Generation of Visible Light Response on the Photocatalyst of a Copper Ion Containing TiO_2

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The generation of photocatalytic activity under the irradiation of visible light (longer than 460 nm) was observed over copper ion containing TiO_2. It is suggested that low valent copper oxide which was produced in the catalyst under the irradiation of UV plays an important role to the generation of the activity under the irradiation of visible light.

It is known that TiO_2 is one of the suitable semiconductors for photocatalyst and is applied to various photocatalytic reactions.[1] However, the properties, not only the photo-efficiency or activity but also the photoresponse, are not sufficient, so that various modifications have been performed to promote the properties and develop new photocatalytic functions.[2-7] Among them, modifications by metal ions and oxides have been performed to improve the activity and photoresponse.[5-7] We have studied the photocatalytic activity of TiO_2 modified with oxides to advance the photocatalytic properties on the conception of the combination of the catalytic oxidation-reduction property of oxides with the photocatalyst system of TiO_2.[6, 7]

In this letter, we report on the photocatalytic property of TiO_2 combined with copper ion, which was prepared from the pyrolysis of the mixture of $Ti(SO_4)_2$ and $Cu(NO_3)_2$. Particularly, the photocatalytic property was investigated on the activity as well as the photoresponse.

The photocatalyst used in this work was prepared by the pyrolysis of the homogeneous mixture of $Ti(SO_4)_2$ and $Cu(NO_3)_2$, which was obtained from evaporating the mixed solution in a crucible with stirring during the evaporation, at 933 K for 10 h, where $Cu(NO_3)_2$ was contained calculated as 1 weight % of CuO in the prepared catalyst. The state of the prepared catalyst was confirmed by XRD and was a mixture of TiO_2 (anatase) and $TiO(SO_4)$. However, informations about the state of the copper ion in the catalyst cannot be obtained from the XRD measurement. The photocatalytic reaction was carried out in a vessel made of Pyrex glass connected with a closed gas circulation system. The photocatalytic activity was evaluated by H_2 production from an aqueous methanol (50 vol%, 100 ml), where methanol was oxidized by hole and photogenerated electron took part in the reduction of proton to H_2. The catalyst (0.5 g) was suspended in well out-gassed aqueous methanol in the vessel and then irradiation (500 W Xe lamp USHIO) was started. The wavelength of irradiation was changed by inserting different optical cut-off filters in the light path. The produced H_2 was analyzed by gaschromatograph. The catalysts were characterized by diffuse reflectance UV-Visible spectrometry (Jasco. U-best 550DS). A series of UV-Vis spectra were particularly measured at every prescribed time after performing the photocatalytic reaction in a UV cell under N_2 atmosphere.

First, the photocatalytic property was investigated under the full arc irradiation of Xe lamp. The time courses of photocatalytic H_2 production over the copper ion containing TiO_2 under full arc irradiation are shown in the full arc part of Figure 1. It is observed in Figure 1 that H_2 was produced constantly after the induction period of 8 hours. The amount of produced H_2 per hour was defined as the photocatalytic activity of the catalyst. The activity of H_2 production under the full arc irradiation in the steady state was 2.4 μmol/h, while that of TiO_2 itself prepared by the same condition is 0.1 μmol/h; the photocatalytic activity of TiO_2 was remarkably enhanced by the addition of Cu ion in TiO_2. In the induction period, the color of the catalyst was changing from white to red-purple with irradiation time. This suggests that the state of the catalyst changed to be an active state for the photocatalytic reaction during the induction period. In order to make clear how the catalyst changes in the induction period, the diffuse reflectance UV-Vis. spectra of the photocatalyst after the various irradiation period were measured.

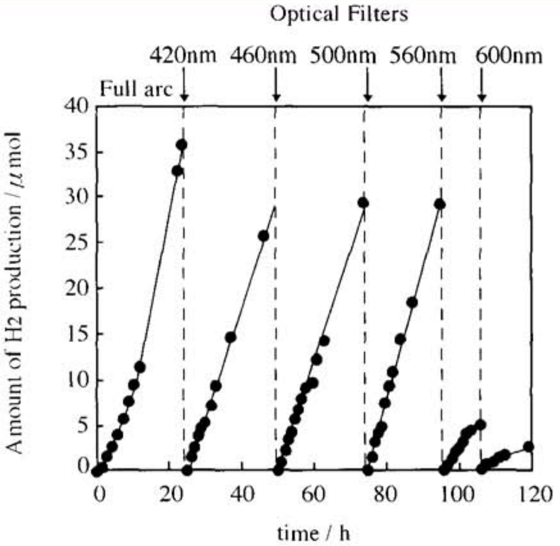

Figure 1. Time courses of photocatalytic H_2 production from aqueous methanol under various irradiation conditions.

UV-Vis spectra of copper ion containing TiO_2 after the full arc irradiation for various time are shown in Figure 2. In the spectra in Figure 2, a strong absorption band below 400 nm was attributable to the absorption of the band-gap of TiO_2. Beside the band below 400 nm, the production of new band whose absorption edge was at 630 nm was observed. The intensity of the 630 nm band was increasing accompanied with irradiation time and saturated at ca. 8 hours. In order to assign the produced band, the spectrum of Cu_2O diluted with TiO_2 was measured. From the result, the spectrum of Cu_2O was good agreement with

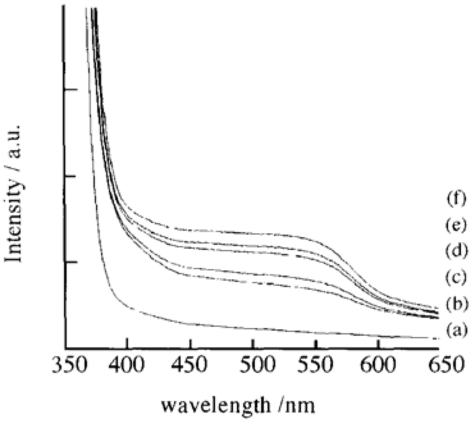

Figure 2. Diffuse reflectance UV-Vis spectra of Cu ion containing TiO2 after the full arc irradiation by Xe lamp for (a) 0 h, (b) 1 h, (c) 2 h, (d) 5 h, (e) 6 h, and (f) 8 h.

the produced new band in Figure 2. These results suggest that the Cu(II) ion in TiO_2 reduced gradually under the induction period in the photocatalytic reaction to form low-valent copper oxide, such as Cu_2O. The condition of the catalyst under the steady state of photocatalytic reaction was the mixture of TiO_2 and low-valent copper oxide, where the copper oxide homogeneously dispersed in TiO_2. From the results in Figures. 1 and 2, it is indicated that the photocatalytic activity improved by changing the Cu(II) ion to low-valent copper oxide in the catalyst.

The reaction was examined in dark and under irradiating visible light after the confirmation of the steady state of photocatalytic reaction under full arc irradiation to investigate the contribution of the produced active state of the catalyst to the photocatalytic reaction. It was confirmed that the production of H_2 stopped completely, when the irradiation was stopped and when the vessel kept in dark.

The results of the time courses of the photocatalytic reaction under irradiating visible lights are also shown in Figure 1. When the irradiation longer than 420 nm was started, H_2 produced constantly from the initial stage of the reaction as shown in Figure 1. The light cut off at 460 and 500 nm resulted in nearly the same photocatalytic activity as that at 420 nm, while the irradiation of light with wavelength longer than 560 and 600 nm markedly decreased the activity. From the results, the photocatalytic reaction was obviously proceeding under irradiation of visible light (longer than 460 nm) where the photocatalytic reaction cannot proceed over TiO_2 itself. Moreover, the photocatalytic behaviors under various irradiating light were well consistent with the photo-absorption of produced low-valent copper oxide. (Figure 2) These results indicate that photogenerated low-valent copper oxide become the active center for proceeding the photocatalytic reaction under the irradiation of visible light. Therefore, the photocatalytic activity can be observed to the irradiation longer than 600 nm.

It has been reported that Cu_2O expressed photocatalytic activity for cleavage H_2O into H_2 and O_2 in stoichiometric ratio under irradiating visible light.[8] In the present system, it is found that the combination of copper ion with TiO_2 become the characteristic photocatalyst which produces an ability for proceeding the photocatalytic reaction under visible light irradiation.

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