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# Surface reduction of ruthenium compounds with long exposure to an X-ray beam in photoelectron spectroscopy

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## Abstract

The reduction of Ru at the surface of commercial  $\text{RuCl}_3$  and  $\text{RuO}_2$  has been observed during XPS analysis. The experiments have been performed with either a non-monochromatized ( $\text{Mg K}_\alpha$ ) or a monochromatized ( $\text{Al K}_\alpha$ ) X-ray beam. Ruthenium reduction is enhanced by increasing the X-ray dose, but the residual pressure exerts only a weak influence. The initial composition of commercial ruthenium (III) chloride hydrate is a complex mixture of chloro or chlorohydroxo species rather than pure  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ .  $\text{RuCl}_3$  is not suitable as a reference compound for ruthenium chloride compounds in XPS analysis, because it contains mainly Ru(IV) which is reduced under X-ray. A similar reduction occurs at the surface of  $\text{RuO}_2$  samples (by reduction of  $\text{RuO}_3$  layers), and on the adventitious carbon. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Carbon; Reduction;  $\text{RuO}_3$ ; Ruthenium; XPS

## 1. Introduction

The literature is relatively poor in reliable reference values of the photoelectron binding energy for ruthenium compounds. The situation is particularly critical for the tervalent state; in order to obtain binding energy references to be compared with those of the literature, a sample of Ru(III) chloride hydrate has been analysed by XPS. Folkesson [1] reported a position of 281.8 eV for the  $\text{Ru 3d}_{5/2}$  peak in  $\text{RuCl}_3$  and Ohyoshi et al. [2] a value of  $282.1 \pm 0.4$  eV in  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ . In our case, we found a value of 282.8 eV in a first analysis for commercial Ru(III) chloride.

However, to improve the signal-to-noise ratio, a long X-ray irradiation time was requested. The analyses were first performed on a spectrometer equipped with an  $\text{Al K}_\alpha$  monochromatized X-ray anode. After a couple of hours, the Ru 3d doublet ( $\text{Ru 3d}_{5/2}$ – $\text{3d}_{3/2}$ ) was shifted slightly with respect to the  $\underline{\text{C}}$ –(C,H) main component of the C 1s peak. Another sample was analysed for comparison on a spectrometer equipped with a  $\text{Mg K}_\alpha$  non-monochromatized X-ray anode. In order to extend the investigation of these effects to other ruthenium compounds, ruthenium dioxide was also analysed.

Reduction or degradation occurring during X-ray photoelectron spectroscopy analyses has been reported in the literature. Wallbank et al. [3] noticed that the extent of Cu(II) reduction in Cu(II) halides and Fe(III) or Co(III) in potassium hexacyanoferrate

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(III) or -cobaltate(III), respectively, does not depend on temperature, vacuum pressure or X-ray flux, but is only a function of the integrated X-ray dose. In this case, the reduction of Fe(III) is almost complete after 17 h. Batista-Leal et al. [4] reported reduction of  $\text{AuCl}_3$ , but pointed out that maintaining the sample at low temperature decreases the reduction rate. Reduction also occurs after heating several metals and oxides [5]. According to the same authors, reduction of adventitious carbon can also occur (shift of about 0.4–0.6 eV for the C 1s peak) after heating in high vacuum. In the case of organic films, Graham et al. [6] stated that X-ray photons are not the main source of damage, but the photo-induced electrons. Direct X-ray irradiation is thought to induce no more than 5–10% of the observed damage.

In the case of damage induced in the Ce 3d core level of ceria samples, El Fallah et al. [7] attributed the energy change in the oxidation state to photo-stimulated oxygen desorption. However, owing to the partially reversible character of this effect and to the main modifications of the Ce 3d final states obtained, they proposed alternative pathways based on intra-atomic rearrangements or oxygen migration towards interstitial sites of the fluorite lattice. To prevent reduction, Iijima et al. [8] recommended the use of a monochromatized X-ray beam (80–90% less reduction). This reduction would be due to slow electrons generated from the X-ray window, which is very close to the sample with non-monochromatized X-rays anodes, and to photoelectrons emitted from the sample surface by X-ray irradiation. More recently, Vreugdenhil et al. [9] reported the chemical transformation of up to one-third of the Pd (from  $\text{PdCl}_2$ /polyvinylpyrrolidone) during XPS analysis.

To our knowledge, there has been no similar report on reduction processes involving high valency states of ruthenium under such conditions.

## 2. Experimental

### 2.1. Materials

$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  and  $\text{RuO}_2$  were provided by Aldrich.  $\text{RuCl}_3$  (ruthenium (III) chloride hydrate) is highly hygroscopic and must be stored under dry air; the

stoichiometry  $\text{RuCl}_3 \cdot 1.5\text{H}_2\text{O}$  was suggested by thermogravimetric analysis. X-ray fluorescence analysis of this sample showed that the atomic ratio Ru/Cl is close to 1/3. The main contaminants were found to be Ca, P, S (<0.5%), and Si (<0.2%).  $\text{RuO}_2 \cdot n\text{H}_2\text{O}$  (ruthenium (IV) oxide hydrate) contains 60% ruthenium (according to the supplier and thermogravimetric analysis).

### 2.2. Instrumentation

The XPS measurements were performed on two different spectrometers.

The SSI X-Probe (SSX-100/206) photoelectron spectrometer from Surface Science Instruments is equipped with a monochromatized aluminium X-ray source (1486.6 eV) focused onto the sample. The anode is powered at 10 kV and 12 mA, the irradiated zone corresponding to the analysed area is an elliptic spot of smallest width 600  $\mu\text{m}$  (area of about 0.5  $\text{mm}^2$ ). In this system, the Bremsstrahlung X-ray radiation is removed by the monochromator. The constant pass energy of the analyser was set at 50 eV, and an electron flood gun (set at 6 eV) with a Ni grid placed 3 mm above the sample was used to over-compensate for sample surface charging during the measurements. Under these conditions, the energy resolution of the spectrometer, as expressed by the full width at half maximum (FWHM) of the Au  $4f_{7/2}$  photopeak, was about 1.1 eV.

The Vacuum Generators (VG) ESCA 3 Mk II spectrometer is equipped with a non-monochromatized Mg anode (1253.6 eV) and a thin Al window. The analysed area, smaller than the irradiated zone, is about 50  $\text{mm}^2$ . The Mg anode is powered at 14 kV and 20 mA. The constant pass energy in the hemispherical analyser of 50 eV and the slit width of 4 mm gave an energy resolution, expressed by the FWHM of the Au  $4f_{7/2}$  peak, of about 2.0 eV.

The powder specimens were pressed in stainless steel holders of 4 and 8 mm diameter for the SSI and the VG spectrometer, respectively, and then introduced into the preparation chamber without previous thermal treatment. They were outgassed overnight and analysed at room temperature under a residual pressure of  $\approx 1 \times 10^{-7}$  and  $1\text{--}5 \times 10^{-7}$  Pa for the SSI and VG spectrometer, respectively. The angle between the normal to the sample surface and the

electron detection direction was  $55^\circ$  and  $45^\circ$  for the SSI and VG spectrometer, respectively.

The use of the  $\underline{\text{C}}-(\text{C,H})$  component of the C 1s (fixed at 284.8 eV) peak of adventitious contamination carbon for charge correction is complicated by the overlap with the Ru 3d doublet, and by the complexity of the C 1s peak itself, which contains a  $\underline{\text{C}}-(\text{C,H})/\underline{\text{C}}-\text{O}/\underline{\text{C}}=\text{O}/\text{O}-\underline{\text{C}}=\text{O}$  ratio of about 10:3:1:1, as determined by Gerin et al. [10]. Nevertheless, the main component ( $\underline{\text{C}}-(\text{C,H})$ ) of the C1s peak is sufficiently well defined to be taken as a reference to calculate the binding energy. The following sequence of spectra was recorded: (i) for  $\text{RuCl}_3$ : C 1s–Ru 3d, Ru 3p, Cl 2p, C 1s–Ru 3d; (ii) for  $\text{RuO}_2$ : C 1s–Ru 3d, Ru  $3p_{3/2}$ , O 1s, C 1s–Ru 3d. Sequences were recorded without time interval during the first hour of analysis. After 2–3 h, recording was performed at different time intervals, with an average of five sequences per day. The sample was permanently bombarded by X-rays. The total analysis time on the VG spectrometer was 79 h.

Peak decomposition of both the SSI and VG spectra was performed using the ESCA 8.3 D software provided by the SSI manufacturer with constraints described below.

The atomic concentration ratios were calculated from normalized peak areas corrected by experimental [11] and manufacturer sensitivity factors for the VG and SSI spectrometer, respectively.

### 3. Results and discussion

The amount of contamination in the analysis chamber due to the pumping system is lower in the SSI (cryogenic pump) than in the VG spectrometer (oil diffusion pump), which explains why the atomic percentage of the corresponding adventitious carbon is lower in the former.

Fig. 1 shows the C 1s–Ru 3d band obtained for  $\text{RuCl}_3$  on the SSI. After 5 h exposure to X-rays, a small shift ( $\approx 0.4$  eV) of the Ru 3d doublet towards lower binding energy with respect to the  $\underline{\text{C}}-(\text{C,H})$  component of the C 1s peak is observed, which could be due to reduction of ruthenium.

The effect of flood gun bombardment on the same SSI spectrometer (energy 10 eV and current of about 50  $\mu\text{A}$ ) was tested on vanadium oxynitride during an

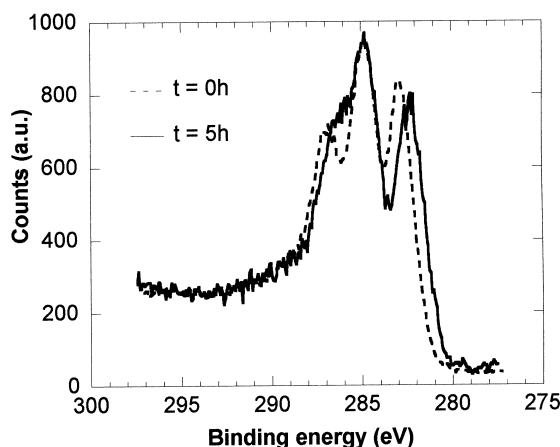


Fig. 1. Reduction of Ru(III) chloride hydrate on the SSI after 5 h of X-ray irradiation.

exposure time of up to 7 h. No vanadium reduction was observed [12]. This was confirmed on copper oxide (T. Curtin, personal communication, 1995). The main source of heating in the SSI spectrometer is the flood gun filament. The temperature at the surface of the sample was not measured, but was roughly evaluated to be around  $40\text{--}50^\circ\text{C}$  after a long exposure time. This effect will be evaluated, but the above-mentioned analyses performed on vanadium oxynitride and copper oxide (under the same conditions) seem to demonstrate that the combined effects of flood gun bombardment and temperature elevation do not provoke any reduction of the sample.

The influence of the vacuum was tested on  $\text{RuCl}_3$  in the VG spectrometer. For this, Ru 3d–C 1s spectra were recorded after about 15 h under vacuum, and again after 79 h under vacuum without bombardment with X-rays in the mean time. Fig. 2 shows the overlapped corresponding peaks. Normalization was made at the intensity of the Ru  $3d_{5/2}$  peak because, during the analysis, the surface was progressively covered by adventitious carbon. The effect of this contamination on the spectrum is enhancement of the C 1s peak intensity and a decrease of the Ru  $3d_{5/2}$  peak intensity. There is only a very small shift (0.2 eV) of the Ru  $3d_{5/2}$  and Ru  $3d_{3/2}$  components with respect to  $\underline{\text{C}}-(\text{C,H})$ , but this last peak (the central one) is more intense due to the increase of sample contamination as a function of the residence time in

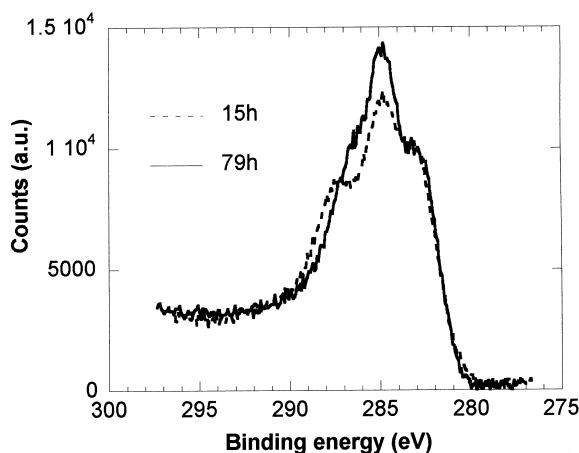


Fig. 2. Influence of the vacuum on Ru(III) chloride hydrate after 15 and 79 h (VG spectrometer).

the analysis chamber of this spectrometer. This small shift (0.2 eV) is similar to the instrumental error.

The reduction caused by electrons ejected from the thin Al window which the X-ray beam passes through, as shown by Iijima et al. [8], must be taken into account in the VG spectrometer, where the sample is very close ( $\approx 1$  cm) to the Al window, but not in the SSI spectrometer, where the distance between the sample and the X-ray window is much larger ( $\approx 20$  cm).

The effects of X-ray bombardment on  $\text{RuCl}_3$  were examined in more detail in the VG spectrometer. Fig. 3a–c display the C 1s–Ru 3d band, respectively, at the beginning ( $t=0$ ), after 20 h ( $t=20$ ) and after 79 h ( $t=79$ ) X-ray exposure. A clear shift ( $\approx 1.2$  eV) of the Ru 3d doublet towards lower binding energies with respect of the  $\text{C}-(\text{C,H})$  reference component (main line) is observed (between the start and the end of the experiment). This shift, attributed to a reduction effect, is confirmed on the Ru  $3p_{3/2}$  peak. Reduction seems to start after about 70 min for the VG spectrometer, and is completed after 35 h (no more peak shift in the band observed). A tentative peak decomposition of the C 1s–Ru 3d band obtained with the VG instrument was performed by fixing the following constraints: the binding energy difference between Ru  $3d_{5/2}$  and Ru  $3d_{3/2}$  was fixed at 4.1 eV and the Ru  $3d_{5/2}$ –Ru  $3d_{3/2}$  area ratio was fixed at 1.5 [13]. In order to “fill in” the rest of the band, peaks attributed to carbon bound to oxygen

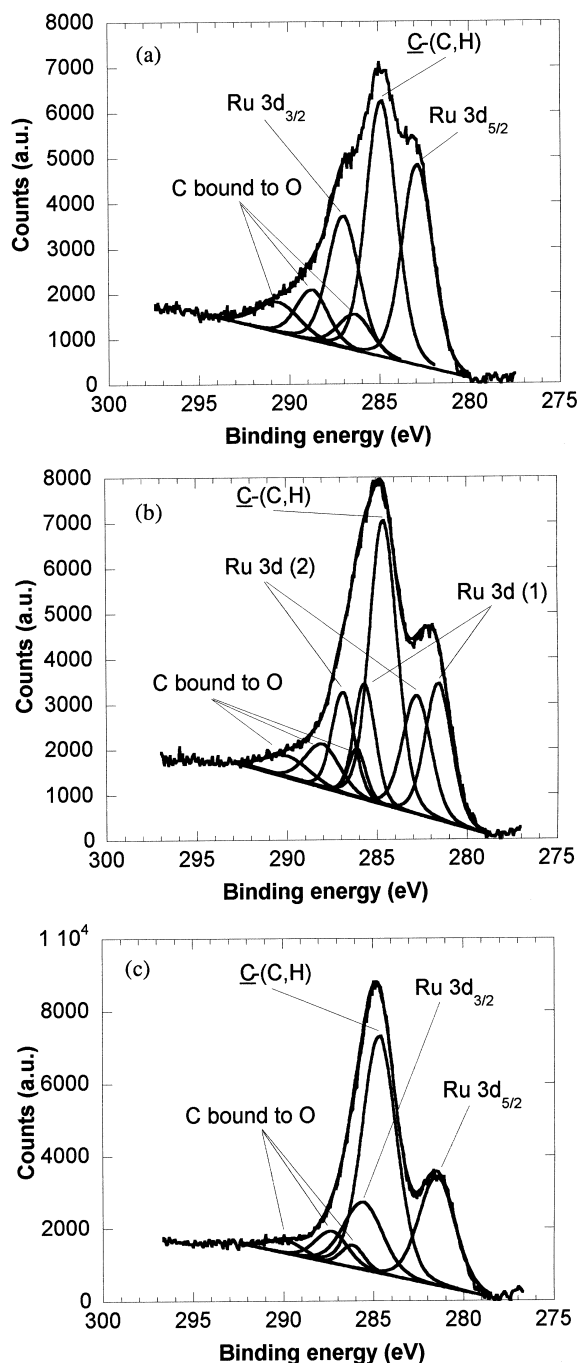


Fig. 3. C 1s–Ru 3d band in Ru(III) chloride hydrate exposed to X-rays for: (a)  $t=0$  h, (b)  $t=20$  h, (c)  $t=79$  h (VG spectrometer).

( $\underline{\text{C}}-\text{O}$ ,  $\underline{\text{C}}=\text{O}$  and  $\text{O}-\underline{\text{C}}=\text{O}$ ) were placed on the higher binding energy side of the C 1s peak [10]. Half widths between 2.0 and 2.1 were observed for both Ru 3d<sub>5/2</sub> and  $\underline{\text{C}}-(\text{C}, \text{H})$  peaks. For the carbon bound to oxygen, the half widths are larger, but do not exceed 2.6 eV. The peak shape is set at 80% Gaussian/20% Lorentzian, with a linear baseline. After peak decomposition, the binding energy of the  $\underline{\text{C}}-(\text{C}, \text{H})$  component is fixed at 284.8 eV exactly and the binding energies of the other components are recalculated thereafter.

A peak decomposition was performed at the start of the experiment ( $t=0$ , Fig. 3a) and at the end (79 h under X-ray irradiation, Fig. 3c), assuming that only one species of ruthenium was present in each case. At intermediate times, the band is composed of two Ru 3d doublets corresponding to two different oxidation states. A decomposition of the photoelectron spectrum obtained after 20 h under X-ray irradiation is also illustrated (Fig. 3b).

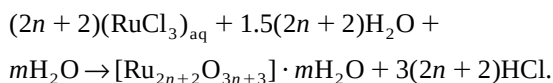
Table 1 shows the binding energies for C 1s, Ru 3d<sub>5/2</sub>, Ru 3p<sub>3/2</sub> and Cl 2p; the Ru/Cl atomic ratios measured at the surface for the three exposure times, calculated from Cl 2p and Ru 3d<sub>5/2</sub> or Ru 3p<sub>3/2</sub> peaks, respectively, are also given. A relatively good fit was obtained in the three cases. However, it is necessary to keep in mind that more than one single solution is possible, especially for “intermediate” spectra.

Between the initial ( $t=0$ ) and the final ( $t=79$  h) analysis, the energy shift of the Ru 3d<sub>5/2</sub> peak was 1.2 eV, and was confirmed by an analogous shift of the Ru 3p peak.

The initial value of the Ru 3d<sub>5/2</sub> binding energy, at 282.8 eV, was significantly higher than the values given by Folkesson [1] at 281.8 eV (the metal

chloride was of lower purity) and by Ohyoshi [2] at 282.1 eV ( $\pm 0.4$  eV). In contrast, at the end of the analysis, the Ru 3d<sub>5/2</sub> binding energy (281.6 eV) was close to the values given in the literature. We consequently assume that we were dealing with two different compounds: one highly oxidised Ru species (Ru 3d<sub>5/2</sub> at 282.8 eV), characterized by a high binding energy value, and a less oxidised species (Ru 3d<sub>5/2</sub> at 281.6 eV). The question arises, therefore, as to whether the initial or the final photoelectron spectrum corresponds to stoichiometrically pure RuCl<sub>3</sub>.

Table 1 gives the Ru/Cl ratio at the surface for the three exposure times, calculated from the Cl 2p and Ru 3d<sub>5/2</sub> or Ru 3p<sub>3/2</sub> peaks, respectively. This ratio is lower than the stoichiometric ratio (0.33), particularly at  $t=0$ . The atomic ratios calculated from the Ru 3d<sub>5/2</sub> peaks are slightly different from those calculated from the Ru 3p<sub>3/2</sub> peak because the former is more dependent on the peak decomposition process. These results suggest that, at the beginning of X-ray exposure, the sample surface does not correspond to RuCl<sub>3</sub>, but to another species. Because it is reasonable to assume a six-fold coordination around the Ru atom, the surface composition of the starting material can be formulated as Ru<sup>(III+x+y)</sup>Cl<sub>3+y</sub>(H<sub>2</sub>O)<sub>3-x-y</sub>(OH)<sub>x</sub>, with an  $x+y$  value between 1 and 2. This would merely be the result of surface reactions involving atmospheric water. Following Tyrlik et al. [14], commercial ruthenium chloride is not an homogeneous substance and the major hydrolysis pathway can be written as



The presence of adsorbed HCl would explain the

Table 1  
Binding energy (eV) of the different peaks and atomic ratios as a function of X-ray exposure time

| Time | C 1s      | Ru 3d <sub>5/2</sub> | Ru 3p <sub>3/2</sub> | Cl 2p | Ru/Cl       |             |
|------|-----------|----------------------|----------------------|-------|-------------|-------------|
| (h)  | [C–(C,H)] |                      |                      |       | From Ru 3d5 | From Ru 3p3 |
| 0    | 284.8     | 282.8                | 464.4                | 198.6 | 0.21        | 0.20        |
| 20   | 284.8     | 283.0 <sup>a</sup>   | 464.8 <sup>a</sup>   | 198.7 | 0.27        | 0.23        |
|      |           | 281.8 <sup>b</sup>   | 463.6 <sup>b</sup>   |       |             |             |
| 79   | 284.8     | 281.6                | 463.2                | 198.4 | 0.27        | 0.24        |

<sup>a</sup> Corresponds to the “higher oxidised state” component of ruthenium.

<sup>b</sup> Corresponds to the “less oxidised state” component of ruthenium.

surface enrichment in Cl. This process also causes some acidity, which can be detected by the corrosion effect developed on the stainless steel holders when they are in prolonged contact with air. Moreover, if  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  is heated under air, oxidation occurs and  $\text{RuO}_2$  is the resulting product [15].

According to these results and to other sources [14,16] the surface of commercial ruthenium (III) chloride hydrate could not correspond to the stoichiometry  $\text{Ru}^{\text{III}}\text{Cl}_3$ , but rather to  $\text{Ru}^{(\text{III}+x+y)}\text{Cl}_{3+y}(\text{H}_2\text{O})_{3-x-y}(\text{OH})_x$ , in fact a complex mixture of chloro and chlorohydroxo species, many of which are polymeric and contain Ru(IV) [16]. The reduction could occur by hydroxyl desorption leading to the formation of  $\text{Ru}^{\text{III}}\text{Cl}_3$ . The justification for this process could be verified by analysis of the O 1s photopeak. Unfortunately, the oxygen component also contains carbon-bound species, and this carbon is also reduced during irradiation (see below), thereby presenting difficulties to quantify each component in a proper way.

Moreover, after 79 h irradiation under vacuum, if the sample is exposed to air (25°C, 1 atm) for 5 min, and then introduced again under vacuum for XPS analysis, a small shift (0.4 eV) of the Ru 3d doublet towards higher binding energy is again observed, corresponding to a partial reoxidation of ruthenium. This is also the case for non-irradiated samples stored under vacuum for 79 h without X-ray bombardment. This could be due to the high hygroscopicity of the powders. Adsorbed water can induce a slight reoxidation [3], and the starting material ( $\text{Ru}^{(\text{III}+x+y)}\text{Cl}_{3+y}(\text{H}_2\text{O})_{3-x-y}(\text{OH})_x$ ) could, at least partially, be regenerated.

The case of adventitious carbon can be examined in more detail. In Table 2 we observe, as expected, that the total amount of carbon at the sample surface increases during the analysis (from 74.7 to 82.8% at the end), due to progressive contamination by hydrocarbonaceous species arising from the pumping

device. The ratio  $[\underline{\text{C}} \text{ bound to O}]/[\underline{\text{C}}-(\text{C,H})]$  is two times lower after 79 h; this corresponds to a reduction of  $\underline{\text{C}}-\text{O}$  into  $\underline{\text{C}}-(\text{C,H})$ .

In order to ascertain this reduction under an X-ray beam, Ru(IV) dioxide hydrate ( $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ ) was also tested. The literature on Ru oxides is more abundant than that on Ru chlorides. The presence of a Ru  $3d_{5/2}$  peak assigned to  $\text{RuO}_2$  at 280.7–281 eV is quite well established. Depending on the various experimental conditions, different authors [17–20] referring to Kim et al. [21] have postulated the presence of a Ru  $3d_{5/2}$  peak from  $\text{RuO}_3$  at 282.5 eV. However, on the basis of UPS and EELS measurements, Cox et al. [22] ruled out the presence of  $\text{RuO}_3$  and postulated the presence of satellite Ru  $3d_{5/2}$  peaks associated with  $\text{RuO}_2$  in place of the Ru  $3d_{5/2}$  peak from  $\text{RuO}_3$ . This is postulated for the following reasons: (1)  $\text{RuO}_3$  does not exist as a discrete solid phase, and its existence as an ill-defined surface species is highly questionable; (2) their own studies of non-metallic Ru(IV) oxides established a typical Ru 3d binding energy of 282.2 eV; and (3) the UPS and EELS data of their study are completely inconsistent with oxidation or reduction of the  $\text{RuO}_2$  surface. A problem remains due to the presence of a double peak in the O 1s region. More recent articles [23–25] have demonstrated the existence of  $\text{RuO}_3$  by the presence of a Ru  $3d_{5/2}$  peak at 282.6 eV.

In agreement with these observations, the present work indicates that the surface of  $\text{RuO}_2$  is covered by ruthenium trioxide ( $\text{RuO}_3$ ), with a Ru  $3d_{5/2}$  peak at 282.5 eV. The analysis performed on the SSI spectrometer actually shows an O/Ru atomic ratio of 2.5 at the beginning of X-ray exposure. In this ratio, a part of the oxygen contribution is attributed to hydration water and oxygen bound to carbon, but the assignment as  $\text{RuO}_3$  is confirmed by the presence or the absence of the corresponding Ru  $3d_{5/2}$  peak as a function of the experimental conditions. For some samples used in the laboratory,  $\text{RuO}_3$  alone can be observed by the presence of a peak at 282.5 eV.

A sample of  $\text{RuO}_2 \cdot n\text{H}_2\text{O}$  was also bombarded for 82 h in the VG spectrometer and analysed at various intermediate stages in order to determine possible reduction under the X-ray beam. A weak shift of the C 1s–Ru 3d band occurs after 82 h, identifiable by enhancement of the gap between the peaks assigned to C 1s and to Ru  $3d_{5/2}$  (Fig. 4), suggesting that

Table 2  
Variation in proportion of the C 1s peak as a function of the X-ray exposure time

|                                                                                 | $t=0$ | $t=20 \text{ h}$ | $t=79 \text{ h}$ |
|---------------------------------------------------------------------------------|-------|------------------|------------------|
| Total (%)                                                                       | 74.7  | 74.7             | 82.8             |
| $[\underline{\text{C}} \text{ bound to O}]/[\underline{\text{C}}-(\text{C,H})]$ | 0.5   | 0.4              | 0.2              |

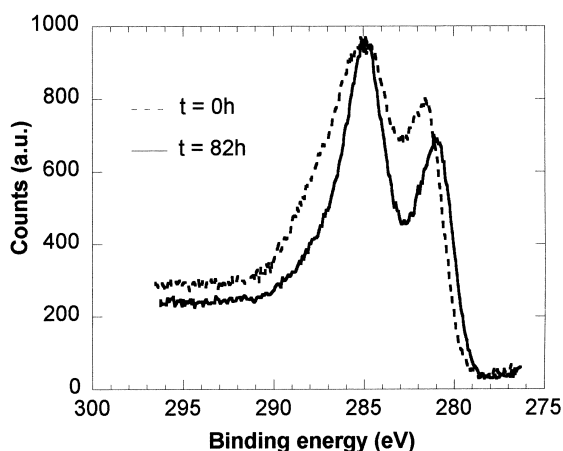


Fig. 4. Reduction of  $\text{RuO}_3$ -covered  $\text{RuO}_2$  under X-ray irradiation for 82 h (VG spectrometer).

$\text{RuO}_3$  is reduced to  $\text{RuO}_2$ . The decomposition of the band leads to the following initial ( $t=0$ ) amounts: Ru(IV) 3.5% and Ru(VI) 5.1%. At the end of exposure, the amounts of Ru(IV) and (VI) are 6.8 and 2.8%, respectively. Unfortunately, as in the case of ruthenium chloride, the atomic ratio O/Ru could not be measured after 82 h because:

- with the SSI, very long exposure times are needed,
- with the VG, the presence of adventitious carbon prevents correct measurements because it is present in large amounts and is also reduced under X-ray exposure.

During the X-ray irradiation, we observed a small increase of the C 1s peak intensity. This was also the case with experiments carried out to test the influence of the vacuum on the reduction process: in this case, no shift of  $\text{Ru } 3d_{5/2}$  seems to appear. In the same way, contaminated  $\text{RuO}_3$  layers at the surface of  $\text{RuO}_2$  were not reduced when submitted only to vacuum, but the reduction was effective under X-ray irradiation.

#### 4. Conclusion

Commercial ruthenium (III) chloride is a mixture of chloro and chlorohydroxo species, and its surface consists mainly of Ru(IV), the reduction of which

under X-ray exposure is effective after a few hours. In the same way, the surface of commercial ruthenium (IV) dioxide is covered by  $\text{RuO}_3$  layers, but its reduction is comparatively much less pronounced. In the case of ruthenium (III) chloride, the initial surface composition is assumed to be close to  $\text{Ru}^{(\text{III}+x+y)}\text{Cl}_{3+y}(\text{H}_2\text{O})_{3-x-y}(\text{OH})_x$ , resulting from the surface reaction between atmospheric water and  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ . Under X-ray irradiation, surface reduction occurs, leading to a composition close to Ru(III) chloride. These observations demonstrate that the use of “ $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ ” as a reference for the binding energy in ruthenium chloride compounds in XPS analysis is not reliable. Moreover, great caution is required when analyzing samples that could contain ruthenium chloride compounds.

Reliable XPS analyses should be performed in a short time, depending on the X-ray dose delivered to the sample by the spectrometer. As far as the spectrometers used in the present work are concerned, the analysis should not exceed 1 h for the VG (ESCA 3 Mk II), and should be restricted to less than 4 h with the SSI (SSX-100/206) spectrometer. These reduction phenomena are minimized by using monochromatized X-ray beams or by performing the analyses at low temperature [8]. The influence of the residual pressure is relatively weak compared to X-ray bombardment, and seems to provoke only dehydration of the sample.

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