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Photoreduction of carbon dioxide catalysed by free and supported zinc and cadmium sulphide powders [1]

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Abstract

Loading of ZnS onto large-surface-area SiO_2 ($340\ m^2\ g^{-1}$) affords photocatalysts for the reduction of carbon dioxide to formate using 2,5-dihydrofuran (2,5-DHF) as reducing agent. A 13% coverage gives the most active powders, producing 7 mmol of formate on irradiation with UV light, and a slight excess of zinc ions improves the yield to 10 mmol. This acceleration, together with the observation that no oxalate is formed, suggests that CO_2 is reduced in a two-electron process. The activity decreases at higher and lower coverages, and photocorrosion to Zn(0) is observed when the latter is below 7%. When the SiO_2 surface is modified by aminopropyl groups, increased activity is observed due to their reducing properties. Analogous experiments with CdS at 40% coverage on irradiation with visible light again affords higher yields of formate than unsupported CdS. However, when 2,5-DHF is replaced by sodium sulphite, the supported catalyst reaches only half of the activity exhibited by the unsupported sulphide. When CdS is platinized by 0.5 or 4.3 mol.% Pt, a mixture of $CO_2/KHCO_3$ affords, in addition to formate, formaldehyde and methanol in amounts of 0.1 and 0.51 mmol. © 1997 Elsevier Science S.A.

Keywords: Cadmium sulphide/SiO_2/2,5-dihydrofuran; Carbon dioxide; Photoreduction; Zinc sulphide

1. Introduction

Carbon dioxide can be photoreduced at colloids, such as ZnS [1-3], CdS [4-6] and TiO_2 [7] or TiO_2/M [8,9], in the presence of 2-propanol, triethylamine, dihydrogenphosphate/sodium sulphide or oxalate as reducing agent. Maximum amounts of products in the range of micromoles to millimoles are formed and their nature depends on the photocatalyst, solvent and reducing agent. Thus the formation of formic acid is preferred at ZnS colloids [1,10,11], whereas CO is the major product at colloidal CdS [6]. Less work has been published on the photocatalytic activity of semiconductor powders, as exemplified by the reactions in the presence of zinc sulphide [10] and the oxides TiO_2/M [11-13], $SrTiO_3$ [14], α-Fe_2O_3 [15] and $CaFe_2O_4$ [16]. Higher reduced C_1 products, such as methanol and methane, are obtained only in the presence of redox catalysts such as Pd [17] and Os [18]. Recently, we have observed that UV irradiation of ZnS powder photocatalyses the production of formate in the presence of 2,5-dihydrofuran (2,5-DHF) as reducing agent [19]. It was proposed that the photogenerated reactive electron-hole pair ($e_r^- + h_r^+$) reduces hydrogen carbonate to formate and oxidizes 2,5-DHF to a mixture of regioisomeric dehydrodimers (Eqs. (1)-(3))

$$ZnS \xrightarrow{2h\nu} 2e_r^- + 2h_r^+ \qquad (1)$$

$$2e_r^- + HCO_3^-(ad) + 2H_3O^+(ad) \rightarrow HCO_2^- + 2H_2O \qquad (2)$$

$$2h_r^+ + 2RH(ad) + 2H_2O(ad) \rightarrow R{-}R(ad) + 2H_3O^+(ad) \qquad (3)$$

Although the redox potentials of e_r^- and h_r^+ are not known, they should be located a few hundred millivolts below and above the conduction and valence band edges, which for ZnS single crystals are positioned at −1.8 and +1.8 V (normal hydrogen electrode (NHE), pH 7) respectively [20]. Comparison with the standard potential $E^\circ(HCO_3^-/HCO_2^-) = -0.41$ V (NHE, pH 7) (calculated from the value of 0.76 V (saturated calomel electrode, SCE) reported for pH 8.9 [21]) indicates the thermodynamic feasibility of CO_2 reduction. By analogy with the photoreduction of CO_2 by 2-propanol in the presence of colloidal zinc sulphide, it seems probable that the two-electron reduction step (Eq. (2)) proceeds via intermediary zinc atoms [2].

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One reason for the low apparent quantum yield of 0.1% [19] may originate from the poor adsorption of carbon dioxide onto the semiconductor surface. One possible way to improve this is the fixation of ZnS on a large-surface-area support such as SiO_2 which may enhance CO_2 adsorption. The corresponding CdS photocatalysts were also investigated using visible light for the photoreduction. Furthermore, the effect of platinization on the nature of the reduction products was determined

2. Experimental details

2.1. General methods

The general methods and apparatus employed are described in Ref. [22]. Specific surface areas were measured by the Brunauer–Emmett–Teller (BET) method. The surface Zn/S ratio was determined by X-ray photoelectron spectroscopy (XPS) from ground samples which were attached to the sample holder by silver paste and dried for 12 h at room temperature before measurement (Al K_α radiation, without monochromator, 5×10^{-10} mbar, penetration depth about 5 nm).

Formate was determined by filtering off 2 ml of the irradiated solution through a micropore filter (0.2 μm pore size) with subsequent washing (2×5 ml) with chloroform to remove 2,5-DHF; 1 ml of the aqueous solution was injected into an ion chromatograph (Dionex Quick Analyser; regeneration agent, 1 ml of concentrated H_2SO_4 in 2 l of H_2O; eluting agent, 1.7×10^{-3} M $NaHCO_3$, 1.8×10^{-3} M Na_2CO_3; conductivity detector for 10, 30 and 100 μS; a calibration curve was obtained with $(0.1\text{–}5) \times 10^{-3}$ M HCO_2Na solutions). Determination by high performance liquid chromatography (HPLC) was performed analogously using a Eurokat-H type B146 column, 0.025 M sulphuric acid, a flow rate of 2 ml min^{-1} and UV detection at $\lambda = 200$ nm.

Methanol was determined by gas chromatography (GC) by heating 3 ml of the irradiated solution for 20 min to 70 °C and withdrawing a sample from the gas phase. Formaldehyde was measured colorimetrically as described in Ref. [23]. $(MV)Cl_2$ (MV^{2+}, methyl viologen) was used as received (Aldrich). Unless noted otherwise, all irradiations were performed with slow CO_2 bubbling in a Pyrex ($\lambda \geq 290$ nm) immersion lamp apparatus equipped with a Philips HPK 150 W high-pressure mercury lamp.

2.2. Preparation of photocatalysts

2.2.1. ZnS, CdS

2.2.1.1. ZnS

An aqueous solution (250 ml) of 24.0 g (0.1 mol) of $Na_2S \cdot 9H_2O$ was added dropwise under an argon atmosphere to a solution of 28.8 g (0.1 mol) of $ZnSO_4 \cdot 7H_2O$ in 250 ml of water. After stirring for 24 h, the powder was filtered off, washed to neutrality with H_2O and dried for 2 weeks over Siccapent. The specific surface area was 220 $m^2\ g^{-1}$ as determined by the BET method. This powder corresponds to ZnS-A described in Ref. [24].

2.2.1.2. CdS

Na_2S (1 M) (50 ml) was added in an argon atmosphere with stirring to 150 ml of a 10% ammonia solution containing 0.33 M of cadmium sulphate. After stirring for 12 h, the powder was washed with water to neutrality and dried for 6 days over Siccapent.

2.2.2. SiO_2-supported powders

2.2.2.1. SiO_2/x% ZnS

SiO_2 (10 g) (Grace type 432, neutral, specific surface area of 340 $m^2\ g^{-1}$) in 100 ml of zinc sulphate solution (Table 1) was stirred under argon at room temperature for 24 h. Thereafter 100 ml of the appropriate sodium sulphide solution was added within 30 min and stirring was continued for another 24 h. After filtration and washing with water (2×50 ml), the samples were dried over Siccapent for 6 days.

2.2.2.2. $[SiO_2]O(CH_2)_3NH_2$/13% ZnS

This was obtained analogously from 10 g of $[SiO_2]O(CH_2)_3NH_2$ (Aldrich) and 50 ml of 0.048 M solutions of the two salts.

2.2.2.3. SiO_2/13% ZnS/Zn^{2+}

This was obtained as described above using 14.2 g (0.0624 mol) of zinc sulphate, 20 g of SiO_2 and 0.048 mol of sodium sulphide.

2.2.2.4. Determination of ZnS loading

To determine the amount of ZnS fixed onto SiO_2, 0.25 g of the powder was heated for 24 h in 100 ml of concentrated HCl and thereafter diluted with 100 ml of water. After filtering, the zinc ion concentration was measured by atomic absorption spectrometry (AAS) employing zinc nitrate as standard.

Table 1

Composition and specific surface area of various SiO_2/ZnS powders compared with unsupported ZnS

Zn^{2+} (theor.) (%)	Zn^{2+} (bulk) (%)	Zn/S (surf.)	$m^2\ g^{-1}$
3	1.68	–	–
6	3.74	1.24/1.00	–
12	7.68	–	–
24	13.16	1.14/1.00	316
36	22.30	1.20/1.00	300
48	28.18	1.20/1.00	271
–	–	1.04/1.00	220

2.2.2.5. *CdS powders*

The corresponding CdS powders were prepared analogously, except that the metal sulphate was dissolved in 10% ammonia solution.

2.2.2.6. *CdS/Pt and SiO_2/40% CdS/Pt*

Powders containing 0.5 or 4.3 mol.% of platinum relative to CdS were obtained according to Ref. [25] by photoplatinization of CdS (1 g) and SiO_2/40% CdS (2.5 g) respectively in the presence of 1 and 8 ml of 0.036 M of H_2PtCl_6.

2.3. *ZnS-catalysed photoreduction to formate by 2,5-DHF*

2.3.1. *Dependence on time*

The appropriate powder (0.2 g) was suspended in 68 ml of H_2O in the immersion lamp apparatus with sonication and CO_2 bubbling for 15 min. Thereafter 8 ml (0.11 mol) of 2,5-DHF was added and the suspension was irradiated ($\lambda \geq 290$ nm) for 6 h. Samples of 2 ml were withdrawn and analysed for formate by ion chromatography as described above. The original pH value of 4.2 changed to 5.2 after irradiation. Blank experiments indicated that 2,5-DHF contained 0.05–0.2 mmol l^{-1} of formate, as also illustrated by the value of 0.1 mmol l^{-1} measured for SiO_2 alone (Fig. 1); no formate was detected when 2,5-DHF was omitted; all values obtained from metal sulphide-containing catalysts in the presence of 2,5-DHF were therefore corrected by subtracting 0.1 mmol l^{-1}. Furthermore, small amounts of acetate were detected which were shown to be released by the micropore filter.

2.3.2. *Dependence on ZnS loading*

To ensure that each sample contained a fixed amount of 50 mg of ZnS, 3 g of SiO_2/1.7% ZnS, 1.33 g of SiO_2/3.7% ZnS, 0.65 g of SiO_2/7.7% ZnS, 0.38 g of SiO_2/13% ZnS, 0.224 g of SiO_2/22% ZnS and 0.178 g of SiO_2/28% ZnS were employed. The suspension was irradiated for 24 h and formate was determined by HPLC as described above; at this time, photocorrosion was detected in the case of SiO_2/1.7% ZnS and SiO_2/3.7% ZnS through the formation of blue $MV^{\cdot +}$ on addition of $(MV)Cl_2$.

2.3.3. *Dependence on the concentration of SiO_2/13% ZnS*

The employed concentrations of 1.3, 2.7, 5.4, 8.1, 10.8 and 14.9 g l^{-1}, after 24 h of irradiation, produced formate at concentrations of 0.0, 1.5, 2.0, 2.0, 1.5 and 1.0 mmol l^{-1} respectively. All other conditions were as described in Section 2.3.1 except that formate was determined by HPLC.

2.3.4. *$[SiO_2]O(CH_2)_3NH_2$/13% ZnS*

0.5 g of the catalyst powder, 1 ml (0.014 mol) of 2,5-DHF in 70 ml of water and an irradiation time of 24 h; formate was determined by HPLC.

2.4. *ZnS-catalysed photoreduction to formate by 2-propanol*

ZnS (50 mg) or 0.20 g of SiO_2/13% ZnS suspended in 68 ml of water was sonicated with CO_2 bubbling for 15 min.

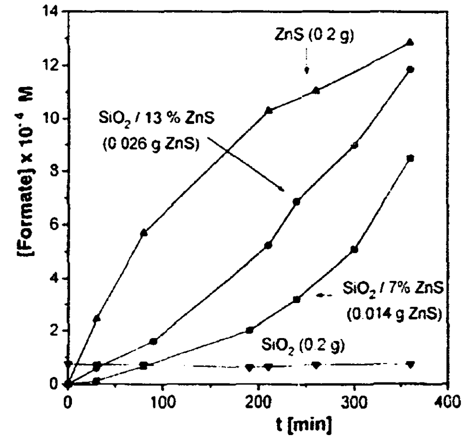

Fig. 1. Dependence of formate formation on irradiation time for various photocatalysts (2.6 g l^{-1}); specific concentration c_s(2,5-DHF) = 0.55 mol g^{-1}; $\lambda \geq 290$ nm.

After adding 8 ml (0.12 mol) of 2-propanol, the suspension was irradiated for 6 h. Samples were withdrawn at different times and analysed as described in Section 2.3.1. Formation of Zn(0) was shown by the production of blue $MV^{\cdot +}$ on addition of $(MV)Cl_2$ after irradiation had been stopped. Pinacol was detected by GC/MS analysis of an evaporated chloroform extract prepared from a sample irradiated for 24 h.

2.5. *CdS-catalysed photoreductions*

2.5.1. *CdS, SiO_2/40% CdS, $[SiO_2]O(CH_2)_3NH_2$/40% CdS*

CdS (0.20 g) or 0.5 g of the supported powder was suspended in 90 ml of 0.005 M Na_2SO_3 and sonicated for 15 min with CO_2 bubbling. When 2,5-DHF was employed as reducing agent, the powder was suspended in 90 ml of water and 6 ml (0.083 mol) of 2,5-DHF was added after sonication. Irradiation was performed with a tungsten–halogen lamp ($\lambda \geq 350$ nm) for 24 h. Samples (3 ml) were withdrawn through the micropore filter and analysed by HPLC; in the case of 2,5-DHF, the samples were washed with chloroform as described in Section 2.1.

2.5.2. *CdS/Pt and SiO_2/40% CdS/Pt*

CdS/Pt (0.2 g) (0.5 or 4.3 mol.%) was suspended in 90 ml of water and sonicated for 15 min with CO_2 bubbling. After the addition of 6 ml (0.083 mol) of 2,5-DHF, irradiation was conducted for 24 h. No formate could be detected when this experiment was repeated without CO_2 bubbling in 90 ml of 0.05 M $KHCO_3$.

SiO_2/40% CdS/Pt (0.5 g) (0.5 or 4.3 mol.%) was suspended in 90 ml of 0.005 M Na_2SO_3 containing 0.05 M $KHCO_3$ and sonicated with CO_2 bubbling for 15 min. The CO_2 stream was turned off and irradiation was conducted for 24 h. Thereafter 5 ml of the suspension was filtered through the micropore filter and formate, methanol and formaldehyde were determined as described in Section 2.1.

3. Results and discussion

3.1. Zinc sulphides

For the preparation of the supported photocatalysts, neutral SiO_2 (340 m^2 g^{-1}) was stirred for 24 h in zinc sulphate solutions of different concentrations. Subsequent addition of sodium sulphide afforded the corresponding SiO_2/ZnS powders (271–316 m^2 g^{-1}) which, in the bulk, contained only little more than half of the theoretically possible amount of Zn^{2+} (Table 1). XPS measurements showed that, in a surface layer about 5 nm thick, the Zn/S ratio was 10%–20% higher than for unsupported ZnS. This may be due to coprecipitation of small amounts of zinc hydroxide. The determination of the Zn/SiO_2 surface ratios for the various powders by XPS revealed values of 0.3/1 to 0.4/1.

The time-dependent formation of formate on irradiation ($\lambda \geq 290$ nm) of various photocatalyst powders in a CO_2-bubbled suspension of 2,5-DHF/H_2O is summarized in Fig. 1. The small and constant amount of formate obtained with the support in the absence of ZnS originates from 2,5-DHF as demonstrated by blank experiments. As reported for unsupported zinc sulphide, 2,5-DHF is oxidized to a regioisomeric mixture of 2,2'-, 2,3'- and 3,3'-bidihydrofuryl, and the overall reaction can be formulated by Eqs. (1)–(3). Since no oxalate could be detected, the reduction of CO_2 should occur by a two-electron process, as also suggested by the positive effect of surplus zinc ions (see Table 2). A two-electron reduction was also proposed for the colloidal ZnS/2-propanol system by Henglein et al. [2], while Kanemoto et al. [11], in the case of colloidal ZnS/DMF/NEt_3, favoured a one-electron reduction via the CO_2^- radical, although no oxalate was detectable.

While unsupported ZnS induces a higher initial rate, the amount of product produced per gram of ZnS after 6 h is higher for the supported powders, as indicated by the values of 57, 42 and 6 mmol g^{-1} calculated for SiO_2/7% ZnS, SiO_2/13% ZnS and ZnS respectively. It cannot be decided whether this positive influence of the support is due to improved adsorption properties or to a more efficient charge separation and interfacial electron transfer at the SiO_2/ZnS contact.

In Fig. 2, it is shown that the formate concentration passes through a maximum at about 13% when the ZnS coverage is varied from 3% to 28%. Only for coverages below 7% was photocorrosion to Zn(0) detected through the formation of the blue $MV^{\cdot+}$ radical cation on addition of $(MV)Cl_2$ after 24 h of irradiation. This suggests that competition between photocorrosion and electron transfer to and from the substrates depends on the nature of the support/semiconductor contact. To keep the concentration of the light-absorbing ZnS component constant, the total amount of SiO_2/ZnS was decreased appropriately with increasing degree of coverage. Accordingly, light scattering should decrease in the same direction and the initial rate increase may partly arise from increasing light absorption. However, this should not lead to a maximum, but rather to a plateau. In agreement with this explanation, the reaction rate does not change when the concentration of SiO_2/13% ZnS is varied from 3 to 8 g l^{-1}, whereas it decreases at higher concentrations. Thus the rate decrease at coverages from about 15% to 22%, corresponding to total catalyst concentrations of 5 to 3 g l^{-1}, probably reflects a decreased availability of SiO_2 surface for adsorption of the substrates and/or an unfavourable change in the photocatalytic properties of the ZnS particles.

Table 2
Formate concentration observed for various ZnS photocatalysts (7.1 g l^{-1}) after irradiation for 24 h in the presence (c_s = 0.028 mol g^{-1}) and absence of 2,5-DHF

Photocatalyst	HCO_2^- (10^{-3} M)
SiO_2/13% ZnS	7.0
SiO_2/13% ZnS/Zn^{2+}	10.3
[SiO_2]O$(CH_2)_3NH_2$/13% ZnS	11.0
[SiO_2]O$(CH_2)_3NH_2$/13% ZnS [a]	8.7 [a]

[a] Without 2,5-DHF.

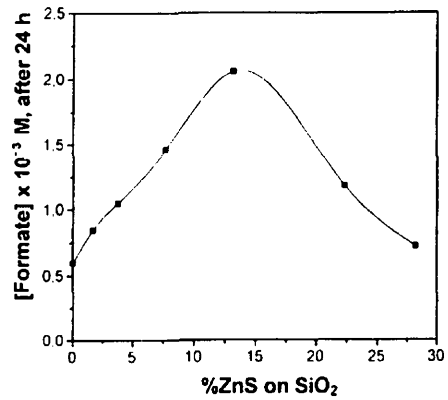

Fig. 2. Dependence of formate formation on the percentage of ZnS loading: total amount of catalyst is 2–39 g l^{-1} corresponding to a constant ZnS concentration of 0.66 g l^{-1} and to c_s(2,5-DHF) = 0.72–0.037 mol g^{-1}; $\lambda \geq 290$ nm.

To promote the adsorption of CO_2 onto the support, the basic silica powder [SiO_2]O$(CH_2)_3NH_2$/13% ZnS, containing 0.9 mmol g^{-1} aminopropyl groups, was also tested as a photocatalyst. However, no improvement was observed since, in addition to 2,5-DHF, the surface amine itself functioned as a reducing agent (Table 2).

In the SiO_2/13% ZnS-catalysed reaction, when 2,5-DHF was replaced by 2-propanol, cathodic photocorrosion to elemental zinc was observed and formate formation became slower (Fig. 3). Pinacol was formed as an oxidation product, as also reported for colloidal ZnS [2], and the oxidative reaction therefore corresponds to Eq. (3) which can be divided into an oxidative deprotonation step (Eq. (4)) and the dimerization of the intermediate radicals (Eq. (5))

$$RH(ad)+h_r^+ +H_2O(ad) \rightarrow R^{\bullet}+H_3O^+ \tag{4}$$

$$2R^{\bullet}(ad) \rightarrow R-R(ad) \tag{5}$$

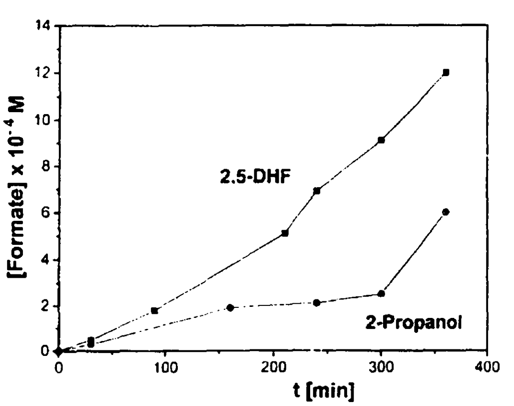

Fig. 3. Dependence of formate formation on irradiation time for SiO_2/13% ZnS in the presence of 2,5-DHF (c_s = 0.55 mol g^{-1}) or 2-propanol (c_s = 0.60 mol g^{-1}); $\lambda \geq 290$ nm.

Since, for 2-propanol, the standard potential of the oxidative step is 0.3 V more positive than for 2,5-DHF, the slower reaction can be rationalized (for the reaction, RH(solv) → R(solv) + H^+(solv), the standard potentials of 1.2 V (2,5-DHF) and 1.5 V (Me_2CHOH) were estimated according to Ref. [2] assuming ΔG(C–H) values of 3.6 eV (2,5-DHF) [26] and 3.9 eV (Me_2CHOH) [2] and −2.4 V for $E^\circ(H^+/H)$ in water [27]; the bond dissociation energy of the α-CH bond can be estimated to be 3.7 eV from the data collected in Ref. [26]; 0.1 eV was subtracted from this value for conversion to ΔG(solv) [27]).

3.2. Cadmium sulphides

Due to the positions of the conduction and valence band edges of −0.9 and +1.5 V (vs. NHE, pH 7) reported for CdS [28,29], we expect that CdS may also be catalytically active in CO_2 reduction. In addition to 2,5-DHF, sodium sulphite was employed as reducing agent. Although its concentration was only 1/300 that of 2,5-DHF, it induced an almost fourfold higher formate yield (Table 3). This can be rationalized by the much stronger reducing properties ($E^\circ = -0.51$ V at pH 7).

Surprisingly, this positive effect of sulphite is almost cancelled out when the supported photocatalyst SiO_2/40% CdS is employed, as indicated by the formate concentrations of 6.3 and 5.6 mmol l^{-1} found for sulphite and 2,5-DHF respectively. Introduction of the support decreases the activity by 58% in the case of sulphite, whereas an increase of 40% is observed for 2,5-DHF. This suggests that sulphite is preferentially adsorbed at SiO_2 and diffusion to the CdS particles is hindered. The same differences between sulphite and 2,5-DHF are observed for the aminopropyl-modified catalyst. As in the case of ZnS photocatalysis, the amino group also acts as a reducing agent.

Since, in the absence of carbon dioxide, the dehydrodimerization of 2,5-DHF and the reduction of water are efficient only when platinized CdS is employed [30], it was tested whether platinization would also increase the rate of CO_2 reduction. Although the usually observable photocorrosion of CdS was absent, the formate concentrations found in the presence of 0.5 and 4.3 mol.% Pt were only 0.3 and 0.23 mmol l^{-1} respectively, as compared with 0.4 mmol l^{-1} for the non-platinized CdS. This unexpected decrease in rate suggests that further products, such as formaldehyde and methanol, may have been formed at the expense of formate. Both reductions are thermodynamically feasible since the corresponding standard potentials are −0.48 and −0.38 V (vs. NHE, pH 7) respectively. Since these new products are volatile, the CO_2 stream was replaced by potassium hydrogen carbonate. In these experiments, supported CdS had to be used since the unsupported sample was inactive. As can be seen from Fig. 4, SiO_2/40% CdS induces methanol and formaldehyde concentrations of 0.1 and 0.01 mmol l^{-1} respectively and 0.23 mmol l^{-1} of formate. For an unsupported CdS powder, Inoue et al. [31] reported 1.17 and 2 mmol of methanol and formaldehyde respectively when CO_2 was bubbled through the suspension. Not unexpectedly, the introduction of the good redox catalyst platinum increases the amount of the four-electron and six-electron reduction products. While formaldehyde increases steadily, methanol passes through a maximum in the case of the SiO_2/0.5% Pt sample. Since formaldehyde is expected to be an intermediate in methanol formation, its further reduction seems to be more efficient for the catalyst containing the lower amount of Pt. The decrease

Table 3
Formate concentration observed for various CdS photocatalysts after irradiation ($\lambda \geq 350$ nm) for 24 h; 2.22 g l^{-1} of CdS and 5.55 g l^{-1} of supported powder; c_s(2,5-DHF) = 0.41 and 0.16 mol g^{-1} and c_s(Na_2SO_3) = 1.35 and 0.54 mmol g^{-1} of CdS and of supported powder respectively

Photocatalyst	Reducing agent	HCO_2^- (10^{-4} M^{-1})
CdS	Na_2SO_3	15.0
SiO_2/40% CdS	Na_2SO_3	6.3
CdS	2,5-DHF	4.0
SiO_2/40% CdS	2,5-DHF	5.6
SiO_2]$O(CH_2)_3NH_2$/40% CdS	Na_2SO_3	10.1
SiO_2]$O(CH_2)_3NH_2$/40% CdS	2,5-DHF	9.8
SiO_2]$O(CH_2)_3NH_2$/40% CdS	–	7.3

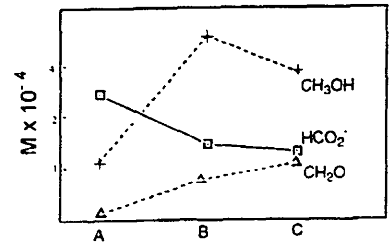

Fig. 4. Influence of platinization on product selectivity: A, SiO_2/40% CdS; B, SiO_2/40% CdS/Pt(0.5 mol.%); C, SiO_2/40% CdS/Pt(4.3 mol.%); 5.55 g l^{-1} of photocatalyst; 9.0 and 0.9 mmol g^{-1} of $KHCO_3$ and Na_2SO_3 respectively; $\lambda \geq 350$ nm.

in formate is in agreement with its known CdS/Pt-catalysed photo-oxidation [32].

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