

Clay-assisted Visible Light Water Photoreduction

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In recent years, several groups have shown the potential of the ruthenium bipyridyl–methyl viologen system in promoting water photoreduction [1]. Heterogeneous catalysts, such as colloidal platinum [2, 5] or platinum deposited upon inorganic supports [4, 5], have been used successfully in this system. Hydrogenase can play the role of these heterogeneous catalysts [6]. Pinnavaia *et al.* have demonstrated the selective catalytic properties of a rhodium complex incorporated into a hectorite [7]. Nitrogen photoreduction has been observed on desert sands [8].

Montmorillonite is a layered alumino-silicate, with expandable inter-layers distances (from 12 to 20 Å), permitting the intercalation of organic substrates [9]. Methyl viologen or ruthenium bipyridyl, two cationic species, are potentially good substrates for incorporation into montmorillonite lamellar spaces. The quenching of ruthenium bipyridyl bound to colloidal kaolin and montmorillonite by inorganic and organic substrates has been studied [10]. Van Damme and co-workers have shown that platinum and ruthenium dioxide supported on a sepiolite clay can catalyze water photosplitting [11].

We have observed hydrogen formation in a natural clay when a buffered system (pH 7) containing methyl viologen and ruthenium bipyridyl, with triethanolamine used as sacrificial donor, is irradiated with visible light (>395 nm).

Experimental

Tris (2,2'-bipyridyl)–ruthenium (II) chloride was purchased from Alfa, the methyl viologen and triethanolamine from Aldrich, and all were used without further purification. The buffer (pH 7.00) was a Fisher solution (monobasic potassium phosphate and sodium hydroxyde). The clay was a Wyoming bentonite (Clay Spur, Wyoming, U.S.A.). A Typical solution was prepared by mixing a solution of 0.0192 g of ruthenium bipyridyl (5.00×10^{-4} M), 0.0771 g of methyl viologen (5.00×10^{-3} M), 0.8 ml of

TABLE I. Production of Hydrogen in Presence of the Tetrameric Iron–Sulfur Cluster Pre-adsorbed on Clay.^a

[Rubipy] (M)	[MV] (M)	[Cluster] (M)	H ₂ produced (nmol, 15 hrs)
5.0×10^{-4}	5.0×10^{-3}	–	250
5.0×10^{-4}	5.0×10^{-3}	6.5×10^{-4}	120
5.0×10^{-4}	5.0×10^{-3}	1.3×10^{-3}	60
–	5.0×10^{-3}	1.3×10^{-3}	–
5.0×10^{-4}	–	1.3×10^{-3}	–

^aIn each case, triethanolamine has a concentration of 5.0×10^{-2} M and the clay is suspended in a 60 ml solution (3.0 g/L); Rubipy = ruthenium bipyridyl, MV = methyl viologen, Cluster = $[n\text{-Bu}_4\text{N}]_2[\text{Fe}_4\text{S}_4(\text{SPh})_4]$.

triethanolamine (1.0×10^{-1} M) in 10 ml of the buffer solution with a suspension of clay in 50 ml of distilled and deaerated water. The reaction mixture was illuminated under argon with a 300 W tungsten–halogen lamp (at 25 cm from the center of the solution) through a 395 nm glass filter (Ealing, GG-395). Quantitative determinations of the hydrogen produced was effected by G.C. analysis on a 5 Å molecular sieve. In some experiments, presence of hydrogen was also checked by mass spectrometry. Tetra-*n*-butylammonium tetrakis [phenyl-thiolato- μ_3 -sulphido–iron] cluster was prepared and purified according to the procedure of Christou and Garner [12]. H-1 nmr (Varian XL-200), U.V. spectra and melting points were in agreement with literature data [13, 14]. Typically, an iron–sulfur pre-adsorbed clay preparation was formed by mixing a solution of the cluster in acetonitrile with a suspension of clay in acetonitrile and evaporated to dryness. Freshly-obtained black powder was used in some experiments (see Table I) in replacement of the clay in the procedure described above.

Results and Discussion

Figure 1 shows the production of hydrogen as a function of the quantity of clay in the medium. The blank experiment (absence of clay) shows no hydrogen production. A maximum is observed at a concentration of 3.0 g per litre of solution. When the clay concentration is enhanced to 5.0, the activity is reduced by a factor of 3. Pre-adsorption of the methyl viologen on the clay gave similar activity as the corresponding usual procedure (Fig. 1). The amount of hydrogen produced is directly proportional to the time of irradiation, for at least

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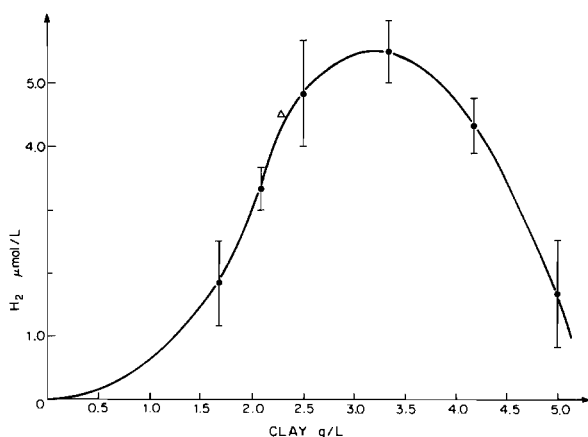


Fig. 1. Amount of hydrogen produced as a function of the clay concentration after 20 hrs of irradiation. The measurement shown as (Δ) corresponds to a methyl viologen pre-adsorbed clay (see text).

24 hrs*. We have calculated an approximate monolayer surface coverage of the montmorillonite by methyl viologen alone. We have used a value of 750 m²/g as the typical surface area of the clay [15] and have estimated the area covered by a methyl viologen molecule as 60 Å². The maximum of activity corresponds to a 70% coverage. The amount of hydrogen produced drops considerably when a surface coverage of 100% in methyl viologen is reached. In these conditions the concentration of the highly polarized water molecules on the acidic mineral surface is reduced and we believe that these water molecules are involved in the photoreduction process. Moreover, electron acceptor sites such as aluminum at the crystal edges can be covered at these high organic substrate/clay ratios. At lower surface coverage (large clay concentrations), the drop in the amount of hydrogen produced can be attributed to the decrease of accessibility of intercalated methyl viologen for reaction with the excited ruthenium bipyridyl, and/or a larger amount of the hydrogen produced that is retained on the clay surface.

Since hydrogenase [16] and iron-sulfur clusters fixed on serum bovine albumin [17] have been shown to act as catalysts in the photoreduction of water in similar systems, we have studied the activity of the clay on which tetrameric iron-sulfur cluster

had been deposited (see Experimental). The use of the clay-cluster preparation inhibits the hydrogen formation (Table I). Surprisingly, the coverage of the clay surface by the anionic cluster and its counter-cation prevents the formation of active sites for electron transfer from the reduced methyl viologen.

We are actively pursuing our investigations on the mechanism by which the clay assists the hydrogen production.

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*Correlation coefficient, $\rho = 0.96$ for 10 pts, with a slope of 11 nmol/L/hr.