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PHOTOASSISTED OXIDATION OF FORMALDEHYDE IN LUMINOPHORE-GRADE CdS-Pt SUSPENSIONS

The photoassisted oxidation of formaldehyde in aqueous solutions with a simultaneous evolution of molecular hydrogen was studied in platinized luminophore-grade CdS suspensions. The course of the reaction depended on illumination time, amount of platinum deposited onto CdS surface and pH of the formaldehyde solution. The apparent first-order reaction rate constant was $1.48 \times 10^{-4} \text{ min}^{-1}$

1. INTRODUCTION

In recent years, progress has been achieved in the application of semiconductor systems as photocatalysts in degradation of water pollutants to innocuous products, e.g. carbon dioxide (KRAEUTLER et al. [1], KAWAI et al. [2], HSIAO et al. [3], MATTHEWS [4]) and ammonia (SAKATA et al. [5]), and energy-storing ones such as hydrogen (SAKATA et al. [5], MATSUMURA et al. [6], BAMWENDA et al. [7], ENEA et al. [11]) and methane (SAKATA et al. [5]).

Photocatalytic activity of semiconductors can be explained in terms of the band gap excitation of electrons. Absorption of photon of energy equal or greater than the energy gap of the semiconductor induces the excitation of an electron from the semiconductor valence band to the conduction band, leaving a positive hole in the valence band. The photogenerated charges (electrons and holes) may diffuse to the semiconductor surface where they may be consumed in electrochemical redox reactions with the solution species absorbed on the surface.

Semiconductors can be used either in the form of electrodes (mono- or polycrystalline) or in the form of suspensions (dispersions or colloidal solutions), the latter being preferred due to their large surface area, simplicity of preparation, and low price. Particulate semiconductors, e.g. cadmium sulfide, titanium dioxide, have been recently used to degrade aldehydes (MATSUMURA et al. [6]), cyanides (FRANK

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et al. [8]), chloromethanes (PRUDEN et al. [9]), phenols (MATTHEWS [4]), and organophosphorous compounds (HARADA et al. [10]).

The work presented was aimed at investigating the photooxidation of formaldehyde on platinized cadmium sulfide suspensions. Cadmium sulfide has been chosen for this study because it exhibits photoactivity under visible light and the photogenerated holes in its valence band have enough potential to oxidize formaldehyde.

2. EXPERIMENTAL

All chemicals used in this work were analytical-grade reagents and were used as received. Solutions were prepared daily (to avoid their aging) with redistilled water. The cadmium sulfide (POCh) used was a luminophore grade powder. Its suspensions were prepared by dispersing 50 to 100 mg portions of cadmium sulfide powder into appropriate amounts of redistilled water ($20\text{--}150\text{ cm}^3$). The suspension was stirred during the experiments by a magnetic stirring bar.

All photoexperiments were performed in three water-jacketed Simax cylindrical photoreactors ($70\text{--}190\text{ cm}^3$) shown in fig. 1. The top of each reactor was equipped with a gas tight silicon septum and a side arm that permitted gas phase sampling and argon bubbling, respectively. The water jacket acted simultaneously as an absorber of infrared radiation in the incident light. Steady-state irradiations were carried out using a LH-21 halogen lamp (Polam). The incident light flux was measured using L-02 (Sonopan) and LM-2 (Carl Zeiss, Jena) radiometers.

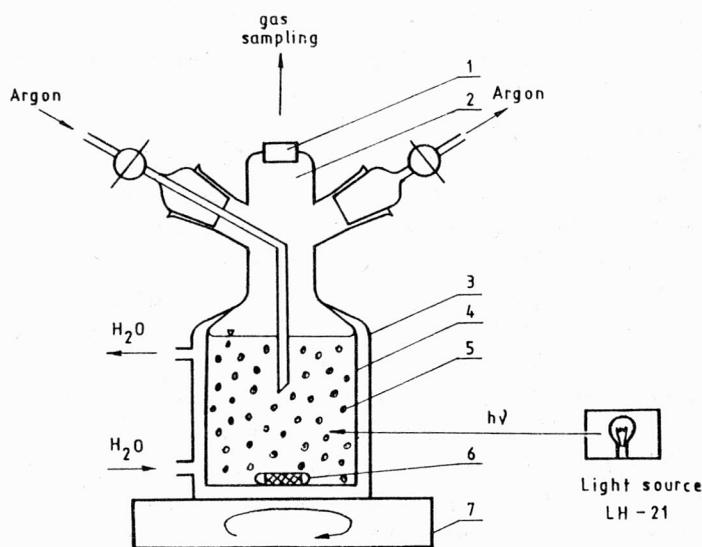


Fig. 1. Schematic representation of photoreactor

1 - silicon septum, 2 - gas phase, 3 - water jacket, 4 - solution, 5 - CdS/Pt particle, 6 - stirring bar, 7 - electromagnetic stirrer

Cadmium sulphide particles were surface platinized by the photoreduction of hexachloroplatinic acid from the deaerated solution of 0.01 M $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 0.5 M HCHO in 2:3 v/v methanol–water mixture. Amounts of platinum deposited on cadmium sulfide were calculated from the difference between its initial and final concentrations in the solution (measured colorimetrically with the use of SnCl_2 method). The gas phase concentration of hydrogen was determined by g.c. using a gas chromatograph (Elwro) with a catharometric detector and stainless steel column (2 m long with an internal diameter of 4 mm) packed with Porapak Q (0.149–0.125 mm). The carrier gas was pure argon passing at a flow rate of $20 \text{ cm}^3/\text{min}$. The column temperature was 24°C .

In most experiments, the course of reactions was monitored by sampling the gas phase. The amount of hydrogen produced was determined intermittently as a function of illumination time. Hydrogen production results were reproducible within an experimental error of $\pm 10\%$.

The amount of formaldehyde consumed during irradiations was determined by measuring the residual amount of carbon in the supernatant solutions. For this purpose a Shimadzu TOC-500 analyser was used. The average experimental error was in the range of $\pm 3\%$.

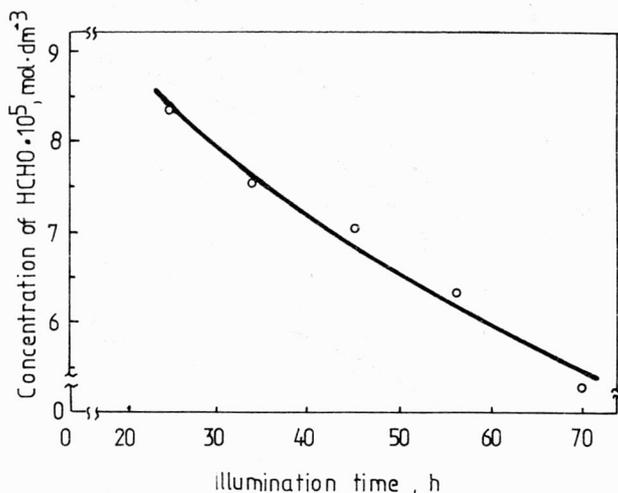


Fig. 2. Changes in formaldehyde concentration as a function of illumination time
 $2 \text{ g}/\text{dm}^3$ CdS/Pt (1.5%), pH 10.8 (NaOH), temperature 27°C , initial concentration of HCHO 0.1 mM, light intensity $1.4 \text{ kJm}^{-2}\text{s}^{-1}$

3. RESULTS AND DISCUSSION

The changes in formaldehyde concentration as a function of illumination time were studied using several suspensions containing an initial concentration of

0.1 mmol HCHO/dm³. The kinetics of the HCHO conversion was monitored by measuring the residual concentration of formaldehyde. Figure 2 shows a steady decrease in HCHO concentration during long period of illumination. A plot of log (HCHO concentration) as a function of time gave a linear relationship implying (at best approximation) a pseudo-first order kinetics. The apparent first-order rate constant, determined from the slope by the linear regression analysis, was $1.48 \times 10^{-4} \text{ min}^{-1}$.

Upon illumination of cadmium sulfide-platinum suspensions in formaldehyde solutions hydrogen was detected in the gas phase. The production of hydrogen continued as the illumination proceeded (fig. 3). The rate of hydrogen production increased remarkably after depositing platinum on cadmium sulfide particles. The use of cadmium sulfide-platinum (2%) instead of unplatitized cadmium sulfide gave an average threefold increase in the rate within the first five hours. This is attributed to the fact that the presence of platinum deposit on cadmium sulfide particles favours trapping and storage of electrons and promotes hydrogen production by allowing the electrons to reach easily the catalytic sites where they are consumed by protons (ENEA et al. [11]).

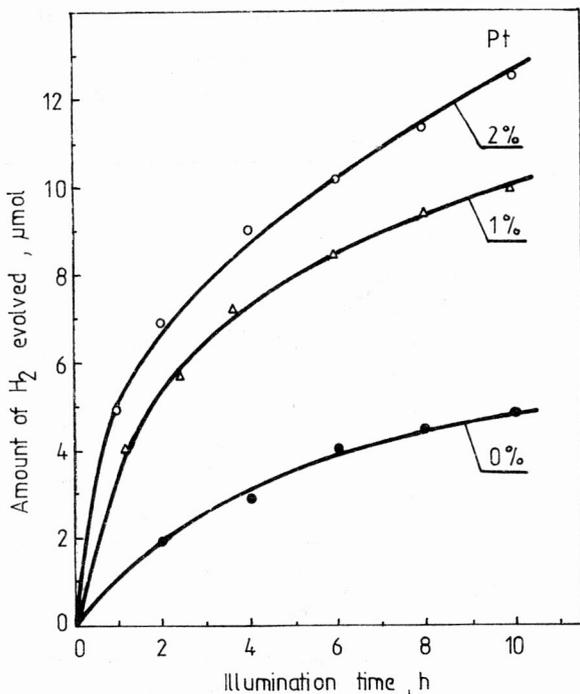


Fig. 3. Time-course of hydrogen evolution

2 g/dm³ CdS/Pt (1.5%), initial concentration of HCHO 2M, pH 5, temperature 27°C, light intensity $1.4 \text{ kJm}^{-2}\text{s}^{-1}$

By varying the initial pH of the suspension, it was observed that the quantity of hydrogen produced and the rates of its production increased gradually with the rise

in pH (fig. 4). The change in rate was remarkable within the pH range from 9 to 11. The pH effect can be explained in terms of a negative shift of cadmium sulfide flat band potential (U_{fb}) with increasing pH. Cadmium sulfide is known (MATSUMURA et al. [6]) to exhibit a negative shift of -40 mV of U_{fb} per pH unit at $pH > 9$. The cathodic shift of U_{fb} might enhance the rate of interfacial electron transfer from cadmium sulfide-platinum particles to the reactant species, resulting in increased hydrogen formation.

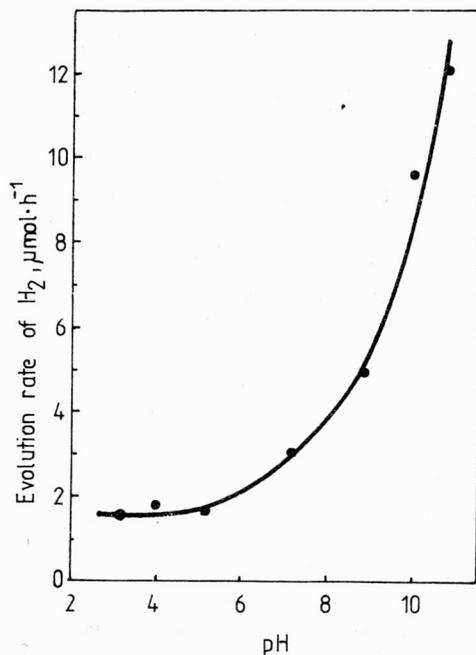


Fig. 4. Rate of hydrogen evolution versus pH

2 g/dm³ CdS/Pt (2%), initial concentration of HCHO 4M, illumination time 24 h, light intensity 1.4 kJm⁻²s⁻¹, temperature 27°C

The photoreaction leading to oxidation of formaldehyde with a simultaneous hydrogen evolution may be explained as follows: irradiation of cadmium sulfide particles with light of an energy equal to or greater than the band gap energy accounts for the absorption of light by these particles and, consequently, for the creation of holes (h^+) and electrons (e^-) according to eq. (1)



After the separation of the charges, holes oxidize formaldehyde to formic acid as follows:



In the second, the formic acid molecules are decomposed to protons and carbon dioxide (eq. (3))



Photogenerated electrons reduce protons to hydrogen according to eq. (4)



Thus, the overall reaction corresponds to the photooxidation of formaldehyde to carbon dioxide with a simultaneous production of hydrogen.

4. CONCLUSIONS

The following general conclusions can be drawn from this study:

1. Formaldehyde in aqueous solutions was decomposed with a simultaneous evolution of hydrogen on platinized luminophore-grade cadmium sulfide suspensions.
2. The reactions investigated may give a promising method to remove formaldehyde from industrial wastewater streams with simultaneous generation of a clean fuel, i.e. hydrogen.

ACKNOWLEDGEMENT

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WSPOMAGANE ŚWIATŁEM UTLENIANIE FORMALDEHYDU NA ZAWIESINIE CdS-Pt O KLASIE LUMINOFORYCZNEJ

Wspomagane światłem utlenianie wodnego roztworu formaldehydu, z jednoczesnym wydzielaniem molekularnego wodoru, badano przy użyciu platynizowanej zawiesiny siarczku kadmu o klasie luminoforycznej. Efektywność reakcji zależy od czasu naświetlania, ilości platyny osadzonej na siarczku kadmu oraz pH roztworu formaldehydu. Stała reakcji I rzędu wynosiła $1,46 \times 10^{-4} \text{ min}^{-1}$.

ВСПОМОГАЕМОЕ СВЕТОМ ОКИСЛЕНИЕ ФОРМАЛЬДЕГИДА НА СУСПЕНЗИИ СУЛЬФИД КАДМИЯ-ПЛАТИНА ЛЮМИНОФОРИЧЕСКОГО КЛАССА

Вспомогаемое светом окисление водного раствора формальдегида с одновременным выделением молекулярного водорода было исследовано при употреблении суспензии сульфид кадмия-платина люминофорического класса. Эффективность реакции зависит от времени экспозиции, количества осажденной на сульфиде кадмия платины, а также pH раствора формальдегида. Постоянная реакции I порядка составляла $1,46 \times 10^{-4} \text{ мин}^{-1}$.