

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

J. KIWI

Institut de Chimie Physique, Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland

and

R. PRINS

Laboratory of Inorganic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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Experimental proof is provided by EPR for the presence of Ru^{3+} ions in a RuO_2/TiO_2 highly dispersed catalyst. A model is proposed for the mode of intervention of Ru^{3+}/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]. RuO_2 , having a low overvoltage for oxygen evolution, has already been suitably stabilized on TiO_2 [2–6] and has been used as a redox catalyst to mediate O_2 evolution in the reaction

$$4Ce^{4+} + 2H_2O \xrightarrow[RuO_2/TiO_2]{\text{catalyst}} 4Ce^{3+} + 4H^+ + O_2. \quad (1)$$

This system consists of Ce^{4+} solution in $1 NH_2SO_4$. In reaction (1), when an RuO_2/TiO_2 particle is in contact with a Ce^{4+} -containing solution, the situation developed is similar to an electrocatalyst under anodic bias. The electrochemical potential imposed on the RuO_2 -TiO₂ particle determines the rate of H₂O oxidation and Ce⁴⁺ 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 RuO_2/TiO_2 catalyst by EPR techniques. The interest in such a study is that redox catal-

0 009-2614/86/\$ 03.50 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division) 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 Fe_2O_3 [8], WO₃ [9] and GaAs [10]. Ru³⁺-states in RuO₂ 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 TiO_2 Degussa P25 with a surface area of 50 m²/g. RuO₂ was deposited on TiO₂ P25 by hydrolysis of RuCl₃ · H₂O Alfa Ventron [4]. In order to determine the RuO₂ particle diameter, TEM was carried out [‡]. The average RuO₂ particle diameter had a size of 20 Å ± 15%. This small cluster size is advantageous both from the point of view of mass transport of the active species as well as

[‡] We thank Dr. W. Hoffmann, Nukem GmbH Karlstein, FRG for having carried out the TEM on the RuO₂/TiO₂ 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 cm⁻¹).

3. Results and discussion

The RuO₂/TiO₂ EPR spectra contained several signals. Fig. 1 shows a Ru³⁺ signal at g = 2.08 for a 1.58% RuO₂/TiO₂ sample. Also a signal at g = 1.92was observed. Such a signal has previously [12] been reported for many noble metal-loaded TiO₂ samples and has been assigned to surface Ti³⁺ ions. For the sample presented in fig. 1 (1.58% RuO₂/TiO₂), the amount of Ru³⁺ shown has been quantified according to the EPR spectrum obtained. The experimental results obtained indicate that 20% of the Ru is present as Ru³⁺. A 3.07% RuO₂/TiO₂ sample showed the same signal height of Ru³⁺, at a receiver gain which is twice as low, indicating that there is also 20% Ru³⁺ present in this sample. The same holds true for a



Fig. 1. X-band EPR spectrum of a 1.58% RuO₂/TiO₂ catalyst recorded at 10 K showing Ru³⁺, O₂ and Ti³⁺ species at g values of 2.08, 1.98 and 1.92 respectively.

0.78% RuO₂/TiO₂ sample. The signal at g = 1.98 in the EPR spectrum (fig. 1) might correspond to O_2^- on the surface of the RuO₂. Similar observations have been reported recently [13].

In the Ru samples one sees the Ru³⁺ state at the surface of the RuO₂ particles. It is unlikely that Ru³⁺ will be present as Ru₂O₃, because in this case the Ru³⁺ 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 Ru⁴⁺ is paramagnetic, normally it does not show an EPR signal. The Ru⁴⁺ ion has a 4d⁴ 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 Ru³⁺ state.

An increase in catalytic activity [5] has been reported for O₂ evolution in reaction (1) and concomitant paramagnetic character of the RuO₂/TiO₂ samples up to $\approx 4\%$ RuO₂/TiO₂. The Ru³⁺/Ru⁴⁺ states responsible for the observed catalysis may find themselves in an even distribution in the RuO₂ existing on TiO₂. The fact that higher loaded samples of RuO₂/TiO₂ intervene more favorably in reaction (1) further substantiates the role of Ru³⁺ (existing in 20% abundance) up to 3.07% Ru on TiO₂. Since Ru³⁺ and Ru⁴⁺ are both paramagnetic states [14], it follows that the combined effect of these two states is effective in facilitating the interaction of H₂O and Ce⁴⁺/Ce³⁺ on RuO₂/TiO₂ dispersions.

 Ru^{3+} states in RuO_2 structures, as observed in our case, are not surprising [15]. Ru^{3+} states have been detected by optical absorption measurements and correspond to d-d acceptor transitions in this oxide. Ru^{3+} has been reported to be present in fully oxidized Ru-doped TiO₂ [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 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 Ru^{3+}/Ru^{4+} states in the oxida-

tion process. A high density of charges is set on the oxide surface and dipoles $Ru^{\delta +} - Ru^{\delta -}$ 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 $RuO_2(Ru^{4+})$. Such a reaction cannot continue for any length of time, and the Ru³⁺ state will allow the discharge of these electrons, causing Ce⁴⁺ oxidation. The catalysis taking place will then be regulated by the electrochemical potential of Ce^{4+}/H_2O couple [6]. The catalysis is then seen to involve a lower oxidation state of Ru. The highly electrostatic Ru⁴⁺ state may preferentially interact with the less charged water dipole across the double layer. The Ru³⁺ states will then interact with Ce⁴⁺ 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 Ru^{3+} ions on RuO_2/TiO_2 also has implifications 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: Ru^{3+} , Ru^{4+} , Pt^{4+} , Rh^{3+} [18]. The density of states at the Fermi level for Ru³⁺ (five d-electrons) is expected to be lower than that of Ru⁴⁺ (four d-electrons) and, as the d-orbitals of the Ru atoms become more occupied (Ru³⁺ 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 Ru³⁺ states, with their characteristic unpaired electrons, would shift the RuO₂/TiO₂ Fermi level in reaction (1).

A last point to examine is the validity of Ru^{3+} and Ru^{4+} states intervening in reaction (1). Ru has been reported to exist with valence states 3+ to 8+ [20]. Intervention of an Ru^{2+} state is discarded since it is not easy to reduce the initial $RuCl_3$ used to prepare the catalyst [4] to Ru^{2+} . The d bands associated with $Ru^{2+}([six d] \text{ electrons})$ [21] are at an energy level that is too high for this to occur. 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 Ce⁴⁺ ion containing solution [20]. In reaction (1) the corrosion of RuO_2 is inhibited by stabilizing it on TiO₂ [3,4]. Low initial Ce⁴⁺ (3.3×10^{-3} M) and RuO₂ concentrations (5×10^{-5} M) as used in reaction (1) also make corrosion of a 3.07% RuO₂-TiO₂ catalyst very unlikely. Therefore, only Ru⁴⁺/Ru³⁺ states seem to play a role in the catalysis shown is reaction (1). Furthermore, by cyclic voltammetry [22] evidence has been provided for oxygen evolution on RuO₂ 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, 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 RuO_2/TiO_2 highly dispersed catalyst.

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