

# EPR evidence for ruthenium variable valence states in active oxidative catalysts

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## EPR EVIDENCE FOR RUTHENIUM VARIABLE VALENCE STATES IN ACTIVE OXIDATIVE CATALYSTS

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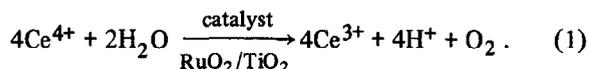
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Experimental proof is provided by EPR for the presence of  $\text{Ru}^{3+}$  ions in a  $\text{RuO}_2/\text{TiO}_2$  highly dispersed catalyst. A model is proposed for the mode of intervention of  $\text{Ru}^{3+}/\text{Ru}^{4+}$  states in oxidative processes.

### 1. Introduction

The problem of oxygen evolution in the dark is a topic of relevant interest in several laboratories working in the area of the conversion of light to chemical energy [1].  $\text{RuO}_2$ , having a low overvoltage for oxygen evolution, has already been suitably stabilized on  $\text{TiO}_2$  [2–6] and has been used as a redox catalyst to mediate  $\text{O}_2$  evolution in the reaction



This system consists of  $\text{Ce}^{4+}$  solution in 1  $\text{NH}_2\text{SO}_4$ . In reaction (1), when an  $\text{RuO}_2/\text{TiO}_2$  particle is in contact with a  $\text{Ce}^{4+}$ -containing solution, the situation developed is similar to an electrocatalyst under anodic bias. The electrochemical potential imposed on the  $\text{RuO}_2\text{--TiO}_2$  particle determines the rate of  $\text{H}_2\text{O}$  oxidation and  $\text{Ce}^{4+}$  reduction. On the other hand, catalytic properties originate from the state of the surface species, and the observed oxygen evolution in reaction (1) will depend on the exact nature of these surface sites. The present study examines more closely the nature of the  $\text{RuO}_2/\text{TiO}_2$  catalyst by EPR techniques. The interest in such a study is that redox catal-

ysis has been reported to be facilitated by variable valence states [7] encountered on the catalyst surface. But until now, only a few studies have appeared giving evidence for this assumption. Of the few examples known, we could mention studies involving  $\text{Fe}_2\text{O}_3$  [8],  $\text{WO}_3$  [9] and GaAs [10].  $\text{Ru}^{3+}$ -states in  $\text{RuO}_2$  as reported in this study lend support to the concept of variable valency being important in the field of redox catalysis.

### 2. Experimental

The titanium dioxide used was  $\text{TiO}_2$  Degussa P25 with a surface area of  $50 \text{ m}^2/\text{g}$ .  $\text{RuO}_2$  was deposited on  $\text{TiO}_2$  P25 by hydrolysis of  $\text{RuCl}_3 \cdot \text{H}_2\text{O}$  Alfa Ventron [4]. In order to determine the  $\text{RuO}_2$  particle diameter, TEM was carried out<sup>†</sup>. The average  $\text{RuO}_2$  particle diameter had a size of  $20 \text{ \AA} \pm 15\%$ . This small cluster size is advantageous both from the point of view of mass transport of the active species as well as

<sup>†</sup> We thank Dr. W. Hoffmann, Nukem GmbH Karlstein, FRG for having carried out the TEM on the  $\text{RuO}_2/\text{TiO}_2$  samples. The magnification used was 500000.

of surface area per gram of catalyst employed [7]. EPR spectra (X-band) were recorded with a Varian E-15 spectrometer equipped with a TE-104 dual sample cavity and a liquid-helium flow cryostat. An in situ cell was used [11] and the temperature of the sample was kept constant at 10 K with a Cryoson CE 5348 temperature controller. Signal intensity and position were calibrated with the aid of the Varian strong pitch ( $g = 2.0028, 3.01 \times 10^{15}$  spins  $\text{cm}^{-1}$ ).

### 3. Results and discussion

The  $\text{RuO}_2/\text{TiO}_2$  EPR spectra contained several signals. Fig. 1 shows a  $\text{Ru}^{3+}$  signal at  $g = 2.08$  for a 1.58%  $\text{RuO}_2/\text{TiO}_2$  sample. Also a signal at  $g = 1.92$  was observed. Such a signal has previously [12] been reported for many noble metal-loaded  $\text{TiO}_2$  samples and has been assigned to surface  $\text{Ti}^{3+}$  ions. For the sample presented in fig. 1 (1.58%  $\text{RuO}_2/\text{TiO}_2$ ), the amount of  $\text{Ru}^{3+}$  shown has been quantified according to the EPR spectrum obtained. The experimental results obtained indicate that 20% of the Ru is present as  $\text{Ru}^{3+}$ . A 3.07%  $\text{RuO}_2/\text{TiO}_2$  sample showed the same signal height of  $\text{Ru}^{3+}$ , at a receiver gain which is twice as low, indicating that there is also 20%  $\text{Ru}^{3+}$  present in this sample. The same holds true for a

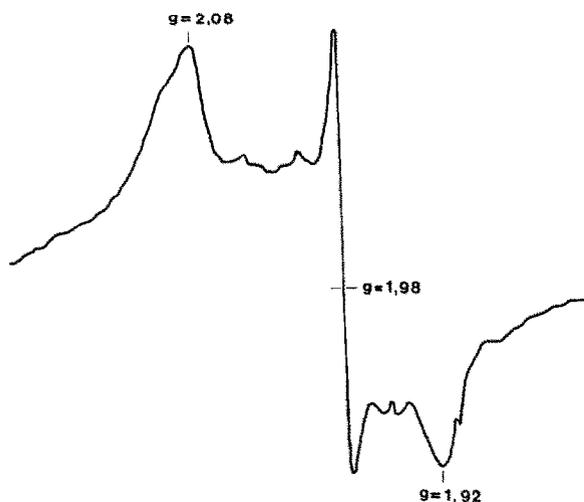


Fig. 1. X-band EPR spectrum of a 1.58%  $\text{RuO}_2/\text{TiO}_2$  catalyst recorded at 10 K showing  $\text{Ru}^{3+}$ ,  $\text{O}_2^-$  and  $\text{Ti}^{3+}$  species at  $g$  values of 2.08, 1.98 and 1.92 respectively.

0.78%  $\text{RuO}_2/\text{TiO}_2$  sample. The signal at  $g = 1.98$  in the EPR spectrum (fig. 1) might correspond to  $\text{O}_2^-$  on the surface of the  $\text{RuO}_2$ . Similar observations have been reported recently [13].

In the Ru samples one sees the  $\text{Ru}^{3+}$  state at the surface of the  $\text{RuO}_2$  particles. It is unlikely that  $\text{Ru}^{3+}$  will be present as  $\text{Ru}_2\text{O}_3$ , because in this case the  $\text{Ru}^{3+}$  ions would be very close together and might couple antiferromagnetically or might broaden the EPR signal dramatically. This was not observed in fig. 1. Although  $\text{Ru}^{4+}$  is paramagnetic, normally it does not show an EPR signal. The  $\text{Ru}^{4+}$  ion has a  $4d^4$  configuration and either a strong zero-field splitting and/or a strong relaxation because of the strong coupling between spin and orbital momentum in an orbitally degenerate state, will make it impossible to observe an EPR signal. Therefore all one sees in Ru samples is the  $\text{Ru}^{3+}$  state.

An increase in catalytic activity [5] has been reported for  $\text{O}_2$  evolution in reaction (1) and concomitant paramagnetic character of the  $\text{RuO}_2/\text{TiO}_2$  samples up to  $\approx 4\%$   $\text{RuO}_2/\text{TiO}_2$ . The  $\text{Ru}^{3+}/\text{Ru}^{4+}$  states responsible for the observed catalysis may find themselves in an even distribution in the  $\text{RuO}_2$  existing on  $\text{TiO}_2$ . The fact that higher loaded samples of  $\text{RuO}_2/\text{TiO}_2$  intervene more favorably in reaction (1) further substantiates the role of  $\text{Ru}^{3+}$  (existing in 20% abundance) up to 3.07% Ru on  $\text{TiO}_2$ . Since  $\text{Ru}^{3+}$  and  $\text{Ru}^{4+}$  are both paramagnetic states [14], it follows that the combined effect of these two states is effective in facilitating the interaction of  $\text{H}_2\text{O}$  and  $\text{Ce}^{4+}/\text{Ce}^{3+}$  on  $\text{RuO}_2/\text{TiO}_2$  dispersions.

$\text{Ru}^{3+}$  states in  $\text{RuO}_2$  structures, as observed in our case, are not surprising [15].  $\text{Ru}^{3+}$  states have been detected by optical absorption measurements and correspond to  $d-d$  acceptor transitions in this oxide.  $\text{Ru}^{3+}$  has been reported to be present in fully oxidized Ru-doped  $\text{TiO}_2$  [15], to compensate for substitutional trivalent impurities.

Such variable-valence ions [16] are often found in materials that occur in non-stoichiometric form and generally involve ionic rather than covalent bonds. Aliovalent  $\text{Ru}^{3+}$  would then induce a difference in electronic densities on the catalyst surface [7-9], providing density fluctuations favorable for charge transfer [17].

A model is hereby suggested to explain the mode of intervention of the  $\text{Ru}^{3+}/\text{Ru}^{4+}$  states in the oxida-

tion process. A high density of charges is set on the oxide surface and dipoles  $\text{Ru}^{\delta+}-\text{Ru}^{\delta-}$  are formed with a potential gradient. Electron migration would then take place at potential values  $>1.23$  V in reaction (1). When water is oxidized, electrons would accumulate on  $\text{RuO}_2(\text{Ru}^{4+})$ . Such a reaction cannot continue for any length of time, and the  $\text{Ru}^{3+}$  state will allow the discharge of these electrons, causing  $\text{Ce}^{4+}$  oxidation. The catalysis taking place will then be regulated by the electrochemical potential of  $\text{Ce}^{4+}/\text{H}_2\text{O}$  couple [6]. The catalysis is then seen to involve a lower oxidation state of Ru. The highly electrostatic  $\text{Ru}^{4+}$  state may preferentially interact with the less charged water dipole across the double layer. The  $\text{Ru}^{3+}$  states will then interact with  $\text{Ce}^{4+}$  ions across this layer. Invoking elementary electrostatic considerations, the system will minimize in this way the energy of repulsion and decrease charge accumulation at the interface.

The existence of  $\text{Ru}^{3+}$  ions on  $\text{RuO}_2/\text{TiO}_2$  also has implications for the Fermi level of the system under consideration. It has been shown that the density of states for metals decreases abruptly above the Fermi level for metals with available d-electrons like:  $\text{Ru}^{3+}$ ,  $\text{Ru}^{4+}$ ,  $\text{Pt}^{4+}$ ,  $\text{Rh}^{3+}$  [18]. The density of states at the Fermi level for  $\text{Ru}^{3+}$  (five d-electrons) is expected to be lower than that of  $\text{Ru}^{4+}$  (four d-electrons) and, as the d-orbitals of the Ru atoms become more occupied ( $\text{Ru}^{3+}$  state), a smaller number of them would be available to interact with water dipoles as proposed in such a model. This effect has been reported to be important in highly dispersed metals and oxides [19] and  $\text{Ru}^{3+}$  states, with their characteristic unpaired electrons, would shift the  $\text{RuO}_2/\text{TiO}_2$  Fermi level in reaction (1).

A last point to examine is the validity of  $\text{Ru}^{3+}$  and  $\text{Ru}^{4+}$  states intervening in reaction (1). Ru has been reported to exist with valence states  $3+$  to  $8+$  [20]. Intervention of an  $\text{Ru}^{2+}$  state is discarded since it is not easy to reduce the initial  $\text{RuCl}_3$  used to prepare the catalyst [4] to  $\text{Ru}^{2+}$ . The d bands associated with  $\text{Ru}^{2+}$  ([six d] electrons) [21] are at an energy level that is too high for this to occur.  $\text{Ru}^{3+}$  [20] on the other hand, is a stable species in strong acid media. Oxidation of Ru to compounds with valence greater than four begins at 1.45 V, the redox potential of the  $\text{Ce}^{4+}$  ion containing solution [20]. In reaction (1) the corrosion of  $\text{RuO}_2$  is inhibited by stabilizing it on  $\text{TiO}_2$

[3,4]. Low initial  $\text{Ce}^{4+}$  ( $3.3 \times 10^{-3}$  M) and  $\text{RuO}_2$  concentrations ( $5 \times 10^{-5}$  M) as used in reaction (1) also make corrosion of a 3.07%  $\text{RuO}_2-\text{TiO}_2$  catalyst very unlikely. Therefore, only  $\text{Ru}^{4+}/\text{Ru}^{3+}$  states seem to play a role in the catalysis shown in reaction (1). Furthermore, by cyclic voltammetry [22] evidence has been provided for oxygen evolution on  $\text{RuO}_2$  anodes at a potential of 1.13 versus SCE, a value considerably smaller than 1.45 V versus SCE shown to be necessary to corrode Ru oxides.

In conclusion,  $\text{RuO}_2$  has been suspected for a long time to have oxidation states affording different valence states intervening in redox processes. This study has provided experimental proof for the existence of two ruthenium states on a  $\text{RuO}_2/\text{TiO}_2$  highly dispersed catalyst.

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