# Catalytic Oxidation of Water mediated by Rhenium Oxides†

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Rhenium oxides ($Re_2O_3$, $ReO_2$, and $ReO_2$–$TiO_2$) show efficient catalytic activity in reaction (i)

$$4D^+ + 2\,H_2O \longrightarrow 4D + 4\,H^+ + O_2 \qquad \text{(i)}$$

where $D^+$ = $Ce^{4+}$ or $[Ru(bipy)_3]^{3+}$ (bipy = 2,2′-bipyridine). The pseudo-first-order rate constant, $k_0$, for this reaction, when D = $Ce^{4+}$, ranges from 0.4 to 0.09 $min^{-1}$ for different [$Ce^{4+}$] : catalyst weight ratios, at 25 °C in 1 N $H_2SO_4$. These rates are higher than the reported rates for reaction (i) when $RuO_2$ powder is used as a catalyst.

Dispersions of noble-metal oxides such as $PtO_2$, $IrO_2$, and $RuO_2$ in aqueous acid solutions[1] have recently been shown to be capable of mediating oxygen evolution from water *via* equation (1). The symbol $D^+$–D stands for a redox pair whose

$$4D^+ + 2\,H_2O \longrightarrow 4D + 4\,H^+ + O_2 \qquad (1)$$

standard potential is more positive than $E^\circ$ ($O_2$–$2H_2O$). These redox catalysts are important since they may be used in artificial light–energy conversion processes.[2] In the search for catalytic materials that are suitable for mediating reaction (1) we have discovered that rhenium oxides have highly desirable properties.

As an electrode material Re distinguishes itself by a low over voltage for $H_2$ evolution from aqueous acid solutions[3] of *ca.* −0.3 V *vs.* s.c.e. (saturated calomel electrode). To the best of our knowledge the rhenium oxides' over potential for $O_2$ evolution has not been reported until now. In the acidic domain of the potentials relevant to $O_2$ production, rhenium oxides display high stability.[4] Rhenium oxides in water form macrodispersions which can be readily brought into contact with their aqueous environment. This work provides the first evidence for rhenium oxides as efficient catalysts for water oxidation, using $Ce^{4+}$ and $[Ru(bipy)_3]^{3+}$ (bipy = 2,2′-bipyridine) as sacrificial donors. Rhenium species have been extensively used in hydrocarbon conversion catalysis[5] but not in thermal oxidation reactions involving electron transfer.

## Results and Discussion

Figure 1 shows the u.v. spectrum for the disappearance of $Ce^{4+}$ ions, in a 2.6 × $10^{-3}$ mol $dm^{-3}$ solution of $Ce(SO_4)_2{\cdot}2H_2O$ in 1 N $H_2SO_4$ when 15 mg of $ReO_2$ are present, as a function of time. Within a time interval of 5 min, the $Ce^{4+}$ absorption has disappeared and is replaced by the $Ce^{3+}$ spectrum. Analysis of the gas evolved during the stirring process showed that $O_2$ is produced from the $Ce^{4+}$ reaction with water.

Figure 2 shows the decrease in $Ce^{4+}$ concentration, and the resulting formation of $O_2$, as a function of time. The rate decreases as the conversion to $Ce^{3+}$ proceeds, the rate law being pseudo-first order with respect to $Ce^{4+}$ concentration. If one takes the concentration ratio $Ce^{4+}$ : $O_2$ for each of the experimental points presented on Figure 2 a value of *ca.* 4 is found. The slight $O_2$ deficiency found after 10 min can be attributed to chemisorption of $O_2$ on $ReO_2$, or the corrosion of the catalyst [as will be discussed later in equation (4)]. Taking this into account, it is concluded that the oxidation of water is quantitative in the presence of the redox catalyst. It is inferred that $O_2$ formation from water takes place when $ReO_2$ is present through reaction (2).

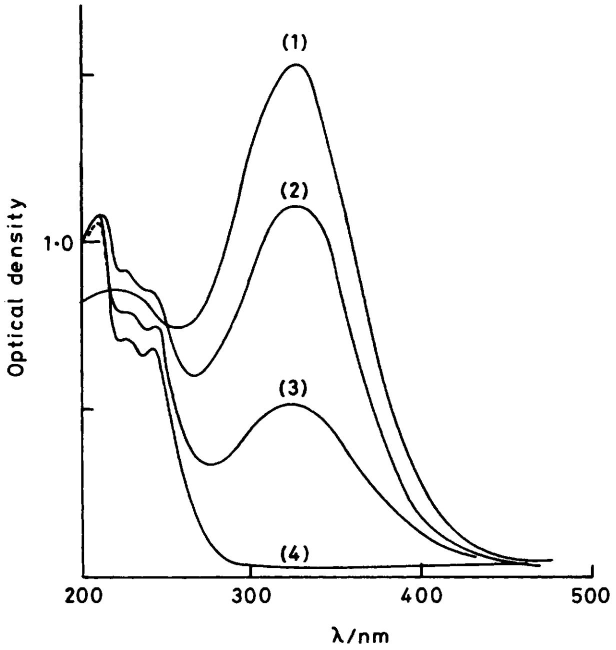

**Figure 1.** (1), Spectrum of a 2.56 × $10^{-3}$ mol $dm^{-3}$ $Ce(SO_4)_2{\cdot}2H_2O$ solution in 1 N $H_2SO_4$. Rhenium dioxide (15 mg) in 25 $cm^3$ of stirred solution at 25 °C. Curves (2), (3), and (4) are after 1, 2, and 5 min respectively

$$4\,Ce^{4+} + 2\,H_2O \xrightarrow{ReO_2} 4\,Ce^{3+} + 4\,H^+ + O_2 \qquad (2)$$

The role of $ReO_2$ is similar to that previously reported[1–3] for $RuO_2$. It would then act as a defect electron storage system, *i.e.* a hole-conducting band is formed in the solid.

When transferring electrons from the catalyst to $Ce^{4+}$, an anodic potential would be imposed on the $ReO_2$ microelectrodes, inducing water oxidation. The standard free energy available to drive reaction (2) is −200 mV *vs.* n.h.e. (normal hydrogen electrode).[4] It can readily be seen that the process under observation is catalytic, since reuse of the catalyst led to $O_2$ evolution during the second cycle. However, the efficiency of the second cycle is diminished, in regard to the previous discussion, with respect to loss of activity of the oxide particle's surface.

A detailed quantitative study of the kinetics of water oxidation as a function of the catalyst employed, *i.e.* $ReO_2$, $ReO_3$, and $Re_2O_3$, and the $Ce^{4+}$ : rhenium oxide ratio has been carried out. The results are shown in the Table, *i.e.* $k_0$ ($min^{-1}$) the rate of oxidation of water by $Ce^{4+}$ under the experimental

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† *Non-S.I. unit employed:* 1 Torr ≈ 133 Pa.

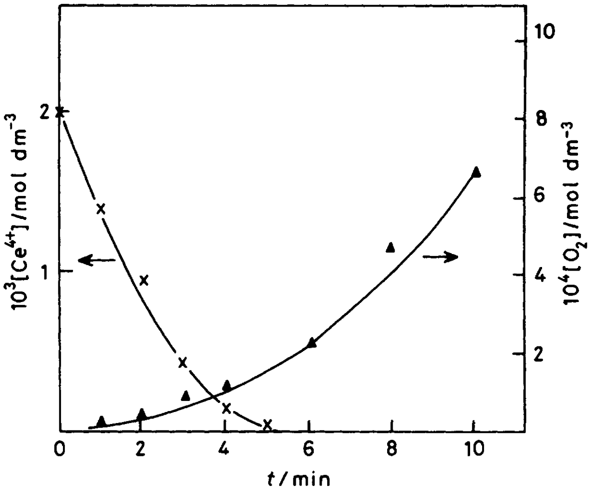

**Figure 2.** Rate of oxygen evolution when $2.56 \times 10^{-3}$ mol $dm^{-3}$ $Ce(SO_4)_2 \cdot 2H_2O$ is stirred in 1 N $H_2SO_4$ (25 $cm^3$) and 15 mg $ReO_2$ added at 20 °C

**Table.** Rate constants and dioxygen yields for the oxidation of water by $Ce^{4+}$ in the presence of different concentrations of rhenium oxide catalysts

| $10^3[Ce^4]$ (mol $dm^{-3}$) | $ReO_2$[a] (mg) | $k_0$ ($min^{-1}$) | $O_2$ Yield[b] |
|---|---|---|---|
| Rhenium(IV) dioxide catalyst, $ReO_2$ | | | |
| 2.56 | 6.00 | 0.134 | 60 |
| 2.56 | 8.00 | 0.142 | 70 |
| 2.56 | 10.00 | 0.315 | 75 |
| 2.56 | 15.00 | 0.391 | 70 |
| Rhenium(VI) trioxide catalyst, $ReO_3$ | | | |
| 2.42 | 6.00 | 0.082 | 20 |
| 2.42 | 8.00 | 0.088 | 22 |
| 2.42 | 10.00 | 0.091 | 22 |
| 2.42 | 15.00 | 0.134 | 30 |
| Dirhenium(III) trioxide catalyst, $Re_2O_3$ | | | |
| 2.57 | 6.00 | 0.087 | 20 |
| 2.57 | 8.00 | 0.132 | 32 |
| 2.57 | 15.00 | 0.230 | 58 |

[a] Milligrams of the rhenium oxide in 25 $cm^3$ of 1 N $H_2SO_4$. The particle dimensions could be determined only by sieving analysis (ASTM norms) resulting in an average particle diameter of 160 μm. This does not mean a regular size distribution, not even after the vigorous magnetic stirring during the reaction. [b] Generated amount of dioxygen expressed as % yield expected from the stoicheiometry of equation (1) and based on the initial concentrations (mol $dm^{-3}$) of $Ce^{4+}$. It is assumed that this reaction proceeds to completion.

conditions used. Pseudo-first-order rates were obtained with respect to $Ce^{4+}$ concentration for almost all the reaction times measured. Values of $k_0$ were determined during the first 8 min of reaction, corresponding to 80 to 90% of the overall reaction. In this time range the relation log $[Ce^{4+}]_0/[Ce^{4+}]_0 - [Ce^{4+}]_t$ *versus* time (min) is perfectly linear, as observed in all cases where the value of $k_0$ was determined. Moreover, at the end of the reaction an important slope change is observed, giving indirect evidence for a change in the surface layers of the catalyst particle. Therefore, the $k_0$ values determined are only comparable in a determined range of the reaction co-ordinates (80—90% of the overall reaction, *i.e.* 8—9 min). Nevertheless, it can be stated that $ReO_2$ is the more efficient catalyst among all the rhenium oxides used in reaction (2).

On the other hand, for high $[Ce^{4+}]$:catalyst weight ratios, changes in the observed rates indicate the possibility of rhenium oxide corrosion. It is known [4,5] that $[ReO_4]^-$ is formed by $OH^{\bullet}$ or $O_2$ action on $Re_xO_n$ ($x = 1$, $n = 2$; $x = 1$, $n = 3$; $x = 2$, $n = 3$) in acidic media in a reaction of the type given by equation (3), where A = ($O_2$ or $OH^{\bullet}$). $ReO_2$ would then

$$2\,H_2O + ReO_2(s) + 3\,A \longrightarrow [ReO_4]^- + 3\,A^- + 4\,H^+ \quad (3)$$

be generated on the surface of rhenium oxides in the course of the reaction.[6] At smaller $Ce^{4+}:Re_xO_n$ ratios a lower reaction rate is observed, reflected in the lower $k_0$ values reported in the Table. The experimental observations could be understood, noting that in equation (2) the redox potential of the $Ce^{4+}$ ions at 25 °C is given by expression (4), while the standard electrode

$$E(\text{n.h.e.}) = 1.44 + 0.059 \log [Ce^{4+}]/[Ce^{3+}] \quad (4)$$

potential of the $H_2O$–$O_2$ and $ReO_2$–$[ReO_4]^-$ couples have values between 1.23 and 1.44 V.[4] Therefore, the electrochemical potential of the powder particle intervening in the catalysis will depend on the rates of oxidation of $Re_xO_n$ and water and reduction of $Ce^{4+}$. These values have limits falling between the potential of the $Ce^{4+}$–$Ce^{3+}$ redox couple and 1.23 V. Therefore, the higher the initial $Ce^{4+}$ concentration and the smaller the amount of $Re_xO_n$ catalyst used, the more positive will be the potential for the $Re_xO_n$ particle [equation (4)]. In this case, the corrosion given by $ReO_2$–$[ReO_4]^-$ will be more likely.

In agreement with these observations, it has been found (Table) that $O_2$ yields are lowest for high $Ce^{4+}:Re_xO_n$ ratios where corrosion of the particles occurs at the expense of water oxidation. Corrosion levels were assessed by analysing a stirred $Ce^{4+}:ReO_2$ solution (ratio = 0.83; Table) and measuring the $[ReO_4]^-$–furil dioxime peak.[7] Under the same experimental conditions described in Figure 2, using 600 mg $l^{-1}$ of $ReO_2$ (600 p.p.m.) the analysis revealed the existence of a complex with a peak at λ = 531 nm (ε = 41 300 $dm^3$ $mol^{-1}$ $cm^{-1}$). This complex of $[ReO_4]^-$–furil dioxime revealed about 0.6—1.2 p.p.m. of Re, indicating corrosion of up to 2% of the catalyst used. Similar results were observed by Mills[8] when $RuO_2$ dispersions were used in sacrificial water oxidation. Subsequently a $ReO_2$–$TiO_2$ catalyst was used and a much lower level of corrosion was observed, in agreement with previous work using $RuO_2$–$TiO_2$[9] to catalyse reaction (2).

Further studies showed that the reduction of tris(2,2′-bipyridine)ruthenium(III) by water, according to equation (5)

$$4[Ru(bipy)_3]^{3+} + 2\,H_2O \xrightarrow{ReO_2} 4[Ru(bipy)_3]^{2+} + 4\,H^+ + O_2 \quad (5)$$

(−200 mV *vs.* n.h.e.) is possible at pH 4.2. Concentrations of $4.85 \times 10^{-3}$ mol $dm^{-3}$ $[Ru(bipy)_3]^{3+}$ were used and spectral changes, as a function of time, were followed spectrophotometrically. In a catalyst-free solution, $[Ru(bipy)_3]^{3+}$ is stable for at least 1 h, which is necessary for completion of reaction (5). Our results show that reaction (5) is less efficient than reaction (2) when catalysing water oxidations. On the other hand, all the results were obtained in the absence of light. Application of the experimental results in the classical photogeneration of dioxygen from water[2] by the photogenerated $[Ru(bipy)_3{}^{3+}]^*$ chromophore are under investigation. This could take the rhenium oxide study into the field of the photocatalytic system of solar energy conversion.

In conclusion, our results show that rhenium oxides efficiently catalyse water oxidation *via* sacrifical systems. The multiple valence states (+1 to +7)[4,5] available in Re seem to provide variable electronic densities which are beneficial in electron transfer processes.[4,5]

## Experimental

*Catalyst Preparation and Characterisation.*—Rhenium dioxide was prepared by the following methods. (*a*) Thermal decomposition of $K_2[ReCl_6]$ or $K_2[ReBr_6]$ in 2 mol $dm^{-3}$ HCl solution, leading to an amorphous black powder, insoluble in water. (*b*) Thermal decomposition of $[NH_4][ReO_4]$ at 300 °C and $10^{-2}$ Torr. (*c*) $ReO_2$ dispersed on $TiO_2$ Degussa P-25 has been prepared by a method already applied in $RuO_2$–$TiO_2$ catalyst preparation. In this way, ammonium rhenate, $[NH_4][ReO_4]$ (60 mg), was hydrolysed in water (100 $cm^3$) at pH 4.5 and 25 °C for 8 d. Subsequent drying was carried out using a Rotavapor at 45 °C and then at 230 °C for 1 h at $10^{-3}$ Torr.

Rhenium trioxide was prepared either by: (*a*), thermal decomposition of $[NH_4][ReO_4]$ at 500 °C in a current of argon or (*b*), heating a 1:1 molar mixture of $Re_2O_7$ and $ReO_2$. Both preparations lead to an amorphous red powder. Rhenium dioxide as well as $ReO_3$ powders were polycrystalline and did not present a defined *X*-ray diffraction pattern. Thermogravimetric analysis showed some superficial water loss up to 200 °C of the order of 10—20% by weight. The initial particle dimensions of all the rhenium oxide powders were determined by sieve analysis resulting in 160 μm in diameter (ASTM norms), before running the catalysis experiments. This was done after drying the sample at 120 °C under an argon atmosphere over 4 d.

*Apparatus and Materials.*—The oxygen evolved was measured *via* a Beckman membrane oxygen electrode. Constant stirring (300 revolutions $min^{-1}$) and temperatures of 25 °C were maintained throughout. Spectral changes observed in reaction (2) were followed by means of a Perkin-Elmer Lambda 3 spectrophotometer using 0.1-cm cells. Cerium(IV) sulphate (AnalaR) was used in all cases. In typical runs using $[Ru(bipy)_3]^{3+}$, 25 $cm^3$ of a $2.45 \times 10^{-4}$ mol $dm^{-3}$ solution were thoroughly degassed and different quantities of rhenium oxides added. The colour changes observed in the solution were followed by registering, spectrophotometrically the increase of the $[Ru(bipy)_3]^{2+}$ 450-nm peak as a function of time.

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