Effect of Lead Oxide Addition to the Photocatalytic Behavior of TiO_2

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The addition of small amount of lead oxide (less than 0.1 wt%) to TiO_2 was effective for improving the photocatalytic activity of H_2 production from aqueous methanol. By the addition of Pb_2O_3 to TiO_2, the characteristic ability of photo-assisted H_2 production was observed under irradiation whose wavelength was longer than 420 nm and was appeared accompanied with the improvement of the photocatalytic activity.

TiO_2 is one of the suitable semiconductors for photocatalyst and has been widely applied to various photocatalytic reactions, not only the reaction on the basis of photoenergy conversion to chemical energy but also other useful reactions.[1] To improve the ability of TiO_2 photocatalyst, various modifications have been performed. Particularly, modification by metals such as platinum was usually carried out,[2-4] while the surface was modified by appropriate metal ion or oxide in some cases.[5-7] Various positive effects to the photocatalytic properties of TiO_2 can be expected, when TiO_2 is combined with metal oxides. However, it is very difficult to clarify the condition how to combine metal oxides with TiO_2. On the basis of the conception, we have been investigating the photocatalytic properties of TiO_2 modified with cerium oxide.[7]

In this paper, we report the photocatalytic properties of TiO_2 modified with lead oxide. Particularly, the conditions of lead oxide in TiO_2 photocatalyst as well as the effect of lead oxide to the photocatalytic activity of TiO_2 were investigated.

The catalysts used in this work were prepared from the calcination of titanium and lead hydroxide mixture, which were obtained from $Ti(SO_4)_2$ and $Pb(NO_3)_2$ mixed solution with NH_4OH, at prescribed temperatures. The initial state of lead oxide added in TiO_2 was measured by XPS (VG ESCALAB). The state of the lead oxide was confirmed as Pb_2O_3 from XPS spectrum of Pb_2O_3(0.5 wt%)/ TiO_2, so that the amount shows as the weight percent of Pb_2O_3 to TiO_2 for convenience. The photocatalytic activity was evaluated by photocatalytic H_2 production from aqueous methanol as a test reaction. In the reaction, proton reduced to H_2 by photo-generated electron in conduction band, while methanol acts as sacrificial regent and oxidized by hole in valence band. Photocatalytic reaction was carried out in a vessel connected with closed gas circulation system equipped with vacuum line and gaschromatograph sample inlet. The catalyst (0.5 g) was dispersed in well-outgassed 100 ml of aqueous methanol (50 vol%) in the vessel and was irradiated by 500 W Xe lamp (USHIO UI-501C). The change of wavelength region was performed by inserting optical filter (Colored Glass L42, HOYA), that can cut off the wavelength shorter than 420 nm. The crystal structure of the catalyst was examined by powder X-ray diffractometer (Shimadzu XD D-1).

The time course of photocatalytic reaction over Pb_2O_3(0.01 wt%)/TiO_2 is shown in Figure 1. It is observed in Figure 1 that H_2 produced constantly after induction period for ca. 3 hours. The amount of produced H_2 for 1 hour under the steady state is defined as the activity of catalyst. During the induction period, it was observed that the color of the catalyst changed from white to deep blue-purple and the color of the end of induction period kept in the steady state. This results are clearly suggesting that photo-reduction of the catalyst selectively proceeded in the induction period and the reduction of proton to H_2 proceeds over the partially reduced catalyst.

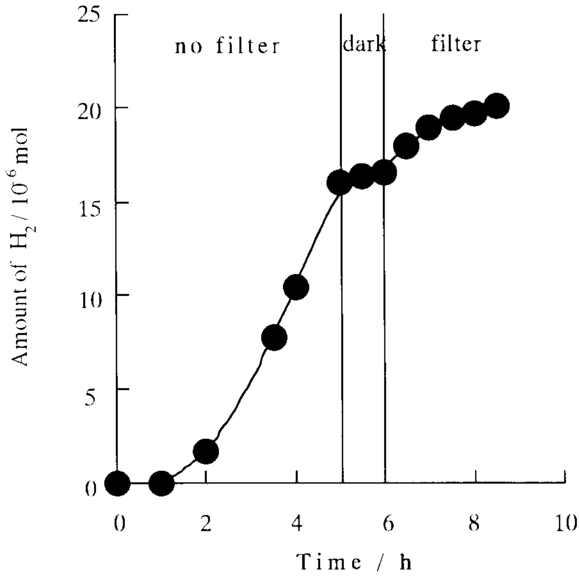

Fig. 1. Time course of photocatalytic H2 production from aqueous methanol over Pb2O3(0.01 wt%)/TiO2.

In order to investigate the contribution of the reduced catalyst to H_2 production, the reaction was observed under the conditions at which the photocatalytic reaction does not proceed, where H_2 production was observed in dark followed by restarting the irradiation, which was cutting off the wavelength shorter than 420 nm by optical filter, after confirming photocatalytic reaction under the steady state. The results are also shown in Fig.1. When the irradiation stopped and the vessel was kept in dark, the production of H_2 almost stopped. When the irradiation restarted by the light cut off the wavelength shorter than 420 nm, the production of H_2 can be confirmed but the amount of produced H_2 was decreasing with passing time accompanied with changing the color of the catalyst from deep-blue purple to white. These results are suggesting that irradiation is necessary for the production of H_2 from the photo-reduced catalyst and the light longer than 420 nm can assist the production of H_2. This property does not observe when TiO_2 is applied to this reaction, so that this is the new ability that appears when lead oxide is added in TiO_2 photocatalyst.

The dependence of the activity upon the amount of Pb_2O_3 added in TiO_2 and the dependence of the activity of Pb_2O_3(0.01 wt%)/TiO_2 upon the calcination temperatures were examined to investigate the conditions of TiO_2 photocatalyst added with lead oxide. The results are shown in Figure 2 and 3, respectively.

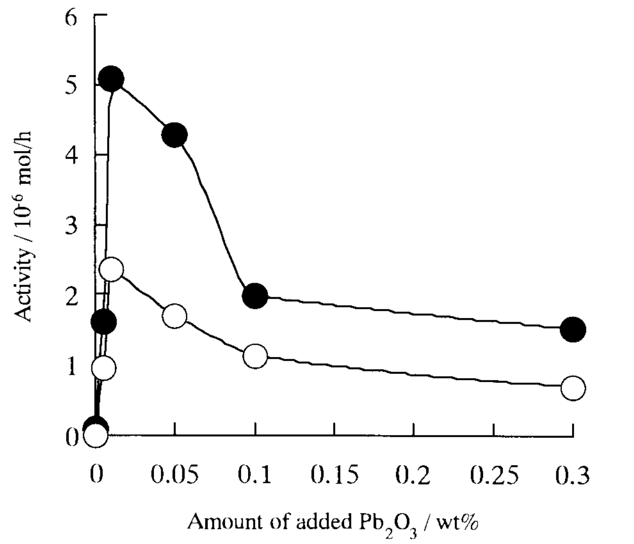

Fig.2. Dependence of the activity upon the amount of added Pb2O3; ●: the activity under steady state, ○: inital activity under irradiation, cut off the wavelength shorter than 420 nm.

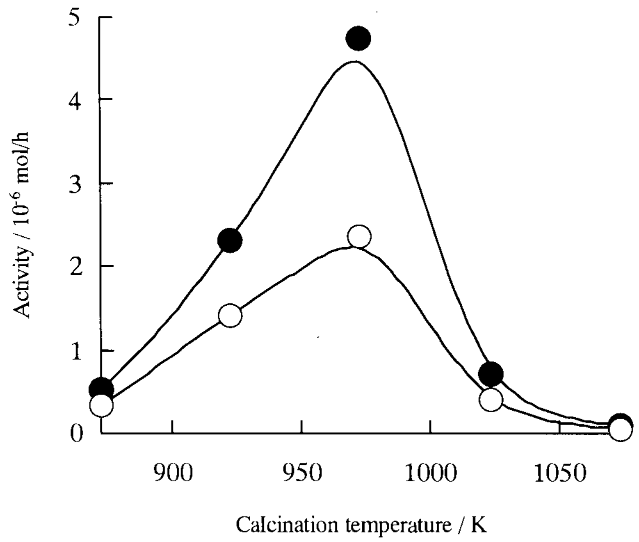

Fig.3. Dependence of the activity of Pb2O3(0.01 wt%)/TiO2 upon calcination temperatures; ●: the activity under steady state, ○: inital activity under irradiation, cut off the wavelength shorter than 420 nm.

The photocatalytic activity under the steady state and the initial rate of H_2 production under the irradiation cutting off the wavelength shorter than 420 nm are shown in both of the figures. These values were evaluated from the time course of reaction as Figure 1. From Figure 2, the photocatalytic activity improved by the addition of Pb_2O_3 and the maximum activity exhibited when Pb_2O_3 in 0.01 wt% was added to TiO_2. However, the activity was decreasing markedly when Pb_2O_3 in more than 0.01 wt% was added. The photocatalytic activity of base TiO_2 which was prepared from $Ti(SO_4)_2$ by precipitation method was 0.1 μmol/h under the same condition, so that the activity improved more than one order of magnitude when Pb_2O_3 is added to TiO_2. These are suggesting that the addition of small amount of lead oxide is effective for improving photocatalytic activity but the excess addition of lead oxide is not desirable for photocatalytic H_2 production.

From Figure 3, the activity noticeably increased by the increase of the calcination temperature and exhibited the maximum activity at 973 K. However, the activity decreased markedly when the catalyst was calcined over 973 K. From the results of XRD examination, anatase pattern was mainly observed on the catalyst calcined below 1023 K, while rutile was mainly observed on them calcined over 1073 K. XRD pattern originated from lead oxide cannot be observed on every catalysts. From these results, it is suggesting that lead oxide highly disperse in TiO_2 and the improvement of the photocatalytic activity probably depends on the condition of lead oxide in TiO_2 rather than the crystal structure of TiO_2. A characteristic condition of lead oxide in TiO_2 is probably effective for the improvement of the photocatalytic activity.

As shown in both of Figure 2 and 3, the initial activity of H_2 production under the irradiation cutting off the wavelength shorter than 420 nm show the same dependencies as the activity under steady state. This results are suggesting that the photocatalytic activity improves accompanied with appearing the ability of photo-assisted H_2 production originated from the addition of lead oxide in TiO_2

The detail condition of the photocatalyst is investigating.

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References

1 K.Zamaraev, M. I. Khramov and V. N. Parmon, Catal. Rev., **36**, 617 (1994).
2 T. Kawai and T. Sakata, J. Chem. Soc., **1980**, 694.
3 K. Yamaguchi and S. Sato, J. Chem. Soc. Faraday Trans.1, **81**, 1237 (1085).
4 B. Ohtani, K. Iwai, S. Nishimoto, and S. Sato, J. Phys. Chem.B, **101**, 3349 (1997).
5 E. Borgarello, J. Kiwi, M. Grätzel, E. Pelizzetti, and M. Visca, J. Am. Chem. Soc., **104**, 2996 (1982).
6 W. Choi, A. Termin, M. R. Hoffmann, J. Phys. Chem., **98**, 13669 (1994).
7 Y. Sakata, Y. Hirata, K. Miyahara, H. Imamura and S. Tsuchiya, Chem. Lett., **1993**, 391.