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Dioxygen Evolution from Inorganic Systems. Water Oxidation Mediated by RuO_2 and TiO_2–RuO_2 Colloids

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The kinetics of reduction of aqueous solutions of Ce^{IV} and $Ru(bpy)_3{}^{3+}$ in the presence of catalytic amounts of RuO_2 colloids stabilized with polybrene and colloidal TiO_2 particles loaded with RuO_2 have been investigated by means of stopped-flow spectrophotometric techniques. The effect of pH, catalyst preparation and loading concentration have been considered. The TiO_2/RuO_2 colloidal particles (45 nm radius) are extremely active catalysts.

Introduction

The formation of dioxygen in the reaction of water with sufficiently powerful oxidants is of interest in ascertaining the chemical mechanism in plant photosynthesis [1] and developing systems affording water cleavage by visible light [2]. Finely divided noble metal oxides (PtO_2, IrO_2, RuO_2) have recently been shown to be capable of mediating O_2 evolution from water [3–5] through the reaction

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

where S^+/S represents the redox couple; production of O_2 was observed when the oxidant was Ce^{4+}, $Ru(bpy)_3{}^{3+}$ or $Fe(bpy)_3{}^{3+}$.

Whether used as a powder [3, 4] or in colloidal form [3, 4, 6–8] or deposited onto some supporting material like TiO_2 [9–11], or CdS [12], or zeolite [5], RuO_2 is generally recognized as one of the best catalysts for dioxygen evolution.

The present paper reports on the reaction kinetics of Ce^{4+} and $Ru(bpy)_3{}^{3+}$ disappearance in the presence of RuO_2 colloids and ruthenium dioxide bound to TiO_2.

Experimental

Reagents

Ruthenium tetraoxide and titanium tetrachloride were obtained from Pierce Inorganics. Polybrene was obtained from Aldrich.

Cerium(IV) sulfate purchased from C. Erba was diluted with H_2SO_4 as required and standardized by oxidimetric titration. $Ru(bpy)_3Cl_2$ was obtained from F. Smith and the corresponding $Ru(bpy)_3^{3+}$ was obtained by electrooxidation and standardized spectrophotometrically at 675 nm ($\epsilon = 420\ M^{-1}\ cm^{-1}$) [13].

Preparation of Catalysts

The colloids of RuO_2 stabilized with polybrene were prepared by mixing equal amounts of a solution of RuO_4 in water (43 mg RuO_4 in 43 mL H_2O at 0 °C, stirred for 30 min) and a solution (0.40 g L^{-1}) of stabilizer. The resulting solution has a green colour and spectra (see Fig. 1) collected at different times were found to be unchanged over one day. Colloidal TiO_2 was prepared by two different methods: (A) by hydrolysis of $TiCl_4$ in water–ice mixture according to procedures previously described [14, 15]. The colloid was then dialyzed and the final pH at the end of the dialysis was adjusted to pH 2.5. (B) The hydrolysis of

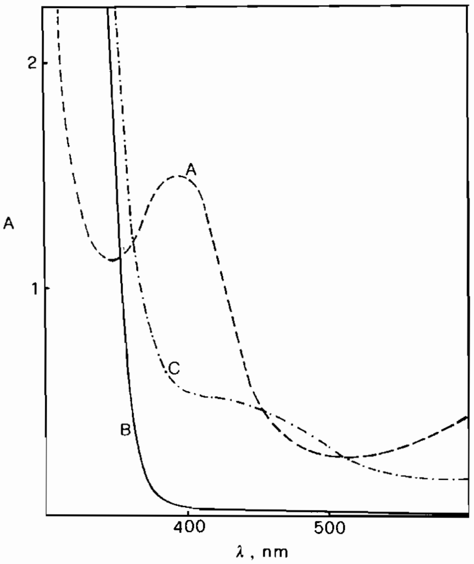

Fig. 1. Spectra of: (A) RuO_2 colloids stabilized with polybrene (0.41 g L^{-1} RuO_2, 0.20 g L^{-1} polybrene; after 90 min). (B) TiO_2 colloids (5 g L^{-1}) prepared according to method (A). (C) TiO_2 colloids, as in (B), loaded with 0.5% RuO_2.

$TiCl_4$ in ice-water was carried out at pH 0–1. After 15 days, a precipitate was formed; after centrifugation (3000 rpm, 5′) and dilution, the aqueous phase contained colloidal TiO_2 particles. This solution, kept at pH 2, was stable for months. The RuO_2 loading was carried out by mixing in the proper proportions RuO_4 (1 g L^{-1}) dissolved in water without stabilizer, with the TiO_2 colloids (5 g L^{-1}) at room temperature; after 30 min the solution turned brown and the spectrum was stable over several weeks for both colloids (A) and (B) (at pH 3) (see Fig. 1). At pH 5 the catalyst (A) flocculates after a few minutes whereas catalyst (B) is stable for at least some hours, and for longer times at pH 12.

The Ti and Ru content was determined by atomic absorption spectroscopy. The particle size of the prepared colloids was determined by photon correlation spectroscopy as described in the next paragraph.

Characterization of the Catalysts

Quasielastic light scattering was used to characterize the colloidal aggregates. The light scattering was detected at 20° (forward scatter) and 90° using the laser light scattering apparatus previously described [16]. The signal from the photomultiplier was put through an amplifier and discriminator to a correlator. The correlation function thus obtained yielded a diffusion coefficient $1/\tau = 2\,DK^2$, where τ is the correlation time and $K = 4\pi n/\lambda \sin \theta/2$ (n is the refractive index and λ the wavelength of the incident beam). The diffusion coefficient in turn, when substituted in the Stokes–Einstein equation gave the hydrodynamic radius (η is the microviscosity of the dispersion medium)

$$R_H = \frac{kT}{6\pi\eta D}$$

The hydrodynamic radii of polybrene stabilized RuO_2 was found to be around 30 nm while those of the TiO_2–RuO_2 catalysts were 5 and 45 nm for colloids prepared by methods (A) and (B), respectively.

Methods

Absorption spectra and slow kinetics were recorded on a Cary 219 spectrophotometer. The faster reaction kinetics were followed with a Durrum stopped-flow spectrophotometer. The Ce^{4+} reactions were monitored at 318 nm ($\epsilon_{318} = 5580\ M^{-1}\ cm^{-1}$) [17], while for $Ru(bpy)_3{}^{3+}$ 452 nm was used ($\epsilon_{452} = 1.35 \times 10^4\ M^{-1}\ cm^{-1}$). pH was controlled with a Metrohm E 388 potentiometer and was brought to the desired value through addition of HCl or NaOH solutions.

Dioxygen evolution was measured by gas chromatograpy (C. Erba) using Ar as a carrier in the system $Ru(bpy)_3{}^{3+}$ (4×10^{-3} *M*) in the presence of TiO_2(B)–RuO_2 (0.05 g L^{-1}, 0.32% RuO_2).

Results and Discussion

The ability of RuO_2 to mediate O_2 evolution from water using the test system Ce^{4+} has been reported by Kiwi and Grätzel [3]. The mechanism of this process has recently been investigated by different groups [18, 19].

The present results show that Ce^{4+} decays at a first order rate (see oscilloscope traces in Fig. 2) in the presence of polybrene stabilized RuO_2 colloids. The first order rate constants are virtually independent of initial Ce^{4+} concentration in the range 2–5×10^{-5} *M* (and in the range 0.0005–0.02 g L^{-1} of RuO_2; the rate constants have however a tendency to increase with decreasing Ce^{4+} concentration at higher $[RuO_2]$ values).

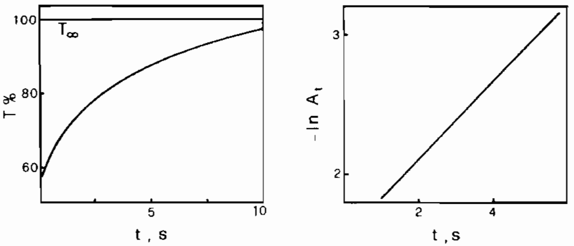

Fig. 2. Oscilloscope trace and first order plot for the Ce^{IV} decay at 318 nm. RuO_2 0.005 g L^{-1}; polybrene 0.015 g L^{-1}; H_2SO_4 0.09 *M*; 25 °C.

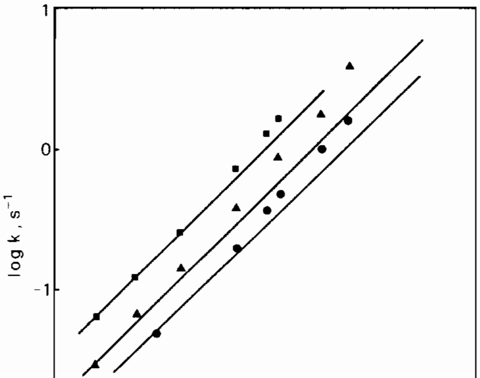

Fig. 3. Dependence of the observed rate constant of Ce^{IV} decay on RuO_2 amount at different temperatures: (●) 25 °C; (▲) 35 °C; (■) 45 °C. Ce^{IV} 4.5×10^{-5} *M*; polybrene 0.015 g L^{-1}; H_2SO_4 0.09 *M*.

Figure 3 shows the dependence of the rate constants on the RuO_2 concentration, at different temperatures. In the investigated range of catalyst concentration a satisfactory linearity can be observed particularly in the first part, while at increasing catalyst concentration (and particularly at lower

[Ce^{4+}]) deviation toward higher orders can be observed. A similar dependence has been reported for the $Fe(bpy)_3^{3+}$ reaction in the presence of copolymer stabilized RuO_2 colloids [6], although in a more restricted concentration range, and in the presence of MnO_2 based catalyst [20]. It is noteworthy that the presence of small amounts of catalyst enhances the Ce^{4+} decomposition by *ca.* three orders of magnitude; *e.g.* at 35 °C, [Ce^{IV}] = 4.5×10^{-5} *M*, [H_2SO_4] = 0.09 *M*, the rate constant of decay in the presence of 0.02 g L^{-1} of RuO_2 is 1.9 s^{-1} (the rate constant is 4.1×10^{-3} s^{-1} in the presence of 0.015 g L^{-1} of polybrene; the decay rate constant increases slightly, *i.e.* from 0.26 to 0.41 s^{-1} in going from 0.005 to 0.021 g L^{-1} of polybrene at [Ce^{IV}] = 4.5×10^{-5} *M*, RuO_2 0.01 g L^{-1}, 25 °C, [H_2SO_4] = 0.09 *M*). The effect of acidity has also been investigated. Table I collects the observed rate constants in the acidity range 0.045–0.45 *M* H_2SO_4. An inverse dependence on [H_2SO_4] seems to be operating in the investigated acidity range. As far as the mechanism of the reaction is concerned, a recent investigation points out that at [Ce^{4+}]/[RuO_2] ratios comparable with the present experimental conditions dioxygen evolution should be the predominant pathway; in addition it was stated that the use of a large catalytic surface area and low initial oxidant concentration should strongly decrease the corrosion of RuO_2 [19].

TABLE I. Catalysed Decay Rate of Ce^{IV} at Different Acidity.[a]

[H_2SO_4], *M*	k_{obs}, s^{-1}
0.045	0.82
0.067	0.57
0.090	0.44
0.135	0.30
0.225	0.19
0.45	0.098

[a] [Ce^{IV}] = 2.3×10^{-5} *M*, RuO_2 = 0.008 g L^{-1}, polybrene = 0.015 g L^{-1}, 25 °C, I = 0.45 *M* (Na_2SO_4).

The polybrene stabilized colloidal RuO_2 catalyst was also investigated with $Ru(bpy)_3^{3+}$ as the electron acceptor. This compound is particularly interesting in connection with photochemical conversion of light energy since the $Ru(bpy)_3^{3+/2+}$ couple can participate in photoredox cycles [2]. The non catalytic reduction of $Ru(bpy)_3^{3+}$ in aqueous solution (and of related complexes such as Fe and Os complexes with 2,2′-bipyridine or 1,10-phenanthroline-like ligands) have been extensively investigated [13, 21]. O_2 evolution was always lower than that stoichiometrically calculated and strongly dependent on the pH of the solution. The decay rate constant of $Ru(bpy)_3^{3+}$ is enhanced by the presence of polybrene stabilized RuO_2 (5×10^{-4} g L^{-1} of RuO_2, 0.005 g L^{-1} of polybrene) by *ca.* 2 orders of magnitude. Figure 4 reports the observed rate constants as a function of pH. The dependence on RuO_2 concentration shows however a deviation from a simple linear dependence (Fig. 5). The vestiges of higher order dependence on catalyst concentration that are hardly evident in Fig. 3 are evident in this system. Such behavior is not unusual in redox catalysis by colloidal particles, as has been reported before [11, 22–24].

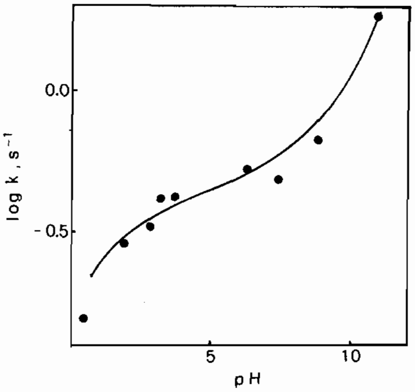

Fig. 4. Dependence of the observed rate constant of $Ru(bpy)_3^{3+}$ decay on pH. $Ru(bpy)_3^{3+}$ 3×10^{-5} *M*; RuO_2 0.0005 g L^{-1}; polybrene 0.005 g L^{-1}; 25 °C (in the range of pH 6–10, the decay is not simply first order and successive reactions take place; the reported values are based on the early part of the reaction).

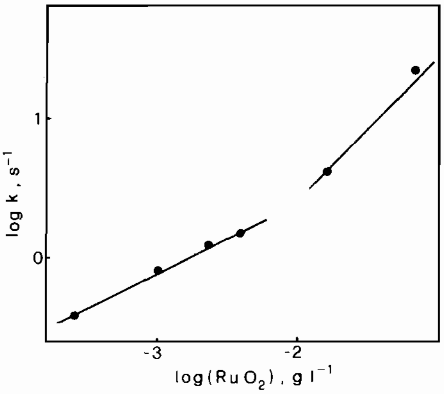

Fig. 5. Dependence of the observed rate constant of $Ru(bpy)_3^{3+}$ decay on RuO_2 amount. $Ru(bpy)_3^{3+}$ 3×10^{-5} *M*; polybrene 0.005 g L^{-1}; pH 2.6; 25 °C (the straight lines are drawn with slope 1 and 2, respectively).

The remarkable properties of catalysts based on semiconductor colloids loaded with redox catalysts have been recently pointed out [2, 25], in particular RuO_2 loaded TiO_2 has been employed in related dioxygen generating and water splitting experiments [9–11, 26]. While O_2 evolution is very low in the absence of catalyst, the addition of colloidal TiO_2–RuO_2 strongly enhances the O_2 yield particularly in the pH range between 8 and 11. These observations are similar to previously reported RuO_2 based

TABLE II. TiO_2 and RuO_2 Effect on $Ru(bpy)_3^{3+}$ Decay.

TiO_2 g L^{-1} [a]	k_{obs} (s^{-1})
0.2	12.3
0.4	7.2
1.0	7.0
2.0	7.7
RuO_2 g L^{-1} [b]	
–	3.7×10^{-3} [c]
5×10^{-3}	7.0
8×10^{-3}	16.1
1×10^{-2}	22.4

$[Ru(bpy)_3^{3+}] = 1.5 \times 10^{-5}$ *M*

pH = 2

[a] $RuO_2 = 0.005$ g L^{-1} constant. [b] $TiO_2 = 1$ g L^{-1} constant. [c] In absence of RuO_2, the rate constant for the decay of $Ru(bpy)_3^{3+}$ is $(3.2 \pm 0.5) \times 10^{-3}$ s^{-1} in the range 1–2 g L^{-1} of TiO_2.

catalytic sytems [4, 5]. The dependence of the rate constants on initial $Ru(bpy)_3^{3+}$ concentration was investigated using colloid prepared by method (A); increasing the initial oxidant concentration decreases the observed rate (*e.g.* with TiO_2 1 g L^{-1}, RuO_2 0.005 g L^{-1}: $[Ru(bpy)_3^{3+}] = 3.2 \times 10^{-5}$ *M*, k = 4.9 s^{-1}; $[Ru(bpy)_3^{3+}] = 1.4 \times 10^{-5}$ *M*, k = 7.5 s^{-1}). However the first-order decay plots were satisfactorily linear up to three half-lives. The effect of different degrees of loading was also investigated. Table II reports the data obtained at constant TiO_2 concentration and different degrees of RuO_2 loading as well as the reverse situation. In going from 0.5 to 2.0 or 2.5% of RuO_2 the rate constant is increased by a factor of 2–3. It was previously reported that the loading has no further relevant effect above these values [11]. Finally the effect of catalyst concentration was explored. Figure 6 shows the results: at high catalyst concentration (>0.5 g L^{-1}) a linear dependence can be observed, whereas at lower values a sharp decrease occurs: k = 1.1 s^{-1} (TiO_2 0.4 g L^{-1}), 0.12 (0.2), 0.04 (0.1). This behavior is not unusual and similar trends were reported in H_2 generation from gold [27] and platinum colloids [22–24]. The TiO_2–RuO_2 colloids prepared by method (B) exhibited a higher catalytic activity compared with catalyst (A) and better stability at pH ⩾ 5. Figure 7 reports the observed rate constants in the presence of TiO_2–RuO_2 (B) catalyst compared with those observed in the presence of TiO_2 alone and in the absence of any added colloids over a wide range of pH.

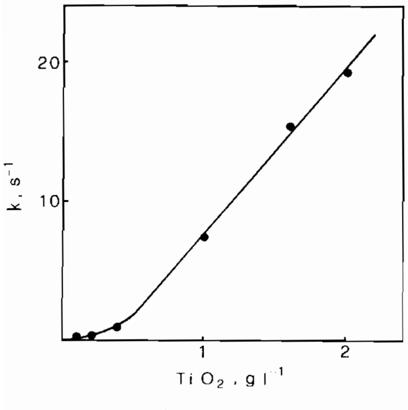

Fig. 6. Effect of the catalyst concentration on the observed rate constant for $Ru(bpy)_3^{3+}$ decay. TiO_2(A); RuO_2 0.5%; $Ru(bpy)_3^{3+}$ 1.4×10^{-5} *M*; pH 2; 25 °C.

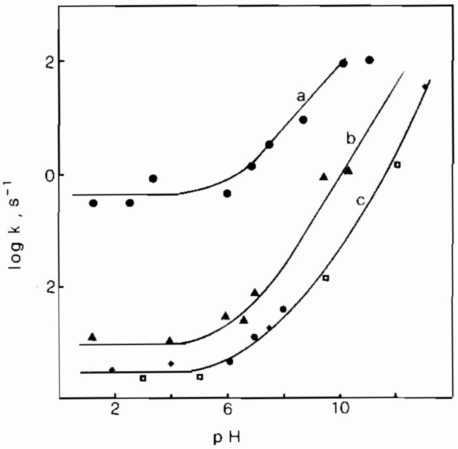

Fig. 7. Effect of pH on the observed rate constant for $Ru(bpy)_3^{3+}$ decay. $Ru(bpy)_3^{3+}$ 1.5×10^{-5} *M*; 25 °C. a) In the presence of TiO_2–RuO_2: TiO_2(B) 0.02 g L^{-1}; RuO_2 0.5%; b) in the presence of TiO_2: TiO_2(B) 0.02 g L^{-1}; c) in the absence of catalyst: (*) present work; (■) ref. 13; (●) ref. 20.

The non catalytic rate constants for the reduction of $Ru(bpy)_3^{3+}$ to $Ru(bpy)_3^{2+}$ are in agreement with previously reported data [13, 20]. Very little improvement can be obtained with TiO_2 colloids, while an increase of about 2–3 orders of magnitude can be observed in the presence of 0.02 g L^{-1} TiO_2 loaded with 0.0001 g L^{-1} RuO_2. At pH < 6 the rate constant is nearly independent of acidity, while between pH 6 and 10 a dependence can be seen. At the higher pH, the rate limit is probably the diffusional encounter between the oxidant and the colloidal particle. From the mechanistic point of view, the role of RuO_2 may be envisaged as a defect electron storage system; similar concepts were previously developed to rationalize redox catalysis by RuO_2 as well as by other colloids [4, 21, 22].

The present results for the TiO_2/RuO_2 catalyst can be compared with a study carried out by means of combined flash photolytic and conductometric techniques on a similar confunctional catalyst [11]; although the preparation and the characteristics of the catalysts exhibit some differences, similar conclusions have been reached.

The present results confirm the superior activity of this supported catalyst over the RuO_2 powder or stabilized RuO_2 colloids in the acceleration of the $Ru(bpy)_3^{3+}$ reaction, particularly in the direction of O_2 evolution [28]. A parallel observation is that a platinum coated TiO_2 colloid showed remarkable catalytic properties toward dihydrogen evolution compared with Pt colloid alone [29]. The extremely high reaction rate observed in the present system, particularly at pH 9–10, makes these colloidal TiO_2 particles loaded with RuO_2 promising catalysts for cyclic water cleavage.

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