Crystal

The UHV measurements were conducted in a stainless steel chamber as described elsewhere (20). RuO$_2$ (110)
Oxidation Reductions over RuO₂

III. RESULTS

III.A. Polycrystalline RuO₂

III.A.1. X-Ray Photoelectron Spectra

X-ray photoelectron spectra of Ru3d for O2-annealed polycrystalline RuO₂, room temperature Ar⁺-sputtered RuO₂, and high-temperature (573 K) H₂-reduced RuO₂ are presented in Fig. 2. The corresponding O (1s) to Ru (3d) ratios are given in Table 1 (also shown is the effect of Ar⁺-sputtering on this ratio). The XPS Ru(3d5/2) is shown at 281.2 ± 0.1 eV with a spin orbit-splitting 3d5/2–3d3/2 of 4.1 ± 0.1 eV. This spectrum is very similar to that reported in Refs. (22, 23). These line positions are those of Ru⁴⁺ cations (22, 23). A component at ca. 282.8 eV is also seen. This contribution is assigned in Ref. (23) to unscreened Ru⁴⁺ cations by comparison with the binding energy of nonmetallic Ru⁴⁺ oxides. In other words, the line at 281.2 eV (in Fig. 2) is due to unscreened Ru⁴⁺ cations since RuO₂ is metallic (24). The full width at half maximum (FWHM) of the Ru(3d5/2) line of 2.0 eV is quite large, in particular if this value is compared to a line width of about 0.6 eV for a well-defined RuO₂(110) surface (see Section III.B.1). We interpret the large value for the FWHM of polycrystalline RuO₂(110) as originating from an inhomogeneous broadening due to the presence of several orientations of RuO₂ surfaces and the presence of defects. A clear shift is seen upon H₂ reduction (Fig. 2c) or Ar⁺-sputtering (Fig. 2b). The shift of 0.7 ± 0.1 eV (XPS Ru(3d5/2) = 280.5 eV) is identical whether the surface has been reduced with H₂ or Ar⁺-sputtered for 40 min. We should note that Ar⁺-sputtering preferentially removes oxygen from the RuO₂ surface. The line at 280.5 eV is probably showing a large contribution from Ru metal, since Ru metal has a binding energy of 280.0–280.3 eV (Table 1) and no other stable Ru cations with oxidation state lower than +4 are known to exist in the solid state. The O (1s) emission occurs at 529.7 eV, indicative of O anions. The tail of the O (1s) peak is most likely a contribution from surface hydroxyls at ca. 532 eV (25) (Fig. 3). Also shown in the figure is the O (1s) obtained after hydrogen reduction as well as after Ar⁺-sputtering. Table 1 shows that one indeed is removing O atoms by H₂ reduction, further confirming the XPS Ru(3d) results. However, the remaining presence of these XPS O (1s) lines indicates the presence of chemisorbed oxygen on and/or within the reduced material. This interpretation is supported by the observed O (1s) peak position at 530.5 eV, which is assigned to chemisorbed oxygen (Fig. 3, see Section III.B.1 for other details). We should emphasize that the bond energy of Ru–O in chemisorbed O on Ru metal is stronger by more than 1 eV than the corresponding bond of RuO₂ (9). In fact, this is why Ru metal is unusually nonreactive compared to other noble metals; once the surface is covered with O atoms, it becomes very difficult to remove them (1, 2, 26). One can measure the extent of reduction by the decrease of the O (1s) to Ru (3d) corrected peak area intensity ratios. This change can also be correlated to the FWHM of the Ru (3d) peaks since this latter decreased with increasing sputtering time. A similar trend is observed in Figs. 4 and 5: sputtering as a function of time (as well as H₂ reduction) does decrease the FWHM of Ru(3d5/2) peaks with concomitant lowering of the binding energy. Also shown is the decreasing of the O (1s)/Ru (3d) lines with...
<table>
<thead>
<tr>
<th>Material</th>
<th>XPS Ru (3d$_{5/2}$) FWHM (eV)</th>
<th>XPS O (1s) (eV)</th>
<th>O(1s)/Ru(3d)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/O Thin film</td>
<td>281.0</td>
<td>529.48</td>
<td>248.88</td>
<td>This work</td>
</tr>
<tr>
<td>Ru/O Powder</td>
<td>280.9</td>
<td>529.48</td>
<td>248.88</td>
<td></td>
</tr>
<tr>
<td>RuO$_2$(110)</td>
<td>280.7</td>
<td>529.48</td>
<td>248.88</td>
<td></td>
</tr>
<tr>
<td>RuO$_2$(100)</td>
<td>280.7</td>
<td>529.48</td>
<td>248.88</td>
<td></td>
</tr>
<tr>
<td>RuO$_2$ Polycryst</td>
<td>280.7</td>
<td>529.48</td>
<td>248.88</td>
<td></td>
</tr>
<tr>
<td>Ar$_2$C-sputtered RuO$_2$ Polycryst</td>
<td>280.9</td>
<td>530.7</td>
<td>249.9</td>
<td>0.75 This work</td>
</tr>
<tr>
<td></td>
<td>280.7</td>
<td>530.7</td>
<td>249.9</td>
<td>0.40 This work</td>
</tr>
<tr>
<td></td>
<td>280.6</td>
<td>530.7</td>
<td>249.9</td>
<td>0.40 This work</td>
</tr>
<tr>
<td>H$_2$-reduced RuO$_2$ Polycryst</td>
<td>280.5</td>
<td>530.4</td>
<td>249.9</td>
<td>0.31 This work</td>
</tr>
<tr>
<td>Ru Polycryst</td>
<td>280.2</td>
<td>530.4</td>
<td>249.9</td>
<td>0.31 This work</td>
</tr>
<tr>
<td>Ru(0001) Single crystal</td>
<td>279.8</td>
<td>0.37</td>
<td>271</td>
<td></td>
</tr>
<tr>
<td>Ru(0001)-(1£1)O</td>
<td>280.95</td>
<td>0.21</td>
<td>262</td>
<td></td>
</tr>
</tbody>
</table>

Increasing sputtering due to preferential oxygen removal as well as the 40-min. Ar$_2$C-sputtered samples might be larger than those expected from pure Ru metal. It does appear that H reduction is at least as good as if not more efficient in reducing RuO$_2$ than Ar$_2$C sputtering.

Because of the presence of chemisorbed oxygen (together with an energy resolution of > 1 eV), the FWHM and the position of the XPS Ru (3d$_{5/2}$) line of the hydrogen-reduced Ru$_2$O$_3$ (Fig. 10).
FIG. 4. XPS of the Ru(3d5/2) region of polycrystalline RuO$_2$ as a function of sputtering time with Ar ions; all other conditions are kept constant. (a) 5 min Ar$^+$-sputtered RuO$_2$, (b) 10 min Ar$^+$-sputtered RuO$_2$, (c) 40 min Ar$^+$-sputtered RuO$_2$, and (d) H$_2$-reduced RuO$_2$.

This is by no means universal, as H$_2$ reduction usually has a marginal effect when compared to Ar$^+$ sputtering for most oxide materials. For example, H$_2$ is thought to adsorb only on defect sites of TiO$_2$(110) surface, with an isosteric heat of adsorption of 83 kJ mol$^{-1}$ (29) while no evidence for its adsorption is found on the fully oxidized Ti foil (30). However, Ar-ion sputtering may reduce up to 75% of the Ti$^{4+}$ cations into Ti$^{x+}$($x < 4$) of single crystal or polycrystalline TiO$_2$ surfaces (31, 32).

III.A.3. Temperature-Programmed Reduction of RuO$_2$

Figure 7 displays two TPR profiles obtained by using sample weights of 102.4 mg and 26.6 mg. Calculating the constant $P$ defined as $P = \beta S_0/Fc_0$ according to Malet and Caballero (36) yields values of 9.8 and 2.5 K, respectively, where $\beta$ is the heating rate, $S_0$ is the amount of reducible species, and $Fc_0$ is the molar H$_2$ flow rate into the reactor. Values of $P$ lower than 20 K were found to be appropriate to obtain good peak resolution (36). Accordingly, a narrow TPR peak with a full width at half maximum of 20 K (solid curve) was obtained. The sharp onset of reduction below 390 K indicates an autocatalytic process triggered by the formation of metallic Ru nuclei providing atomic hydrogen. Both the peak position at 391 K and the low FWHM are in good agreement with the TPR results obtained by Hurst.
et al. (37). Decreasing $S_0$ by a factor of 4 yields an even higher resolution (dotted curve). This TPR profile consists of a very narrow peak at 388 K and a broader peak at 398 K. The latter may originate from an inhibiting influence of water on the reduction kinetics.

The degree of reduction was calculated based on the following equation:

$$\text{RuO}_2 + 2\text{H}_2 \rightarrow \text{Ru} + 2\text{H}_2\text{O}.$$  \[1\]

Averaging the amount of H$_2$ consumed in six TPR experiments yields a value of 99.7%, which indicates full reduction to metallic Ru within the experimental accuracy. The presence of polycrystalline metallic Ru at the end of the TPR was also confirmed by XRD.

III.A.4. Temperature-Programmed Reactions over RuO$_2$

Figure 8 shows TPD after methanol adsorption at room temperature over polycrystalline RuO$_2$. Formaldehyde ($m/e$ 29, 30), methyl formate ($m/e$ 60), CO ($m/e$ 28), CO$_2$ ($m/e$ 44), H$_2$ ($m/e$ 2), and water ($m/e$ 18) were observed, in addition to unreacted methanol ($m/e$ 31) (Table 2). All primary alcohols have their strongest signal at $31 m/e$ due to CH$_2$OH species. It is more accurate to consider the $m/e$ 31 signal for quantitative analysis rather than the parent molecule because of its high intensity. This is particularly important in the case of methanol when TPD is conducted at pressure above ca. $10^{-8}$ Torr because its parent molecule ($m/e$ 32) interferes with O$_2$ from the background. Quantitative analyses were computed following the methods described in Refs. (17, 18), where the major fragmentation patterns (up to 5) of each product were accounted for. Products desorbed in three temperature domains. The first (below 390 K) consisted of methanol, formaldehyde, methyl formate, H$_2$O, and H$_2$. As summarized in Table 2 these desorptions combined contributed 2.7% of the overall carbon products. In Fig. 8 H$_2$ is shown to desorb at a slightly higher temperature than formaldehyde (about 10 K).

Several runs were conducted addressing this particular observation. H$_2$ desorption temperature was seen either exactly at the formaldehyde peak temperature or shifted by up to 10 K higher (as seen in Fig. 8). The shift was not consistent from one run to the other. It is most likely that cooling the reactor under O$_2$ had an effect on the state of the RuO$_2$ surface. A stabilization effect due to surface oxygen on the recombinative desorption of H$_2$ where surface O atoms have indeed delayed D$_2$ desorption over U metal has been observed by other workers (38). Since the experiments were conducted over RuO$_2$ that has been cleaned with O$_2$ at 573 K and cooled under O$_2$ to 300 K before evacuation, it is not unreasonable to consider that some weakly held oxygen left on the surface retards the recombinative of H atoms.

The second desorption domain (380–520 K) mainly consisted of CO and CO$_2$ with some formaldehyde and H$_2$. This latter desorption contributed over 97% of the total carbon products. The third desorption domain (510–750 K) contained H$_2$O with some H$_2$. No carbon-containing products are observed in this temperature region with the probable exception of some formaldehyde.

Three main points are worth noting. (i) All adsorbed methanol (saturation coverage) has reacted, as evidenced by a desorption of only 1.7% of the initial amount (the surface was exposed to 18 $\times$ 10$^3$ torr of methanol prior to TPD). (ii) The total decomposition mainly gave CO$_2$ (a CO$_2$/CO of ca. 9), indicating that oxygen anions are easily removed from the surface. (iii) Some formaldehyde ($m/e$ 30) is left (0.44%) and some has reacted via Tishchenko reaction (ester formation) to give methyl formate (0.58%) (see Refs. 12 and 13 for more details on this reaction).

![FIG. 8. TPD after methanol adsorption at 300 K over polycrystalline RuO$_2$. RuO$_2$ has been O$_2$-annealed at 573 K (1 atm) and cooled under O$_2$ to 300 K.](image-url)
III.A.5. Temperature-Programmed Reactions over Reduced RuO₂

TPD measurements of methanol over H₂-reduced RuO₂ were also conducted. Considerable differences in the product distribution are observed (Fig. 9 and Table 3). First, all products desorbed at lower temperatures. Second, an early CO₂ desorption is clearly seen with a peak at 360 K. Both the 360 and 450 K desorption contributed 50% of the desorption products. CO desorption accompanied the low-temperature CO₂ peak and contributed ca. 11% of the carbon yield. Formaldehyde, which was observed in trace amounts on the stoichiometric surface, has increased severalfold, accounting for 20% of the overall products. Similarly, methyl formate desorption has increased ca. 20× and contributes ca. 11% of the desorption products. CO desorption accompanied the low-temperature CO₂ peak and contributed ca. 11% of the carbon yield. Formaldehyde, which was observed in trace amounts on the stoichiometric surface, has increased severalfold, accounting for 20% of the overall products. Similarly, methyl formate desorption has increased ca. 20× and contributes ca. 11% of the desorption products.

TABLE 3

<table>
<thead>
<tr>
<th>Reactant/product</th>
<th>Temperature (K)</th>
<th>Carbon yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol (m/e 31)</td>
<td>360</td>
<td>6.82</td>
</tr>
<tr>
<td>Formaldehyde (m/e 30)</td>
<td>360</td>
<td>20.63</td>
</tr>
<tr>
<td>Methyl formate (m/e 60)</td>
<td>360</td>
<td>11.25</td>
</tr>
<tr>
<td>CO₂ (m/e 44)</td>
<td>360 and 450</td>
<td>49.97</td>
</tr>
<tr>
<td>CO (m/e 28)</td>
<td>360 and 440</td>
<td>11.32</td>
</tr>
<tr>
<td>H₂ (m/e 2)</td>
<td>360</td>
<td>—</td>
</tr>
<tr>
<td>H₂O (m/e 18)</td>
<td>370</td>
<td>—</td>
</tr>
</tbody>
</table>

FIG. 9. TPD after methanol adsorption at 300 K over H₂-reduced RuO₂ (573 K, 1 atm).

Due to the high concentration of formaldehyde (Scheme B) because 2 mol of formaldehyde may react, giving 1 mol of methyl formate (Tishchenko reaction).

Scheme A

\[
\begin{align*}
\text{CH}_3\text{OH} + \text{O} & \rightarrow \text{CH}_2\text{O} \text{ (a)} + \text{OH} \text{ (a)} \quad \text{OH dissociation} \\
\text{CH}_3\text{O} \text{ (a)} & \rightarrow \text{CH}_2\text{O} \text{ (g)} + \text{H} \text{ (a)} \quad \text{Dehydrogenation} \\
\text{H} \text{ (a)} + \text{OH} \text{ (a)} & \rightarrow \text{H}_2\text{O} \text{ (g)} \quad \text{Water removal} \\
\text{CH}_2\text{O} \text{ (a) + 2O (g)} & \rightarrow \text{CO}_2 \text{ (g) + H}_2\text{O} \text{ (g)} \quad \text{Decomposition} \\
\text{CH}_2\text{O} + \text{O} & \rightarrow \text{CO} \text{ (g) + H}_2\text{O} \text{ (g)} \quad \text{Decomposition}
\end{align*}
\]

Scheme B

\[2\text{CH}_3\text{O} \text{ (a)} \rightarrow \text{H}_2\text{O(OCH}_3\text{ (g)} \quad [7]\]

Yields in Tables 2 and 3 are carbon-based and not molar-based. In other words about 1/3 of the formaldehyde left is forming methyl formate (assuming no other reaction of the latter).

III.B. UHV Experiments

III.B.1. X-Ray Photo Emission Data of RuO₂(110) Single Crystals

High-resolution core level shift (HRCLS) experiments of a well-defined RuO₂(110) surface in comparison with the Ru(0001)-(1×1)O were performed at the beamline I311 at MAXII in Lund, Sweden (39). The photon energies used were \(h\nu = 380\text{ eV} \) and \(680\text{ eV}\) for Ru(3d) and O(1s), respectively. The energy resolutions of the Ru(3d₅/₂) and O(1s) spectra were set to 80 MeV and 180 MeV, respectively (to be compared with the 1.1 eV in the polycrystalline experiments). The HRCLS spectra of Ru(3d₅/₂) and O(1s) were taken at 100 K and are depicted in Fig. 10. Upon oxidation of the Ru(0001)-(1×1)O surface clearly two well-resolved Ru(3d₅/₂) peaks are visible; these are assigned to bulk Ru(3d₅/₂) (280.12 eV, FWHM: 0.21 eV) and Ru coordinated to three oxygen atoms in the surface layer (281.05 eV, FWHM: 0.39 eV). The corresponding O(1s) photoemission line is at 530.07 eV (FWHM: 0.55 eV) (Fig. 10a; see also Table 1). \(\Delta_1 = (\text{O(1s)} - \text{Ru(3d₅/₂)})\) (where Ru(3d₅/₂) is at 280.12 eV) is equal to 249.95 eV. This value is very close to that obtained for polycrystalline oxide that has been Ar-ion sputtered or etched in Section II, as well as in Refs. (3, 21, 39), RuO₂(110).
O(1s) (from 530.07 to 529.48 eV) together with that of the main Ru atoms to higher binding energy (from 280.12 to 280.8 eV) contributing to $\Delta_1 = (O(1s) - Ru(3d_{5/2})) = 248.88$ eV is very close to that observed on polycrystalline materials (Table 1).

III.B.2. CO and O$_2$ Reactions over RuO$_2$(110) Single Crystal

i. LEED spot intensity measurements. Oxygen exposure to the clean RuO$_2$(110) surface leads to the stabilization of a weakly held oxygen species that desorbs with a peak at 420 K (see Fig. 1). This weakly held oxygen has been shown to adsorb over cus-Ru atoms (9). The weakly held oxygen serves as a precursor state to heal the missing bridging oxygen atoms of the RuO$_2$(110) surface. This behavior is clarified in Fig. 11, in which the spot intensity of a RuO$_2$(110) related LEED beam is shown as a function of the CO exposure (as well as O$_2$ exposure) at a sample temperature of 520 K. With increasing CO exposure the LEED intensity decreased; a change in slope is observed at about 90 L. Oxygen postexposure was able to recover a large part of the original LEED intensity signal. A saturation is reached after an O$_2$ exposure of 80 L. The main point to make from this figure is that the oxidation-reduction cycle of this oxide single crystal surface can be conducted and monitored under mild conditions (low temperatures and relatively low exposures). To completely restore the LEED signal a more prolonged exposure to O$_2$ or several O$_2$-TPD runs, as shown in Fig. 1, are required.

ii. Temperature-programmed reaction of CO over RuO$_2$(110). Successive CO-TPD experiments (after CO exposure at 170 K) were conducted over stoichiometric RuO$_2$(110)—as the starting material, but without regeneration with O$_2$ molecules in between runs. The amount of CO$_2$ produced decreased with successive runs upon a cumulative exposure of 2.5 L, down to below the detection limits of the QMS (Fig. 12a). This is due to removal of available surface oxygen (most likely the two-fold bridging oxygen atoms; see Section IV). This behavior is in fact observed only if the ramping stops just after CO and CO$_2$ desorptions have taken place (450 K). In contrast, if CO-TPD runs are conducted up to elevated
temperatures, a different TPD profile is observed (Fig. 12b). In this latter situation postdosing of CO (at 293 K) results in a gradual increase of peak areas of desorbed CO$_2$. Saturation is achieved by ca. 570 K. This latter observation provides clear evidence of self-regeneration of the active sites due to a temperature effect. Comparison with STM pictures, collected under similar conditions (3), indicates that this behavior may be associated with oxygen migration from the threefold sites to the twofold (bridging) sites (see Section IV). In other words, this behavior is not necessarily due to bulk to surface diffusion of lattice oxygen.

iii. Temperature-programmed reaction of methanol over RuO$_2$(110). In Fig. 13 we present the thermal desorption data after the clean RuO$_2$(110) surface has been exposed to 2.4 L methanol at 200 K. The main product (ca. 70%) leaving the surface after a rise in the sample temperature is CO$_2$. The main peak appears at ca. 480 K and is accompanied by a small peak at 380 K. These peak positions compare favorably with those of the high-pressure experiments (Fig. 8). CO desorption took place at the same temperatures (380 and 480 K) but with a different distribution. The low-temperature desorption was about twice as large as the high-temperature desorption (see Table 4 for quantitative analysis). The similarity with Fig. 8 is easily noticed. Methanol desorption takes place at 380 K. Most of the formaldehyde leaves the surface at 380 K (a large peak) although a small desorption at 500 K is also observed. Both methanol and formaldehyde desorptions appear at the same position as those observed in the high-pressure work (compare Figs. 8 and 13).

IV. DISCUSSION

Several main points resulting from the above study are worth mentioning.

1. Ru cations in polycrystalline RuO$_2$ can be easily reduced (either by H$_2$ or upon Ar$^+$ sputtering) as evidenced by a shift of the XPS Ru(3d$^5$=2) line by 0.7 eV (from 281.2 to 280.5 eV) (Fig. 2). This shift is consistent with that observed by HRCLS from model surfaces of Ru(0001)–(1$\times$1)O and RuO$_2$(110) single crystals (from 281.05 to 280.05 eV) (Fig. 10).

2. One can measure the shift as a $\Delta$, where $\Delta = XPS O(1s) − XPS Ru(3d_{5/2})$. $\Delta$ was equal to 248.88 and 248.5 eV for RuO$_2$ single crystal and polycrystalline materials, respectively. On the reduced (either by H$_2$ or by Ar$^+$ bombardment) RuO$_2$ polycrystalline surface $\Delta = 249.9$ eV, which is identical to that of Ru(0001)–(1$\times$1)O single crystal ($\Delta = 249.95$ eV) (Table 1).

3. XRD (Fig. 6) as well as TPR (Fig. 7) has indicated that H$_2$-reduced polycrystalline RuO$_2$ has been bulk transformed to Ru metal. Although the O(1s) to Ru(3d) peak-area ratios decreased dramatically (Figs. 4 and 5), the

| Reactant/product Temperature (K) Carbon yield (%) |
|-----------------------------------------------|------------------|
| CH$_3$OH ($m/e$ 31) 390 13.0 |
| HCHO ($m/e$ 30) 390 24.2 |
| CO$_2$ ($m/e$ 44) 385 13.0 485 27.2 |
| CO ($m/e$ 28) 385 15.4 485 7.2 |
| CO$_2$/CO 1.78 |
| CO$_2$+HCHO 64.4 |

FIG. 13. Successive TPD after CO adsorption over RuO$_2$(110) single crystal surface without (a) and with (b) surface regeneration; regeneration was conducted by heating the surface to the indicated temperature.
TABLE 5
Formaldehyde Yield during Methanol-TPD over Several Oxide Single Crystals and Computed Activation Energies of Formaldehyde Desorption

<table>
<thead>
<tr>
<th>Oxide single crystals</th>
<th>Yield (%)</th>
<th>Peak temperature (K)</th>
<th>Activation energy (kcal/mol)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutile TiO$_2$(110)$^a$</td>
<td>0—45</td>
<td>1–2</td>
<td>520</td>
<td>32 (0.03–0.06)$^r$</td>
</tr>
<tr>
<td>Rutile TiO$_2$(001)-f(011)</td>
<td>0—460</td>
<td>4</td>
<td>640</td>
<td>40 (0.1)</td>
</tr>
<tr>
<td>Wurtzite ZnO(0001)–Zn$^d$</td>
<td>1–25</td>
<td>40</td>
<td>28 (0.36–0.72)</td>
<td>42</td>
</tr>
<tr>
<td>Rutile RuO$_2$(110)$^c$</td>
<td>0—10–20</td>
<td>15</td>
<td>450</td>
<td>28 (0.54)</td>
</tr>
<tr>
<td>Rutile RuO$_2$(111)$^c$</td>
<td>24</td>
<td>30</td>
<td>24 (1)</td>
<td>This work</td>
</tr>
</tbody>
</table>

$^a$ Molecular adsorption at room temperature, UPS data; no other products were observed.

$^b$ Other products included CH$_4$ and CO.

$^c$ Dissociative adsorption, XPS data; no other products were observed.

$^d$ Peak areas and yield were computed from Fig. 1 in Ref. 40.

$^r$ Given value = 11%. Variations from run to run put a yield value between 10 and 20% (42).

$^e$ Estimated by Redhead analysis, assuming first-order pre-exponential factor (10$^{13}$ s$^{-1}$) (49).

$^f$ Yield (%)/activation energy (kcal/mol).

The residual presence of O atoms at binding energy higher than that of O(1s) in RuO$_2$, together with the absence of the RuO$_2$ phase in XRD, suggests the formation of some dissolved or chemisorbed oxygen on metallic Ru. The shift in the XPS O(1s) peak position to higher binding energy (Fig. 3 and Table 1) is also indicative of chemisorbed oxygen atoms.

4. The surface of RuO$_2$(110) could be regenerated by dosing O$_2$ molecules (<1 L, direct dosing) at room temperature (Fig. 1).

5. The self-regeneration of the active centers for CO oxidation to CO$_2$ was clearly shown to occur when one heats the RuO$_2$(110) to 570 K and above.

6. Both polycrystalline RuO$_2$ and RuO$_2$(110) surfaces behaved similarly toward methanol oxidation to formaldehyde, as well as toward its total decomposition to CO and CO$_2$ (Figs. 8 and 13).

In addition to the above six points, results from previous and parallel works (1–3, 7, 8) have indicated that CO adsorption occurs preferentially on cus-Ru (DFT calculation (7, 8), STM (3)). Similarly, LEED-I-V analyses have suggested that methanol adsorption occurs also on these same sites (8).

Points 1 to 4 indicate one single conclusion. It is a simple task to make reduction-oxidation cycles on RuO$_2$ single crystal and polycrystalline surfaces using H$_2$ or CO as reducing agents and O$_2$ as the oxidizing agent.

RuO$_2$(110) single crystal is unique for its activity toward CO to CO$_2$ and as such no comparison can be made to other oxides. However, its reactivity toward methanol oxidation to formaldehyde can be compared to that of other oxides such as ZnO(0001)–Zn (40), TiO$_2$(001)-(011) facetted (41), SnO$_2$(110) (42), ZrO$_2$(110) (43), and CeO$_2$(111) (44) single crystals. TiO$_2$(110) (45), MgO(100) (46), and ZrO$_2$(100) (43) single crystals showed no activity toward methanol oxidation to formaldehyde. Interestingly all these oxide single crystals have surface cations with at least one coordinative unsaturation. Table 5 shows the TPD yield, the peak temperature, and a computed activation energy of formaldehyde desorption for these oxides together with those of RuO$_2$(110) single crystal. RuO$_2$ is indeed more active than the other oxides. One may estimate the efficiency of the reaction by dividing the reaction yield (%) by the activation energy (or peak temperature). The higher the number, the more active the surface. These numbers were found as low as 0.03 mol/kcal for ZnO(0001)–Zn and rose to 1 mol/kcal for RuO$_2$(110) single crystal. Equally important, the other two rutile oxides with a (110) surface orientation are not active (see also Table 5). In other words, the coordinative unsaturation is not the sole requirement for making the oxidation. Other surface properties enter into consideration and these are discussed below.

We have asked three questions in the introduction and we attempt to answer them with the help of this study below.

Since RuO$_2$(110) is very active toward adsorption as well as oxidation reactions, the difference from the other oxides must lie somewhere else. It has been demonstrated that CO oxidation obeys the Mars-van Krevelen mechanism (3), where the undercoordinated surface oxygen anions (bridging oxygen anions) are consumed as a result of their reaction with adsorbed CO making CO$_2$. The surface defects created
that way are regenerated by gas-phase oxygen adsorption. In other words, there are at least three requirements for the reaction to occur.

(a) An active lattice oxygen must be available to react with adsorbed CO (such as the undercoordinated bridging and terminal bonded oxygen atoms).
(b) Strong adsorption sites for the reactant must be present.
(c) There must be an efficient dissociative adsorption of O$_2$ molecules to regenerate lattice oxygen ions.

Requirement (a) has been clearly shown in this study by the following:

(i) Adsorption of CO on RuO$_2$(110) single crystal gives large amounts of CO$_2$. This amount decreases with successive runs (on the nonregenerated surface) until its disappearance. Yet, it can be easily switched back by simply flashing the surface to 570 K (lattice oxygen migration to the active sites) (Fig. 13).
(ii) Comparing the methanol TPD runs over the stoichiometric and the H$_2$-reduced polycrystalline RuO$_2$, we observe that the amount of CO$_2$ decreased by almost 50% and that of formaldehyde (the partial oxidation product) increased to 20% of the product yield (Table 3).

Requirement (b) is indeed fulfilled. As mentioned in the introduction, the adsorption energy of CO over cus-Ru in the rutile RuO$_2$(110) structure (1.2 eV (3)) is ca. 4 and 5 times stronger than the corresponding adsorption over custrTi of TiO$_2$(110) or cus-Sn of SnO$_2$(110), respectively. A weak adsorption will result in an easy displacement of the reactant by other reactants/products (such as water) and the surface becomes nonreactive, particularly if the oxidation process is to occur at low temperatures. Requirement (c) is also met on RuO$_2$. Dosing O$_2$ molecules followed by flashing the surface to ca. 600 K (to remove on-top oxygen) over RuO$_2$(110) single crystal (Fig. 1) fully restored the surface. This is also evidenced by LEED spot intensity measurements (Fig. 11).

One of the intriguing results of this present study is that temperature-programmed reactions under UHV (single crystal) and high-pressure conditions (polycrystalline samples) are virtually identical. This also means that the reaction pathways are very much alike and therefore the active centers on RuO$_2$ are the same. Moreover, we also know that the efficiency for CO oxidation does not depend very much on the orientation of RuO$_2$ (47), at least not when we compare the (110), (100), and (101) orientations—all three surfaces contain cus-Ru. We conclude from this observation that the presence of cus-Ru atoms is an important requirement for the high activity of RuO$_2$. The (110), (100), and (101) surfaces of RuO$_2$ are low-energy surfaces that should equally be the prevailing orientations found on polycrystalline RuO$_2$.

The binding energies of bridging O and on-top O were computed to be 4.6 and 3.1 eV, respectively (values are given with respect to neutral atomic oxygen in the gas phase (9)). Therefore one would expect that the CO oxidation reaction would start by consuming the on-top O species first and then the bridging O species. This has been shown in recent HREELS experiments (48). It was observed that the intensity of on-top O species has decreased with CO exposure at room temperature (i.e., reacted with CO to give CO$_2$). Once all on-top O atoms have been removed, the intensity of the signal from bridging O atoms decreased. When all the available bridging oxygen atoms were consumed (complete disappearance of their signal), the CO oxidation reaction stopped. This result can be compared to those of Fig. 13, where CO oxidation stops when the available surface oxygen atoms are consumed.

In summary, this work has shown that detailed analysis of a well-defined surface can shed light on a complex reaction such as CO or methanol oxidation, over a polycrystalline oxide. The fact that RuO$_2$ is metallic, and thus allows extensive LEED and electron spectroscopy studies, together with its unusually high activity toward oxygen and CO adsorptions and reactions has been of tremendous help in comparing the activity of a well-defined surface of RuO$_2$(110) to that of the polycrystalline material.

**REFERENCES**

38. Lloyd, J. A., Mann, W. L., and Paffett, M. T., manuscript in review.