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Reaction Rate Enhancement in Water Oxidation Catalyzed by Colloidal RuO_2

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It is well known that dioxygen evolves when alkali is added to a tris(2,2′-bipyridine)iron(III) solution, according to the reaction

$$4Fe(bpy)_3^{3+} + 4\ OH^- \rightarrow 4Fe(bpy)_3^{2+} + 2H_2O + O_2 \qquad (1)$$

Detailed analysis of the kinetic data concerning (1) and related reactions have been reported [1–4].

The photodecomposition of water into its elements is a very important goal in the field of solar energy conversion [5]; since in this process one step may be the water oxidation to dioxygen *via* a thermal electron transfer reaction, like (1), remarkable efforts have been devoted to the development of redox catalysts that could mediate this reaction.

Among these, RuO_2 based catalysts has showed a remarkable efficiency in reducing the pH requirement for dioxygen evolution, and their activity was correlated with particle size [6].

Recently, a high monodisperse colloid has been employed in operation of a dioxygen producing half-cell with a near stoichiometric reaction yield [7].

In the present note we report the effect of the RuO_2 based colloidal catalyst on the reaction rate of system (1), followed by means of a stopped-flow spectrophotometric technique.

Experimental

The catalyst was prepared from RuO_4 (Alfa) as described [7]. With this procedure the mean particle radius of the protected RuO_2, measured by quasi-elastic laser light scattering, was about 300 Å, with quite high monodispersity. The RuO_2 content is 1.75 mg/cm^3. $Fe(bpy)_3^{3+}$ was obtained by oxidation with an excess of PbO_2 of the corresponding Fe(II) complex in 2 *M* H_2SO_4, and subsequent precipitation of the perchlorate salt, as reported early [8].

Borate buffers (concentration 6.25×10^{-2} *M*) were used to adjust the pH in the range 8.7_5–9.5_5 and NaOH (1.33–6.33×10^{-2} *M*) for the measurements performed at higher pH (the ionic strength of these experiments was brought to 0.12 *M* with NaCl).

TABLE I. Observed Rate Constants and Catalytic Factors (f).[a]

pH	8.7_5	9.0	9.3	9.5_5
10^2 k_{obs} (s^{-1})	2.8	4.1	6.2	11
f	120	250	150	90

10^2 [NaOH], *M*	1.33	3.83	6.33
k_{obs} (s^{-1})	0.44	1.77	3.0
f	16	5	4

[a] Conditions: $[Fe(bpy)_3^{3+}]_o = 3$–8×10^{-6} *M*; RuO_2 3.5×10^{-3} mg/cm^3; 25.0 °C.

Kinetic runs were carried out with a Durrum stopped-flow spectrophotometer by monitoring the $Fe(bpy)_3^{2+}$ formation at 522 nm (ϵ = 8650 M^{-1} cm^{-1}).

After mixing, the solution was stable for at least 15–20 minutes; after this time, flocculation begins to occur probably due to the presence of the electrolytes. Measurements were not possible at high ionic strength (1.0 *M* NaCl).

Results and Discussion

In the presence of the colloidal catalyst, the reaction obeys the kinetic law previously reported [1–4].

In Table I, the observed rate constants and the catalytic factors, measured in the presence of 3.5×10^{-3} mg/cm^3 of RuO_2, are reported. It can be noted that the maximum in the catalytic activity was observed at pH *ca.* 9, that is the same pH at which the highest dioxygen yield was measured [7], whereas the rate increase was lower in strongly alkaline media, where it reaches only a factor of 4 at the highest NaOH concentration.

RuO_2 is known to exhibit a high electrocatalytic activity in the oxygen evolution process at electrodes with RuO_2 coatings[9]. The mechanism of water oxidation is not simple to elucidate, but RuO_2 can probably mediate certain steps with high energy intermediates.

Some measurements were performed by varying the catalyst concentration and an approximately linear relationship between the observed rate and the amount of RuO_2 was observed (Table II). Then, the increase in the RuO_2 colloidal particle concentration, improves the contact area of the catalyst with the aqueous solution, resulting in a higher efficacy.

TABLE II. Dependence of the Observed Rate Constants on the Catalyst Concentration.[a]

RuO_2 (10^4 mg/cm^3)	0	1.7_5	3.5	8.7_5	$17._5$	35
k_{obs} (s^{-1})	0.028	0.24	0.42	0.77	1.6	3.3

[a]Conditions: $[Fe(bpy)_3^{3+}]_o$ = 3–8 × 10^{-6} *M*; pH 8.7_5; 25.0 °C.

Experiments performed about 1 month after the colloidal catalyst preparation showed an activity drop to a 30–40% of the initial factor and a decrease in stability of the RuO_2 containing solutions even in the presence of a moderate ionic strength. On the basis of these preliminary kinetic results, work is continuing in an attempt to elucidate the factors governing the catalytic activity also on other redox reactions.

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