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Photocatalytic Activity of Titanium Dioxide Loaded with Cerium Oxide

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A cerium oxide loaded TiO_2 catalyst exhibited a high photocatalytic activity of H_2 production from methanol aqueous solution. It was confirmed that this catalyst pretreated by H_2 and O_2 has an ability for photocatalytic decomposition of H_2O in NaOH aqueous solution into H_2 and O_2 (10 M NaOH).

TiO_2 is well known as a typical photocatalyst and has been applied to various photocatalytic reactions. However, the photocatalytic activity of itself is poor.[1)] In order to improve the activity, various modifications were carried out for preparing active sites. Those were usually performed by the addition of transition metals, such as platinum.[1-3)] On the other hand, some oxides have interesting properties originated from its oxidation-reduction properties.[4,5)] CeO_2 is one of the oxides and known some characteristic behaviors.[4-6)] In this work, we take notice of the abilities of CeO_2 and have investigated the photocatalytic activity of TiO_2 which is modified by CeO_2.

The CeO_2-supported TiO_2 catalysts used in the present work were prepared by the calcination of titanium and cerium hydroxide mixture, which was prepared by hydrolysis of $Ti(SO_4)_2$ and $Ce(NO_3)_3$ mixed solution by NH_4OH, at 953 K. The crystal structure of the prepared catalyst was measured by XRD. Only anatase pattern of TiO_2 was observed. The catalyst (0.5 g) was dispersed on a bottom of reaction vessel which was connected to a closed gas circulation system. The vessel was irradiated through the bottom by high pressure mercury lamp (100 W). The evolved gas was analysed by gaschromatograpy.

Dependence of photocatalytic activity of H_2 production from methanol aqueous solution upon amounts of CeO_2 on TiO_2 is shown in Fig. 1. The activity was defined by the amount of H_2 production per hour under steady state. From Fig. 1, it was observed that the H_2 production rate was markedly increased with increasing the amount of CeO_2. The catalyst loaded about 0.5 wt% of CeO2 exhibited the maximum activity. The increase of the amount of CeO_2 more than 0.5 wt% of TiO_2, the rate was notably decreased. It suggests that H_2 production site was formed over the catalyst by the addition of CeO_2. However, the excess addition of CeO_2, more than 0.5 wt % of TiO_2, decreased the activity. From the results of XRD measurement, it was observed that the diffraction pattern became broad by the increase of the amount of CeO_2. It suggests that excess addition of CeO_2 disturbed the crystallization of TiO_2. This may be one of the cause of decreasing the activity at CeO_2 high loaded catalyst.

Various pretreatments were carried out to CeO_2 (0.5 wt%)/TiO_2 catalyst. The results of the photocatalytic activity of H_2 evolution from methanol aqueous solution and O_2 evolution from $AgNO_3$ solution (0.1 M) over the pretreated catalysts are listed in Table 1. The activities of TiO_2 alone and platinum loaded TiO_2 are also listed in Table 1. For H_2 production, it was observed that the activity of the catalyst which was reduced by hydrogen at 723 K was extensively developed compared to that of TiO_2 alone and that the value was the same order of the Pt/TiO_2 photocatalyst system. For O_2 production, the activity was nearly the same at various catalyst. It was confirmed that the reduction of TiO_2 itself did not take place further under this pretreatment condition. Therefore, under the condition, the supported CeO_2 was mainly reduced. These results suggest that partially reduced CeO_2 over TiO_2 plays an important role on the H_2 production site.

Table 1.
Photocatalytic activities of CeO_2/TiO_2

Catalyst	Pretreatment[a)] K	Activity 10^{-5} mol h^{-1} H_2[b)]	O_2[c)]
CeO_2(0.5 wt%)/TiO_2	N	1.4	0.52
	673 E	1.5	0.53
	673 O	1.6	0.51
	673 R	2.8	0.53
	723 R	5.1	0.54
Pt(0.5 wt%)/TiO_2	N	2.9	0.52
	723 R	3.7	0.52
TiO_2	N	0.02	0.55
	723 R	0.3	0.53

a)N:no treated, E:evacuated, O:oxidized, R:reduced.
b)H_2 production from methanol aqueous solution (50 vol.%).
c)O_2 production from silver nitrate solution (0.1 mol/l).

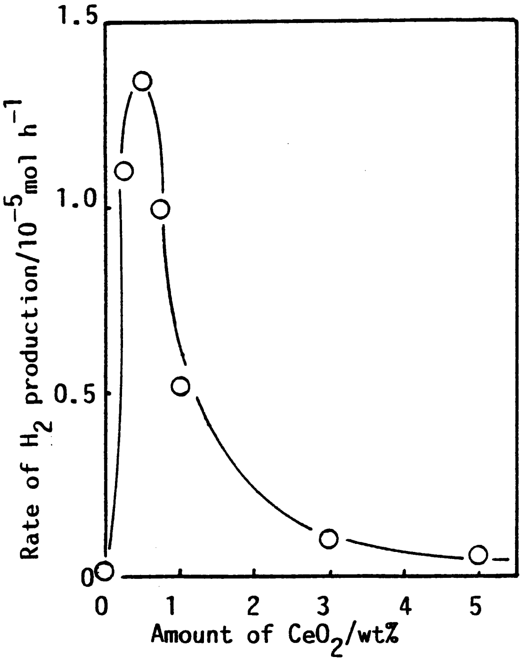

Fig. 1. Dependence of the activity of H_2 evolution from methanol aqueous solution upon the amount of loaded CeO_2.

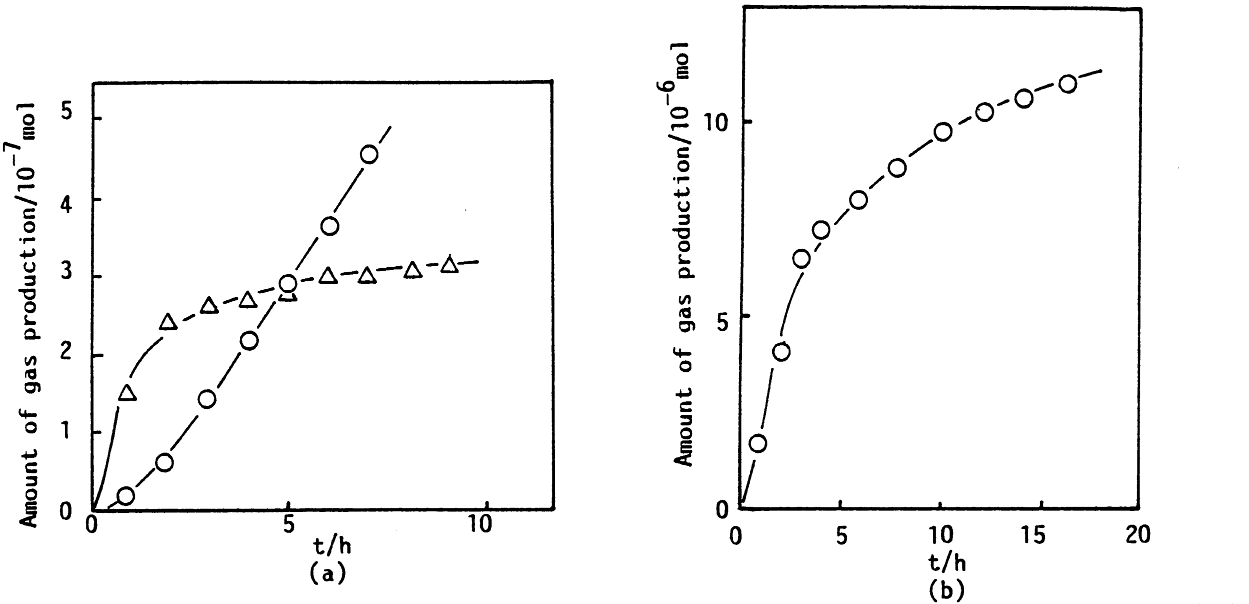

Fig. 2. Time course of photocatalytic decomposition of H_2O over (a) oxidized and (b) reduced CeO_2 (0.5 wt%)/TiO_2. ○: H_2, △: O_2.

The photocatalytic decomposition of H_2O was investigated over the same catalyst. Photocatalytic decomposition of pure H_2O over oxidized and reduced CeO_2(0.5 wt%)/TiO_2 are shown in Fig. 2. For oxidized catalyst, it was observed that O_2 was produced selectively in the initial stage of the reaction and H_2 was produced after 2 or 3 hours of induction period as shown in Fig. 2(a). For reduced catalyst, it was observed that only H_2 was produced with high activity that was nearly the same order as the photocatalytic H_2 production from methanol aqueous solution. The activity of H_2 production was gradually decreased with passing time as shown in Fig. 2(b). These results suggest that the active site for H_2 evolution was formed over the surface of the oxidized catalyst in the initial stage of the reaction, while, for reduced catalyst, reoxidation of the catalyst was proceeded. From these results, reoxidation to the reduced catalyst under mild conditions were performed. The reoxidation was performed by contacting small amount of O_2 that can oxidize the reduced catalyst at about 80%. For the reoxidized catalyst, it was observed that H_2 was produced accompanied with small amount of O_2 from pure H_2O. The effects of the condition of the reactant solution were investigated. The results are shown in Fig. 3. Figure 3(a) shows the time course of photocatalytic decomposition of H_2O over reoxidized catalyst in NaOH aqueous solution (10 M). Figure 3(b) shows the dependence of the photocatalytic activity upon the concentration of NaOH in the solution. The photocatalytic H_2 and O_2 production in stoichiometric ratio were observed from the initial stage of the reaction as shown in Fig. 3(a). From Fig. 3(b), it was observed that the activities of H_2 and O_2 production were increased with increasing the concentration of NaOH and the H_2 and O_2 production rates were approaching

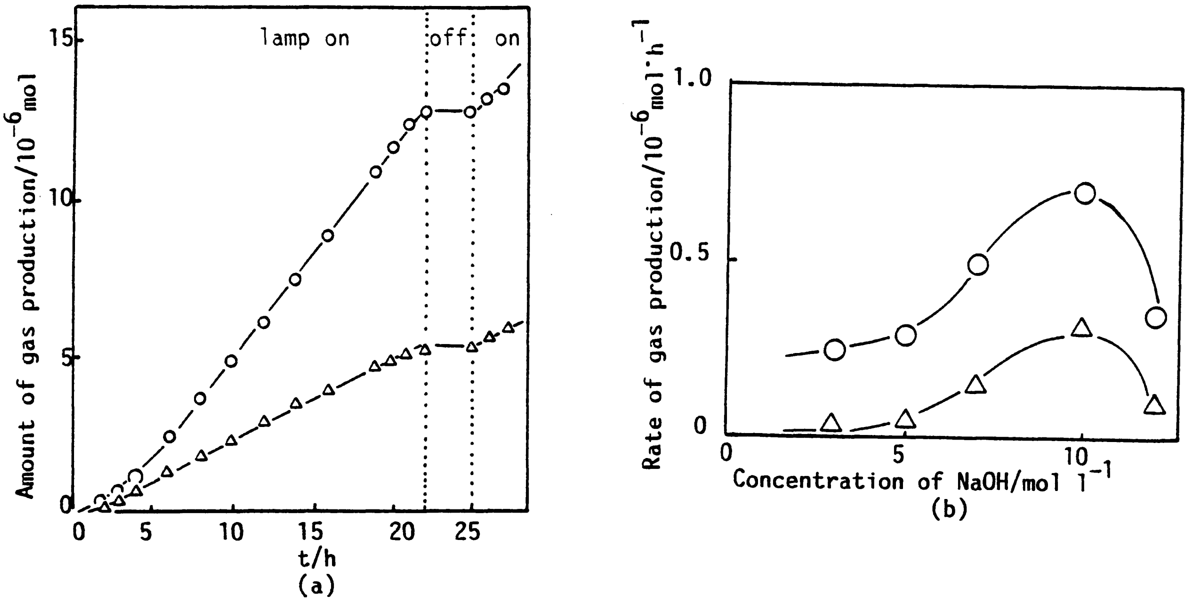

Fig. 3 Photocatalytic decomposition of H_2O in NaOH aqueous solution over reoxidized CeO_2(0.5 wt%)/TiO_2. (a): time course of reaction (10 M NaOH) (b): relation between the activity and concentration of NaOH. ○: H_2, △: O_2.

to the stoichiometric ratio of H_2O decomposition. It suggests that NaOH acted as a promoter of the catalyst and the concentration of NaOH around 10 mol/l was suitable for decomposition of H_2O. In high concentration of NaOH solution that is more than 10 mol/l, the activity was decreased. That may be caused by the increase of the viscosity of the solution.

There are some reports about the photocatalytic decomposition of H_2O over modified TiO_2.[2,3,8,9] H_2O, however, was not able to be decomposed in stoichiometric ratio, except for a few cases such as NaOH coated Pt/TiO_2,[8] pretreated NiO/TiO_2,[9] and Pt/TiO_2 in Na_2CO_3 solution.[10] It is interesting to note that pretreated CeO_2/TiO_2 become one of a photocatalyst that can decompose H_2O into H_2 and O_2 stoichiometrically. It is clear that cerium oxide becomes an effective site on TiO_2 photocatalyst.

References

1) T. Kawai and T. Sakata, J. Chem. Soc., Chem. Commun., 1980, 694.
2) A. Kudo, K. Domen, K. Maruya, and T. Onishi, Chem. Lett., 1987, 1019.
3) A. Mills and G. Porter, J. Chem. Soc., Faraday Trans. 1, 78, 3659 (1982).
4) J. Kiwi and C. Morrison, J. Phys. Chem., 88, 6164 (1984).
5) K. Otsuka, S. Murakoshi, and A. Morikawa, Fuel Process. Technol., 7, 203 (1983).
6) K. Otsuka, M. Hatano, and A. Morikawa, J. Catal., 79, 493 (1983).
7) A. Laachir, V. Perrichon, A. Badri, J. Lamotte, E. Catherine, J. C. Lavalley, J. E. Fallah, L. Hilaire, F. le Nomand, E. Quemere, G. N. Sauvion, and O. Touret, J. Chem. Soc., Faraday Trans., 87, 1601 (1991).
8) K. Yamaguchi and S. Sato, J. Chem. Soc., Faraday Trans. 1, 81, 1237 (1985).
9) A. Kudo, K. Domen, K Maruya, and T. Onishi, Chem. Phys. Lett., 133, 517 (1987).
10) K. Sayama and H. Arakawa, J. Chem. Soc., Chem. Commun., 1992, 150.

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