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Effects of RuO_2 on activity for water decomposition of a $RuO_2/Na_2Ti_3O_7$ photocatalyst with a zigzag layer structure

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Sodium trititanate, $Na_2Ti_3O_7$, with a zigzag layer structure produces a surface lattice O^- radical upon UV irradiation and has the ability to decompose water to hydrogen and oxygen when ruthenium oxide is highly dispersed on the titanate.

Barium tetratitanate, $BaTi_4O_9$, with a pentagonal-prism tunnel structure and alkaline metal hexatitanates, $M_2Ti_6O_{13}$ (M = Na, K, Rb), with a rectangular tunnel act as good photocatalysts to decompose water to oxygen and hydrogen in combination with ruthenium oxide.[1–3] The common features of these titanates are that both have tunnel structures and give rise to surface lattice O^- species in the presence of gases at 77 K upon UV irradiation.[4–6] These results lead to a view that photocatalysis by the titanates is closely related to the surface lattice O^- radical generated by UV irradiation.

In a series of titanates with the chemical formula $Na_2Ti_nO_{2n+1}$ to which $Na_2Ti_6O_{13}$ belongs, $Na_2Ti_3O_7$ has a zigzag layer structure.[7] Fig. 1 shows a schematic structure of $Na_2Ti_3O_7$, together with the rectangular tunnel structure of $Na_2Ti_6O_{13}$. When RuO_2 was supported on $Na_2Ti_3O_7$ by the same conventional impregnation method using $RuCl_3$ aqueous solutions as employed for $BaTi_4O_9$ and $M_2Ti_6O_{13}$ (M = Na, K, Rb), poor photocatalytic performance for water decomposition has been known to occur. It is of particular importance to clarify the reasons for the photocatalytic differences between the tunnel and the layer titanate and to confirm whether or not a correlation between photocatalytic activity and the surface lattice O^- radical formation holds for the layer titanate, for better understanding of the photocatalysis mechanism.

Since the photocatalytic processes in water decomposition on RuO_2-deposited titanates are composed of photoexcited charge formation in the titanates and charge transfer to the surface reactants through RuO_2, each step has to be examined separately in order to shed light on the differences between the two types of titanates. In the present study, the ability of photoexcited charge formation was examined by an electron paramagnetic resonance (EPR) method, and that of charge transfer by changing the effects of RuO_2 deposited on the titanates and then by high resolution transmission electron microscopic (HRTEM) observation. We have discovered that a layered titanate of $Na_2Ti_3O_7$ has a high ability for photoexcited charge formation and the effects of RuO_2 dispersion are important for photocatalysis: $Na_2Ti_3O_7$ is a promising photocatalyst when ruthenium oxide is dispersed as small particles on the titanate.

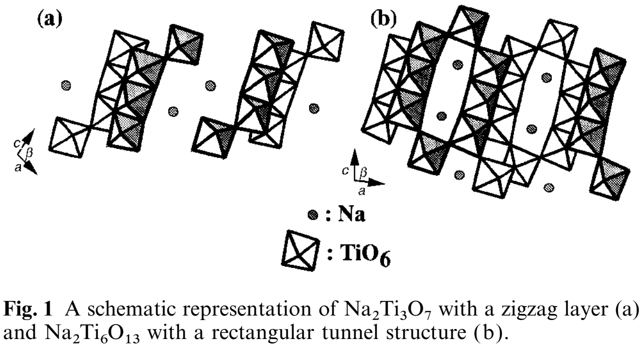

Fig. 1 A schematic representation of $Na_2Ti_3O_7$ with a zigzag layer (a) and $Na_2Ti_6O_{13}$ with a rectangular tunnel structure (b).

$Na_2Ti_3O_7$ was prepared by calcining an equimolar ratio of TiO_2 (high purity grade, Soekawa Chemical Co.) and Na_2CO_3 (high purity grade, Soekawa Chemical Co.) in air at 1073 K for 16 h. The formation of these titanates was confirmed by X-ray diffraction. For measurements of EPR signals, about 300 mg of the titanates were placed in a quartz cell and degassed at 573 K in high vacuum. The *g* values were calibrated by Mn^{2+} in MgO, the error of which was within ± 0.001. For the preparation of a photocatalyst, $Na_2Ti_3O_7$ was impregnated with the two kinds of ruthenium compounds: one consisted of $RuCl_3$ aqueous solutions which were the same as used in the previous procedures,[1–3] and the new other was dodecacarbonyltriruthenium, $Ru_3(CO)_{12}$, dissolved in tetrahydrofuran. The Ru metal loading was 0.7 wt%, unless otherwise specified. The impregnated titanate was dried at 353 K and then subjected to reduction at 673 K in a H_2 atmosphere for 4 h, followed by oxidation in air at 623 K. Ruthenium oxides prepared using $RuCl_3$ and $Ru_3(CO)_{12}$ are referred to as RuO_2(CL) and RuO_2(CB), respectively. A powdered photocatalyst (250 mg) was dispersed in a quartz reaction cell filled with distilled and deionized pure water (20 cm^3), stirred by bubbling with Ar gas, and irradiated through a water filter with a Xe lamp operated at 400 W. Hydrogen and oxygen produced were analyzed by a gas chromatograph directly connected to the reaction system.

The HRTEM images of the RuO_2-dispersed titanates were obtained with a JEOL 2010 transmission electron microscope operated at 200 kV. The energy-dispersive X-ray (EDS) spectra were collected for nanometer-sized areas of the samples with a Voyager energy dispersive analyzer (Noran Instruments) installed on the microscope.

Fig. 2 shows the EPR signals of $Na_2Ti_6O_{13}$ and $Na_2Ti_3O_7$ obtained at 77 K in 4 kPa O_2 under UV irradiation by a 500 W

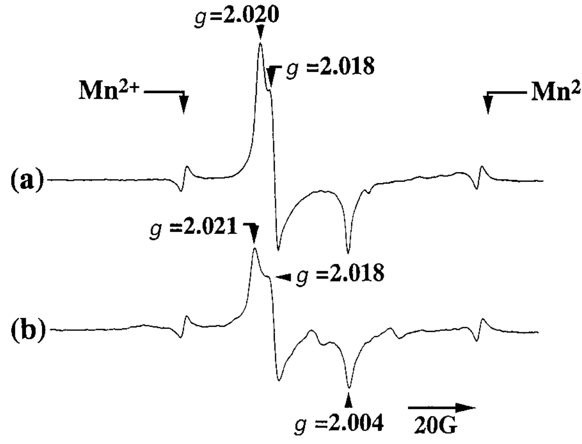

Fig. 2 Comparison of EPR signals of $Na_2Ti_6O_{13}$ (a) and $Na_2Ti_3O_7$ (b) with UV irradiation. The signals were recorded at 77 K in the presence of 4 kPa oxygen. The signal of $Na_2Ti_6O_{13}$ was the same as reported previously (*cf.* ref. 4).

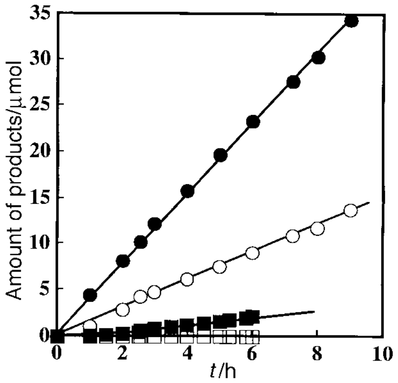

Fig. 3 Production of hydrogen and oxygen from water by a RuO_2(CB) and RuO_2(CL)/$Na_2Ti_3O_7$ photocatalyst with a zigzag layer structure. ●, H_2; ○, O_2 for RuO_2(CB)/$Na_2Ti_3O_7$; ■, H_2; □, O_2 for RuO_2(CL)/$Na_2Ti_3O_7$.

high pressure mercury lamp. As reported previously, the tunnel structure $Na_2Ti_6O_{13}$ provided a strong signal with $g = 2.020$, $g = 2.018$ and $g = 2.004$, which is assigned to a surface lattice O^- radical.[4,6] For $Na_2Ti_3O_7$, nearly the same signal with $g = 2.021$, $g = 2.018$, and $g = 2.004$ was observed. The close similarity clearly indicates that $Na_2Ti_3O_7$ is able to produce the surface lattice O^- radical. Since the formation of the radical is associated with highly efficient photoexcited charge separation in $BaTi_4O_9$ and $Na_2Ti_6O_{13}$,[8] $Na_2Ti_3O_7$ is concluded to have the ability of photoexcited charge formation.

Fig. 3 shows water decomposition on a RuO_2(CB)-deposited $Na_2Ti_3O_7$ [referred to as RuO_2(CB)/$Na_2Ti_3O_7$] photocatalyst, together with a RuO_2(CL)/$Na_2Ti_3O_7$ photocatalyst. In addition to hydrogen, the evolution of oxygen occurred from an initial stage and continued at a constant rate as long as the sample was irradiated. Note that a RuO_2(CL)/$Na_2Ti_3O_7$ photocatalyst which underwent the same reduction and oxidation resulted in little evolution of oxygen, although a small amount of hydrogen was produced.

Fig. 4 shows HRTEM images of RuO_2 deposited $Na_2Ti_3O_7$. For RuO_2(CL)/$Na_2Ti_3O_7$, large egg-shaped black spots, whose sizes were around 20–30 nm, were observed. On the other hand, for RuO_2(CB)/$Na_2Ti_3O_7$ spherical dark spots of 2–4 nm in diameter were mostly distributed uniformly on the regular lattice image of $Na_2Ti_3O_7$. EDS analysis showed that the dark egg-like and spherical spots are composed of ruthenium. Note that RuO_2(CB) produces smaller, better distributed RuO_2 particles than does RuO_2(CL).

In order to compare the roles of RuO_2(CL) and RuO_2(CB) in photocatalysis, these Ru oxides were supported on $Na_2Ti_6O_{13}$ with a rectangular tunnel structure. Fig. 5 shows the photocatalytic activities of RuO_2(CL)/ and RuO_2(CB)/$Na_2Ti_6O_{13}$. RuO_2(CL)/$Na_2Ti_6O_{13}$ produced hydrogen and oxygen in nearly the stoichiometric ratio. These results exclude the possibility that the poor performance of the RuO_2(CL)/$Na_2Ti_3O_7$ photocatalyst is due to a Cl residue which might remain on the surface. Interestingly, the photocatalytic activity was higher by a factor of 2.2 for RuO_2(CB)/$Na_2Ti_6O_{13}$ than for RuO_2(CL)/$Na_2Ti_6O_{13}$. This indicates that a larger number of active sites are produced in the former, thus suggesting that RuO_2(CB) is superior to RuO_2(CL) in the formation of smaller RuO_2 particles. The surface geometric effect of a pentagonal-prism tunnel structure of $BaTi_4O_9$ has been previously described as playing the role of a 'nest' in the accommodation of Ru oxides, which presents a barrier for the aggregation and growth of RuO_2 particles and keeps Ru oxide particles small.[1] Thus, the differences in particle sizes between RuO_2(CL) and RuO_2(CB) are considered to be rather small in $Na_2Ti_6O_{13}$ in view of the tunnel structure. For a layered titanate of $Na_2Ti_3O_7$ which has no tunnel space, there is little geometric effect to suppress the aggregation and growth of RuO_2. This leads to significant differences in RuO_2 particle sizes and shapes between RuO_2(CL) and RuO_2(CB), as shown in Fig. 4.

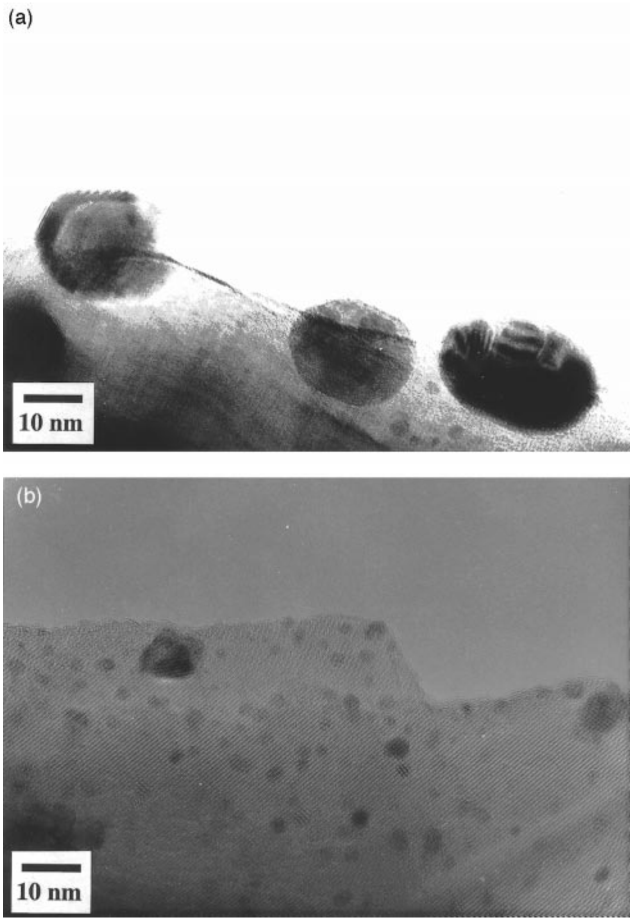

Fig. 4 HRTEM images of RuO_2(CL)/$Na_2Ti_3O_7$ (a) and RuO_2(CB)/$Na_2Ti_3O_7$ (b).

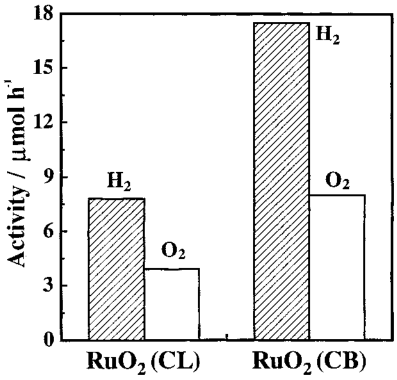

Fig. 5 Photocatalytic activities of RuO_2(CL)/ and RuO_2(CB)/$Na_2Ti_6O_{13}$. Ru content: 1 wt%.

It is likely that the larger RuO_2 particles produce an oxygen-deficient state in the interior of the particles, because of the difficulty of complete oxidation, and/or weak interactions at interface between RuO_2 and the titanate surface, which has unfavorable influences on the photoexcited charge transfer in photocatalysis. These considerations lead to the view that the good photocatalytic performance of H_2 and O_2 production observed for RuO_2(CB)/$Na_2Ti_3O_7$ is due to the presence of smaller RuO_2 particles.

In conclusion, there is no intrinsic difference in photocatalysis between the tunnel and layer structures: a $Na_2Ti_3O_7$ titanate with a zigzag layer structure makes a good photocatalyst which produces H_2 and O_2 when RuO_2 is highly dispersed. The view that the ability to form O^- surface radicals upon

UV irradiation is correlated with the photocatalytic activity may be also applicable to the layered titanate. For the design of efficient photocatalysts, in addition to the choice of titanates which permit the formation of O^- radicals upon UV irradiation, it is also important to have well dispersed small RuO_2 particles.

Notes and references

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