Photo-oxidation of Water on the Surface of Hectorite using *trans*-Diaquabis-(2,2′-bipyridine)ruthenium(2+) as Catalyst

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Summary *trans*-Ru(bpy)$_2$(H$_2$O)$_2^{2+}$ (bpy = 2,2′-bipyridine) was shown to be an efficient redox catalyst for the oxidation of water and allowed the construction of a catalytic water photo-oxidation system within an adsorbed layer.

THE photocatalytic splitting of water with transition-metal complexes as sensitizers has attracted much attention during the last few years. A large variety of homogeneous and heterogeneous systems are currently being investigated, the most promising being the heterogeneous or micro-heterogeneous ones. Indeed, such systems offer an improved possibility of avoiding back reactions, stabilizing high-energy intermediates, or catalysing difficult redox reactions. Charge separation for instance was shown to be very efficient in micellar media or on the surface of chemically modified polymers.[1] Catalytic oxidation or reduction of water was achieved with colloidal metal or oxide particles in numerous systems.[2]

Our approach to the water-splitting problem has been to use organometallic compounds adsorbed on solid surfaces[3,4] in order to achieve the separation of the H_2- and O_2-producing systems at the molecular level, by taking advantage of the heterogeneous character of the surface or of the adsorption selectivities for instance. An obvious problem in this type of system is the design of selective catalysts, for H_2 and O_2 production respectively, which can be adsorbed on the surface.

We report here on a system for the photooxidation of water, using exclusively adsorbed components. This system, which is conceptually similar to the one first proposed by Lehn *et al.*,[5] was composed of a sensitizer [Ru(bpy)$_3^{2+}$, bpy = 2,2′-bipyridine], a 'sacrificial' electron acceptor [Co(NH$_3$)$_5$Cl^{2+}], and a redox catalyst [*trans*-Ru(bpy)$_2$-(H$_2$O)$_2$]$^{2+}$. All these components were adsorbed by cation exchange on the surface of a Na-hectorite clay. The concentrations of the three components on the surface were as follows: Co(NH$_3$)$_5$Cl^{2+}: 60% of the cation-exchange capacity (C.E.C.); Ru(bpy)$_3^{2+}$: 1% of C.E.C.; Ru(bpy)$_2$-(H$_2$O$_2$)$_2^{2+}$: 1% of C.E.C.

The reaction was carried out in a static reaction system containing 50 ml of a 6% (w/w) aqueous suspension of the reactive clay at pH 4·2 (acetate buffer). This suspension was illuminated with two 500 W quartz-halogen lamps (less than 1% spectral radiance below 400 nm) with appropriate heat filters and continuous stirring. Control experiments performed with a u.v. cut-off filter (370 nm) gave results similar to the experiments performed without the filter, showing that the effective radiation is in the visible region [λ_{max} of Ru(bpy)$_3^{2+}$ = 450 nm].

The results are summarized in Figure 1. A rapid evolution of gas is observed until the acceptor is consumed. Experiments performed with one of the components missing showed that all three are necessary for gas evolution. It should be noted that, in homogeneous solution, the reaction proceeds at the same rate. What is demonstrated is that all components seem to be also equally mobile on a clay surface, opening a route for a catalytic water-splitting system within adsorbed layers.

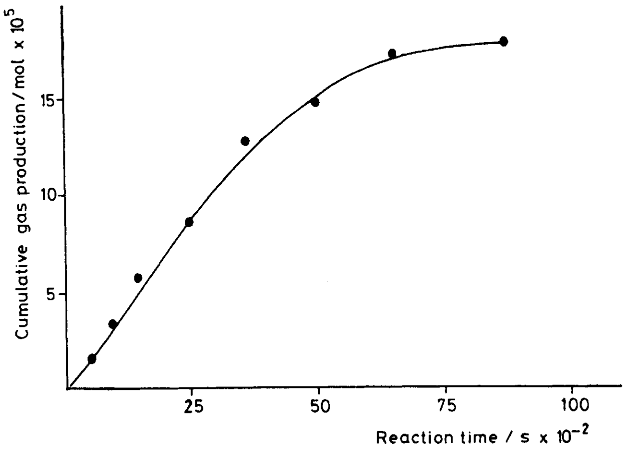

FIGURE 1. Cumulative gas production from 50 ml of the described suspension *vs.* reaction time.

Chromatographic analysis of the evolved gas shows, however, that it is composed of O_2 and N_2 in a *ca.* 50:50 ratio. It was assumed that the N_2 originated from the decomposition of NH_3 molecules produced by the decomposition of the acceptor complex after reduction: $Co(NH_3)_5Cl^{2+} + e^- \rightarrow Co(NH_3)_5Cl^+ \rightarrow Co^{2+}_{aq.} + 5NH_3 + Cl$.

In order to verify this hypothesis, the reaction was carried out under the same conditions but with helium flowing continuously through the suspension. This allowed on-line analysis of the reaction gases to be performed at determined intervals. The results are shown in Figure 2, which shows that initially only O_2 is produced by the reaction and that N_2 is only produced later on, probably from the NH_3

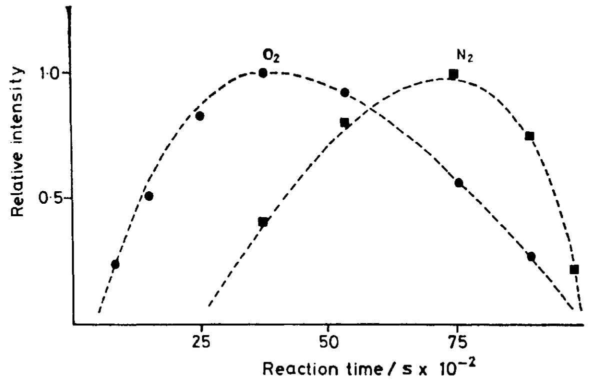

FIGURE 2. Relative peak intensities of O_2 (●) and N_2 (■) from on-line chromatographic analysis of effluents from the described reaction system *vs.* reaction time.

formed concomitantly with O_2. This was verified by adding an ammonium salt to the reaction mixture. In this case, N_2 was indeed produced from the beginning of the experiment. This shows that *trans*-$Ru(bpy)_2(H_2O)_2^{2+}$ is also an efficient catalyst for ammonia oxidation.

Calculation of the turnover number shows that 20 electrons are transferred per molecule of catalyst and per molecule of sensitizer, demonstrating the truly catalytic nature of the reaction. Higher turnover numbers can hardly be obtained in this system because of the limited amounts of reactants that can be adsorbed on the clay surface.

A few comments should be made concerning the real nature of the catalyst. It has previously been shown that $Ru(bpy)_2(H_2O)_2^{2+}$ adsorbed on hectorite is converted into a μ-oxo dimer of Ru^{III}, $(bpy)_2(H_2O)Ru\text{–}O\text{–}Ru(H_2O)(bpy)_2^{4+}$, in the presence of oxygen and under dry conditions (air-dried clay powders).[4] Experiments performed with this dimer adsorbed on hectorite did not lead to oxygen production suggesting that the catalytic redox cycle involves the $Ru^{II} \rightleftharpoons Ru^{III} \rightleftharpoons Ru^{IV}$ conversion of a monomeric species, in agreement with what has been shown for the electrocatalytic oxidation of alcohols using $(trpy)(bpy)Ru(H_2O)_2^{2+}$ (trpy = 2,2′,2″-terpyridine) as catalyst.[6]

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