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The photoreduction of acetylene by band-gap irradiation of TiO_2 using Mo_2O_4(diethyldithiocarbamate)$_2$ as a catalyst

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Abstract

The photoreduction of acetylene is catalyzed by Mo_2O_4(dedtc)$_2$ (dedtc, diethyldithiocarbamate) in the presence of 5–8 nm diameter colloidal TiO_2. This photocatalytic process exhibits optimum activity at pH 6 and a loading of 30 catalyst molecules per TiO_2 particle. The same catalytic site(s) are responsible for C_2H_2 reduction to C_2H_4 and C_2H_6 and H^+ reduction to H_2. The overall photonic efficiency is 1.3% for the transfer of reducing equivalents to products at full lamp intensity, and increases with decreasing intensity. The effects of pH, temperature, intensity and loading on the catalytic process are consistent with a mechanism in which the catalytic site associated with the TiO_2 surface promotes the transfer of H atoms or electrons to the bound substrate. The photocatalytic properties of this neutral molecular complex are compared with those observed for other Mo-containing catalysts. © 1997 Elsevier Science S.A.

Keywords: Acetylene; Band-gap irradiation; Mo_2O_4(dedtc)$_2$ catalyst; Photoreduction; TiO_2

1. Introduction

The study of light-induced redox reactions on semiconductor surfaces is a very active area and has been the subject of recent reviews [1–4]. Colloidal TiO_2 is often the semiconductor of choice because of its high surface area and resistance to photocorrosion. Band-gap irradiation of TiO_2 leads to electron–hole pairs which are trapped at the surface of the small particles. The holes are thought to be initially trapped either as subsurface oxygen anion radicals [5] or on surface OH groups [6], and have the capability to oxidize many organic species. In the presence of sacrificial electron donors which remove the trapped holes, electrons accumulate on the particle surface. Both bulk and surface modifications to the semiconductor can enhance the efficiency and rate of charge separation following light absorption [3].

Molybdenum-based compounds are effective catalysts in many redox processes and have the potential to induce multielectron reduction processes, such as N_2 fixation. We are particularly interested in exploring the utility of Mo-based compounds as catalysts for interfacial electron transfer from irradiated colloidal TiO_2. The catalytic photoreduction of acetylene in colloidal aqueous suspensions of TiO_2, and the accompanying reduction of H_2O, have been used to examine the capabilities of several ionic molybdenum species in this regard [7–12]. Tetrathiomolybdate and other thio anions of molybdenum are nearly as effective as Pt for transferring photoproduced electrons to water (H_2 production) [10] or to alkynes and alkenes [9].

Due to the nature of the reaction medium (dilute aqueous solutions), direct characterization of the catalytically active species is very difficult or impossible, and information about the process comes from comparative studies. Earlier studies have found that ionic compounds of Mo are much better photoreduction catalysts than oxo ions [9]. However, because of the tendency of Mo compounds to polymerize, it is not known whether the effective catalyst should be identified with the monomeric precursor or an aggregate of the starting materials. Stable molecular complexes, such as $[MoOCl(dppe)_2]^+Cl^-$ (dppe, 1,2-bis(diphenylphosphino)ethane), which are expected to maintain, at least qualitatively, their structural integrity during the catalytic process, help to overcome this tendency to form polynuclear species, and this complex has been shown to retain catalytic activity [12].

The study described here is a continuation of the examination of molybdenum complexes as photoreduction catalysts. In particular, this study focuses on the reasonably stable $[Mo_2O_4^{2+}]$ core which has been complexed to diethyldithiocarbamate (dedtc) to form the neutral complex Mo_2O_4(dedtc)$_2$. This ligating system was chosen to determine whether a significant increase in catalytic efficiency of the

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$[Mo_2S_4(S_2C_2H_4)_2]^{2-}$ ion [9] over the $Mo_2O_4^{2+}$ aquo ion [8] requires the presence of S in the Mo_2S_4 core or whether the presence of S in the ligating system is adequate.

2. Experimental section

Preparation of transparent sols of TiO_2 and their characterization have been described previously [7,8]. To 8 ml of a stock solution containing 5–8 nm diameter TiO_2 particles at pH 1.6 was added 3 ml of 2% polyvinylalcohol (PVA), 4 ml of H_2O and 3 ml of MeOH and the pH was adjusted with NaOH or HCl. Because of the limited solubility and instability in air-saturated solutions, the catalyst, $Mo_2O_4(dedtc)_2$, was prepared daily by dissolving the appropriate amount of weighed solid in a minimum amount (less than 0.2 ml) of CH_2Cl_2, and then diluting with 2 ml of MeOH. This solution was added dropwise to the TiO_2 solution during deaeration and saturation with the appropriate gas. The final solution had a volume of 20 ml and contained the appropriate amount of catalyst (1.0 g dm^{-3} TiO_2, 3.0 g dm^{-3} PVA in a 5 : 15 (v/v) MeOH–H_2O solution). PVA served as a colloidal stabilizer and sacrificial electron donor. Solutions were deaerated and saturated with C_2H_2, C_2H_4 or N_2 by bubbling for 30 min, and placed in a thermostatically controlled irradiation cell. Irradiations were carried out with a 200 W high pressure Hg lamp filtered with water and a 320 nm cut-off filter. The intensity available to the sample in the 320–385 nm range, at which the TiO_2 sol absorbs most of the radiation, was 0.79×10^{-3} einsteins h^{-1}. A few experiments to determine the photonic efficiency were carried out with a Corning 7-60 broad-band filter with a peak transmission of 68% at 360 nm and a measured bandwidth (FWHM) of approximately 30 nm. Neutral density filters were inserted in the lamp beam for intensity dependence measurements. The lamp intensities were determined by ferrioxalate actinometry.

C_2H_2 was prepurified by bubbling through three water traps prior to introduction into the reaction vessel. All other reagents were of the highest purity commercially available, and were used without further purification.

$Mo_2O_4(dedtc)_2$ was prepared by reaction of $MoCl_5$ with diethyldithiocarbamate as described by Schultz et al. [13]. Minor impurities were removed by silica gel column chromatography using CH_2Cl_2 as eluent.

Product formation was monitored by analysis of the headspace gases in the photolyzed vessel. The vessel was equipped with an evacuable calibrated sampler into which aliquots of the headspace gases could be expanded without contaminating the photolysis mixture with O_2. Aliquots were withdrawn from the sampler by gas syringe and analyzed chromatographically. A 6 ft × 1/4 in Porapak N column was used for hydrocarbon products (He carrier, TCD) and a 5 ft × 1/4 in Molecular Sieve 5A for H_2 analysis (N_2 carrier, TCD).

Duplicate experiments performed several months apart typically reproduced the yields to within 10%–15%. This fluctuation was primarily due to drifts in the lamp intensity over long periods of use. No correction was attempted. Blank experiments with missing TiO_2, but otherwise identical compositions, gave no detectable products.

3. Results and discussion

The absorption of $Mo_2O_4(dedtc)_2$ in methanol shows a λ_{max} value at 270 nm with a weak shoulder at 320 nm. In the presence of TiO_2, this absorption is completely obscured by the band-gap absorption of the semiconductor and no corrections were made for direct light absorption by the catalyst.

In acetylene-saturated solutions containing the standard reactant mixture, but without catalyst, C_2H_4 is the only reduction product observed. In the presence of catalyst, C_2H_6 and H_2 are also produced (Fig. 1). A chromatographic search reveals no heavier hydrocarbon products. After an initial "catalyst preparation" period, the yields of all products increase linearly with time over at least the 8 h irradiation period used for most of these studies. A linear least-squares fit of the production data after the preparation period was used as the effective photocatalytic rate for a comparison of the factors affecting the catalytic process. CH_2Cl_2 is an excellent electron trap, and its presence even at the low concentrations necessary for solubilization of the catalyst would be expected to decrease the efficiency of the photoreduction of acetylene. However, the reproducibility of the yields over several months indicates that either the CH_2Cl_2 interference is reproducible or that it is destroyed during the "catalyst preparation" period.

3.1. Effect of pH

The bulk pH of the mixture was determined to remain within 0.3 pH units of the initial preparation during photolysis due to the natural buffering action of titania. The formation rates of the reduction products as a function of the initial pH are shown in Fig. 2. Within experimental uncertainty, ethyl-

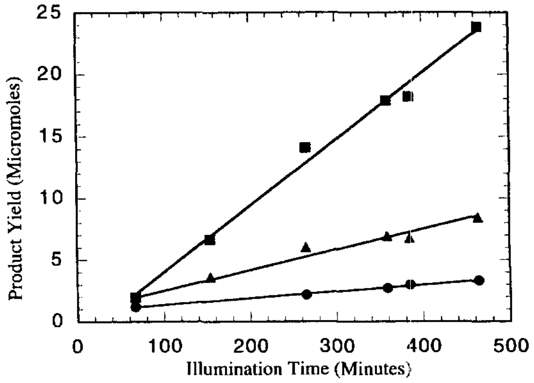

Fig. 1. Yields of H_2 (●), C_2H_4 (■) and C_2H_6 (▲) as a function of irradiation time. Irradiations were performed using a 200 W high pressure Hg lamp filtered below 320 nm. The available intensity was 0.79×10^{-3} einsteins h^{-1} in the 320–385 nm region. All solutions were at pH 6 and contained 30 catalyst molecules per TiO_2 particle.

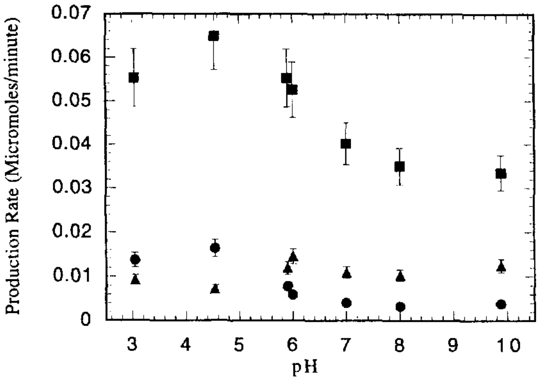

Fig. 2. Effect of pH on the rates of product formation: H_2 (●); C_2H_4 (■); C_2H_6 (▲). Error bars represent plus or minus one standard deviation of the production rate determination.

ene formation is relatively constant below pH 6, and then decreases in more basic solutions. Ethane production is relatively constant over the pH range, but appears to maximize at around pH 6. Hydrogen production is significant in acidic solutions, but decreases to near zero in basic solutions. The total rate of C_2H_2 photoreduction, evaluated as electron equivalents from the product yields, is relatively constant over the low pH range, and then decreases above pH 6 (Table 1). Even if H_2 is not included in the counting of electron equivalents, these data show that photoreduction proceeds more efficiently at pH 6 and below. Similar systems with anionic or cationic catalytic species also exhibit a maximum photocatalytic efficiency in this pH region [7–12].

In order for electron trapping by the catalyst to compete with electron–hole recombination, intimate contact between the catalyst and the colloidal surface must be achieved. The surface charge of colloidal TiO_2 is sensitive to the pH and impurities and should have a Point of zero zeta Potential (PZZP) around pH 4.6 [14]. Neutrally charged $Mo_2O_4(dedtc)_2$ would not initially be expected to interact strongly with the colloidal surface, but partial reduction during the preparation period could provide for either electrostatic interaction or partial ligand exchange with surface TiO^-, $TiOH_2^+$ or TiOH groups. The redox potential of the conduction band electrons also increases linearly with pH [15], and thus electron transfer should become more favorable at higher pH values. A combination of these factors may account for the relatively flat pH profile of the catalytic action. Subsequent studies were conducted at pH 6, since this region gives optimum yields of acetylene photoreduction products.

Table 1
Effect of pH on the rate of photoreduction[a]

pH	R(electrons)[b]	R(electrons)[c]
3.0	0.18	0.15
4.5	0.19	0.16
5.9	0.17	0.16
6.0	0.18	0.16
7.0	0.13	0.12
8.0	0.12	0.11
9.9	0.12	0.12

[a] All solutions contain a ratio of 30 catalyst molecules per TiO_2 particle. Photoreduction rates are reported as micromoles of electron equivalents per minute produced by irradiation by an Hg lamp with an average intensity of 0.79×10^{-3} einsteins h^{-1} in the 320–385 nm region.

[b] Total electron equivalent rates calculated as: $(R(H_2) \times 2 + R(C_2H_4) \times 2 + R(C_2H_6) \times 4)$.

[c] Acetylene electron equivalents calculated as: $(R(C_2H_4) \times 2 + R(C_2H_6) \times 4)$.

3.2. *Effect of loading*

The effect of catalyst concentration on the rate of photocatalytic reduction is shown in Fig. 3. Because of the uncertainty in the degree of attachment of the catalytic species to the TiO_2 surface, data are presented as the ratio of the number of catalyst molecules to TiO_2 particles, where the TiO_2 particle concentrations were calculated from an average diameter of 6 nm [7,12], a density of 3.8 g cm^{-3} and a concentration of 1.0 g l^{-1}. Even low concentrations of catalyst lead to the evolution of H_2 and C_2H_6 and greatly increase the rate of production of C_2H_4, with a maximum efficiency attained at approximately 30 molecules of catalyst per TiO_2 particle. The study was terminated at loading numbers above 40, since the limited solubility of the catalyst led to partial precipitation from solution at this loading. At optimum loading, C_2H_4 yields are approximately three times greater than those obtained from the bare TiO_2 surface. The change in reduction efficiency and the appearance of new reduction products clearly implicate a new catalytic site(s) derived from the presence of $Mo_2O_4(dedtc)_2$.

3.3. *Effect of intensity*

Decreases in lamp intensity increase the photonic efficiency for the production of C_2H_4 and C_2H_6 and decrease the H_2 production efficiency. Fig. 4 shows the normalized rate of production as a function of the percentage of full intensity of the lamp. Hoffmann et al. [3] describe the effect of intensity on interfacial charge transfer as being due to two competitive processes: a rapid competition between charge carrier (h^+,

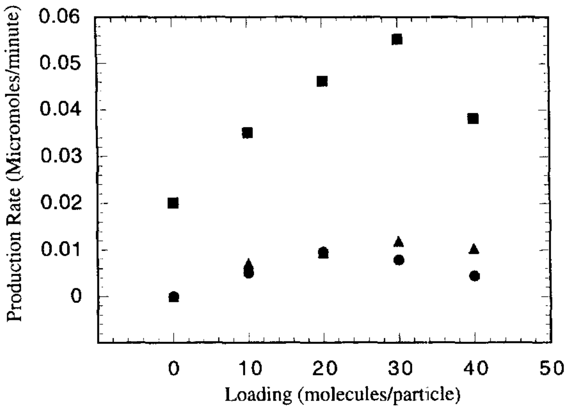

Fig. 3. Effect of catalyst loading on the production rate: H_2 (●); C_2H_4 (■); C_2H_6 (▲). The loading is calculated as the number of moles of catalyst per mole of TiO_2 particles as described in the text.

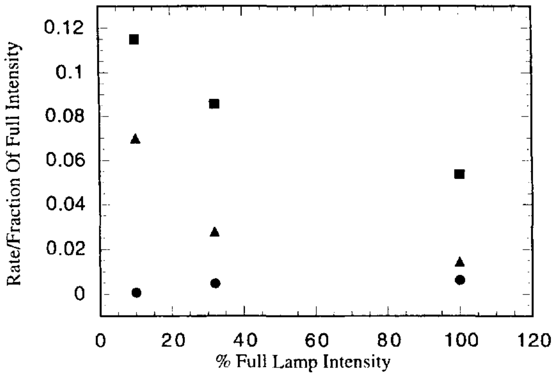

Fig. 4. Production rates as a function of the lamp intensity: H_2 (●); C_2H_4 (■); C_2H_6 (▲). The lamp intensity was modified with neutral density filters. The rates at the lower intensities were normalized to those at full intensity (i.e. observed rate/fractional intensity).

e^-) recombination and trapping, followed by a slower competition between trapped carrier (h_{tr}^+, e_{tr}^-) recombination and interfacial charge transfer, with the recombination processes being favored at higher intensities. The increased efficiency seen here as the intensity is lowered undoubtedly results from the second process. In a previous study using $[MoOCl(dppe)_2]^+Cl^-$ as a catalyst, with essentially the same system configuration and lamp intensity, the photoreduction yields varied linearly with intensity [12], suggesting that the removal of e_{tr}^-, either by direct transfer to the catalyst or through H_{tr} precursors, competes favorably with h_{tr}^+–e_{tr}^- recombination. Thus the intensity data suggest that the rate of this transfer limits the efficiency of the catalyst in this study.

3.4. Effect of temperature

The similar effects of pH, loading and intensity on the production of ethylene and ethane suggest a common catalytic precursor. The production rates of all products increase with temperature over the range 26–45 °C with apparent activation energies of 12–15 kJ mol^{-1}. Due to the uncertainty of the mechanism, it is not possible to assign the origin of these low barriers.

3.5. Photonic efficiency

The photonic efficiency ζ_r [16,17], describing the effectiveness of light conversion to product in heterogeneous, light-scattering systems, is directly proportional to the quantum yield, and may be considered to be a lower limit to this more commonly used measure of light efficiency. An estimate of the photonic efficiency of the present system utilized a Corning 7-60 broad-band filter, which was chosen to narrow the excitation wavelength regime while trying to mimic the full spectral absorbance of the reaction mixture. The results of these measurements are given in Table 2. For comparison, the production rate and photonic efficiency calculated from full-band irradiation in the 320–385 nm region are included.

The approximately 40% reduction in intensity occasioned by the use of the 7-60 filter was expected to show only modest changes in ζ_r for all products (see Fig. 4). However, the data show an enhancement for C_2H_6 only, with ζ_r decreasing for C_2H_4 and H_2. This effect is attributed to the different wavelength distribution in the filtered beam. Such differential effects between 313 nm and 365 nm excitation have been reported previously [12]. The 7-60 filter removes most light below 330 nm, while the full output of the lamp with a 320 nm cut-off filter has a significant intensity between 320 and 330 nm. The cause of this effect has not been identified, although we can speculate that irradiation in the band-gap region (360–380 nm), as favored by the 7-60 filter, may selectively excite larger TiO_2 particles, and their photocatalytic activity may be somewhat size dependent.

The photonic efficiency is quite modest, utilizing just over 1% of the absorbed light to result ultimately in separated reduced products at full intensity, and increasing to an estimated 3% at the lowest intensity studied. A comparison of the photonic efficiencies observed for C_2H_2 reduction with molybdenum oxo ions on TiO_2, collected in the same apparatus with similar intensity and wavelength conditions, is given in Table 3. The overall efficiencies of the Mo-based catalysts are quite comparable. The two dimeric $Mo(V)_2$ species have nearly identical overall efficiencies, but $Mo_2O_4(dedtc)_2$ favors two-electron reduction to a greater extent than $Mo_2O_4^{2+}$. It is possible that sulfur-containing

Table 2
Photonic efficiency of the photocatalytic reduction of $C_2H_2^a$

Product	Rate	PE (%)	Rate	PE (%)
	Corning 7-60 filter[b]		Full intensity[c]	
H_2	0.024	0.005	0.41	0.05
C_2H_4	1.07	0.22	3.24	0.41
C_2H_6	0.64	0.13	0.71	0.09
Electron equivalents[d]	4.74	0.99	10.5	1.33

[a] Solutions were at pH 6 with a loading of 30. Rates are reported as micromoles per hour.
[b] Intensity determined to be 0.48×10^{-3} einsteins h^{-1} by ferrioxalate actinometry.
[c] Intensity is 0.79×10^{-3} einsteins h^{-1} based on an average wavelength of 350 nm.
[d] Electron equivalents defined in Table 1.

Table 3
Comparison of the photonic efficiencies of several molybdenum species[a]

Catalyst	C_2H_4	C_2H_6	Total	Reference
MoO_4^{2-}	0.30	0.43	0.73	[11]
$Mo_2O_4^{2+}$	0.52	0.60	1.12	[11]
$Mo_3O_4^{4+}$	0.30	0.28	0.58	[11]
$Mo_2O_4(dedtc)_2$	0.82	0.36	1.18	This work
$PtCl_6^{2-}$	0.52	0.72	1.24	[11]

[a] All data are reported as electron equivalents for each product found with optimum loading at pH 6 with full light intensity.

ligands create a more favorable pathway for the two-electron process. However, the dedtc ligands do not promote the nearly twofold enhancement of the photonic efficiency observed when sulfur is present in the $Mo(V)_2$ core (e.g. $Mo_2S_4(S_2C_2H_4)_2^-$) under similar conditions [11]. The total efficiency depends not only on the catalyst, but also on the efficiency of the hole scavenger. For example, Pt deposits, produced from the in situ photoreduction of $PtCl_6^{2-}$ on TiO_2 (Table 3), are excellent electron traps, but are not much more effective at reducing C_2H_2 than the Mo-based catalysts. However, the reported study did not quantitate the concurrent H_2 production from the Pt systems which later studies demonstrated to be significant [10]. Increasing the effectiveness of hole scavenging through the addition of ethylenediaminetetraacetic acid (EDTA) can increase the overall reduction efficiency by a factor of two or three [10].

3.6. Turnover studies

A long-term (68 h) irradiation was performed to ensure that the process was catalytic rather than stoichiometric, and to determine the catalyst stability. These data, shown in Table 4, indicate that the catalytic activity decreases by 50%–65% in 68 h. The total number of acetylene molecules converted to ethylene or ethane (T) was approximately 40 over this period, verifying the catalytic nature of the process.

3.7. Reactions involving other substrates

Saturation of the sol with C_2H_4 or N_2 instead of C_2H_2 also results in photocatalytic reduction with H_2 as the principal product (Table 5). N_2 and C_2H_4 exhibit similar overall reduction rates, measured as electron equivalents, which are somewhat lower than those observed for C_2H_2. In the presence of C_2H_4, the low yield of C_2H_6 indicates that C_2H_4 is not reduced at the catalytic site. Thus unbound C_2H_4 is almost certainly not the precursor for C_2H_6 formation when C_2H_2 is the substrate. The rates at which electron equivalents appear in the reduction products are nearly substrate and product independent. Since H_2 and C_2H_6 are not formed in the absence of catalyst, these results appear to suggest that the transfer of the reducing species to the catalytic site precedes product formation in these systems.

Table 4
Turnover studies[a]

Product	Initial rate	Average rate		T^b
		28 h	68 h	
H_2	0.007	0.004	0.003	5
C_2H_4	0.054	0.026	0.019	32
C_2H_6	0.012	0.007	0.005	8
Electron equivalents[c]	0.16	0.089	0.064	110

[a] Initial and average rates are reported as micromoles per minute.
[b] T refers to the number of moles of product per mole of catalyst initially present.
[c] Defined in Table 1.

Table 5
Comparison of substrate efficiencies[a]

Product\substrate	C_2H_2	C_2H_4	N_2
H_2	0.007	0.069	0.066
C_2H_4	0.050	–	n.d.[b]
C_2H_6	0.012	0.00087	n.d.[b]
Electron equivalents[c]	0.18	0.14	0.13

[a] Studies were conducted under identical conditions of pH 6 and a loading of 30. Rates are reported as micromoles per minute at a full intensity of 0.79×10^{-3} einsteins h^{-1}.
[b] None detected.
[c] Defined in Table 1.

3.8. Mechanistic considerations

Hydrogen appearing in the reduction products originates from the solvent mixture. The higher photoreduction yields below pH 6 (where the TiO_2 surface would be heavily protonated) are consistent with the formation of trapped H atoms (H_{tr}) at the TiO_2 surface. The presence of H_{tr} may explain the photoreduction of C_2H_2 to C_2H_4 at the TiO_2 surface in the absence of catalyst. When catalyst is present, spillover of H_{tr} from the support to the catalytic site may lead to either recombination to form H_2 or sequential reduction of bound C_2H_2. This spillover mechanism has been suggested in the formation of molybdenum bronzes on TiO_2 [18,19]. With this mechanism, the efficiency of photoreduction would be limited, in part, by access of H_{tr} to the catalytic site. Surface migration of H_{tr} is apparently limited, since recombination to form H_2 is not detected in the absence of catalyst. Consequently, the low photoreduction efficiencies may result from the required close proximity of the catalytic site and H_{tr}. An alternative mechanism involving direct transfer of e_{tr} from TiO_2 to the catalytic sites has been detailed earlier [12]. Either mechanism can explain the observations of this study.

There is no direct evidence that the catalytic species are bound to the colloidal surface, and it is possible that they exist in dynamic equilibrium with the solution. The strongly peaked C_2H_4 production at a loading of approximately 30 $Mo_2O_4(dedtc)_2$ per TiO_2 particle is consistent, however, with a more constant surface population. We suggest that $Mo_2O_4(dedtc)_2$ becomes attached to the TiO_2 surface during the induction period, either by reduction or partial ligand exchange, and remains on the surface throughout the irradiation period. The catalyst, depicted generically as TiO_2/Mo_2L_2 ($L \equiv$ dedtc)

$$TiO_2 + xh\nu(+PVA) + Mo_2O_4(dedtc)_2 \rightarrow TiO_2/Mo_2L_2(+PVA^{ox}) \quad (1)$$

serves to transfer electrons or hydrogen atoms to bound substrates, or facilitates recombination to form H_2. H_2 production by oxidative elimination from methanol or PVA

$$TiO_2(2h^+) + CH_3OH \rightarrow CH_2O + H_2 + TiO_2 \qquad (2)$$

should occur with equal efficiencies in all preparations, which is inconsistent with the absence of H_2 when no catalyst is present. Saturation with N_2 or C_2H_4 leads to similar H_2 yields, indicating that neither of these substrates prevents the formation of H_2 at the catalytic site. In the presence of C_2H_2, the photoreduction is dominated by the transfer of reducing species to C_2H_2 giving, formally, both two-electron and four-electron reductions. Since the catalytic site is ineffective in transferring H to C_2H_4, it is unlikely that C_2H_4, once released from the catalytic site, is the precursor of C_2H_6. Therefore intermediates in the C_2H_6 formation process must be retained at the catalytic site during the reduction process. A mechanism consistent with these observations is given below.

$$TiO_2/Mo_2L_2 + C_2H_2 \rightleftharpoons TiO_2/Mo_2L_2(C_2H_2) \qquad (3)$$

$$TiO_2/Mo_2L_2(C_2H_2) + 2(H) + PVA \rightarrow TiO_2/Mo_2L_2(C_2H_4) + PVA^{ox} \qquad (4)$$

$$TiO_2/Mo_2L_2(C_2H_4) \rightarrow TiO_2/Mo_2L_2 + C_2H_4 \qquad (5)$$

$$TiO_2/Mo_2L_2(C_2H_4) + 2(H) + PVA \rightarrow TiO_2/Mo_2L_2 + C_2H_6 + PVA^{ox} \qquad (6)$$

This mechanism, utilizing a common catalytic site for all photoproducts, is consistent with the pH, loading and temperature data for the C_2H_2 reduction products. The decrease in photonic efficiency above pH 6 is due to the decreased availability of H^+. The increase in photonic efficiency as the intensity is lowered is consistent with an increasing probability of interfacial electron transfer to H^+ or the catalytic site. The mechanism does not explain, however, why H_2 shows a decrease in photonic efficiency as the light intensity decreases, whereas C_2H_4 and C_2H_6 show an increase in photonic efficiency. One possibility is that H_2 production is a light-assisted process requiring the photochemical elimination of H or H_2 from the catalytic site. Further investigations of these observations are underway.

4. Conclusions

$Mo_2O_4(dedtc)_2$ is a relatively stable neutral molecular complex of molybdenum which, like most other molybdenum compounds, serves as a catalyst for the reduction of C_2H_2. The product mix and photonic efficiency afforded by this catalyst are very similar to those found for the $Mo_2O_4^{2-}$ aquo ion. Consequently, it appears that the $Mo(V)_2$ core is primarily responsible for the catalytic activity, and this activity is not greatly affected by the sulfur content of the ligands. Although the efficiency of the process is determined as much by the rate of hole removal by the sacrificial electron donor (PVA) as by the capture of conduction band electrons either by surface H^+ or the catalyst, a threefold increase in the photonic efficiency as the light intensity is reduced suggests that the transfer of the reducing species to the catalyst is inefficient compared with trapped charge carrier recombination.

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References

[1] A.L. Linsebigler, G. Lu, J.T. Yates Jr., Chem. Rev. 95 (1995) 735.

[2] A. Hagfeldt, M. Grätzel, Chem. Rev. 95 (1995) 49.

[3] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.

[4] M.A. Fox, M.T. Dulay, Chem. Rev. 93 (1993) 341.

[5] O. Micic, Y. Zhang, K.R. Cromack, A.D. Trifunac, M.C. Thurnauer, J. Phys. Chem. 97 (1993) 7277.

[6] S.T. Martin, H. Herrmann, W. Choi, M.R. Hoffmann, J. Chem. Soc., Faraday Trans. 90 (1994) 3315.

[7] Z.-S. Cai, R.R. Kuntz, Langmuir 4 (1988) 830.

[8] S. Al-Thabaiti, R.R. Kuntz, Langmuir 6 (1990) 782.

[9] L. Lin, R.R. Kuntz, Langmuir 8 (1992) 870.

[10] L. Lin, S. Al-Thabaiti, R.R. Kuntz, J. Photochem. Photobiol. A: Chem. 64 (1992) 93.

[11] L. Lin, R.R. Kuntz, J. Photochem. Photobiol. A: Chem. 66 (1992) 245.

[12] R.R. Kuntz, J. Photochem. Photobiol. A: Chem. 84 (1994) 75.

[13] F.A. Schultz, V.R. Ott, D.S. Rolison, D.C. Bravard, J.W. McDonald, W.E. Newton, Inorg. Chem. 17 (1978) 1758.

[14] G.T. Brown, J.R. Darwent, P.D.I. Fletcher, J. Am. Chem. Soc. 107 (1985) 6446.

[15] D. Duonghong, J. Ramsden, M. Grätzel, J. Am. Chem. Soc. 104 (1982) 2977.

[16] N. Serpone, R. Terzian, D. Lawless, P. Kennepohl, G. Sauvé, J. Photochem. Photobiol. A: Chem. 73 (1993) 11.

[17] N. Serpone, G. Sauvé, R. Koch, H. Tahiri, P. Pichat, P. Piccinini, E. Pelizetti, H. Hidaka, J. Photochem. Photobiol. A: Chem. 94 (1996) 191.

[18] P. Pichat, M.-N. Mozzanega, J. Phys. Chem. 92 (1988) 467.

[19] V.C. Hoang, O. Zegaoui, B. Pommier, P. Pichat, Stud. Surf. Sci. Catal. 63 (1991) 679.