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PHOTOACTIVITY OF TERNARY LEAD–GROUP IVB OXIDES FOR HYDROGEN AND OXYGEN EVOLUTION

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The relative photocatalytic activity of a series of lead-IVB group oxides ($PbCrO_4$, $PbMoO_4$, and $PbWO_4$) was studied for hydrogen evolution from aqueous methanol solution and for oxygen evolution from aqueous silver nitrate solution. Among the compounds, only $PbMoO_4$ and platinized $PbMoO_4$ powders acted as photocatalysts for oxygen and hydrogen evolution reactions from aqueous solutions, with an activity for oxygen evolution on $PbMoO_4$ comparable to that observed on TiO_2.

1. Introduction

From the earliest studies of photoelectrochemical (PEC) reactions on semiconductor electrodes and in particle suspensions, new materials have been sought as photocatalysts [1]. Oxides, such as TiO_2, have been of particular interest, since they show high stability under irradiation and are photocatalytically active for many reactions, including the oxidation of organic materials and oxygen evolution. For example, a number of binary [2] and ternary [3] oxides were investigated as photoelectrodes.

Lead oxides are known to be semiconductors [4–6] and a study of the photoelectrochemical behavior of an oxidized Pb surface [2] attributed the anodic photocurrents observed to a PbO layer that was, at least partially, oxidized to higher oxides under irradiation. Although photoelectrochemical studies of lead oxides have been used to characterize anodic films on Pb electrodes [7–9], no

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reports have been published in the photocatalytic activity of lead oxides for oxygen or hydrogen evolution, probably because they are unstable under irradiation in aqueous solution. However, stabilization of the lead oxide structure could occur when it is incorporated into the lattice to form a ternary oxide. For example, the oxides $PbFe_{12}O_{19}$ and $Pb_2Ti_{1.5}W_{0.5}O_{6.5}$ were investigated as photoanodes and were reported to be stable in some electrolytes [3].

In this study, the photocatalytic activity of particulate suspensions of the ternary lead oxides $PbCrO_4$, $PbMoO_4$, and $PbWO_4$ is described. Hydrogen evolution from aqueous methanol and oxygen evolution from aqueous silver nitrate solution are reported.

2. Experimental

$PbCrO_4$ (Mallinckrodt Chemical), $PbMoO_4$ (Morton Thiokol Inc.), $PbWO_4$ (Alfa Products), PbO (Johnson Matthey), MoO_3 (Aldrich Chemical), and TiO_2 (MCB) powders were used. The crystal structures were confirmed by X-ray diffraction (Philips, Cu K_α, 35 mA, 20 kV). UV-visible diffuse reflectance spectra of the powders were recorded in order to determine the band gaps (Varian Model DMS300 spectrometer, scan rate: 200 nm/min). Methanol (J.T. Baker) and silver nitrate (Johnson Matthey) were used without further purification as reducing or oxidizing reagents for hydrogen and oxygen evolution. In hydrogen evolution experiments, aqueous H_2PtCl_6 solution (1 wt% as Pt) was added to the oxide suspension. Under such conditions, an active catalyst will cause photodeposition of Pt on the surface of the metal oxide [10], producing a metal island capable of acting as a hydrogen evolution site.

The photocatalytic reactions were carried out in a closed gas circulation system equipped with a vacuum line and a gas chromatography sampling inlet [11]. The catalyst was dispersed in the solution by sonication prior to the reaction. A mixture of the catalyst (0.3 g) and the aqueous solution (80 mL) was stirred magnetically in a reaction cell equipped with an optically flat Pyrex window and degassed at least 30 min by vacuum evacuation. After degassing and adding 100 Torr of Ar, we irradiated the suspension using a high pressure mercury lamp (Ushio, USH = 205, DPA, 200 W). The amount of hydrogen and oxygen evolved were determined by gas chromatography (Varian Model 90-P, Ar carrier, molecular sieve 5A column, thermal conductivity detector).

3. Results and discussion

The observed catalytic activities for hydrogen and oxygen evolution of four ternary lead oxides, MoO_3, and TiO_2 are presented in table 1. Only $PbMoO_4$ and TiO_2 show appreciable photoactivity. The activity for oxygen evolution on the

Table 1
Photocatalytic activity of several ternary and binary metal oxides H_2 and O_2 evolutions from aqueous solution.

Catalyst [a]	Evolved gas (μmol) [b]	
	H_2 [c]	O_2 [d]
$PbCrO_4$	0	0
$PbMoO_4$	59	97
$PbWO_4$	0	0
PbO	0	0
MoO_3	0	0
TiO_2	477	120

[a] 0.3 g in 80 mL solution; [b] reaction time: 2 h, light source: 200 W high pressure Hg lamp; [c] from aq.Ch_3OH (90:10 H_2O:MeOH, 80 mL), H_2PtCl_6 (1 wt% Pt) was added; [d] from aq.$AgNO_3$ (0.01 M, 80 mL).

$PbMoO_4$ powder was reproducibly comparable to that observed on TiO_2, but the activity for hydrogen evolution was significantly lower. In the discussion which follows, we assume that methanol is oxidized and dihydrogen evolves from water when aqueous methanol solutions are irradiated, and that Ag^+ is reduced and oxygen evolves from water when aqueous silver nitrate solutions are irradiated.

Platinum deposition was indispensable for the hydrogen evolution on $PbMoO_4$ powder. The irradiation of Pt-free $PbMoO_4$ suspended in distilled water produced no hydrogen and only small amounts of oxygen (6 μmol after 2 h); simultaneously the color changed from light yellow to dark brown, suggesting that $PbMoO_4$ itself was reduced. This accounts for the absence of hydrogen evolution and presumably results from the lack of hydrogen evolution sites on the surface of native $PbMoO_4$.

In contrast, PbO and MoO_3 show no activity. These materials probably fail to photocatalyze hydrogen evolution because their conduction band edges are not sufficiently negative (compared with the potential required for water reduction). When MoO_3 was irradiated in aqueous methanol solution, its color turned to deep blue, as would be consistent with metal oxide reduction. Thus, the photooxidation of methanol proceeds on MoO_3, but evolution of dioxygen does not. When PbO powder is irradiated in aqueous silver nitrate, silver is photodeposited, judging from the change of the color (from yellow to grey). In this case, PbO is probably oxidized to either Pb(III) or Pb(IV) at the expense of oxygen evolution [2].

The time course of hydrogen and oxygen evolution on Pt/$PbMoO_4$ and $PbMoO_4$ is shown in fig. 1. The oxygen evolution rate is relatively constant, although it ultimately decreased gradually with time because of the deposition of Ag metal in the surface, the change of pH, etc. Photocatalyzed hydrogen evolution stopped after 2 h.

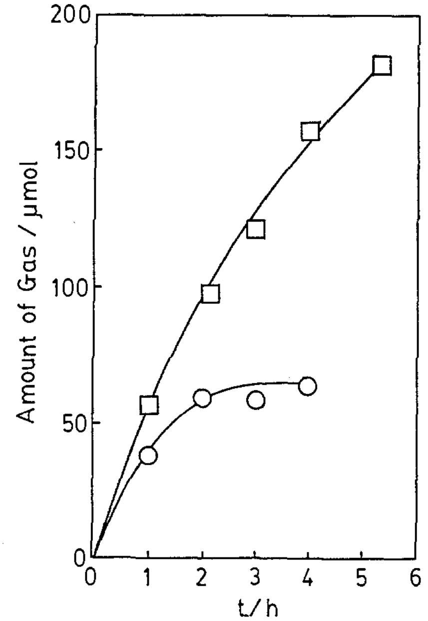

Fig. 1. H_2 evolution from aqueous CH_3OH and O_2 evolution from aqueous $AgNO_3$ solutions. Open circles: H_2 from aq. CH_3OH over Pt (1 wt%)/$PbMoO_4$. Open squares: O_2 from aq. $AgNO_3$ over $PbMoO_3$. In both cases, 0.3 g of catalyst was used and the light source was a 200 W high pressure Hg lamp.

In photocatalytic reaction research, the moles of evolves gas should always be compared with the moles of catalyst. In this study, $PbMoO_4$ (0.3 g or 820 µmol) was used. Since $4h^+$ (holes) are required for each molecule of O_2 produced, 720 µmol of holes are needed to evolve 180 µmol of oxygen (after 5 HO, while 120 µmol of electrons are needed to form 60 µmol of hydrogen (after 4h) from fig. 1. Based on these values and the fact that oxygen evolution shows no signs of diminishing, we conclude that oxygen evolves photocatalytically. The situation for hydrogen evolution is unclear.

Diffuse reflectance spectra of $PbCrO_4$, $PbMoO_4$, and $PbWO_4$ powders are shown in fig. 2. The band gaps of $PbCrO_4$, $PbMoO_4$, and $PbWO_4$ powders were estimated to be 2.2, 3.2, and 3.8 eV respectively. Band gap excitation of $PbMoO_4$, which showed significant photocatalytic activity in this study, should occur via the electron transfer from the valence band (electron density localized at Pb^{2+}) to the conduction band (localized in moO_4^{2-}) [12].

Both $PbMoO_4$ and $PbWO_4$, which have a Scheelite structure, have been studied as photoconductors [13]. Only $PbMoO_4$ showed appreciable photocatalytic activity, despite its photophysical similarity to $PbWO_4$. The reason is unclear. One factor tending to reduce the measured activity is the larger band gap (3.8 eV), which is smaller than but comparable to the optical cut-off of Pyrex (~ 4 eV). This factor alone cannot account for the absence of activity, so subtle electronic/

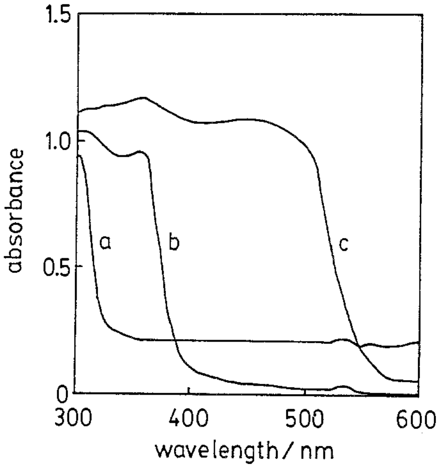

Fig. 2. Diffuse reflectance spectra of (a) $PbWO_4$, (b) $PbMoO_4$, and (c) $PbCrO_4$ powders.

chemical factors must be important. $PbCrO_4$ did not show photoactivity, despite its small band gap (2.2 eV). Perhaps recombination between electrons and holes is too fast to allow interfacial electron transfer at the photocatalyst surface to compete. As for $PbWO_4$, the absence of active sites on the surface is another possible explanation.

4. Summary

Following the empirical observation that photocatalytic activity of oxides occurs along certain diagonals of the periodic table (for the cation); we tested a set of ternary Pb-IVB-oxygen compounds -PbO, $PbCrO_4$, $PbMoO_4$, and $PbWO_4$. Of these, only $PbMoO_4$ shows any photoactivity for sacrificial water decomposition. Platinized $PbMoO_4$ was photoactive for dihydrogen evolution from Ag^+-containing water solutions. The activity for dioxygen evolution was comparable to TiO_2. Thus, $PbMoO_4$ emerges as a new material showing competitive photoactivity.

Acknowledgment

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References

[1] M. Gratzel, In: *Energy Resources through Photochemistry and Catalysis* (Academic Press Inc., New York, 1983).

[2] K.L. Hardee and A.J. Bard, J. Electrochem. Soc. 124 (1977) 215.

[3] H.H. Kung, H.S. Jarrett, A.W. Sleight and A.J. Ferretti, J. Appl. Phys. 48 (1977) 2463.

[4] D.E. Scaife, Solar Energy 24 (1980) 41.

[5] W. Mindt, J. Electrochem. Soc., 116 (1969) 1077.

[6] L.C. Schumacher, I.B. Holzheter and M.J. Dignam, J. Electroanal. Chem. 261 (1989) 331.

[7] G.H. Brilmyer, in: *Advances in Lead Batteries*, eds. K. Bullock and D. Pavlov (Electrochem. Soc., Pennington, NJ (1984) (Proceedings Vol. 84–14) pp 142–153.

[8] D. Pavlov, S. Zanova and G. Papozov, J. Electrochem. Soc. 124 (1977) 152.

[9] D. Pavlov, J. Electroanal. Chem. 118 (1981) 167.

[10] B. Krauetler and A.J. Bard, J. Am. Chem. Soc. 100 (1978) 2239.

[11] K. Domen, A. Kudo and T. Onishi, J. Catal. 102 (1986) 99.

[12] M. Bohn, O. Erb and A. Scharmann, Phys. Stat. Sol. 84 (1984) 291.

[13] W.V. Loo, Phys. Stat. Sol. 27 (1975) 565.

[14] M. Shibata, A. Kudo, A. Tanaka, K. Domen, K. Maruya and T. Onishi, Chem. Lett. (1987) 1017.