Photocatalytic Activity of Sodium Hexatitanate, $Na_2Ti_6O_{13}$, with a Tunnel Structure for Decomposition of Water

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Sodium hexatitanate, $Na_2Ti_6O_{13}$, with a tunnel structure, combined with oxidized Ru, was found to be an efficient photocatalyst for the complete decomposition of water.

In view of the current interest in light-energy storage, the development of an effective semiconducting photocatalyst has been of particular importance. In a previous study, we suggested that host–guest type oxides may be photocatalytically useful.[1] In an attempt to obtain a new photocatalyst with this in mind, we have found that sodium hexatitanate, $Na_2Ti_6O_{13}$, with a tunnel structure has a potentially interesting photocatalytic function. This report deals with its photocatalytic properties for the decomposition of water.

Sodium hexatitanate, $Na_2Ti_6O_{13}$ (referred to as NTO), was prepared by calcining sodium carbonate and titanium dioxide in a molar ratio of 1 : 6 between 1173 and 1273 K for 18 h and cooling slowly to room temperature. The formation of NTO oxide was confirmed by the *X*-ray diffraction pattern. Photocatalysts were prepared by impregnating the oxide with metals, *e.g.* Ru, Pt, or Rh, from their aqueous chloride solution. The metal loading was 0.2—0.3 wt%. The catalysts were heat treated as follows for activation. The Ru impregnated catalyst was oxidised in air at 823 K (to give RuO_x/NTO, Ru being considered to be in an oxidized state). The Pt catalyst was reduced in an H_2 atmosphere at 573 K (Pt/NTO) and the Rh catalyst reduced at 673 K after being heated at 873 K (Rh/NTO). The photocatalytic reactions were carried out using *ca.* 250 mg of the photocatalyst with *ca.* 20 ml of distilled pure water at pH 7, illuminated by a Xe lamp light (400 W) through a water filter. The amounts of H_2 and O_2 were analysed by gas chromatography (on a molecular sieve 5 Å column) directly connected to the reaction system.

Figure 1 shows results for the decomposition of water on the RuO_x/NTO photocatalyst. In an initial induction period, more H_2 than O_2 was produced, the rates of production of both continuing to increase with illumination time. After 8 h, the activity reached a constant level at which H_2 and O_2 were produced in almost the stoichiometric ratio. This stationary behaviour with nearly complete decomposition of water can be seen clearly in the second run after evacuation of the gas phase.

Figure 2 shows the effects of the metals on the photocatalytic activities of the NTO oxides. There was little activity in the absence of the metals. On addition of Pt or Rh, the activity for H_2 production increased by a factor of *ca.* 3 but no significant production of O_2 occurred in either case. These

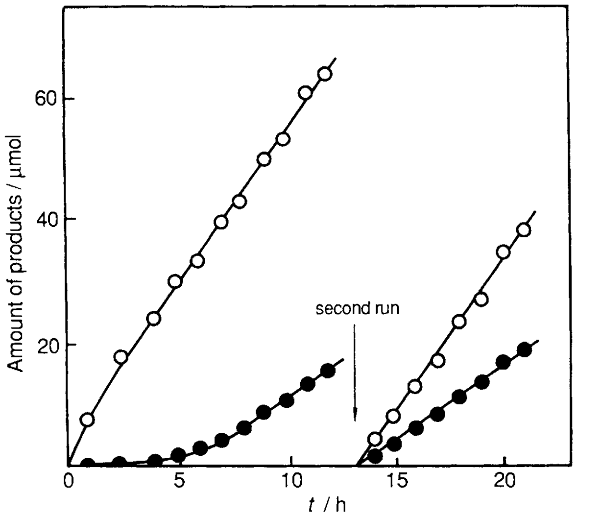

Figure 1. Photodecomposition of water on a $RuO_x/Na_2Ti_6O_{13}$ catalyst. ○, H_2; ●, O_2.

activities were much lower than that of the RuO_x/NTO catalyst. The higher efficiency of the RuO_x/NTO catalyst for O_2 production is partly related to the higher capability of RuO_2 in decreasing the overvoltage for the oxidation. Also, the active RuO_x/NTO catalyst is not subjected to any reduction treatment in its preparation; activation of the oxide by reduction is not required, either before or after the deposition of the active metal phases. The interesting feature of the present system is that the NTO oxide can be activated under oxidative conditions unlike other conventional titanium oxides such as TiO_2 and $SrTiO_3$ which need reduction at high temperatures. This evidently leads to a favourable surface state for oxidation, since it is frequently considered that the take-up of oxygen by the lattice defects of reduced semiconducting oxides is partly responsible for the lack of gaseous oxygen. Such properties might offer an advantage in developing photocatalysts with a stable long-term activity.

The present NTO oxide is one (M = Na, $n = 6$) in a series of oxides having the chemical formula $M_2Ti_nO_{2n+1}$ (M = alkali metal). Each Ti atom has six oxygen atoms at the corner of a distorted octahedron, and the geometric structures differ depending on whether the TiO_6 octahedra are edge- or corner-shared. The most interesting structural feature of the hexatitanate is the presence of a framework enclosing tunnels which are formed by corner- and edge-shared TiO_6 octahedra.[2] The present results suggest that this tunnel structure is able to provide stable sites to facilitate a strong interaction with the active phase of RuO_x and thus lead to a higher efficiency in the transfer of the photoexcited carriers.

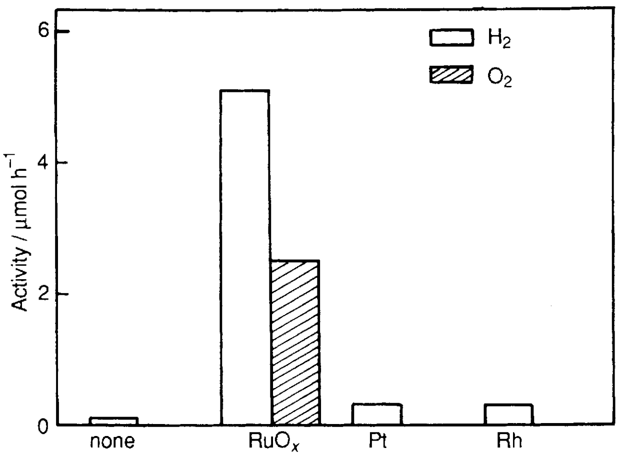

Figure 2. Effects ot active phases deposited upon the photocatalytic activity.

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