Photocatalytic Decomposition of Water into H_2 and O_2 over Novel Photocatalyst $K_3Ta_3Si_2O_{13}$ with Pillared Structure Consisting of Three TaO_6 Chains

Akihiko Kudo* and Hideki Kato
Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162

(Received May 15, 1997; CL-970370)

The novel catalysts of native and NiO-loaded $K_3Ta_3Si_2O_{13}$ with pillared structure consisting of three linear TaO_6 chains showed luminescence and high photocatalytic activities for the decomposition of distilled water into H_2 and O_2 in stoichiometric amounts under UV irradiation.

The photocatalytic decomposition of water has been studied extensively since the Honda-Fujishima effect was found.[1] However, the number of photocatalyst materials found is limited. Titanium oxides such as TiO_2 and $SrTiO_3$ have mainly been employed as active photocatalysts for the water decomposition which produce reasonable amounts of H_2 and O_2 in a stoichiometric amount.[2] In order to show the activity, however, they need co-catalysts such as Pt,[3-5] Rh,[3,6] and NiO.[7,8] Recently, $K_4Nb_6O_{17}$,[9] $Na_2Ti_6O_{13}$,[10] and $BaTi_4O_9$[11] have been found to be active for the photocatalytic water decomposition. These materials have structural regularities such as layered and tunneling structures. Therefore, it seems to be important to develop new photocatalyst materials from the standpoint of the structural regularity.

$K_3Ta_3Si_2O_{13}$ has been reported to possess a unique crystal structure as shown in Figure 1.[12] It consists of pillars formed by corner sharing of three linear TaO_6 chains. The TaO_6 pillars are linked by Si_2O_7 ditetrahedral units resulting in the creation of pentagonal tunnel space, in which potassium cations exist. The length of the longest diagonal of the pentagonal neck in Figure 1 is ca. 5.4 Å. Thus, $K_3Ta_3Si_2O_{13}$ has the characteristic one dimensional structure with respect to the octahedral TaO_6 units and with the microporous structure. Therefore, the photochemical properties of $K_3Ta_3Si_2O_{13}$ are of particular interest. This paper reports the luminescence properties and high efficiency photocatalytic decomposition of distilled water into H_2 and O_2 over $K_3Ta_3Si_2O_{13}$ and NiO-loaded $K_3Ta_3Si_2O_{13}$.

$K_3Ta_3Si_2O_{13}$ was synthesized by calcination of the mixture of K_2CO_3 (Kanto Chemicals, purity; 99.5%), Ta_2O_5 (Wako Pure Chemical, purity 99.8%), and SiO_2 (Kanto Chemicals, purity; 99.95%) in air at 1620 K for 10 h using a platinum crucible.[12] The product was confirmed to be a single phase by an X-ray diffraction method. NiO (1.3 wt%) was loaded by an impregnation method using an aqueous $Ni(NO_3)_2$ solution and then calcined at 720 K for 4 h in air. The NiO-loaded $K_3Ta_3Si_2O_{13}$ catalyst was used without any pretreatments. The photocatalytic decomposition of water was conducted by suspending 1g of the catalyst in 350 ml of distilled water in an inner irradiation quartz reaction cell attached to a gas-closed circulation system. The light source was a 400 W high pressure mercury lamp. A gas chromatograph (MS5A column, argon carrier) was used for the determination of H_2 and O_2 evolved. Diffuse reflection spectra and luminescent spectra were obtained using a UV-VIS-NIR spectrometer (Jasco, Ubest V-570) and a fluorospectrometer (Spex, Fluoromax™), respectively. The diffuse reflection spectrum was converted to an absorbance mode by means of the Kubelka-Munk method.

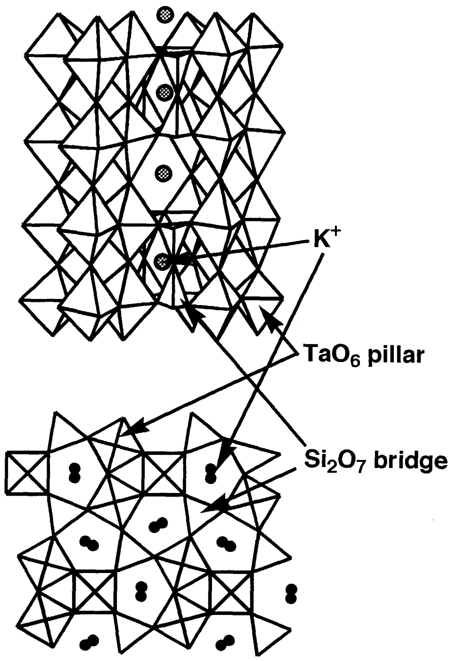

Figure 1. Structure of $K_3Ta_3Si_2O_{13}$.[12]

Figure 2 shows the diffuse reflection spectrum at 300 K, and excitation and emission spectra at 77 K of $K_3Ta_3Si_2O_{13}$ which give us the information of the energy state of the photocatalyst. In this material, the pillars consisting of TaO_6 units are photoactive. The broad yellow-green emission at 500 nm was observed. The onset of excitation spectrum was around 300 nm and corresponded with that of the diffuse reflection spectrum. The similar emission spectra have been reported for $K_3Nb_3Si_2O_{13}$ with the same structure as $K_3Ta_3Si_2O_{13}$.[13] The energy gap of $K_3Ta_3Si_2O_{13}$ was estimated to be ca. 4.1 eV. The wavelength for the absorption and excitation of $K_3Ta_3Si_2O_{13}$ was longer than that of isolated TaO_6 units as seen in Ba_3NaTaO_6 (the excitation maximum; 245 nm)[14] whereas it was shorter than those of semiconductor Ta_2O_5 and $KTaO_3$ materials with three dimensional bulk structures.[15] In general, the absorption and excitation spectra in which the excitation energy is delocalized are observed at longer wavelength sides than those in the case of localization.[16] These facts suggest that the excitation energy or the electron-hole pair in $K_3Ta_3Si_2O_{13}$ is delocalized in the one dimensional TaO_6 pillars, more or less.

Figure 3 shows the photocatalytic decomposition of distilled water without any sacrificial reagents over $K_3Ta_3Si_2O_{13}$ and NiO (1.3 wt%)-loaded $K_3Ta_3Si_2O_{13}$. It is noteworthy that the

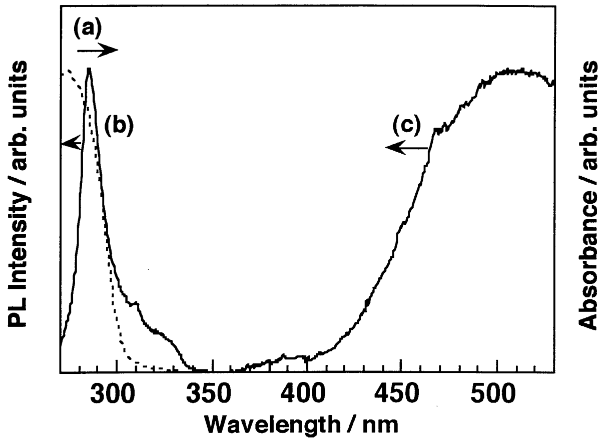

Figure 2. (a) Diffuse reflection spectrum at 300 K and (b) excitation and (c) emission spectra at 77 K of $K_3Ta_3Si_2O_{13}$.

native $K_3Ta_3Si_2O_{13}$ photocatalyst produced both H_2 (43 μmol/h) and O_2 (19 μmol/h) in a stoichiometric amount. The reported photocatalysts which can produce H_2 and O_2 from distilled water in a stoichiometric amount without any assistance by co-catalysts such as Pt are only $K_4Nb_6O_{17}$[9] and ZrO_2.[17] The activity was increased by NiO-loading; H_2 (368 μmol/h) and O_2 (188 μmol/h) were produced. The amount of O_2 at the initial stage was large. This is probably due to the partial reduction of NiO. The activity was maintained for more than 30 h. The total amounts of electrons and holes reacted were more than the amount of the catalyst. These results clearly indicate that the reaction proceeds photocatalytically. Some NiO-loaded photocatalysts have been reported to be active for the water decomposition.[7-9,15] For all cases, the pretreatment of H_2 reduction and O_2 oxidation was indispensable for activating the catalysts. In contrast to them, NiO-$K_3Ta_3Si_2O_{13}$ was active even without such a pretreatment.

The photocatalyst material found at the present study is the tantalum oxide system although the reported photocatalysts for the water decomposition are mainly the titanate system so far.[2-8]

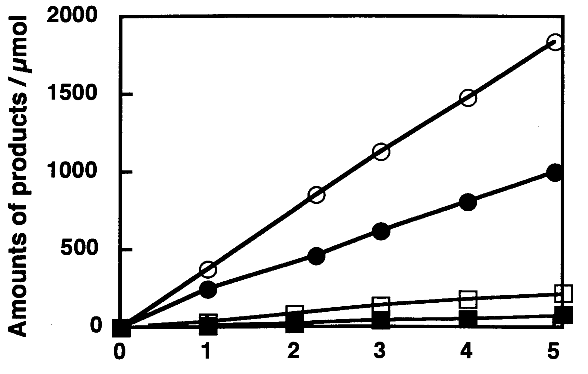

Figure 3. Photocatalytic decomposition of water over $K_3Ta_3Si_2O_{13}$ (□ ; H_2, ■ ; O_2) and NiO(1.3 wt%)-$K_3Ta_3Si_2O_{13}$ (○; H_2, ●; O_2). Catalyst; 1g, distilled water; 350 ml, reaction cell; inner irradiation quartz cell, light source; 400 W high pressure mercury lamp.

Ta_2O_5, $KTaO_3$, and $Rb_4Ta_xNb_{6-x}O_{17}$ which have bulk or layered structures have also been reported as tantalum oxide photocatalysts.[15] $K_3Ta_3Si_2O_{13}$ consists of the one dimension pillared structure which is substantially different from the structure of other tantalate photocatalysts.

On transition metal oxides with octahedral units, the energy migration occurs relatively easily when the angle of O-M-O-M-O bonds is close to 180°.[18] From this fact and the excitation and absorption spectra as shown in Figure 2, the electron and/or energy migration in one dimensional linear TaO_6 chains seem to play an important role for the luminescent and photocatalytic properties.

Thus, the characteristics of $K_3Ta_3Si_2O_{13}$ are different from those of other reported photocatalysts and has arisen as a new type of photocatalyst material for high efficiency photocatalytic water decomposition. This material will also be available as a photoactive microporous host.

The financial support by the 1st. Toyota High-tech Research Grant Program and Mitsubishi Petrochemical Co. is gratefully acknowledged. This work was also supported by a Grant-in-Aid (No. 09640696) from the Ministry of Education, Science, Sports, and Culture, Japan.

References

1 A. Fujishima and K. Honda, *Nature (London),* **238**, 37 (1972).
2 T. Sakata, in " Photocatalysis: fundamentals and applications", ed by N. Serpone and E. Pelizzetti, New York (1989), Chapt. 10, p 311 and references therein.
3 K. Yamaguchi and S. Sato, *J. Chem. Soc., Faraday Trans. 1,* **81**, 1237 (1985).
4 K. Sayama and H. Arakawa, *J. Chem. Soc., Chem. Commun.,* **1992**, 150.
5 S. Tabata, H. Nishida, Y. Masaki, and K. Tabata, *Catal. Lett.,* **34**, 245 (1995).
6 J.-M. Lehn, J.-P. Sauvage, R. Ziessel, and L. Hilaire, *Israel J. Chem.,* **22**, 168 (1982).
7 K. Domen, A. Kudo, and T. Ohnishi, *J. Catal.,* **102**, 92 (1986).
8 A. Kudo, K. Domen, K. Maruya, and T. Onishi, *Chem. Phys. Lett.,* **133**, 517 (1987).
9 A. Kudo, K. Sayama, A. Tanaka, K. Asakura, K. Domen, K. Maruya, and T. Onishi, *J. Catal,* **120**, 337 (1989).
10 Y. Inoue, T. Kubokawa, and K. Sato, *J. Phys. Chem.,* **95**, 4059 (1991).
11 Y. Inoue, T. Niiyama, Y. Asai, and K. Sato, *J. Chem. Soc., Faraday Trans. 1,* **90**, 797 (1994).
12 J. Choisnet, N. Nguyen, D. Groult, and B. Raveau, *Mat. Res. Bull.,* **11**, 887 (1976).
13 G. Blasse and B. Raveau, *J. Solid State Chem.,* **31**, 127 (1980).
14 G. Blasse, G.J. Dirksen, and P. Zhiwu, *Chem. Phys. Lett.,* **215**, 363 (1993).
15 K. Sayama, H. Arakawa, and K. Domen, *Catal. Today,* **28**, 175 (1996).
16 J. Alarcon and G. Blasse, *Phys. Status Solidi A,* **135**, 627 (1993).
17 K. Sayama and H. Arakawa, *J. Phys. Chem.,* **97**, 531 (1993).
18 J. Alarcon and G. Blasse, *J. Phys. Chem. Solids,* **53**, 677 (1992).