SELECTIVE PHOTOREDUCTION OF CARBON DIOXIDE TO METHANOL WITH HYDROUS CUPROUS OXIDE

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Summary

An aqueous suspension of hydrous cuprous oxide $(Cu_2O \cdot xH_2O)$ is found to photoreduce carbonic acid selectively to methanol, but is itself sacrificed. The high yield and selectivity is attributed to strong chemisorption of carbon dioxide, highly negative flat-band potential and multielectron transfer.

1. Introduction

There are three chemical reactions whose photocatalytic initiation would be of tremendous economic importance: (1) the decomposition of water into oxygen and hydrogen; (2) the reduction of dinitrogen to ammonia; (3) the reduction of carbon dioxide to C_1 or C_2 compounds [1 - 6].

The virtues of the photodecomposition of water are well known and during the past decade a large number of model systems have been studied [1, 2, 7 - 13]. Unfortunately, their quantum efficiencies are small and a promising practical device is not yet available.

The photoreduction of dinitrogen [14 - 17] presents the following additional difficulties: (i) the reduction of one molecule of dinitrogen involves the transfer of six electrons compared with the two electrons needed for the production of one molecule of hydrogen from water; (ii) ammonia accumulates in the solution and participates in back reactions, *i.e.* the oxidation of

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ammonia into nitrates, nitrites or nitrogen; (iii) the reduction of dinitrogen presents a strong activation barrier; (iv) nitrogen is poorly chemisorbed on catalyst surfaces.

Unlike water or nitrogen, carbon dioxide can be reduced in a series of steps to yield formic acid, formaldehyde, methanol and methane

 $CO_{2} + 2H^{+} + 2e^{-} \longrightarrow HCOOH$ (1) $CO_{2} + 4H^{+} + 4e^{-} \longrightarrow HCHO + H_{2}O$ (2) $CO_{2} + 6H^{+} + 6e^{-} \longrightarrow CH_{3}OH + H_{2}O$ (3) $CO_{2} + 8H^{+} + 8e^{-} \longrightarrow CH_{4} + 2H_{2}O$ (4)

Each step requires a transfer of two additional electrons. Carbon dioxide generally chemisorbs strongly on most catalysts and involves little activation energy during reduction. Thus it seems that the reduction of carbon dioxide is relatively easy, when compared with dinitrogen. However, the constraint set by back reactions is very severe in the reduction of carbon dioxide. The reduction products of carbon dioxide (*i.e.* formic acid, formaldehyde) are themselves excellent electron donors. As their concentration increases, the oxidative back reactions become more favourable. Consequently, the photolysis of carbonic acid in the presence of semiconductor catalysts yields trace quantities of formic acid, formaldehyde, methanol and methane [5, 18 - 22]. With semiconductor catalysts such as TiO_2 and $SrTiO_3$, the yield of the first reduction product, *i.e.* formic acid, is higher than that of formaldehyde and methanol by more than one order of magnitude [5].

Unlike the photoreduction of water, photoreduction of carbon dioxide cannot be enhanced by incorporating strong electron donors in the solution. The reason for this is that the reduction products of carbon dioxide are themselves powerful electron donors which get readily chemisorbed into the catalyst particles. One way to overcome this problem is to employ semiconductor catalysts that undergo self-sacrifice with the rapid consumption of photogenerated holes. In our studies we have found that hydrous cuprous oxide possesses this property. The photolysis of a suspension of hydrous cuprous oxide is found to produce methanol selectively and the yield obtained is higher than that observed in previous systems reported in the literature.

2. Experimental details

The catalyst was prepared by the hydrolysis of CuCNS as described in ref. 22. As drying was found to inactivate the catalyst, moist material was used in all experiments and the equivalent amount of Cu_2O was estimated from the quantity of CuCNS employed. The band gap of the material

deduced from the reflectance spectrum is 2.5 eV [22] (compared with 2.3 eV for dehydrated material). The Hall test performed with desiccator-dried compound shows that it is a p-type material. Furthermore, surfaces coated with $Cu_2O \cdot xH_2O$ show cathodic photoresponse in electrolytic media [22].

The photolysis experiments were carried out in a 200 ml glass bulb where the suspension of $Cu_2O \cdot xH_2O$ was stirred magnetically. Purified carbon dioxide (passed through wash bottles containing chromic acid and water to remove organic matter and the spray) was bubbled through the flask at a rate of 0.6 l min⁻¹. The light source used was a 200 W medium pressure mercury lamp (full spectrum).

The photolysis product was tested for formic acid, formaldehyde and methanol by the following methods. The contents of the flask were filtered and distilled. A portion of the filtrate was treated with Tollen's reagent and estimated for formaldehyde turbidimetrically. Another portion was digested with aluminium amalgam and redistilled. In this process any formic acid present is reduced into formaldehyde. From the two estimations of formaldehyde, the formic acid concentration was determined. To estimate methanol, a third portion of the original distillate was reacted with acidified dichromate, then re-distilled and estimated for formaldehyde. The presence of methanol was also confirmed by gas chromatographic analysis. Hydrogen was detected using a polarographic detector (Applied Photophysics) and confirmed by gas chromatography (Shimadzu GC - 9AM).

3. Results and discussion

The variation in the concentration of methanol and formaldehyde during photolysis is presented in Fig. 1. Formic acid and formates are not



Fig. 1. Variation in the yields of methanol (a) and formaldehyde (b) as a function of time (the quantity of $Cu_2O \cdot xH_2O$ used was equivalent to 20 mg of Cu_2O).

detected. Formaldehyde and methanol concentrations reach peak values in approximately 30 min and 45 min respectively. The yields of these compounds are more than two orders of magnitude higher than those obtained with $SrTiO_3$ suspensions of similar absorbance under similar conditions. The optimum yields of formic acid, formaldehyde and methanol are compared in Table 1. It is important to note that with $SrTiO_3$, the substance produced in the highest concentration is formic acid. The photochemical reactions which occur can be represented as follows

$$CO_{2} + 4H^{+} + 4e^{-} \longrightarrow HCHO + H_{2}O$$
(5)
$$\uparrow$$
conduction band
$$2Cu_{2}O \cdot xH_{2}O + 4OH^{-} + 4h^{+} \longrightarrow 4CuO + 2(x + 1)H_{2}O$$
(6)
$$\uparrow$$
valence band
$$CO_{2} + 6H^{+} + 6e^{-} \longrightarrow CH_{3}OH + H_{2}O$$
(7)
$$\uparrow$$
valence band
$$3Cu_{2}O \cdot xH_{2}O + 6OH^{-} + 6h^{+} \longrightarrow 6CuO + 3(x + 1)H_{2}O$$
(8)
$$\uparrow$$
valence band

The oxidation of hydrous cuprous oxide can be seen as a darkening of the suspension. The almost complete absence of formic acid is an indication that the transfer of two electrons is less probable than four or six electrons.

TABLE 1

A comparison of the optimum yields of C_1 products from $Cu_2O \cdot xH_2O$ and $SrTiO_3$ under similar conditions

Catalyst	$HCOOH$ ($\mu mol l^{-1}$)	<i>HCHO</i> (μmol l ⁻¹)	$CH_3OH \ (\mu \mathrm{mol}\ \mathrm{l}^{-1})$
$\operatorname{Cu}_2 \operatorname{O} \cdot x \operatorname{H}_2 \operatorname{O}$	0.00	3.5	24.0
SrTiO ₃	0.70	0.02	0.03

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The presence of methanol in large excess over formaldehyde suggests that the successive two-step electron transfer is not the mechanism of the reaction. An interesting question is: why are electron transfers of higher multiplicity favoured? A possible explanation is as follows. In a p-type semiconducting particle, the photogenerated electrons accumulate in the bulk of the material and holes readily diffuse towards the surface. In the present case, holes are quickly removed by capture on OH^- ions adsorbed at the surface, followed by self-sacrifice of the sensitizer. The rapid removal of holes results in a build-up of the electron density within the particles, making multielectron transfers more probable. The stepwise reductions cannot be completely ruled out.

In a separate experiment, we have observed that when a suspension of $Cu_2O \cdot xH_2O$ in aqueous formaldehyde (10^{-3} M) is irradiated, more than 30% is reduced to methanol in about 45 min. When the same experiment is repeated with SrTiO₃ only trace quantities of methanol are produced. Here, the predominant reaction is oxidative degradation of formaldehyde with concomitant evolution of hydrogen. This observation clearly demonstrates that in the $Cu_2O \cdot xH_2O$ system, holes are consumed exclusively in its own oxidation. A suspension of hydrous cuprous oxide in water photogenerates hydrogen on irradiation (Fig. 2). However, in carbonic acid medium, hydrogen evolution is not detected. Undoubtedly this is a consequence of the fact that carbon dioxide (or carbonate and bicarbonate ions) is strongly chemisorbed in $Cu_2O \cdot xH_2O$.

It is important to note that dehydrated cuprous oxide neither photogenerates hydrogen from water nor reduces carbonic acid. The flat-band potential of Cu_2O is not favourable for these reduction processes. Although we have not succeeded in determining the exact value of the flat-band potential of $Cu_2O \cdot xH_2O$, a comparison of the onset potentials of Cu_2O and $Cu_2O \cdot xH_2O$ shows that the latter is distinctly shifted in the negative direction [22]. The shift is more pronounced when the pH is increased [22].



Fig. 2. Hydrogen photogeneration from water (the quantity of $Cu_2O \cdot xH_2O$ used was equivalent to 20 mg of Cu_2O ; numbers indicated near each curve are the pH values).

Thermodynamically, both water and carbon dioxide reduction are favoured at low pH. In the reduction of water with $Cu_2O \cdot xH_2O$, the rate of reaction is optimum at around pH 11. The origin of an optimum pH can be understood as arising from the combined effect of the above two factors. However, in the reduction of carbon dioxide, an increase in pH in the alkaline direction leads to a rapid decrease in the reaction rates. The reason could be that the active species involved in carbon dioxide reduction is the bicarbonate ion, whose presence is favoured when the pH is acidic.

The decrease in the concentration of methanol on prolonged irradiation could result from the following reactions: (i) the reduction of methanol to hydrogen or methane; (ii) the oxidation of methanol by the degraded catalyst containing cupric oxide which is completely reduced to Cu_2O (nonhydrous). We did not have the facilities to detect methane; however, photolysis of methanol with $Cu_2O \cdot xH_2O$ yields detectable quantities of hydrogen.

4. Conclusion

The selective production of methanol and the high yield make the above system interesting. Photochemical reactions where the sensitizer undergoes self-sacrifice deserve more attention. If a method could be found to regenerate the sensitizer, devices of this type would become of practical importance. If a second light reaction was found, which converted the degraded sensitizer containing CuO into $Cu_2O \cdot xH_2O$, then our process would closely mimic natural photosynthesis with $CuO-Cu_2O \cdot xH_2O$ as the sensitizer as well as the intermediate redox couple. We have also noted that hydrous cuprous oxide has the ability to photoreduce dinitrogen to ammonia [22].

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References

- 1 G. Porter, in J. D. Coyle, R. R. Hill and D. R. Roberts (eds.), Light, Chemical Change and Life, Open University Press, Milton Keynes, 1982.
- 2 M. Gratzel (ed.), Energy Resources through Photochemistry and Catalysis, Academic Press, New York, 1983.
- 3 A. Heller, Nouv. J. Chim., 11 (1987) 187.
- 4 G. N. Schrauzer and T. D. Guth, J. Am. Chem. Soc., 99 (1971) 7188.
- 5 T. Inoue, A. Fujishima, S. Konushi and K. Honda, Nature, 277 (1979) 637.
- 6 K. Tennakone, S. Wickramanayaka, C. A. N. Fernando, O. A. Ileperuma and S. Punchihewa, J. Chem. Soc., Chem. Commun., (1987) 1078.
- 7 A. J. Bard, J. Phys. Chem., 88 (1982) 2.

- 8 J. M. Lehn, J. P. Sauvage and R. Ziessel, Nouv. J. Chim., 4 (1980) 623.
- 9 D. Duonghong and M. Gratzel, J. Chem. Soc., Chem. Commun., (1984) 1579.
- 10 E. Yesodharan, S. Yesodharan and M. Gratzel, Sol. Energy Mater., 10 (1984) 287.
- 11 K. Tennakone and S. Pushpa, J. Chem. Soc., Chem. Commun., (1985) 1433.
- 12 G. Blondeel, A. Harriman and D. Williams, Sol. Energy Mater., 9 (1983) 217.
- 13 A. Mills and G. Porter, J. Chem. Soc., Faraday Trans. 1, 78 (1982) 3659.
- 14 S. Grayer and M. Halman, J. Electroanal. Chem., 170 (1984) 363.
- 15 H. Miyama, N. Fujii and Y. Nagal, Chem. Phys. Lett., 74 (1980) 523.
- 16 G. N. Schrauzer, N. Strampach, L. N. Hui, M. R. Palmer and J. Salehi, Proc. Natl. Acad. Sci. U.S.A., 50 (1985) 3873.
- 17 E. Endoh, J. K. Lelane and A. J. Bard, J. Phys. Chem., 90 (1986) 6223.
- 18 J. C. Hemminger, R. Carr and G. A. Somorjai, Chem. Phys. Lett., 57 (1978) 100.
- 19 B. Aurian-Blajeni, M. Halmann and J. Manassen, Sol, Energy, 25 (1980) 165.
- 20 A. H. A. Tinnemans, T. P. M. Koster, D. H. M. W. Thewissen and C. W. De Kreuk, J. Electroanal. Chem., 145 (1983) 449.
- 21 M. Ulman, A. H. A. Tinnemans, A. Mackor, B. Aurian-Blajeni and M. Ulman, Int. J. Sol. Energy, 1 (1982) 213.
- 22 K. Tennakone, K. R. S. S. Kekulawala, A. H. Jayatissa and S. Punchihewa, Chem. Phys. Lett., 150 (1988) 511.