# Photocatalytic Decomposition of $H_2O$ into $H_2$ and $O_2$ over $Ga_2O_3$ Loaded with NiO

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Photocatalytic decomposition of $H_2O$ over NiO-loaded $Ga_2O_3$, one of the oxides with a $d^{10}$ electron configuration, was confirmed. Without pretreatment, both $H_2$ and $O_2$ have been continuously produced in stoichiometric amounts under the irradiation of high pressure Hg lamp.

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Decomposition of $H_2O$ into $H_2$ and $O_2$ using a suitable photocatalyst is an attractive research target and various photocatalyst systems that are effective in this reaction have been found.[1] In particular, oxides and mixed oxides of $Ti^{4+}$, $Nb^{5+}$, $Zr^{4+}$, and $Ta^{5+}$, which have a $d^0$ electron configuration, are effective photocatalyst systems, generally in combination with loaded NiO or $RuO_2$ as promoter for the photocatalytic decomposition of $H_2O$. Recently, the mixed oxides of $Ga^{3+}$,[2] $In^{3+}$,[3–7] $Sn^{4+}$,[3] and $Sb^{5+}$,[3,8] with a $d^{10}$ electron configuration and promoted with $RuO_2$ have also been found to be effective photocatalysts for the decomposition of $H_2O$ into $H_2$ and $O_2$. However, the photocatalytic property of these oxides with $d^{10}$ electron configuration with respect to the decomposition of $H_2O$ has not been investigated so far. $Ga_2O_3$ is one of the series of these oxides and has relatively wide band gap.[9] The photocatalytic properties of both $Ga_2O_3$ and the corresponding solid solution with $In_2O_3$ have been studied. The photocatalytic properties were evaluated using either $H_2$ or $O_2$ production from aqueous solutions of methanol or $AgNO_3$ as photo-produced hole and electron scavenger.[9] This means that this oxide has a potential as photocatalyst to produce $H_2$ and $O_2$ from $H_2O$ decomposition, yet few investigations have applied $Ga_2O_3$ as a photocatalyst for the direct decomposition of $H_2O$.

In this work, we have studied the photocatalytic properties of $Ga_2O_3$ as a pure oxide photocatalyst with $d^{10}$ configuration. Here we report the photocatalytic behavior of NiO-loaded $Ga_2O_3$ to the overall splitting of $H_2O$.

The $Ga_2O_3$ photocatalyst used in this work was obtained from High Purity Chemical. The structure of crystal was shown to be monoclinic in XRD measurements. In the UV-diffuse reflectance spectrum of the $Ga_2O_3$, a strong absorption band, originating from band-gap excitation, was observed at a wavelength shorter than 274 nm. The band-gap energy is estimated to be 4.5 eV from the absorption edge of the spectrum. The loading of NiO was carried out by impregnation. Powdered $Ga_2O_3$ was suspended in Ni $(NO_3)_2$ (Wako Pure Chemical) aqueous solution and dried over a steam bath. The obtained Ni $(NO_3)_2/Ga_2O_3$ was oxidized in air at 473 K to obtain $NiO/Ga_2O_3$. The catalyst was not changed substantially after loading with NiO at the any content confirmed by XRD analysis. The photocatalytic reaction was carried out in an inner irradiation type photo-reaction cell made of quartz. The cell was attached with closed gas circulation system equipped with sample inlet for analysis and vacuum line. The catalyst (1 g) was suspended in well-outgassed $H_2O$ in the cell and irradiation from high pressure Hg lamp (450 W USHIO UM-452) started. The evolved gases were analyzed by gaschromatograph.

The progress of the photocatalytic reaction of $H_2O$ decomposition over the $Ga_2O_3$ loaded with 2 wt % of NiO (NiO (2 wt %)/$Ga_2O_3$) is shown in Figure 1. Production of $H_2$ and $O_2$ was observed after an initial induction period for 2 h from which the irradiation from the high pressure Hg lamp started. In the initial stages of the reaction, it is noticeable that more $O_2$ was produced than the stoichiometric ratio of the decomposition of $H_2O$. Moreover, the color of the photocatalyst changed from light gray to dark purple. In previous papers studying NiO supported on photocatalysts, such as $NiO/SrTiO_3$,[10–12] the preferable condition of the NiO promoter was the mixture of Ni metal, NiO, and the hydroxide. Therefore, pretreatments of reduction and re-oxidation of NiO were necessary to activate the photocatalysts. This result indicates that reduction of supported NiO occurs in the initial stages and is accompanied by the production of $O_2$. After this induction period, the state of NiO over $Ga_2O_3$ has become the preferable condition for this promoter for the photocatalytic decomposition of $H_2O$. A similar property has been observed in some other NiO-loaded photocatalyst systems for $H_2O$ decomposition, such as $NiO/NaTaO_3$ and $NiO/Sr_2Ta_2O_7$.[13,14]

As shown in Figure 1, the reaction was observed for 29 h during the first run and a constant rate of production of $H_2$ and $O_2$ was confirmed. Then, the irradiation was stopped and the gas phase was evacuated. The reaction cell was kept in dark for 1 h, the absence of production of $H_2$ and $O_2$ was confirmed, and then the irradiation of second run started.

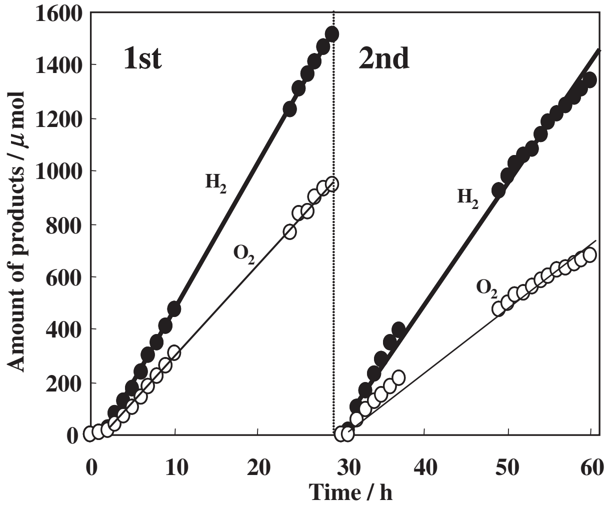

**Figure 1.** Evolution of $H_2$ and $O_2$ in time during photocatalytic decomposition of $H_2O$ over NiO (2 wt %)/$Ga_2O_3$.

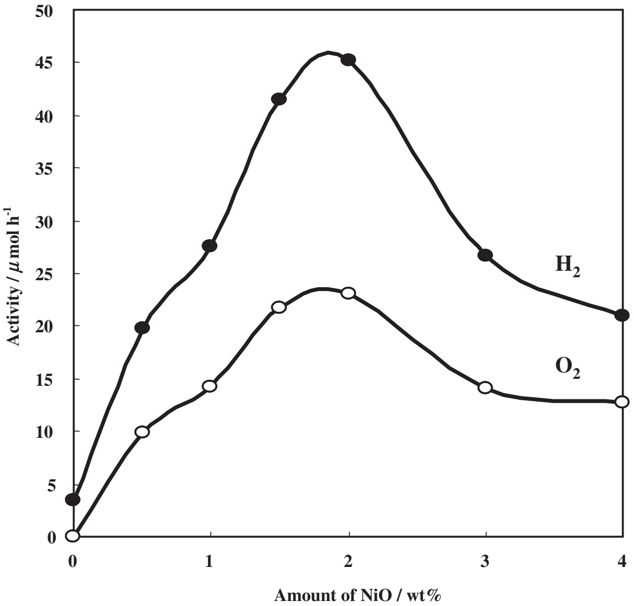

**Figure 2.** Dependence of the photocatalytic activity for $H_2$ and $O_2$ evolution from $H_2O$ on the amount of NiO over $Ga_2O_3$.

In the second run, it was confirmed, see Figure 1, that $H_2$ and $O_2$ were produced at a constant rate in stoichiometric ratio from the beginning of the irradiation and that the production rates were the same as in the first run. These results clearly demonstrate that the photocatalyst of $Ga_2O_3$ loaded with NiO has a potential for the photocatalytic decomposition of $H_2O$ into $H_2$ and $O_2$. In order to understand the effect of NiO promoter over $Ga_2O_3$ in the photocatalytic decomposition of $H_2O$, the photocatalytic reaction was carried out over $Ga_2O_3$ loaded with the various amount of NiO.

Figure 2 shows the dependence of the photocatalytic activity of $H_2O$ decomposition over $Ga_2O_3$ on the amount of loaded NiO. The photocatalytic reactions were carried out in the same manner as the examination of NiO (2 wt%)/$Ga_2O_3$ as shown in Figure 1. The activity shown in Figure 2 was defined as the amount of evolved $H_2$ and $O_2$ in 1 h during the 2nd run. It can be seen that only $H_2$ production was observed when $Ga_2O_3$ itself was used as the photocatalyst without NiO loading. The activity was also relatively low.

When NiO-loaded $Ga_2O_3$ was used, the photocatalytic activity remarkably improved with increasing the amount of loaded NiO and the simultaneous evolution of $H_2$ and $O_2$ in the stoichiometric ratio was observed. It is also observed that the photocatalytic activity to the production of $H_2$ and $O_2$ was dependent on the amount of loaded NiO. Particularly, $Ga_2O_3$ loaded with 2 wt% of NiO exhibited maximum activity, with the activity decreasing when more than 2 wt% NiO was loaded. These results suggest that NiO loading is necessary for the photocatalytic decomposition of $H_2O$ into $H_2$ and $O_2$, and that $Ga_2O_3$ loaded with 2 wt% of NiO is the preferable photocatalyst for the photocatalytic decomposition of $H_2O$.

In conclusion, we have demonstrated the photocatalytic decomposition of $H_2O$ into $H_2$ and $O_2$ over NiO loaded $Ga_2O_3$, one of the pure oxides with a $d^{10}$ electron configuration. NiO loading is necessary to induce the stoichiometric formation of $H_2$ and $O_2$ by photocatalytic decomposition of $H_2O$. Although further detailed examination is necessary, the results obtained in this investigation are important to report, together with this new photocatalyst system for $H_2O$ decomposition.

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## References

1 A. Kudo, *Hyoumen*, **36**, 625 (1998) and the references there in.
2 K. Igarashi, J. Sato, H. Kobayashi, N. Saito, H. Nishiyama, and Y. Inoue, *J. Phys. Chem. B*, **106**, 9048 (2002).
3 J. Sato, N. Saito, H. Nishiyama, and Y. Inoue, *J. Phys. Chem. B*, **105**, 6061 (2001).
4 J. Sato, N. Saito, H. Nishiyama, and Y. Inoue, *Chem. Lett.*, **2001**, 868.
5 J. Sato, H. Kobayashi, N. Saito, H. Nishiyama, and Y. Inoue, *J. Photochem. Photobiol., A*, **158**, 139 (2003).
6 J. Sato, N. Saito, H. Nishiyama, and Y. Inoue, *J. Phys. Chem. B*, **107**, 7965 (2003).
7 J. Sato, H. Kobayashi, and Y. Inoue, *J. Phys. Chem. B*, **107**, 7970 (2003).
8 J. Sato, N. Saito, H. Nishiyama, and Y. Inoue, *J. Photochem. Photobiol., A*, **148**, 85 (2002).
9 A. Kudo and I. Mikami, *J. Chem. Soc., Faraday Trans.*, **94**, 2929 (1998).
10 K. Domen, S. Naito, M. Soma, T. Onishi, and K. Tamaru, *J. Chem. Soc., Chem. Commun.*, **1980**, 543.
11 K. Domen, S. Naito, T. Onishi, K. Tamaru, and M. Soma, *J. Phys. Chem.*, **86**, 3657 (1982).
12 K. Domen, A. Kudo, T. Onishi, N. Kosugi, and H. Kuroda, *J. Phys. Chem.*, **90**, 292 (1986).
13 H. Kato and A. Kudo, *Catal. Lett.*, **58**, 153 (1999).
14 A. Kudo, H. Kato, and S. Nakagawa, *J. Phys. Chem. B*, **104**, 571 (2000).