Photocatalytic Activity of RuO_2-loaded Pb_xWO_4 ($x = 0.2$–1.1) for Water Decomposition

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In the presence of RuO_2, Pb-deficient lead tungstates, Pb_xWO_4 ($x < 1.0$), showed higher photocatalytic activity compared to stoichiometric $PbWO_4$ for water decomposition. The highest activity was obtained at $x = 0.75$ in the range $x = 0.2$–1.1. The effects of the electronic structures on the photocatalysis are suggested.

In a previous paper,[1] we reported that RuO_2-loaded $PbWO_4$ had an ability of photocatalytically decomposing water. This is an interesting discovery, since the transition-metal oxides[2] so far developed as a photocatalyst for water decomposition have been confined to those consisting of Ti^{4+}, Zr^{4+}, Nb^{5+}, and Ta^{5+}, and thus $PbWO_4$ is the first example of a photocatalytically active metal oxide involving W^{6+} ion. In a study of the influences of preparation conditions on the photocatalytic properties of $PbWO_4$, we have found that the activity increased when the amount of Pb used for $PbWO_4$ preparation decreased from the stoichiometric ratio. Since a partial deficiency of one component metal ion in compounds generally leads to a significant or at least considerable deactivation of photocatalysis, the activity enhancement of Pb_xWO_4 ($x < 1.0$) is an interesting phenomenon, and thus the characteristic photocatalytic properties of Pb_xWO_4 were investigated in the x range of 0.2–1.1.

PbO (Nacalai Tesque, GR) and WO_3 (Nacalai Tesque, for analytical use) were used as starting materials. To obtain Pb-deficient and Pb-rich lead tungstate, the ratio of PbO to WO_3 in the mixture was changed from 0.2 to 1.1. Pb_xWO_4 ($x =$ 0.2–1.1) was synthesized by a solid-state reaction at high temperatures in air and under vacuum-sealed conditions. In the former, the mixture was calcined at 923 K for 16 h (denoted here as (A)Pb_xWO_4). In the latter, a mixture of PbO and WO_3 was placed in a quartz tube, vacuum-sealed and heated at 923 K for 16 h ((Q)Pb_xWO_4). RuO_2 was loaded on prepared Pb_xWO_4 surfaces by a procedure reported previously.[3] The photocatalytic reaction was carried out in a closed gas circulation reaction system using a quartz reaction cell. The powder photocatalysts (250 mg) were dispersed in distilled water (30 mL) by stirring with Ar gas (13.3 kPa) bubbling and illuminated by an outer Hg–Xe lamp operated at 200 W. The evolved gases were analyzed by an on-line gas chromatograph.

Figure 1 shows the X-ray diffraction patterns of (A)Pb_xWO_4 ($x = 0.6$–1.1). The pattern for $x = 1.0$ was consistent with that reported previously for the tetragonal structure,[4] and a complete single phase pattern was obtained. The main features of the diffraction patterns were similar in the range of $x = 0.6$–1.1. Additional small peaks due to Pb_2WO_5 were observed for $x = 1.1$. Small peaks due to WO_3 appeared at $x = 0.875$ and grew with decreasing x. The quantitative analysis of Pb and W

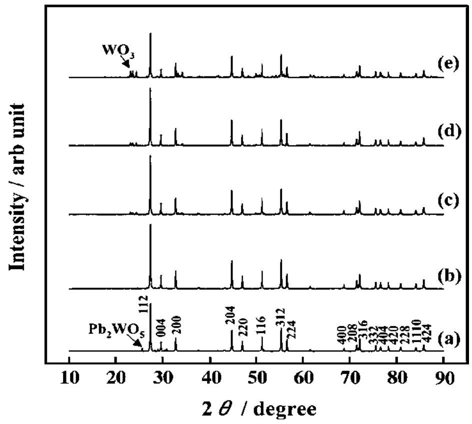

Figure 1. XRD patterns of (A)Pb_xWO_4 at $x = 1.1$ (a), 1.0 (b), 0.875 (c), 0.75 (d), and 0.6 (e).

elements in $PbWO_4$ and $Pb_{0.75}WO_4$ by means of electron probe microanalysis showed that the ratios of Pb/W were 0.90 and 0.68 for (A)$PbWO_4$ and (A)$Pb_{0.75}WO_4$, and were 0.93 and 0.70 for (Q)$PbWO_4$ and (Q)$Pb_{0.75}WO_4$, respectively. Thus, it is evident that the Pb to W ratios in Pb_xWO_4 prepared in air and under vacuum conditions were close to those expected. In the UV–vis diffuse reflectance spectra, light absorption occurred at a wavelength of 330 nm and leveled off at 300 nm for $x = 1.0$. With decreasing x, no significant changes in the main absorption characteristics were observed, although a broad bump due to WO_3 appeared in the range 330–450 nm.

Figure 2 shows water decomposition on RuO_2-loaded (A)$Pb_{0.75}WO_4$. Upon UV irradiation both H_2 and O_2 increased in nearly proportion to irradiation time. After a considerable decrease in the second run, the production remained nearly unchanged after the third run, indicative of the stability of the photocatalyst.

Figure 3 shows the photocatalytic activity of RuO_2-loaded (A)$PbWO_4$ as a function of x. The photocatalytic activity at $x =$

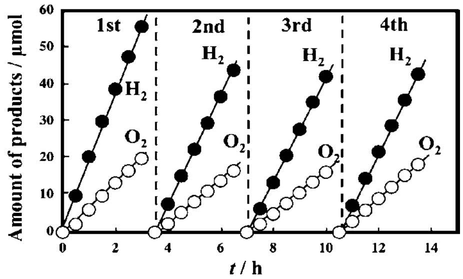

Figure 2. Overall water splitting by 1 wt% RuO_2-loaded (A)$Pb_{0.75}WO_4$ (●; H_2, ○; O_2).

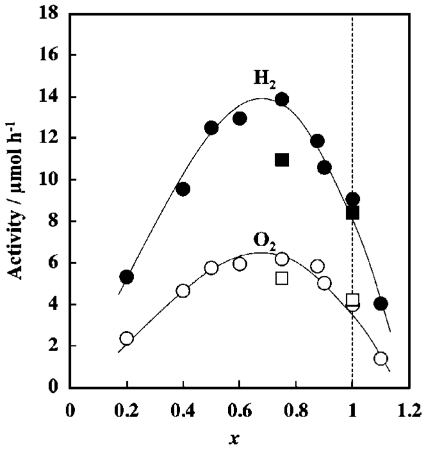

Figure 3. Photocatalytic activity of 1 wt% RuO_2-loaded (A)Pb_xWO_4 ($x = 0.2$–1.1, ●; H_2, ○; O_2) and 1 wt% RuO_2-loaded (Q)Pb_xWO_4 ($x = 0.75$ and 1.0, ■; H_2, □; O_2) as a function of x.

1.1 was approximately one-half that at $x = 1.0$. The excess amount of Pb had negative influences on the activity. On the other hand, with decreasing x, the activity increased, attained to a maximum at around 0.75, above which it decreased markedly. The highest activity at $x = 0.75$ was larger by a factor of 1.5 than that at $x = 1.0$. Figure 3 also shows the result for (Q)$PbWO_4$ and (Q)$Pb_{0.75}WO_4$. The photocatalytic activity of the latter was larger than the former by a factor of 1.3. As shown in Figure 1, a WO_3 phase remained unreacted for $x < 0.875$. The coexistence of WO_3 and $PbWO_4$ might be responsible for the enhancement of photocatalytic activity. However, the deliberate addition of a small amount of WO_3 to $PbWO_4$, followed by calcination, lowered the photocatalytic activity of $PbWO_4$ significantly. The activity of RuO_2-loaded Pb_2WO_5 was negligible.

As Pb-deficient lead tungstates, $Pb_{0.9375}WO_4$ and $Pb_7W_8O_{28.8}$ were reported.[5,6] These provide nearly the same X-ray diffraction patterns as that of $PbWO_4$: for example, differences in a main peak due to 112 plane among the three tungstates were within 0.03°, which was below accuracy for measurements. Thus, it was difficult to confirm the formation of $Pb_{0.9375}WO_4$ and $Pb_7W_8O_{28.8}$ by the diffraction patterns. The SEM images provided similar morphology between $PbWO_4$ and $Pb_{0.75}WO_4$, although the particle sizes were considerably larger for the latter. There is a possibility that the activity enhancement of Pb_xWO_4 with decreasing x is attributable to the formation of $Pb_{0.9375}WO_4$ and/or $Pb_7W_8O_{28.8}$. The previous DFT calculation for $PbWO_4$ showed that the valence and the conduction bands had considerably large dispersions, because of hybridization of O2p with Pb6s orbital and that of W5d with O2p + Pb6p orbitals, respectively.[7] The electronic structures were different from flat structure frequently observed for alkaline metal and alkaline earth metal tungstates such as photocatalytically inactive $CaWO_4$. These results show that the role of Pb6s and -6p orbitals is important to enhance photocatalytic performance. The preliminary DFT calculation for $Pb_7W_8O_{28.8}$ showed that the contributions of Pb6s and -6p orbitals to the valence and conduction bands increased, compared to $PbWO_4$. Figure 4 shows photoluminescence for (A)Pb_xWO_4 ($x = 0.6$–1.0) upon UV excitation at 250 nm. It increased with decreasing x, became the strongest at around $x = 0.75$–0.875, and significantly decreased at $x = 0.6$. Raman spectra showed that a peak due to A_{1g} appearing at $904\,cm^{-1}$ became broader when Pb decreased to $x = 0.75$. These results indicate that the deficiency of Pb in $PbWO_4$ has the effects on the interaction between Pb^{2+} and W^{6+} metal ions, which is likely responsible for an increase in activity.

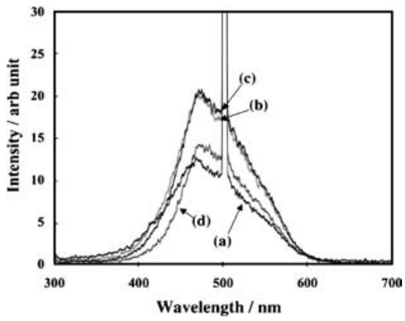

Figure 4. Photoluminescence of (A)Pb_xWO_4 at $x = 1.0$ (a), 0.875 (b), 0.75 (c), and 0.6 (d). A sharp peak at 500 nm is due to excitation light.

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References and Notes

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