CHEMISTRY LETTERS, pp. 1017-1018, 1987.

Photocatalytic Activities of Layered Titanium Compounds and Their Derivatives for H_2 Evolution from Aqueous Methanol Solution

Mutsumi SHIBATA, Akihiko KUDO, Akira TANAKA,[+] Kazunari DOMEN,*
Ken-ichi MARUYA, and Takaharu ONISHI*
Research Laboratory of Resources Utilization, Tokyo Institute
of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 227
[+]Nippon Kogaku K. K., 1773 Asamizodai, Sagamihara, 228

The photocatalyst prepared from H^+-exchanged $K_2Ti_2O_5$ with a layered structure exhibited a high activity (quantum yield = ca. 10%) for H_2 evolution from aqueous methanol solution without any assistance of other materials such as Pt.

Titanium oxides, especially TiO_2(anatase, rutile and colloid) and $SrTiO_3$, have been widely used as photocatalysts for various reactions. However, as the activities of those materials for the H_2 evolution are poor by themselves,[1)] they are usually modified by other materials such as Pt.

Recently, the authors reported $K_4Nb_6O_{17}$ as a novel photocatalyst.[2, 3)] $K_4Nb_6O_{17}$ has a layered structure and the pottasium ion can be exchanged by various cations. Interestingly, the H^+-exchanged $K_4Nb_6O_{17}$ exhibited a high efficiency for the H_2 evolution from aqueous methanol solution, i.e. the quantum yield was ca. 50% at 330 nm, without any assistance of other materials. It has also been known that there are several layered titanium compounds[4-8)] which possess an ion exchange capabilities as is $K_4Nb_6O_{17}$. In this study, therefore, the photocatalytic activities of those compounds were examined for the H_2 evolution from aqueous methanol solution. $Na_2Ti_3O_7$, $K_2Ti_2O_5$, and $K_2Ti_4O_9$ prepared from each stoichiometric mixture of K_2CO_3(Na_2CO_3) and TiO_2 powder which were heated at 1073-1373 K.[4, 5)] All of these compounds have layered structures. $K_2Ti_6O_{13}$ was prepared from $K_2Ti_2O_5$.[5)] The structures of those materials were confirmed by means of the X-ray diffraction method. The replacement of K^+ by H^+ was carrried out in aqueous H_2SO_4 solution at room temperature. The amount of exchanged K^+ was estimated by

Catalyst	H_2 evolution rate / µmol·h⁻¹			
	Original		H^+ exchanged[a)]	
	alone	Pt[b)]	alone	Pt[b)]
$Na_2Ti_3O_7$	2.9	19.0	1.9	5.5
$K_2Ti_2O_5$	20.8	34.7	33.4(110)[c)]	41.9
$K_2Ti_4O_9$	3.5	4.8	3.2	13.8
$K_2Ti_6O_{13}$	4.2	60.7	15.1	83.2
TiO_2[d)] (anatase)	0.5	171.1	—	—

Table 1. Activities of H_2 evolution from aqueous MeOH solution over various titanate compounds.
Catalyst = 0.5 g, solution: MeOH(50 ml) + H_2O(200 ml), light source: Xe lamp(USHIO, 500 W) a) Degree of H^+ exchange _ 80%. b) amount of Pt = 0.5 wt%. c) Calcined at 623 K, see Fig. 1. d) Purchased from MCB.

atomic absorption analysis. Pt was deposited by the photodeposition method during the photacatalytic reaction in aqueous methanol solution.

In Table 1, the activities of the original and H^+-exchanged catalysts for the H_2 evolution from aqueous methanol solution are summarized. All of these activities were stable during the reactions(10 h) after short induction periods(2 h). In general, potassium (sodium) titanates showed higher activities for the H_2 evolution than TiO_2(anatase) although the activity of TiO_2(anatase) increased markedly by the Pt deposition as is known well. Among H^+-exchanged catalysts, the activities of $K_2Ti_2O_5$ and $K_2Ti_6O_{13}$ were higher than those of original forms. When Pt was deposited, $K_2Ti_2O_5$ and $K_2Ti_6O_{13}$ showed relatively high activities.

As H^+-exchanged $K_2Ti_2O_5$ (the degree of ion exchange was ca. 100%) showed the highest activity without Pt, it was examined in more detail. After the ion exchange, it was found by XRD that the layered structure was maintained. In Fig. 1, the dependence of the activity on the calcination temperature is shown. The activity increased with the increase of the calcination temperature and showed the maximum at almost 623 K. Above the temperature, the activity decreased and was very low at 1123 K, and the crystal structure changed completely into TiO_2(anatase). The quantum yield of the H_2 evolution at the calcination temperature of 623 K was ca. 10% at 330-360 nm, and the activity was stable during the reaction (10 h). At the calcination temperatures of 463-623 K, no clear pattern was observed by XRD, which suggested the amorphous-like structure during the transformation from layered to anatase. It should be emphasized that without any assistance of other materials, H^+-exchanged $K_2Ti_2O_5$ exhibits such a high efficiency for the H_2 evolution reaction. To our knowledge, it is an unusual behavior for titanium compounds. To reveal the reason for the high activity, further investigations are now proceeding.

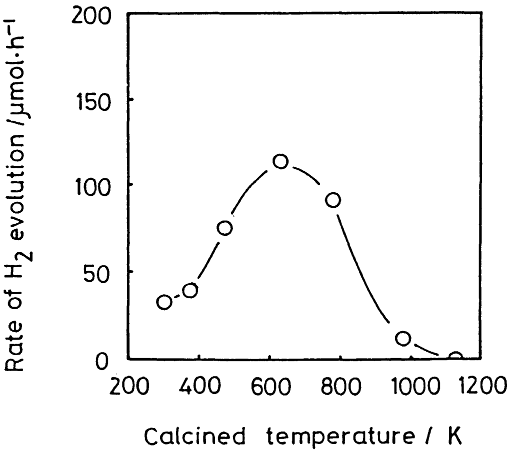

Fig. 1. Dependence of the activity of H^+-exchanged $K_2Ti_2O_5$ for H_2 evolution from methanol aqueous solution upon the calcination temperature.
Catalyst = 0.5 g, solution: MeOH(50 ml) + H_2O(200 ml), light source: Xe lamp(USHIO, 500 W). Every sample was calcined for 3 h in air. Degree of H^+-exchange was about 100%.

References
1) T. Kawai and T. Sakata, J. Chem. Soc., Chem. Commun., 1980, 694.
2) K. Domen, A. Kudo, A. Shinozaki, A. Tanaka, K. Maruya, and T. Onishi, J. Chem. Soc., Chem. Commun., 1986, 356.
3) K. Domen, A. Kudo, A. Shibata, A. Tanaka, K. Maruya, and T. Onishi, J. Chem. Soc., Chem. Commun., 1986, 1706.
4) H. Izawa, S. Kikkawa, and M. Koizumi, J. Phys. Chem., 86, 5023 (1982).
5) Y. Fujiki and T. Ohsawa, Yogyo Kyokai Shi, 90, 27 (1982).
6) K. L. Berry, V. O. Aftandilian, W. W. Gilbert, E. P. H. Meibohm, and H. S. Young, J. Inorg. Nucl. Chem., 14, 231 (1960).
7) S. Anderson and A. D. Wadsley, Nature, 187, 499 (1960).
8) S. Anderson and A. D. Wadsley, Acta Crystallogr., 14, 1245 (1961).

(Received February 7, 1987)