Photocatalytic Water Splitting over Spontaneously Hydrated Layered Tantalate $A_2SrTa_2O_7{\cdot}nH_2O$ (A=H, K, Rb)

Ken-ichi Shimizu,* Yoshihiro Tsuji, Masato Kawakami, Kenji Toda, Tatsuya Kodama,† Mineo Sato,† and Yoshie Kitayama†
Graduate School of Science and Technology, Niigata University, Ikarashi-2, Niigata 950-2181
†*Department of Chemistry & Chemical Engineering, Faculty of Engineering, Niigata University, Ikarashi-2, Niigata 950-2181*

(Received August 9, 2002; CL-020672)

A series of layered perovskite-type tantalates with hydrated interlayer space, $A_2SrTa_2O_7{\cdot}nH_2O$ (A=H, K, Rb), exhibited efficient photocatalytic activity for water splitting into H_2/O_2 mixture under UV irradiation without loading metal co-catalysts.

In view of the current importance of hydrogen as a clean energy source, the development of new photocatalyst for water splitting is an important theme. A variety of photocatalysts, mainly Ti, Nb and Ta based oxides, have been reported to be effective for photocatalytic decomposition of water under UV irradiation.[1–9] Domen and co-workers[5] reported that some ion-exchangeable layered oxides, such as $K_4Nb_6O_{17}$ and $K_2La_2Ti_3O_{10}$, were advantageous for this reaction as compared to the non-hydrous bulk type catalysts such as $SrTiO_3$. Recently, the bulk type Ta-based oxides, such as $NiO/NaTaO_3$ and $NiO_x/InTaO_4$, have been reported as an another group of effective catalysts for water splitting.[6–9] However, in order to obtain photocatalysts exhibiting high activities for water splitting, it is essential to load a transition metal co-catalysts. We expect that Ta based materials with hydrous layered structure may be an effective photocatalysts for water splitting, though such an attempt has been unsuccessful so far.[9] This paper reports the first successful example of the above strategy; layered perovskite-type tantalates with hydrated interlayer space, $A_2SrTa_2O_7{\cdot}nH_2O$ (A=H, K, Rb), act as highly active catalysts for the photocatalytic decomposition of water into H_2 and O_2 without loading co-catalysts.

A series of Ruddlesden-Popper type double-layered perovskites were prepared as follows. According to the previous reports,[10–12] $A_2SrTa_2O_7$ (A=Li and K) powders were prepared by a conventional solid state reaction.[13] $Rb_2SrTa_2O_7$, which is a new compound, was prepared by calcination of the mixture of stoichiometric amounts of $SrCO_3$ (Kanto Chemical, purity; 99.9%), Ta_2O_5 (Rare Metallic, purity; 99.9%) and 150% molar excess of Rb_2CO_3 (Kanto Chemical, purity; 99.5%) at 1173 K for 24 h in air. $H_2SrTa_2O_7$ was prepared by the K^+/H^+ exchange; $K_2SrTa_2O_7$ (3 g) was added to 150 mL of dilute HNO_3 aqueous solution (0.3 M) at room temperature for 24 h with constant stirring.[11] The crystal structure of the obtained materials was confirmed by X-ray diffraction (MAC Science; MX Labo). The band gap energy estimated by UV diffuse reflectance spectroscopy (Jasco; V-550) was around 3.9 to 4.0 eV, irrespective of the alkali metal cations at the interlayer space. The photocatalytic decomposition of water was performed with a gas-closed circulating system. The catalyst powder (0.5 g) was dispersed in 200 mL of pure water by a magnetic stirrer in an inner irradiation cell made of quartz. The light source was a 400 W high-pressure mercury lamp. The amounts of evolved H_2 and O_2 were determined using an on-line gas chromatography (Hitachi, TCD, molecular sieve 5A column and Ar carrier).

In the XRD pattern of $K_2SrTa_2O_7$ recorded immediately after calcination, all the observed lines could be indexed on a tetragonal cell ($I4/mmm$, a = 3.9072 Å, c = 21.6006 Å),[10,11] indicating that this compound consists of a single phase of layered perovskite, $K_2SrTa_2O_7$.[14] As reported previously,[11] $K_2SrTa_2O_7$ allowed intercalation of water when exposed to humid air; anhydrous form of $K_2SrTa_2O_7$ completely disappeared after exposing it to humid air for 24 h, and the corresponding hydrated phase, $K_2SrTa_2O_7{\cdot}nH_2O$,[15] appeared simultaneously. The thermogravimetric analysis of $K_2SrTa_2O_7{\cdot}nH_2O$ showed a distinct loss of water at a temperature range of $373\,K < T < 743\,K$, which could be due to the transformation of hydrate to anhydrous layered material $K_2SrTa_2O_7$. The number of hydration in the formula of $K_2SrTa_2O_7{\cdot}nH_2O$ estimated by the analysis was $n = 0.9$. In the XRD patterns of $H_2SrTa_2O_7$ and $Rb_2SrTa_2O_7$, recorded after exposing it to humid air for 24 h, all the lines could be indexed on a primitive cell ($P4/mmm$, a = 3.9038 Å, c = 9.7742 Å) and a primitive cell ($P4/mmm$, a = 3.9727 Å, c = 12.7632 Å),[16] respectively. Hence, these materials consist of a single phase of layered perovskite in a hydrated form, $A_2SrTa_2O_7,{\cdot}nH_2O$. From the thermogravimetric analysis, the hydration numbers of $H_2SrTa_2O_7{\cdot}nH_2O$ and $Rb_2SrTa_2O_7{\cdot}nH_2O$ were estimated to be $n = 0.6$ and $n = 3.6$, respectively. In the XRD pattern of $Li_2SrTa_2O_7$, recorded after exposing it to humid air for 24 h, all the observed lines could be indexed on a tetragonal cell ($I4/mmm$, a = 3.8470 Å, c = 18.1094 Å), indicating that this compound consists of a single phase of layered perovskite, $Li_2SrTa_2O_7$.[12] The XRD pattern of $Li_2SrTa_2O_7$ was essentially the same after the dispersion of the sample to the distilled water for 6 h, followed by drying at ambient temperature. This indicates that water intercalation does not occur on this material.

Figure 1 shows a typical time course of gas evolution for the photocatalytic decomposition of water on $H_2SrTa_2O_7{\cdot}nH_2O$. The catalyst produces H_2 and O_2 in a stoichiometric ratio ($H_2/O_2 = 2/1$). The rates of H_2 and O_2 formation were 769 and 358 $\mu mol\,h^{-1}$ (g-cat.)$^{-1}$, respectively, which were much higher than those of reported photocatalysts without co-catalysts under the similar reaction conditions. After evacuating the system, almost the same rate was reproduced in the second and third runs. The total amount of H_2 and O_2 evolved during these runs reached 21.2 and 11.2 mol (mol cat.)$^{-1}$, respectively, which confirms that the reaction proceeded catalytically. The XRD pattern of the catalyst after the reaction confirmed the preservation of the catalyst structure.

The rate of gas evolution over various Ta-based catalysts are summarized in Table 1. The H_2 evolution rate of $A_2SrTa_2O_7({\cdot}nH_2O)$ depended on alkali cation and decreased in

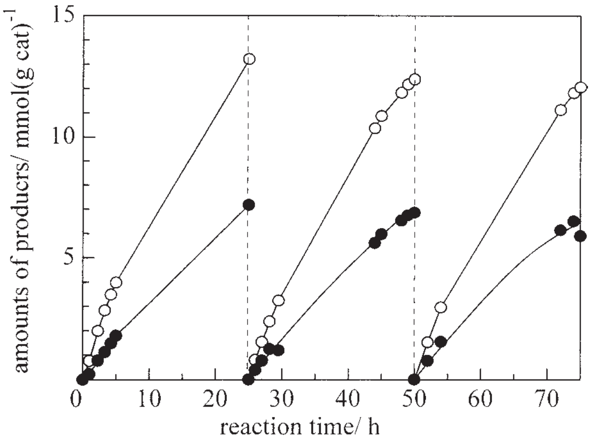

Figure 1. Time courses of H_2 (○) and O_2 (●) evolutions from distilled water on $H_2SrTa_2O_7{\cdot}nH_2O$.

Table 1. Rates of gas evolution over various tantalates

catalyst	evolution rate/μmol h^{-1} (g-cat.)$^{-1}$	
	H_2	O_2
$H_2SrTa_2O_7{\cdot}nH_2O$	769	358
$Li_2SrTa_2O_7$	29.7	0
$K_2SrTa_2O_7{\cdot}nH_2O$	747	384
$Rb_2SrTa_2O{\cdot}nH_2O$	176	44.7
$KTaO_3$	49.3	6.6
$NaTaO_3$	76.0	0

the sequence of $H \fallingdotseq K > Rb > Li$. Note that the layered perovskite-type tantalates with hydrated interlayer space, $A_2SrTa_2O_7{\cdot}nH_2O$ (A=H, K, Rb), showed higher H_2 formation rate than anhydrous layered tantalate, $Li_2SrTa_2O_7$. We have also studied the reaction over the non-hydrous tantalates, $NaTaO_3$ and $KTaO_3$, which were reported to catalyze this reaction.[6] These materials showed the activity for H_2 evolution, though the rate of H_2 evolution was lower than those of $A_2SrTa_2O_7{\cdot}nH_2O$ (A=H, K, Rb). Taking into account the result that the anhydrous layered tantalate, $Li_2SrTa_2O_7$ was less effective than hydrous $A_2SrTa_2O_7{\cdot}nH_2O$ (A=H, K, Rb), one can conclude that the presence of hydrated interlayer space is important for improving the photocatalytic activity of Ta-based catalysts. In the case of hydrous tantalates, electron-hole pairs may be easily migrated to the interlayer surface consisting of TaO_6 before their recombination, and thus intercalated H_2O molecules may be effectively decomposed.

In conclusion, a series of layered perovskite-type tantalates with hydrated interlayer space, $A_2SrTa_2O_7{\cdot}nH_2O$ (A=H, K and Rb), have been found to be efficient photocatalysts for water splitting into H_2 and O_2.

References and Notes

1 J. Lehn, J. Sauvage, R. Ziessel, and L. Halaire, *Isr. J. Chem.*, **22**, 168 (1982).
2 K. Domen, A. Kudo, and T. Onishi, *J. Catal.*, **102**, 92 (1986).
3 Y. Inoue, T. Kubokawa, and K. Sato, *J. Chem. Soc., Chem. Commun.*, **1990**, 1298.
4 Z. Zou, J. Ye, K. Sayama, and H. Arakawa, *Nature*, **414**, 625 (2001).
5 A. Kudo, A. Tanaka, K. Domen, K. Maruya, K. Aika, and T. Onishi, *J. Catal.*, **111**, 67 (1988); T. Takata, Y. Furumi, K. Shinohara, M. Hara, J. N. Kondo, and K. Domen, *Chem. Mater.*, **9**, 1063 (1997).
6 A. Kudo and H. Kato, *Chem. Phys. Lett.*, **331**, 373 (2000).
7 T. Ishihara, H. Nishiguchi, K. Fukamachi, and Y. Takita, *J. Phys. Chem. B*, **103**, 1 (1999).
8 Z. Zou, J. Ye, K. Sayama, and H. Arakawa, *Nature*, **414**, 625 (2001).
9 M. Machida, J. Yabunaka, and T. Kijima, *Chem. Mater.*, **12**, 812 (2000).
10 T. A. Kodenkandath and J. B. Wiley, *Mater. Res. Bull.*, **35**, 1737 (2000).
11 M. P. Crosnier-Lopez, F. Le Berr, and J. L. Fourquet, *J. Mater. Chem.*, **11**, 1146 (2001).
12 N. S. P. Bhuvanesh, M. P. Crosnier-Lopez, H. Duroy, and J. L. Fourquet, *J. Mater. Chem.*, **9**, 3093 (1999).
13 Stoichiometric amounts of $SrCO_3$ and Ta_2O_5 with a 150% molar excess of alkali carbonates (Li_2CO_3 or K_2CO_3) were mixed together and calcined at 1173 K for 24 h in air.
14 The structure of anhydrous $K_2SrTa_2O_7$ can be described as formed from two TaO_6 octahedra thick slabs of a perovskite lattice cut along the *c* direction; these alternate layers are shifted by $(a + b)/2$ (body centered), with the large Sr cations fully occupying the 12-coordination sites. The potassium ions are located in a rock salt type coordination (C.N. = 9).
15 In the XRD pattern of $K_2SrTa_2O_7{\cdot}nH_2O$, all the observed lines could be indexed on a primitive cell (*P4/mmm*, a = 3.9974 Å, c = 12.133 Å). Upon hydration, the adjacent layers are stacked immediately above each other in the same arrangement leading to a halving of the c-axis length.
16 The structure of $Rb_2SrTa_2O_7{\cdot}nH_2O$ has not been reported. The Rietveld method with the RIETAN2000 profile refinement program[17] was used to refine the structure in the space group *P4/mmm* (no. 139) with a starting model for the perovskite slabs similar to that observed in $K_2SrTa_2O_7{\cdot}nH_2O$.
17 F. Izumi, in "The Rietveld Method," ed. by R. A. Young, Oxford University Press, Oxford (1993), Chap. 13.