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Photocatalytic hydrogen production from glycerol and water with NiOx/TiO2 catalysts

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Abstract

The surface of a TiO2 material was modified by loading NiOx in 10 wt% by impregnation with nickel nitrate followed by calcination in air at different temperatures. The TiO2 and NiOx/TiO2 samples prepared were applied for photocatalytic H2 production from glycerol and water at 50 ºC. The H2 evolution was enhanced by NiOx loading and was dependent on calcination temperature. A maximum H2 evolution was observed with 450 ºC calcined NiOx/TiO2 sample. The properties of those TiO2 and NiOx/TiO2 samples were characterized by nitrogen adsorption, XRD, UV/Vis, and XPS measurements to examine factors responsible for the enhancement of photocatalytic H2 evolution with NiOx loaded and calcined TiO2 samples.

Keywords: Photocatalytic activity, Glycerol reforming, Hydrogen production, Nickel doping, Titanium dioxide
1. Introduction

The useful application of biomass derived materials is attracting much attention from industry and academia. One of interesting applications is the production of H\textsubscript{2} from chemical and photochemical transformations of those materials [1-3]. The photocatalytic H\textsubscript{2} production can be performed under mild conditions and several authors studied different biomass derived model materials including alcohols, glycerol, glucose, sugars, and so on. Recently a larger amount of glycerol is produced as a byproduct in the production of biodiesel and so it is desirable to find its application [4]. The heterogeneous photocatalytic H\textsubscript{2} production from aqueous glycerol solutions (Scheme 1) were studied by several authors using TiO\textsubscript{2} based catalysts loaded with Pt [5-8], Pd [9], and CuOx [10-12]. Fornasiero et al. prepared active Cu/TiO\textsubscript{2} catalysts by a water-in-oil microemulsion method, in which Cu nanoparticles were embedded in the TiO\textsubscript{2}, and these were active for the H\textsubscript{2} production from glycerol and water under visible light irradiation conditions [10]. The doping of NiO\textsubscript{x} onto the surface of TiO\textsubscript{2} is effective for the preparation of p-type (NiO\textsubscript{x}) - n-type (TiO\textsubscript{2}) junction [13]. Such NiO\textsubscript{x}-doped TiO\textsubscript{2} catalysts were recently reported to show good performance of photocatalytic degradation of organic compounds of methyl orange [14], methylene blue [15], and 2-naphthol and p-cresol [16]. In the present work, the authors prepared NiO\textsubscript{x}/TiO\textsubscript{2} catalysts by conventional impregnation and tested their performance in photocatalytic H\textsubscript{2} production from a mixture of glycerol and water under UV/Vis irradiation conditions. We could find few published study that has considered the use of NiO\textsubscript{x}/TiO\textsubscript{2} photo-sensitive materials for such a H\textsubscript{2} production from biomass derived compounds.

Scheme 1

2. Experimental

2.1. Catalyst preparation

A TiO\textsubscript{2} material supplied by Catalysis Society of Japan was used, which was a mixture of anatase and rutile TiO\textsubscript{2}. The structural properties will be presented later (Table 1). The doping of Ni species was made by conventional impregnation with nickel nitrate (Wako) and the loading of Ni species was 10 % by weight assuming Ni species was in the form of NiO. A weighed TiO\textsubscript{2} (1 g) was dispersed in 10 cm\textsuperscript{3} Ni(NO\textsubscript{3})\textsubscript{2}
aqueous solution (0.15 M) and the slurry formed was continuously stirred overnight for sufficient impregnation. The mixture was kept in an oven at 80 °C for 12 h to remove the solvent (water). Then, the solid sample was ground and calcined in a muffle furnace while passing air at 50 cm$^3$ min$^{-1}$ at 250, 450 and 650 °C for 3 h. The catalysts so prepared are denoted by NiO$_x$/TiO$_2$ hereinafter.

2.2. Catalyst characterization

The surface and bulk properties of NiO$_x$/TiO$_2$ samples prepared were characterized by different methods. BET surface area was measured by N$_2$ adsorption at -196 °C (Quantachrome NOVA 1000). Prior to N$_2$ physisorption, the samples were degassed under vacuum at 150 °C for 2 h. Structural properties were examined by powder X-ray diffraction (XRD) (Rigaku D/Max-2500 PC) with Cu K$_\alpha$ radiation and a Ni filter. XRD patterns were measured from 20° to 80° at a rate of 1° min$^{-1}$. Diffuse reflection UV/Vis spectra were recorded under ambient conditions (Shimadzu UV-3100PC) using BaSO$_4$ matrix as background under ambient conditions. The spectra measured were converted to the absorption spectra by using the Kubelka-Munk function. X-ray photoelectron spectroscopy (JEOL JPS-9200) was used to examine the surface properties and all the binding energies were referenced with respect to the Ti 2p at 485.5 eV [17].

2.3. Photocatalytic reaction

Photocatalytic reactions were conducted in the same reactor as used previously, which was a 50 cm$^3$ stainless steel autoclave with two quartz windows (diameter 1 cm) [18]. It was previously used for photocatalytic water splitting in the presence of pressurized CO$_2$. A weighed sample (20 mg) was suspended in a mixture of 10 cm$^3$ water and 2 cm$^3$ glycerol (Wako) in the reactor. The air remaining in the reactor was removed by purging with 1 MPa N$_2$ for five times. The reactor was placed on a heating plate and wrapped by a heating tape. The temperature was monitored by a thermocouple embedded in the reactor wall. The reactor was heated while stirring the reaction mixture by a magnetic stirrer. The reaction mixture was illuminated using a 500 W high-pressure Hg lamp (Ushio USH-500SC) at 50 °C for 4 h. The lamp emits predominantly the light of wavelengths at 365 nm, 405 nm, and 436 nm. After the reaction, the gaseous products evolved were collected in a gas trap. The amount of H$_2$ was determined by a gas chromatograph (Shimadzu GC-8A, molecular sieve 5A packed column, TCD detector, N$_2$ carrier) and those of CO, CO$_2$, and CH$_4$ by another gas chromatograph (Shimadzu
GC-8A, Porapak Q packed column, FID detector, N\textsubscript{2} carrier) with a methanizer converting those gases into CH\textsubscript{4}.

3. Results and discussion

In the present work, 10 wt\% NiO\textsubscript{x}/TiO\textsubscript{2} catalysts calcined at different temperatures were used for the photocatalytic H\textsubscript{2} production from aqueous glycerol solution. The 10 wt\% NiO loading approximately corresponds to monolayer coverage of NiO species over the surface of TiO\textsubscript{2} used that has a BET surface area of 50 m\textsuperscript{2} g\textsuperscript{-1}. The state of NiO\textsubscript{x} dispersion (namely, the state of NiO\textsubscript{x}-TiO\textsubscript{2} junction/contact) was varied by changing the calcination temperature.

3.1. Catalytic performance

First, the performance of NiO\textsubscript{x}-unloaded TiO\textsubscript{2} samples calcined at different temperatures was examined for photocatalytic H\textsubscript{2} production from a mixture of glycerol and water at 50 °C. Fig. 1 shows the rates of evolution of H\textsubscript{2} and other gaseous products of CO\textsubscript{2} and CO in photocatalytic reforming of glycerol at 50 °C. The evolution of CH\textsubscript{4} was not detected. When the calcination temperature was raised, the rate of H\textsubscript{2} evolution increased, had a maximum at 450 °C, and then decreased. The maximum H\textsubscript{2} evolution was 320 µmol g\textsuperscript{-1} h\textsuperscript{-1} under the conditions used. The amount of CO\textsubscript{2} evolved did not change so much but that of CO increased with the temperature. The evolution of H\textsubscript{2} was larger than that of CO\textsubscript{2} and CO for the catalysts calcined at 450 °C or below but smaller for the one at 650 °C. In addition, blank experiments were conducted in the absence of light and/or catalyst under the same reaction conditions. No H\textsubscript{2} production was detected in these blank reactions, indicating that both the light and the TiO\textsubscript{2} catalyst are required for the photocatalytic H\textsubscript{2} production from glycerol and water.

Figure 1

Then, the catalytic performance of NiO\textsubscript{x}-loaded TiO\textsubscript{2} samples was tested and the results obtained are also shown in Fig. 1. The rate of H\textsubscript{2} evolution changed with the calcination temperature in a similar manner as observed with the NiO\textsubscript{x}-unloaded samples. The maximum H\textsubscript{2} evolution appeared at the same temperature of 450 °C, being 900 µmol g\textsuperscript{-1} h\textsuperscript{-1}. It was about three times larger compared to the maximum with the NiO\textsubscript{x}-unloaded sample calcined at 450 °C. Thus, the loading of NiO\textsubscript{x} to TiO\textsubscript{2} can
improve its photocatalytic performance. The total amount of CO\textsubscript{2} and CO formed was comparable to that of H\textsubscript{2} evolved for either 250 °C or 450 °C calcined NiO\textsubscript{x}/TiO\textsubscript{2} catalyst. However, the ratio of CO\textsubscript{2} against CO is different, being 1.8 and 5.4 for the former and latter catalysts, respectively. CH\textsubscript{4} was also detected to form for the 650 °C calcined sample.

In addition, the performance of NiO alone was tested under the same reaction conditions. The NiO powder was prepared by calcining Ni(NO\textsubscript{3})\textsubscript{2} at 450 °C in an air stream of 50 cm\textsuperscript{3} min\textsuperscript{-1} for 3 h and grinding in a mortar. This treatment changed Ni(NO\textsubscript{3})\textsubscript{2} to NiO, which was confirmed by XRD (not shown). It was found that H\textsubscript{2}, CO, and CH\textsubscript{4} were evolved at rates of 91, 2124, and 917 \mu\text{mol g}^{-1} h^{-1}, respectively. That is, compared to the above-mentioned NiO\textsubscript{x}/TiO\textsubscript{2} sample calcined at the same temperature, the amount of H\textsubscript{2} was even smaller while those of CO and CH\textsubscript{4} were even larger. Hence, reactions with NiO alone are different from those with NiO\textsubscript{x}/TiO\textsubscript{2} catalysts and so NiO is not effective for our target H\textsubscript{2} production from aqueous glycerol solution, for which the significance of NiO\textsubscript{x} - TiO\textsubscript{2} junction/contact is again illustrated.

Hydrogen could be produced through the two reactions in which one is photo-splitting of water and the other is photo-reforming of glycerol with water (Scheme 1). To examine the significance of the two reactions, the NiO\textsubscript{x}/TiO\textsubscript{2} samples calcined at 250 °C, 450 °C, and 650 °C were also tested for the photocatalytic H\textsubscript{2} production from water in the absence of glycerol. The maximum H\textsubscript{2} production was observed to occur for the 450 °C calcined sample. However, it was only 6.6 \mu\text{mol g}^{-1} h^{-1}, which was smaller by two orders of magnitude than that in the presence of glycerol. Hence, for a mixture of glycerol and water, the H\textsubscript{2} was evolved through photocatalytic reaction between the two.

The most active 450 °C calcined catalyst was further tested for longer reaction periods of time. Fig. 2 indicates the time profile obtained, showing that the H\textsubscript{2} production continued to occur at an almost fixed rate during the reaction up to 12 h and so the catalyst did not change in its activity.

In our reaction runs, gas chromatograph analysis was tried to detect possible liquid products of CH\textsubscript{3}OH, HCOOH, CH\textsubscript{3}OH, and C\textsubscript{2}H\textsubscript{5}OH. We failed to detect such products, which may be ascribed to low conversion of glycerol (< 0.05 % estimated
rough from the initial amount of glycerol used and the total amount of H₂ evolved in 4 h with the most active catalyst) and/or these should easily be changed to gaseous products by action of NiO.

The photocatalytic production of H₂ from aqueous glycol solution was recently studied over TiO₂ catalysts in the absence of costly noble metals [10-12]. Fornasiero et al. prepared several types of CuOₓ/TiO₂ catalysts by different methods and showed that Cu nanoparticle embedded TiO₂ catalysts prepared by a water-in-oil microemulsion method have superior performance compared to conventional Cu/TiO₂ catalysts prepared by impregnation [10, 11]. The performance of our NiOₓ/TiO₂ catalysts prepared by conventional impregnation is comparable to their Cu/TiO₂ catalysts. Lalitha et al. also studied the performance of CuOₓ/TiO₂ catalysts prepared by impregnation and calcination at 350 ºC and 450 ºC [12]. The photocatalysts of Fornasiero et al. and Lalitha et al. are visible light sensitive. (Our NiOₓ/TiO₂ catalysts have not been tested under visible light conditions due to the limitation of experimental setup.)

3.2. Catalyst characterization

The properties of NiOₓ-loaded and unloaded TiO₂ samples calcined at different temperatures were examined by different methods. Table 1 shows the results of N₂ adsorption. The 650 ºC calcined sample had a markedly decreased surface area of 14 m² g⁻¹. In contrast, the surface area of NiOₓ-unloaded TiO₂ was observed to decrease to 43 m² g⁻¹, indicating that the significant decrease in the surface area of NiOₓ-loaded TiO₂ by the calcination at 650 ºC is induced by the doping of NiOₓ. Fig. 3 gives XRD patterns and the bulk phase composition and other parameters determined thereof. The anatase/rutile ratio was 83/17 and the size of TiO₂ was 21 nm for NiOₓ-unloaded mother TiO₂ sample. These structural parameters did not change by the NiOₓ-loading and the following calcination at 250 ºC and 450 ºC. After the calcination at 650 ºC, however, the phase composition changed drastically to an anatase/rutile ratio of 9/91. The phase composition also changed by the calcination for NiOₓ-unloaded TiO₂ but less markedly; the anatase/rutile ratio decreased to 59/41 by the calcination at 650 ºC. Thus, the phase transformation of TiO₂ during the calcination was assisted by the presence of NiOₓ species. The average TiO₂ crystallite size increased with the temperature but marginally. For the NiOₓ-loaded samples calcined at 250 ºC and 450 ºC, NiO was detected, the size being 4 - 6 nm; NiO was highly dispersed on the surface of TiO₂. On calcination at 650 ºC, the NiO changed to NiTiO₃ with an average size of 51 nm and the BET surface
decreased significantly to 14 m² g⁻¹.

Table 1, Figure 3

Fig. 4 shows UV/Vis spectra of those NiOₓ-loaded and unloaded TiO₂ samples. The loading of 10 wt% NiOₓ was found to have a significant impact on the absorption at wavelength > 350 nm. The NiOₓ loading strengthened the absorption in this range of wavelength, depending on the calcination temperature used. These data were reformed to a plot of (Absorbance·Energy)¹/² against Energy in Fig. 4(b). For NiOₓ-unloaded TiO₂, the band gap was estimated to be 2.75 eV; while, for the NiOₓ-loaded samples calcined at 250 ºC and 450 ºC, it was lowered to 2.17 eV. The difference was 0.58 eV. The decrease in the band gap energy may be one of factors responsible for the enhanced H₂ production rate observed with the 250 ºC and 450 ºC calcined NiOₓ/TiO₂ catalysts (Fig. 1). The band gap of TiO₂ depends on its structure, being 3.2-3.3 eV for anatase TiO₂ [19, 21] and 3.0-3.1 eV for rutile TiO₂ [20, 21]. In our samples, the phase composition did not change by the loading of NiOₓ and the calcination at temperatures of 250 ºC and 450 ºC (Table 1). Therefore, the decrease in the band gap observed should result from the formation of NiOₓ and TiO₂ junction. This desirable N - P junction was likely to be destroyed after the calcination at a higher temperature of 650 ºC, at which NiOₓ changed to NiTiO₃ (Fig. 3).

Figure 4

The catalysts were further characterized by XPS measurements. Fig. 5 shows Ni₂p, Ti₂p, and O₁s XPS spectra collected with the NiOₓ unloaded and loaded TiO₂ samples calcined at different temperatures. For the unmodified TiO₂, the binding energy (BE) values of Ti 2p₃/2 and Ti 2p₁/2 were 458.5 eV and 464.5 eV, respectively, the difference being 6 eV. These peaks may come from anatase TiO₂ species and a shoulder peak at 457 eV from rutile TiO₂ species. The loading of NiOₓ and the following calcination caused significant changes: the 650 ºC calcined sample had a peak at a BE of 464 eV but no other peaks were detected, in which the surface Ti species should be in a structure different from anatase and rutile TiO₂ species. The 450 ºC calcined sample also had a peak at a similar BE along with a small peak at about 457 eV. The latter peak indicated that a small amount of Ti species of rutile structure remained on its surface. The 250 ºC calcined may be on a way of changing from a mixture of anatase and rutile Ti species to other structures. A similar significant change was observed for O 1s. The NiOₓ-unloaded TiO₂ sample had a peak at 529.5 eV while the 450 ºC and 650 ºC
calcined ones had a peak at a larger BE of 535 eV. According to the literature, the BE values of NiO and Ni₂O₃ are 529.7 eV and 531.5 eV, respectively. The spectra of Ni 2p were a little noisy but the peaks were detected at 860 eV and 865 eV. The BE values of Ni 2p₃/2 of metallic Ni, NiO, NiAl₂O₅, and NiWO₄ are 852.3 eV, 853.3 eV, 857.2 eV, and 857.6 eV, respectively, [17], which are smaller compared to the peaks observed with the NiOₓ-loaded calcined TiO₂ samples. At present, unfortunately, it is difficult to determine the surface Ni-Ti-O structure but it may be assumed that the above-mentioned NiOₓ-TiO₂ junction was formed for the calcined NiOₓ/TiO₂ samples. Very recently Iwaszuki et al. investigated the performance of NiOₓ-loaded TiO₂ catalysts for the photocatalytic degradation of 2-naphthol and p-cresol and discussed their high performance after considering their structural features estimated theoretically by density functional theory simulations [16]. It is assumed that NiO clusters have a strong interaction with the surfaces of anatase and rutile TiO₂ through Ni-O-Ti bonds and additional Ni-Ti bonds for rutile TiO₂. These structural changes caused by NiO loading can reduce the band gap energy.

Hence, it can be said that the loading of NiOₓ onto TiO₂ and the following calcination cause the band gap energy to lower by 2.5 eV and this is one of factors responsible for the enhancement of the photocatalytic activity in H₂ production from glycerol and water. The maximum H₂ evolution is obtained with 450 °C calcined NiOₓ/TiO₂ sample. However, when the calcination temperature is raised to 650 °C, the surface properties (XPS and UV/Vis) are similar to those of the 450 °C calcined sample but the BET surface area is markedly lowered and so this results in a lower activity.

Under the reaction conditions used, the conversion of glycerol was so small that it was difficult to determine its conversion and detect liquid products. These pieces of information may be necessary to make a discussion on reaction mechanisms over NiOₓ/TiO₂ catalysts. A few authors discuss the mechanisms of photocatalytic reforming of glycerol over Pt/TiO₂ [5] and CuOₓ/TiO₂ [12]. Daskalaki and Kondarides assume that hydroxyl radicals and other oxidants are photogenerated from water and these oxidize and change organic compounds towards lower molecular weight compounds, eventually to CO₂. The photocatalytic reforming of glycerol producing H₂ should occur through those reaction processes. Lalitha et al also assume several processes for the photocatalytic production of H₂ from glycerol over CuOₓ/TiO₂ catalysts [12].
4. Conclusions

NiO$_x$-loaded TiO$_2$ catalysts are active for the photocatalytic production of H$_2$ from aqueous glycerol solution at 50 ºC. The activity can remain unchanged in a long time of 12 h at least. The catalytic performance of NiO$_x$/TiO$_2$ depends significantly on calcination temperature. The maximum activity can be achieved after the calcination at 450 ºC. The calcination temperature would influence the formation of n-type (NiO$_x$) and p-type (TiO$_2$) junction. The calcination at 450 ºC decreased the band gap energy by 0.58 eV with respect to the mother TiO$_2$ material, which was responsible for the improved H$_2$ production. The calcination at a higher temperature of 650 ºC caused a significant decrease in the surface area, reducing the catalytic performance.

Acknowledgements

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References

Scheme, Figures, Table in the order of appearance:

Scheme 1 Photocatalytic reaction between glycerol and water

\[
\text{OH} \quad + \quad 3\text{H}_2\text{O} \quad \xrightarrow{\text{hv}} \quad 7\text{H}_2 \quad + \quad 3\text{CO}_2
\]
Fig. 1  Evolution of H₂ (upper) and other gaseous products (bottom) in photocatalytic reaction at 50 °C between glycerol and water with NiOₓ-unloaded and loaded TiO₂ samples uncalcined and calcined at 250 °C, 450 °C, and 650 °C.
Fig. 2  Time profile of the H$_2$ evolution in photocatalytic reaction between glycerol and water at 50 ºC with NiO$_x$/TiO$_2$ catalyst calcined at 450 ºC
Table 1 Structural properties of NiO\textsubscript{x}/TiO\textsubscript{2} catalysts determined by N\textsubscript{2} adsorption and XRD measurements

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<th>Catalyst</th>
<th>Anatase/rutile ratio</th>
<th>Crystallite size\textsuperscript{a} (nm)</th>
<th>Surface area (m\textsuperscript{2} g\textsuperscript{-1})</th>
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<td>21</td>
<td>50</td>
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<td>NiO\textsubscript{x}/TiO\textsubscript{2} 250 °C\textsuperscript{b}</td>
<td>80/20</td>
<td>22</td>
<td>54</td>
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<tr>
<td>NiO\textsubscript{x}/TiO\textsubscript{2} 450 °C\textsuperscript{b}</td>
<td>80/20</td>
<td>23</td>
<td>50</td>
</tr>
<tr>
<td>NiO\textsubscript{x}/TiO\textsubscript{2} 650 °C\textsuperscript{b}</td>
<td>9/91</td>
<td>27</td>
<td>14</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The average crystallite size of TiO\textsubscript{2} was calculated by following equation: 

\[ D_{ave} = D_a \cdot \frac{[I_a/(I_a+I_r)] + D_r \cdot [I_r/(I_a+I_r)]}{[I_a/(I_a+I_r)] + [I_r/(I_a+I_r)]}, \]

where \( D_{ave} \) is average crystallite size and \( D_a \) and \( D_r \) are crystallize size of anatase \( d(101) \) and rutile \( d(110) \), respectively. \( I_a \) and \( I_r \) are the peak intensity of anatase \( d(101) \) and rutile \( d(110) \), respectively. The ratio of anatase and rutile was determined by the equation 

\[ W_r = \frac{1}{[1+0.8 \cdot (I_a/I_r)]} \quad \text{and} \quad W_a = 1 - W_r, \]

where \( W_a \) and \( W_r \) are the mole ratio of anatase and rutile. The average crystallite size of NiO and NiTiO\textsubscript{3} were calculated by the Scherrer’s formula, 

\[ D = 0.9 \cdot \lambda / (\beta_{1/2} \cdot \cos \theta), \]

\( \lambda \) is the wavelength (0.15418 nm Cu K\textsubscript{α} radiation) of the X-ray, \( \beta_{1/2} \) line-width at medium height of anatase \( d(101) \), rutile \( d(110) \), NiO \( d(200) \) and NiTiO\textsubscript{3} \( d(104) \), and \( \theta \) the diffraction angle. For these calculation procedures, see Refs. [22-24].

\textsuperscript{b} Calcination temperature.
Fig. 3  XRD patterns (left) for NiOₓ-unloaded TiO₂ samples untreated (a) and calcined at 250 ºC (b), 450 ºC (c), and 650 ºC (d) and (right) for NiOₓ-unloaded (a) and loaded TiO₂ samples calcined at 250 ºC (b), 450 ºC (c), and 650 ºC (d)
Fig. 4  (a) UV/Vis spectra measured for NiO$_x$-unloaded (1) and loaded TiO$_2$ samples calcined at different temperatures of 250 °C (2), 450 °C (3), and 650 °C (4). (b) Plot of (Absorbance·Energy)$^{1/2}$ against Energy obtained from the data (a).
Fig. 5 XPS spectra of Ti 2p, O 1s, and Ni 2p for the NiOₓ-unloaded (a) and loaded TiO₂ samples calcined at 250 °C (b), 450 °C (c), and 650 °C (d)