The Photoproduction of O_2 from a Suspension Containing CeO_2 and Ce^{4+} Cations as an Electron Acceptor

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Herein we report the first finding on the photocatalytic production of oxygen from the irradiation of a CeO_2-H_2O-Ce^{4+}_{aq} aqueous suspension. The O_2 yield strongly depended on the duration of irradiation, CeO_2 concentration, concentration of Ce^{4+}_{aq} cations, and pH of the suspension. The optimum photoproduction for O_2 was obtained under the following operating conditions: Illumination time > 15 h, CeO_2 concentration: 2.5-5 g dm^{-3}, $[Ce^{4+}]$: 4-5 mM, pH < 2, and illumination wavelength < 450 nm. The studied system utilizes CeO_2 to accomplish the initial light absorption, charge separation, and O_2 evolution from the interaction of H_2O molecules with holes in the CeO_2 valence band, in the presence of Ce^{4+}_{aq} species as an acceptor of conduction band electrons.

The photocatalytic splitting of water to hydrogen and oxygen is of considerable interest due to the possible applications for storage of solar energy in the form of chemical energy. For the last two decades most of the research work concentrated mainly on the photocatalytic decomposition of water to produce hydrogen, and a large number of findings has been reported in the literature.[1-2] More recently, interest on the second half reaction, i.e., O_2 evolution has been growing steadily. Recent research has seen an increased effort in the search for new materials for photosplitting of water to produce O_2. The obtained data suggest that metal oxide semiconductors are best suited for this reaction as far as activity and long-term stability are concerned.[3-5]

The purpose of this work has been to investigate the performance of CeO_2 as a material for photoassisted water splitting to produce oxygen, and to determine the optimum reaction conditions for the reaction. The choice of CeO_2 was prompted by the fact that among the metal oxides we have tested so far CeO_2 has interesting economical and physicochemical properties. CeO_2, is nontoxic, cheap, and abundant. Furthermore, CeO_2 is semiconducting material with a bandgap energy of between 2.7-3.1 eV.

On the other hand, cerium has +1, +3, and +4 oxidation states. These oxidation states makes cerium cations to be an attractive species as an electron acceptor or sacrificial agent in aqueous photoelectrochemical reactions since they can oxidize and reduce reversibly ($E^{\circ}_{Ce3+/Ce4+} = + 1.44$ V). Despite the fact that Ce^{3+}/Ce^{4+} is a simple redox couple, its use in photocatalytic reactions has not been explored. In this work, we use the transfer of an electron from the photoexcited CeO_2 particle to surface-adsorbed Ce^{4+} as way of improving the e^--h^+ charge separation and the subsequent migration of the charges to active centers on the CeO_2 surface.

Powdered CeO_2 (99.9% purity, 9.5 m^2 g^{-1}, Wako Chemical Co.) was white-yellowish and its onset of absorption was ~ 422 nm, which corresponds to the bandgap energy of ca. 2.94 eV. The Cerium sulfate (99%) was used as supplied. The absorption edge for the 4 mM Cerium sulfate solution was ~ 410 nm.

Experiments were performed using a stirred 350 cm^3 CeO_2+Ce^{4+} aqueous suspension and a Pyrex annular reactor, under an initial 7 kPa of argon. Oxygen was analyzed by GC equipped with a TCD and molecular sieves (5A) at 318 K.

The variation of the O_2 yield as a function of the amount of illumination time (t_i) and on CeO_2 concentration in the suspension is displayed in Figure 1. No O_2 yield was noted in the absence of CeO_2. After an initial induction period of ~1 h, the yield of O_2 increased with illumination time reaching about 300 μmol after 7 h of irradiation for suspension containing 4.6 g CeO_2 dm^{-3} and 4 mM Ce^{4+}. For comparison, the O_2 yield from 2.3 g TiO_2 dm^{-3}+4 mM Ag^{+}_{aq} was 101 μmol O_2 in 7 h. In addition, the O_2 yield increased in proportion to the CeO_2 content in the suspension, and leveled off at $C_{CeO2} > 5$ g dm^{-3}.

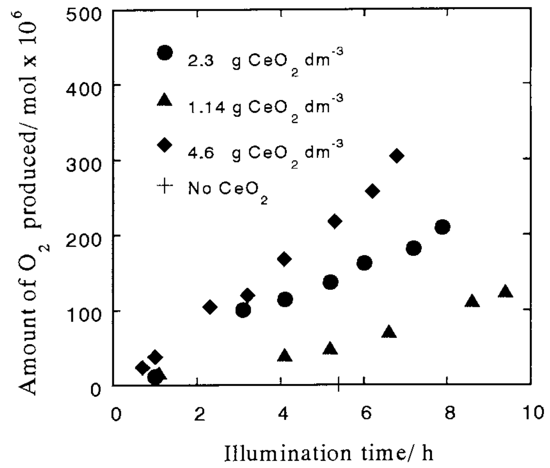

Figure 1. Activity of CeO_2 for O_2 evolution as a function of irradiation time and CeO_2 concentration. Conditions: 1.1 dm^{-3} annular reactor; suspension: 0.35 dm^{-3}; 400 W Hg lamp; $\lambda_i \geq 300$ nm; electron acceptor: 4 mM Ce^{4+}.

The amount of O_2 produced was found to be dependent on the initial concentration of Ce^{4+} species in the suspension, as illustrated in Figure 2. The O_2 yield increased in proportion to Ce^{4+} concentration passing through a maximum at ~ 4 mmol Ce^{4+} dm^{-3}. This result may be partly explained by the fact that an increase in Ce^{4+} concentration will lead to higher interfacial concentrations of these species and higher surface coverage. This in turn increases the probability of interaction between photogenerated electrons and Ce^{4+} species, thus improving the charge separation and overall reaction rate. The decline in the O_2 yield at high Ce^{4+} concentrations can be attributed, among other things, to the change of the net surface charge, and potential distribution across the inter-phase layer, and to inter-phase diffusion limitations. For example, the transport of Ce^{4+} to the

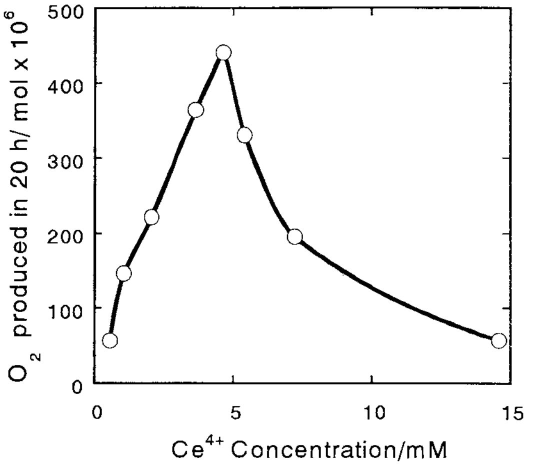

Figure 2. Dependence of O_2 yield on the Ce^{4+}concentration. C_{CeO2}= 2.3 g dm^{-3}. Other conditions as in Figure 1.

close proximity of a CeO_2 particle and the ability of produced Ce^{3+} ions to migrate away into solution. Another explanation is the increase in the inner filter effect by Ce^{4+} with increase in Ce^{4+} concentration.

The pH dependence on the reaction was also investigated and the O_2 production as function of pH is plotted in Figure 3. As seen, the amount of O_2 evolved was strongly dependent upon the initial pH. The pH values below pH 2 gave better O_2 yields, whereas increase in pH resulted in a considerable decrease in the O_2 yield. One of the significant result is the feasibility of producing O_2 in suspensions with pH > 6. Most of the active electron acceptors used previously had a tendency of forming light absorbing precipitates at pH > 4.[3] The variation of the O_2 yield with pH can be attributed to the following: change of the ionic strength of the suspension with varying pH, shift of CeO_2 flatband potential with pH, change in adsorption and the coordination of ions in the solution onto CeO_2 particles and the resulting charge compensation. Another reason might be the variation of $E^{\circ}_{Ce3+/Ce4+}$ with pH of the suspension and the salt counter ion.

The overall reaction scheme for the O_2 production noted here can be envisaged as follows: Following photoexcitation of CeO_2, electron and holes migrate to the inter-phase layer and are trapped on the CeO_2 surface. The surface-adsorbed Ce^{4+} scavenges away the trapped electrons at the interface forming its reduced state, e.g., Ce^{3+}. Simultaneously, the trapped holes may oxidize water molecules in a four-electron exchange process to give oxygen. The formed Ce^{3+} may also participate in scavenging of the electrons but the rate of this reaction is thirty times slower than that noted with Ce^{4+}species, as observed in runs where Ce^{3+} was used as an electron acceptor.

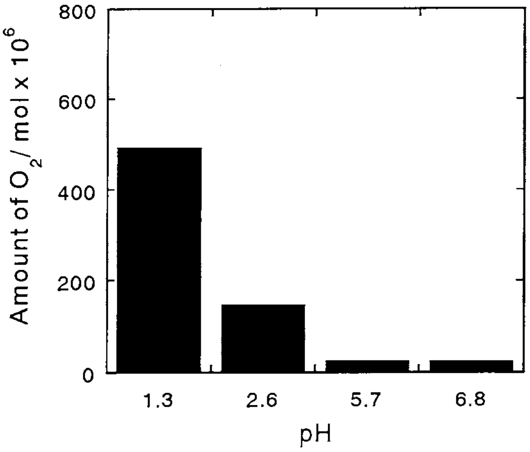

Figure 3. Influence of pH on the yield of O_2. $[Ce^{4+}]$ = 1.1 mM; C_{CeO2}= 2.3 g dm^{-3}; t_I= 20 h.

Further work is in progress so as to investigate the CeO_2-H_2O-Ce^{4+}-hv system in detail.

References and Notes

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