Hydrothermal Synthesis of Potassium Hexatitanate Photocatalyst under Supercritical Water Conditions

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Abstract
Hydrothermal synthesis of potassium hexatitanate (KTO) was carried out under supercritical water conditions. Characterization of the hydrothermally synthesized (ht-) KTO samples by XRD and TEM revealed that fibrous materials can be obtained with the crystal growth in the direction of (010). To determine the optimum Ru loading for highly active photocatalyst, Ru ion exchange on the ht-KTO was examined with the variation of RuCl₃ concentration. The maximum photocatalytic activity of RuO₂ loaded ht-KTO was achieved when the Ru loading was 1.0 wt% which was much higher in comparison with the solid-state synthesized KTO.

1 Introduction
Alkali-metal hexatitanate is one of the semiconducting photocatalysts which has the capability of invoking a photocatalytic decomposition of water to produce H₂ and O₂ in the presence of ruthenium oxide as a promoter. [1-5] The structure of potassium hexatitanate (KTO) is one in which the octahedral TiO₆ units share an edge at one level in a linear group of three, giving rise to a rectangular tunnel structure. [6] The presence of these tunnels in the structure has the advantage of being able to accommodate ruthenium oxide, thus enhancing further catalytic activity. In previous studies, the synthesis of KTO employed for photocatalytic studies, so far has been by the solid-state reaction. In synthesizing catalytic support materials, generally a method that can produce large surface area and nanostructure products is desirable.

Supercritical hydrothermal processing is a prospective method to obtain highly crystalline nanoparticles, because supersaturation degree is higher compared to under subcritical conditions due to low solubility of metal oxide and dehydration of hydrous metal oxide proceeds under supercritical conditions owing to low dielectric constant. [7-8] We have demonstrated hydrothermal synthesis of KTO under various subcritical and supercritical water conditions and the photocatalytic activity for water decomposition over RuO₂ loaded KTO synthesized under supercritical conditions was remarkably higher than that over RuO₂ loaded KTO synthesized under subcritical conditions because the crystallinity of the KTO is beneficial to a certain extent for highly photocatalytic activity as well as large surface area. [9]

In the present paper, ruthenium ion exchange reaction on KTO was examined to elucidate the mechanism of ruthenium uptake and determine the optimum Ru loading for photocatalytic decomposition of water to prepare a highly active photocatalyst compared with the conventional solid-state synthesized KTO.
2 Experimental

2.1 Synthesis

KTO was hydrothermally synthesized using KOH and titanium tetraisopropoxide in a K:Ti molar ratio of 1:2. Heating temperature of 400 °C and heating duration of 5 h were employed. The products were allowed to cool slowly followed by filtering, washing with distilled water and finally drying at 50 °C for 24 h. KTO was also synthesized by the solid-state reaction using K₂CO₃ and TiO₂ in a K:Ti molar ratio of 1.1:6 and heating at 1130 °C for 5 h. KTOs synthesized by the hydrothermal method and the solid state method were described as ht-KTO and ss-KTO, respectively.

2.2 Ion exchange reaction

To determine the cation exchange capacity of KTO, Na uptake was measured at various hydrothermal temperatures. An ion exchange reaction of Na ions on KTO was carried out by a batchwise operation. A 0.5 g of KTO was immersed in a sealable autoclave with 0.1 M NaOH solution at a constant temperature ranging from 50 to 450 °C. The solid phase was filtered off, dried at 50 °C overnight, and dissolved in conc. H₂SO₄. The metal concentration was analysed by ICP emission spectroscopy to estimate the Na uptake and K remained. Loading of Ru on KTO by ion-exchange reaction was carried out using RuCl₃ aqueous solutions with various concentrations for 48 h at room temperature with a magnetic stirrer. The filtrate was analysed for the metal concentrations by ICP emission spectroscopy to calculate the Ru loading and K released. The solid phase was filtered, dried at 50 °C overnight, and calcined at 450 °C for 2 h to activate the ruthenium oxide.

2.3 Photocatalytic decomposition of water

Photocatalytic reaction was carried out in a closed gas-circulation system at 30 °C. The catalyst (ca.0.3 g) was placed in a Pyrex glass reactor containing a 500 cm³ distilled water and was kept in suspension by stirring continuously with a magnetic stirrer. The UV source was an inner radiation type high-pressure Hg lamp (400 W) placed in the Pyrex glass reactor circulating with cooling water. The evolved hydrogen gas was analyzed by a gas chromatograph connected directly to the reaction system.

3 Results and Discussion

3.1 Synthesis of potassium hexatitanate

Figure 1 shows the Scanning electron micrographs of the KTO samples synthesized by the hydrothermal method and the solid-state reaction method. The micrograph of the ht-KTO sample showed similar morphology of long, felt-like fibrous structure, while that of ss-KTO sample exhibited sword-like structure with larger particle size as compared to ht-KTO sample. The X-ray diffraction patterns of ht-KTO and ss-KTO samples can be assigned to K₂Ti₆O₁₃ (JSPDS40-0403), in which the peak at d(020) is more intense for the ht-KTO sample than that for the ss-KTO sample.

Fig. 1 SEM photographs of KTO as synthesized by (a) hydrothermal condition at 400 °C; (b) solid-state condition at 1130 °C.
perpendicular to the sheet of the rectangular tunnels.

3.2 Ion exchange property

At first, Na exchange capacity was measured at various temperatures. Figure 2 shows hydrothermal temperature dependence of Na uptake, K remained, and Na+K content analyzed after the solid phase was digested with conc. H₂SO₄. The Na uptake was almost constant in the temperature range up to 350 °C. Complete ion-exchange reaction occurred at 450 °C, though the structure was transformed to Na₂Ti₃O₇(JSPDS31-1329). It should be noted that only 20% of K ions can be extracted from the KTO, suggesting that the remaining K ions are fixed in the tunnel structure. Thus, Na⁺ exchange capacity can be estimated to be 0.3 mmol/g.

To elucidate the Ru uptake mechanism on the KTO, Ru ion-exchange reaction was carried out with the variation of Ru concentration. Figure 3 exhibits Ru uptake, K released, and K/Ru molar ratio, as a function of initial Ru concentration. The Ru uptake linearly increases with the Ru concentration and saturated to 0.18 mmol/g. The amount of K released also increases with the Ru concentration, whereas the saturation occurs at lower Ru concentration. The K/Ru molar ratio decreases with the Ru concentration from 3 to unity. This is not in accord with the former result that Na/Ru molar ratio was 2 in different Ru concentrations.[1] The equilibrium pH decreases with an increase in the Ru concentration, which suggests that hydrolysis occurs at the higher Ru concentration. Therefore, K ions are presumably exchanged with Ru(OH)₂⁺ at high Ru concentration.

The ht-KTO sample having larger surface area is expected to have better dispersion of ruthenium oxide. The higher dispersion of ruthenium oxide will increase the efficiency of photoexcited charge separation and transfer to the surface reactants, thus, giving raise to the higher activity. On the other hand, in the larger particles of ss-KTO sample, the photoexcited charges generated might have recombined in the KTO and transfer of charge to the surface through the ruthenium oxide might not take place at all.

3.3 Photocatalytic decomposition of water
Figure 4 shows the dependence of hydrogen evolution rate from water upon the amount of loaded Ru over ht-KTO photocatalyst. The hydrogen evolution rate increase and reaches the maximum at 1.0 wt% of Ru loading, then decreases with an increase in the Ru loading. Similar profile was observed in ss-KTO photocatalyst in which the maximum was observed at 0.23 wt% of Ru loading. Large surface area might be the reason why the maximum hydrogen evolution rate shifted to higher Ru loading for ht-KTO photocatalyst. Moreover, the Ru loaded ht-KTO photocatalyst exhibits higher activity compared to the Ru loaded ss-KTO photocatalyst (4.8 μmol/hg at 0.3 wt% of Ru loading).

On the basis of the TEM observation for the Ru loaded ss-KTO sample, larger spots with a diameter of 3-5 nm are uniformly dispersed on the surface, which spherical spots can be attributed to the rutenium oxide. On the other hand, in the micrograph of the Ru loaded ht-KTO sample, these spots can not be easily observed at low Ru loading. These results suggest that ruthenium oxide might be dispersed in the inner lattice of the ht-KTO sample at low Ru loading. The larger amount of the optimum Ru loading for the catalyst of smaller particle size is due to its higher surface area. Rutemum oxides deposited inside the tunnel structure are available for separation of reaction products as well as separation of charges. However, excess loading of Ru produces agglomeration of ruthenium oxides at the surface, a part of which works as the recombination center.

In summary, this study has demonstrated the advantage of the hydrothermal synthesis in supercritical water to prepare a highly active photocatalyst compared with the conventional solid-state reaction. The fibrous structure with large surface area accounts for the dispersion of ruthenium oxides in the inner lattice of the ht-KTO.

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References