Photocatalytic Hydrogen Evolution from Aqueous Methanol Solution on Niobic Acid

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(Received December 18, 1991)

Niobic acid powders, H_3NbO_4 and $H_8Nb_6O_{19}$, obtained by hydrolysis from aqueous potassium niobate (K_3NbO_4 and $K_8Nb_6O_{19}$) solutions with sulfuric acid showed a high photocatalytic activity for hydrogen evolution from an aqueous solution including methanol as a sacrificial reagent without supporting any other materials, such as Pt (quantum yield; ca. 10% at 330 nm). The activity depended on the calcination temperature. H_3NbO_4 powder dried at 380 K was the most active one. As the calcination temperature was increased, the H_3NbO_4 photocatalyst was transformed into $HNbO_3$ (or $Nb_2O_5 \cdot H_2O$) and Nb_2O_5 by dehydration. The BET surface area and the band gap of the powder decreased with the phase transformation. It is concluded that both the surface area and hydrated state strongly affect the activity for sacrificial hydrogen evolution on the niobic acid photocatalysts.

It is important to develop new photoresponsible materials from the standpoint of solar energy conversion. Photocatalysts, on which charge separation and chemical reactions occur at the same time, are powerful materials for light energy conversion to chemical energy. A photocatalytic reaction is a convenient method to evaluate the photoresponsibility of materials.

The present authors have recently reported that some alkali-niobium layered oxides ($K_4Nb_6O_{17}$,[1-5] $Rb_4Nb_6O_{17}$,[6] $KSr_2Nb_3O_{10}$,[7] $CsNbTiO_5$[8] etc.) show high activity for photodecomposition of water as well as for hydrogen evolution from an aqueous methanol solution. These results suggest that some other niobates may possess similar photocatalytic activity.

$K_4Nb_6O_{17}$, which can decompose water into H_2 and O_2 in stoichiometric amounts,[1,3-5] has a layered structure.[9] The octahedral units of NbO_6 form two-dimensional macro anion sheets stacked along the *b*-axis of an orthorhombic unit cell. It has been revealed that the characteristic behaviors of $K_4Nb_6O_{17}$-based photocatalysts are mainly due to this layered structure.[4] It is, therefore, important to examine the photocatalytic activity of the corresponding polyacids or polyanions, which can be regarded as having a subdivided structure of the layers.

An acid treatment changes both the hydrate state and functional groups by accompanying a proton-exchange at the interlayer of the layered niobates. This greatly enhances the photocatalytic activity for hydrogen evolution.[2,7,8] On the other hand, niobic acids can be obtained by the hydrolysis of niobates using an acid. The surface state of niobic acids is expected to be favorable for photocatalyzed hydrogen evolution, as observed regarding the proton-exchanged layered niobates. The characteristic properties of niobic acids, which can be regarded as being a niobic oxide including water, may be different from those of other heterogeneous photocatalysts, such as TiO_2, which has been extensively studied.

In this study, new photoresponsible materials based on niobium were surveyed and the photocatalytic activity for hydrogen evolution from aqueous methanol solutions over polyanions of niobium ($NbO_4{}^{3-}$ and $Nb_6O_{19}{}^{8-}$) and niobic acids (H_3NbO_4 and $H_8Nb_6O_{19}$) were examined.

Expeprimental

Preparation of Niobic Acid Photocatalysts. K_3NbO_4 was prepared by calcining a mixture of K_2CO_3 and Nb_2O_5 at 1400 K in air. $K_8Nb_6O_{19} \cdot 16H_2O$ (Soekawa Chemicals) and Nb_2O_5 (Kanto Chemical) were used as received. $Nb_2O_5 \cdot xH_2O$, which is called niobic acid, was supplied from CBMM. Niobic acid powders of H_3NbO_4 and $H_8Nb_6O_{19}$ were prepared by hydrolyzing the aqueous K_3NbO_4 and $K_8Nb_6O_{19}$ solutions with an aqueous sulfuric acid solution. After K_3NbO_4 or $K_8Nb_6O_{19}$ (5—10 g) was dissolved in distilled water (200 mL), an aqueous sulfuric acid solution (2.5 mol dm^{-3}, 100 ml) was added into the solution. The white precipitate (H_3NbO_4 or $H_8Nb_6O_{19}$) obtained by the hydrolysis was filtered and, subsequently, washed with distilled water. The H_3NbO_4 powder was calcined at 380, 510, 600, 750, and 900 K in air for 5 h. The structure of $H_8Nb_6O_{19}$ has been studied,[10-14] while that of H_3NbO_4 has not. The form of H_3NbO_4 might be similar to that of $H_8Nb_6O_{19}$ in an aqueous solution,[12] since $6H_3NbO_4$ is regarded as $H_8Nb_6O_{19} \cdot 5H_2O$. However, niobic acids prepared from K_3NbO_4 and $K_8Nb_6O_{19}$ are denoted H_3NbO_4 and $H_8Nb_6O_{19}$, respectively in this paper.

Procedure of Photocatalytic Reaction. The reaction of hydrogen evolution from an aqueous methanol solution was carried out in a closed gas-circulation system. The niobic acid photocatalyst (1 g) was dispersed in an aqueous methanol solution (CH_3OH 10 ml+H_2O 290 ml) by stirring it in an inner irradiation reaction cell made of Pyrex. Subsequent to degassing, the aqueous solution or the suspension was irradiated under an argon atmosphere (100 Torr, 1 Torr=133.3 N m^{-2}) by using a high-pressure mercury lamp (Ushio, UM-452, 450 W). The quantum yield was measured by chemical actinometory using ammonium iron(III) oxalate. The amount of evolved H_2 was determined by gas chromatography (MS-5A column, Ar carrier).

Characterization of Niobic Acid Photocatalysts. The composition of the catalysts was determined by thermogravimetry (TG) and differential thermal analysis (DTA; a rate of elevating temperature; 10 K min^{-1}). The crystal form was determined by X-ray diffraction (XRD; Rigaku, scan speed; 2° min^{-1}). The UV diffuse reflectance (DRS; JASCO, UVIDEC-505) was measured in order to see the absorption edge. X-Ray photoelectron spectroscopy (XPS; Shimadzu, ESCA 750) and BET measurements were also carried out.

Results and Discussion

Photocatalytic Activity of Potassium Niobates and Niobic Acids. The effect of the addition of sulfuric acid on the photocatalytic activity for hydrogen evolution by K_3NbO_4 dissolved in an aqueous methanol solution is shown in Fig. 1. Dissolved K_3NbO_4, itself, showed no activity. It polymerized, and a white precipitate of niobic acid was obtained when the pH of the aqueous solution of niobium polyanion was decreased.[11] As soon as the white precipitate was produced through the addition of sulfuric acid at 0.5 of a ratio of added H^+ to K^+, the activity increased drastically, establishing that the white precipitate of niobic acid is an active species. Subsequent adding more sulfuric acid had no effects on the activity. A similar result was obtained in the case of $K_8Nb_6O_{19}$, as shown in Fig. 2. Also in this case, the activity substantially increased when a white precipitation was formed by the addition of sulfuric acid. Polyanion of niobium ($Nb_6O_{19}^{8-}$), itself, shows little activity, as has been reported previously.[15]

The activity of hydrogen evolution from aqueous methanol solutions on a niobium oxide and niobic acids is summarized in Table 1. These niobium oxides show activity without supporting other materials such as Pt, which is one of the important characteristics of niobium oxide photocatalysts. Especially, $H_8Nb_6O_{19}$ and H_3NbO_4 prepared by the hydrolysis of their potassium salts ($K_8Nb_6O_{19}$ and K_3NbO_4) show high activity. For conventional TiO_2, $SrTiO_3$, and CdS photocatalysts, the activity for hydrogen evolution is drastically increased by Pt deposition. However, the presence of Pt did not increase the activity of the niobic acid photocatalyst at all, as had been observed on a proton-exchanged

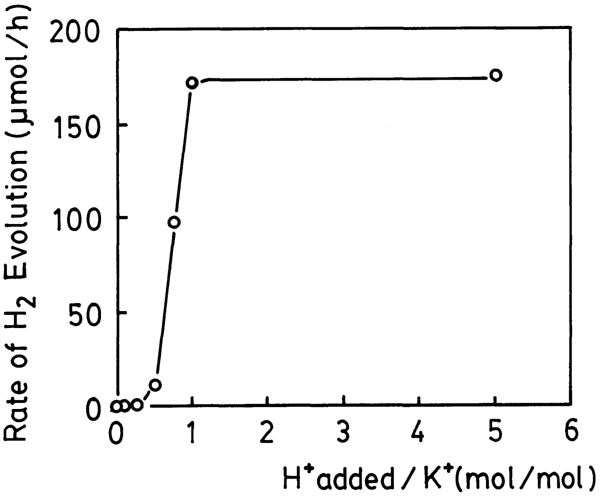

Fig. 1. Effect of H_2SO_4 addition on H_2 evolution from an aqueous methanol solution (H_2O 290 ml+CH_3OH 10 ml) by K_3NbO_4 (1 g).

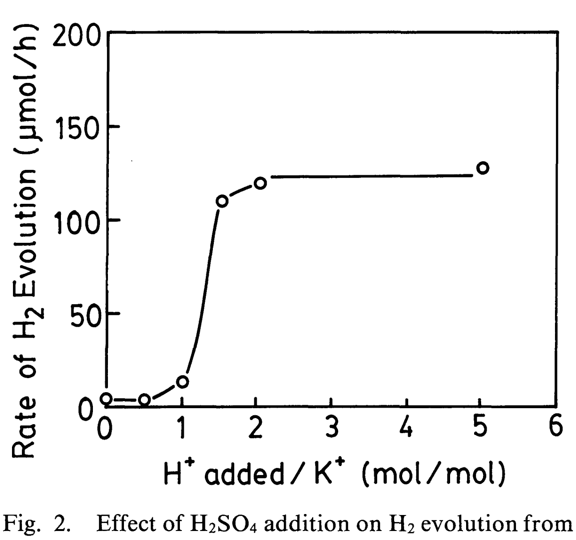

Fig. 2. Effect of H_2SO_4 addition on H_2 evolution from an aqueous methanol solution (H_2O 290 ml+CH_3OH 10 ml) by $K_8Nb_6O_{19}$ (1 g).

Table 1. H_2 Evolution from Aqueous Methanol Solutions (H_2O 290 ml+CH_3OH 10 ml) on Some Niobium Oxide Catalysts

Catalyst	Activity/μmol h^{-1}
Nb_2O_5	21
$Nb_2O_5 \cdot xH_2O$	11
$H_8Nb_6O_{19}$	240
H_3NbO_4	370

Catalyst; 1 g, light source; high pressure mercury lamp (450 W).

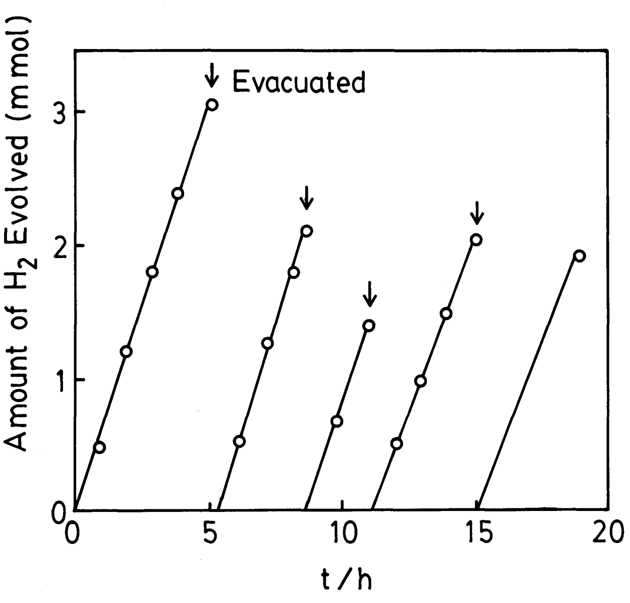

Fig. 3. H_2 evolution from an aqueous methanol solution (H_2O 290 ml+CH_3OH 10 ml) on H_3NbO_4 (1 g).

$K_4Nb_6O_{17}$ photocatalyst.[2] This implies that the acid-treated surface of niobic acid has an efficient catalyst property for H_2 evolution.

Hydrogen steadily evolves on H_3NbO_4 powder for a long time without any deactivation, as shown in Fig. 3. Moreover, the amount of hydrogen evolved for 18 h was 10 mmol, and exceeded the amount of niobium atom in the catalyst (Nb atom; 6 mmol in 1 g of the catalyst). Actually, the number of active sites of niobium atoms on the surface is much less than 6 mmol. Therefore, we conclude that the reaction proceeded photocatalytically.

The dependence of the activity of the precipitated H_3NbO_4 photocatalyst upon the calcination temperature is shown in Fig. 4. The maximum activity (quantum yield at 330 nm: ca. 10%) was obtained for the H_3NbO_4 catalyst calcined at ca. 380 K. One of the reasons for the lower activity of uncalcined catalyst than that of a dried one at 380 K is probably due to a difference in the amount of niobic acid. Even though the same weight of catalysts was used for the reaction, the amount of niobic acid in the uncalcined catalyst would be less than that in the dried catalyst, since the former contained much water. The activity decreased with an increase in the calcination temperature over the range above 380 K. A similar dependence was observed on the H^+-exchanged $K_2Ti_2O_5$ photocatalyst.[16]

The reaction path for the photocatalytic hydrogen evolution on niobic acid powders can be described as follows:

$$H_xNbO_y \xrightarrow[h\nu]{} e^-_{(CB)} + h^+_{(VB)}, \qquad (1)$$

$$Nb^{5+}\text{-}O^{2-} \xrightarrow[h\nu]{} Nb^{4+}\text{-}O^-, \qquad (1')$$

$$2e^-_{(CB)} + 2H^+ \longrightarrow H_2, \qquad (2)$$

$$2Nb^{4+} + 2H^+ \longrightarrow 2Nb^{5+} + H_2, \qquad (2')$$

$$h^+ + R \longrightarrow Ox, \qquad (3)$$

$$Nb^{4+}\text{-}O^- + R \longrightarrow Nb^{4+}\text{-}O^{2-} + Ox, \qquad (3')$$

and

$$Nb^{4+}\text{-}O^-\text{-}Nb^{5+} + R \longrightarrow Nb^{4+}\text{-}\sqcup\text{-}Nb^{4+} + Ox. \qquad (3'')$$

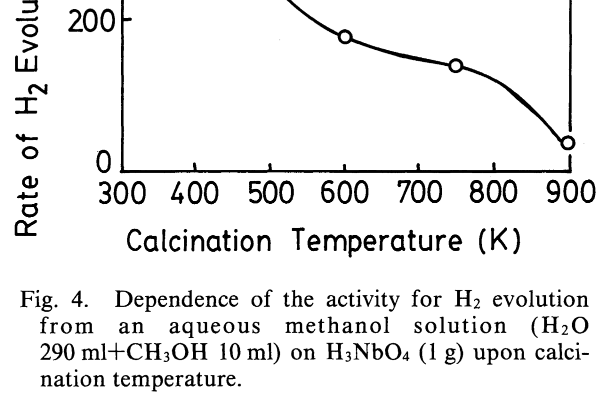

Fig. 4. Dependence of the activity for H_2 evolution from an aqueous methanol solution (H_2O 290 ml+CH_3OH 10 ml) on H_3NbO_4 (1 g) upon calcination temperature.

Here, R, Ox, and $\sqcup$ denote a reducing reagent (methanol in the present study), its oxidized form, and an oxygen vacancy, respectively. Electrons and holes are generated by band-gap irradiation according to Eq. 1, which may be alternately described as in Eq. 1′. The color of the catalysts calcined at high tempepratures (>750 K) turned from the original white into blue, suggesting an accumulation of electrons or Nb(IV) ions by photoreduction of the catalyst, itself, in an aqueous methanol solution (Eqs. 3′ or 3″); the active catalysts calcined at low temperatures (<580 K), however, remained white. The change in color indicates that, for the catalysts calcined at high temperatures, hydrogen evolution (Eqs. 2 or 2′) is a rate-determining step, probably because the protonated surface is dehydrated by the calcination and the number of active sites for the hydrogen evolution is decreased. On the other hand, for catalysts calcined at low temperatures, the rate determining step is electron-hole pair formation (Eqs. 1 or 1′) or oxidation of a reducing reagent (Eqs. 3 or 3′ or 3″) but not hydrogen evolution. Therefore, adding platinum as hydrogen evolution sites did not enhance the hydrogen evolution, as mentioned above.

Characterization of Niobic Acid Photocatalysts. X-Ray diffraction patterns of H_3NbO_4 powder calcined at various temperatures are shown in Fig. 5. An amorphous phase was obtained below 750 K of the

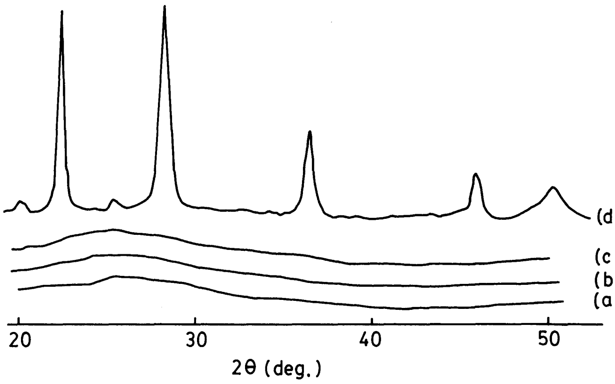

Fig. 5. X-Ray diffraction patterns of H_3NbO_4 calcined at different temperatures. (a); 300 K, (b); 600 K, (c); 750 K, (d); 900 K, 800 cps, 2° min^{-1}.

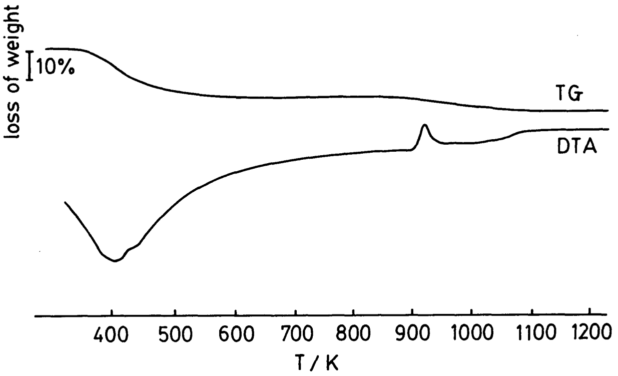

Fig. 6. Thermogravimetry and differential thermal analysis curves of H_3NbO_4.

calcination temperature, while crystallized Nb_2O_5 was formed above 900 K. The active catalyst obtained in this study was, therefore, found to be amorphous.

Thermogravimetry and differential thermal analysis curves of H_3NbO_4 are shown in Fig. 6. For the H_3NbO_4 powder, weight losses due do dehydration of two stages at around 400 and 900 K were observed. An endothemic change was observed with the dehydration and desorption of water at around 400 K, and an exothermic one at around 900 K. The exothermic change is due to a phase transformation from amorphous niobium acid to Nb_2O_5, as observed by XRD; it is partly canceled by the endothermic process of dehydration. From TG, it was found that the composition of H_3NbO_4 changed upon dehydration. The composition can be calculated from the amount of the dehydration, supposing that niobic acid becomes Nb_2O_5 by calcination at 1200 K. $H_3NbO_4\cdot 0.8H_2O$, which was obtained by drying in a desiccator with silica gel, successively turned into $HNbO_3$ (or $Nb_2O_5\cdot H_2O$) and Nb_2O_5 phases upon calcination. The TG curve well corresponds to the effect of the calcination temperature upon hydrogen evolution activity (Fig. 4), establishing that H_3NbO_4 (or $Nb_2O_5\cdot H_2O$), which is the most hydrated state among niobic acids, is the most active phase.

In Table 2, the results of BET, diffuse reflectance spectroscopy, and X-ray photoelectron spectroscopy measurements of H_3NbO_4 powder calcined at various temperatures are summarized. The band gap was determined from the absorption edge of an UV diffuse reflectance spectrum. In XPS measurements, the binding energies of Nb $3d_{5/2}$ and O 1s did not change, although a shoulder of O 1s was observed at the higher binding energy on catalysts calcined at low temperatures, indicating the existence of adsorbed water and/or the surface hydroxyl groups. These results establish that the surface of a catalyst calcined at low temperatures is well hydrated. The surface area decreases with an increase in the calcination temperature in the range above 380 K. The surface area at 300 K is smaller than that at 380 K; this is probably caused by the absorbed water in micropores. The band gaps of H_3NbO_4, $HNbO_3$, and Nb_2O_5 prepared from niobic acid were determined to be 3.3, 3.1, and 3.0 eV, respectively, while those of $Nb_2O_5\cdot xH_2O$ (CBMM) and Nb_2O_5 (Kanto Chemical) were 3.3 and 3.0 eV. Even though the number of available photons for a catalyst calcined at lower temperatures is less than that for a catalyst calcined at higher temperatures, the activity of the former is higher. The change in the surface area corresponds to that of the activity. On a $SrTiO_3$ photocatalyst, the surface area has been shown to be an important factor for hydrogen evolution from an aqueous methanol solution.[17]

From characterizations of TG and XPS, and the color change of the catalyst during the photoreaction, it is clear that not only the surface area, but also the hydrated state of the catalyst, strongly affects the activity for the H_2 evolution on niobium acid photocatalysts.

Conclusion

It was revealed that niobic acids, prepared from soluble potassium niobates by hydrolyzing, acted as new photocatalysts and showed high activity for hydrogen evolution from aqueous methanol solutions without any assistance of other materials, such as Pt. H_3NbO_4 obtained by calcination at 380 K showed the highest activity. The activity strongly depends on the calcination temperature, suggesting that the hydrated state and the surface area are important factors for a sacrificial hydrogen evolution reaction on niobic acid photocatalysts.

References

1) K. Domen, A. Kudo, A. Shinozaki, A. Tanaka, K.

Table 2. Characterization of H_3NbO_4 Powder Calcined at Various Temperatures

Calcination temp	Surface area	Band gap	Binding energy/eV	
K	$m^2\ g^{-1}$	eV	Nb $3d_{5/2}$	O 1s
300	86	3.3	207.4	530.9
380	183	3.3	207.4	530.9
510	131	3.2	207.5	530.8
600	69	3.1	207.5	530.8
750	58	3.1	207.5	530.8
900	29	3.0	207.5	530.7

Maruya, and T. Onishi, *J. Chem. Soc., Chem. Commun.*, **1986**, 356.

2) K. Domen, A. Kudo, M. Shibata, A. Tanaka, K. Maruya, and T. Onishi, *J. Chem. Soc., Chem. Commun.*, **1986**, 1706.

3) A. Kudo, A. Tanaka, K. Domen, K. Maruya, K. Aika, and T. Onishi, *J. Catal.*, **111**, 67 (1988).

4) A. Kudo, K. Sayama, A. Tanaka, K. Asakura, K. Domen, K. Maruya, and T. Onishi, *J. Catal.*, **120**, 337 (1989).

5) K. Sayama, A. Tanaka, K. Domen, K. Maruya, and T. Onishi, *Catal. Lett.*, **4**, 217 (1990).

6) K. Sayama, A. Tanaka, K. Domen, K. Maruya, and T. Onishi, *J. Catal.*, **124**, 541 (1990).

7) K. Domen, J. Yoshimura, T. Sekine, A. Tanaka, and T. Onishi, *Catal. Lett.*, **4**, 339 (1990).

8) T. Sekine, J. Yoshimura, A. Tanaka, K. Domen, K. Maruya, and T. Onishi, *Bull. Chem. Soc. Jpn.*, **63**, 2107 (1990).

9) M. Gasperin and M.T. Le Bihan, *J. Solid State Chem.*, **33**, 83 (1980); *ibid.*, **43**, 346 (1982).

10) B. K. Sen, A. V. Saha, and N. Chatterjee, *Mat. Res. Bull.*, **16**, 923 (1981).

11) B. K. Sen and A. V. Saha, *Mat. Res. Bull.*, **17**, 161 (1982).

12) B. K. Sen, P. Bandyopadhyay, and A. V. Saha, *Mat. Res. Bull.*, **17**, 611 (1982).

13) B. K. Sen, P. Bandyopadhyay, S. Sen, and A. V. Saha, *Mat. Res. Bull.*, **18**, 19 (1983).

14) R. Matters, H. Bierbusse, and H. Fuchs, *Z. Anorg. Allg. Chem.*, **385**, 230 (1971).

15) C. L. Hill and D. A. Bouchard, *J. Am. Chem. Soc.*, **107**, 5148 (1985).

16) M. Shibata, A. Kudo, A. Tanaka, K. Domen, K. Maruya, and T. Onishi, *Chem. Lett.*, **1986**, 1017.

17) A. Kudo, A. Tanaka, K. Domen, and T. Onishi, *J. Catal.*, **111**, 296 (1988).