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PHOTOCATALYTIC HYDROGEN EVOLUTION FROM AN AQUEOUS METHANOL SOLUTION OVER CERAMICS-ELECTROCATALYST/TiO_2

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The activities of TiO_2 powders loaded with various kinds of transition metal borides, nitrides, phosphide, carbides for the photocatalytic hydrogen evolution from an aqueous methanol solution have been examined. It has been found that WC/TiO_2 has the highest activity among them going up one fourth of that of platinum black/TiO_2.

In recent years, numerous studies have been made on the photocatalytic hydrogen evolution from water, 1) aqueous solution of organic 2) and inorganic 3) compounds over powder semiconductors. Loading of electrocatalyst is required to lower the hydrogen overvoltage for these hydrogen evolution systems. Precious metals and their oxides have been used for the purpose. From a practical point of view, cheaper electrocatalyst has to be found and developed. To our knowledge, only Co, Re, 1a) and a few transition metal oxides 1b) other than those have been used up to the present. So, search of non-precious-metal electrocatalyst for these systems seems insufficient. It seems that compounds used as anode of hydrogen fuel cell can also be used as electrocatalyst for photocatalytic hydrogen evolution, though some difference is present between those two systems. A few transition metal carbides 4)5) and borides have been used as the anode for the fuel cell. So, the author have tried to use ceramics other than oxides as electrocatalyst for the photocatalytic hydrogen evolution.

In the present study, the activities of TiO_2 powders loaded with various kinds of transition metal borides, nitrides, phosphide, and carbides have been examined and compared with those of precious metal-loaded TiO_2 powders, where the photocatalytic hydrogen evolution from an aqueous methanol solution presented below has been selected as the common reaction. It has been found that WC/TiO_2 has the highest activity among them going up one fourth of that of Pt black/TiO_2.

$$CH_3OH + H_2O \xrightarrow[\text{photocatalyst}]{h\nu} H_2 + CO_2(+HCHO,\ HCOOH,\ etc.)^{2a),2b)}$$

All the compounds used in the present study were identified by X-ray diffraction pattern. Average particle diameters of precious metals and WC were determined by a centrifugal automatic particle analyzer(Horiba, CAPA-500). Every photocatalyst was prepared by grinding one of the ceramics(or precious metals; 5 mg) and TiO_2(45 mg; Fuji Titan TP-2, anatase, 0.26 μmϕ) in an agate mortar for 3 minutes. Judging from appearance, it was more difficult to support the ceramics including the two kinds of WC on the TiO_2 uniformly than to support the precious metals on it probably because the ceramics are less malleable than the precious metals.

The reaction was performed in a Pyrex Schlenk tube(110 cm^3) with a rectangular-parallelepiped lower part(35 x 35 x 60 mm) and a septum. The reaction mixture, consisting of one of the photocatalysts(25 mg; electrocatalyst, 10 wt%) spread uniformly on the bottom of the reactor and the aqueous solution of methanol(30 cm^3 containing 15 cm^3 of methanol) in an argon atmosphere, was irradiated through the bottom by a 500 W ultra-high-pressure Hg-lamp(Ushio). The amount of hydrogen evolved during the reaction was determined by gaschromatography.

Table 1 shows the hydrogen evolution rate at the initial few hr. All the data have fairly good reproducibilities. In every case, the rate was lower than 0.001 cm^3/hr when irradiated through 420-nm cut-off filter. Therefore, it is assumed that almost all the hydrogen evolution presented in the Table proceeded through absorption of light by the TiO_2. Among the TiO_2 powders loaded with the ceramics, those loaded with borides and carbides of VI-B metals, Ni_2B, and Co_2P revealed higher activities than the others. The order of activity obtained with various carbides is nearly consistent with that reported for electrocatalytic oxydation of H_2.5) No data is available for the order of activity with borides and nitrides. The two kinds of WC/TiO_2 revealed the highest activities, which were one fourth of that of the Pt black/TiO_2. 14.4 cm^3 of H_2 was evolved over WC(1)/TiO_2(10 mg) on irradiation for 19 hr. In this case, the turnover numbers of H_2 on WC and on TiO_2 (mole of H_2/mole of WC or TiO_2) were 130 and 5.8, respectively. This assures that the H_2 evolution over WC(1)/TiO_2 is really photocatalytic.

It is worthy of remark that WC/TiO_2 revealed activity higher than that of the

Table 1. Hydrogen evolution rate(cm^3 at S.T.P./hr) over electrocatalyst/TiO_2 (25 mg; electrocatalyst,[a] 10 wt%)

Borides	rate	Nitrides & Phosphide	rate	Carbides	rate	Others	rate
TiB_2	0.16	TiN	0.060	ZrC	0.037	none[d]	< 0.001
ZrB_2	0.14	ZrN	0.034	VC	0.050		
NbB	0.17	VN	< 0.001	NbC	0.097	Pt black[e]	10.6
TaB	0.019	TaN	0.061	Cr_3C_2	0.28	Ru black[f]	1.5
CrB	0.96	Mo_2N	< 0.001	Mo_2C	0.32	RuO_2[g]	2.5
Mo_2B_5	0.016			WC(1)[b]	3.0		
Ni_2B	0.96	Co_2P	0.75	WC(2)[c]	3.3	Pt/TiO_2[h]	16.2

a) All the ceramics are products of Cerac(purity $\geq$99%, 325 mesh), unless otherwise stated. b) Kennametal Ink, 0.57 μmϕ. c) prepared through carburization of WO_3 by Dr. H. Okamoto, Hitachi Central Research Laboratory; contains no appreciable amount of precious metals, 0.30 μmϕ. d) only TiO_2, 25 mg. e) Nakarai Chemical, $<$0.20 μmϕ. f) Nippon Engelhard, $<$ 0.20 μmϕ. g) Nippon Engelhard, 0.36 μmϕ. h) Pt/TiO_2(1 wt%) prepared by impregnation-H_2 reduction(200 °C, 4 hr) method.

Ru black/TiO_2 and not so much lower than that of the Pt black/TiO_2 in spite of the facts that the two kinds of WC were more difficult to load uniformly on the TiO_2 by grinding and have larger particle size than the Ru black and the Pt black.

The present result seems much different from the data that the ratio of specific activity in the electrocatalytic hydrogen oxidation for Pt/Ru/WC is $1/7x10^{-2}/10^{-4}$.[4] The ratio of specific activity for (Pt black/TiO_2)/(Ru black/TiO_2) obtained in the present experiment is nearly consistent with the reported value. The activity of WC/TiO_2 in the present study, however, is 3000 times that expected from the ratio of activity reported for Pt and WC. This may be due to the difference of the electrochemical character of those three kinds of WC, because it has been known that various kinds of WC are prepared depending on the preparation methods and conditions.[4] Or, the present result may reflect the difference of catalytic effect of WC, Pt,and Ru not only on the reduction of proton, but also on the other rate-determining step, which might be the dissociation of methanol on the TiO_2 [2b] in the present system when highly active electrocatalyst is loaded. Further study is required to clarity this point. Anyhow, it was indicated that the TiO_2 powder with fairly high activity for the photocatalytic hydrogen evolution was obtained by loading of WC.

It seems that the difference of activities between the Pt black/TiO_2 and the Pt/TiO_2(1 wt%) in the Table reflects the difference in the states of dispersion of Pt and contact of Pt with the TiO_2. It is expected that more active WC/TiO_2 is prepared by devising more appropriate loading method of WC, for example, carburization of WO_3 chemically loaded on TiO_2.

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