Ni 담지 $CsLa_2Ti_2NbO_{10}$의 재산화시간에 따른 물분해 수소생산 영향에 관한 연구

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The influence of reoxidation time interval of Ni-loaded $CsLa_2Ti_2NbO_{10}$ on the photocatalytic hydrogen production by water decomposition reaction

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Introduction

Photocatalytic water splitting has been extensively studied from the viewpoint of photon energy conversion. It has been reported that some oxides show reasonable activities for splitting water into H_2 and O_2 in a stoichiometric ratio under UV irradiation.

Recently, it is reported that a family of ion-exchangeable layered perovksite with a general formula of $A_{2-x}La_2Ti_{3-x}Nb_xO_{10}$ with Ni loading shows the photocatalytic activity for water decomposition [1]. The loaded Ni on external surface of the catalyst played the active center of H_2 evolution in the ion-exchangeable layered perovskite as reported previously in $K_4Nb_6O_{17}$ [2]. From these results, the existence of Ni on the photocatalysts and the pretreatment of Ni such as reduction and reoxidation is necessary to enhance the H_2 evolution from water decomposition.

In our study, the influence of the reoxidation time interval of Ni-loaded $CsLa_2Ti_2NbO_{10}$ on photocatalytic activity was investigated. The relationship between the activities and the characteristics of Ni on the catalyst was elucidated. To determine the catalyst structure, UV-vis, XRD, TEM and TPR were carried out.

Experimental

Preparation of $CsLa_2Ti_2NbO_{10}$ layered perovskites

$CsLa_2Ti_2NbO_{10}$ was prepared by solid state reaction. Appropriate quantities of Cs_2CO_3, La_2O_3, TiO_2(anatase), Nb_2O_5 (Aldrich 99.99%) were mixed. Excess (25 mol%) of Cs_2CO_3 was added to compensate for the loss due to volatilization. La_2O_3 was pretreated at 1000 ^{o}C for 12 hrs before mixing. the mixture of precursors was pressed in the form of pellets. Pellets were heated at 1150 ^{o}C for 2 days in air followed by the grinding of pellets into powder below 50 μm. The products were washed with distilled water and dried at 100 ^{o}C. Ni was deposited on the oxide by impregnation of aqueous nickel (II) nitrate solution followed by drying and then calcined at 300 ^{o}C for 2 hrs. The loading of Ni metal was 1 wt%. The Ni-loaded oxides were pretreated in a closed gas circulation system. Each sample was reduced by H_2 (30 cm^3/min) at 500 ^{o}C for 2 hrs and then oxidized by air (30 cm^3/min) at 200 ^{o}C for 1 hr, 1.5 hrs, 2 hrs and 4 hrs.

Photocatalytic activity

Photocatalytic H_2 evolution from water was conducted in an inner irradiation quartz cell, which was connected to a closed circulation system using a high pressure Hg lamp (450W). 300 mg of the powder sample was suspended in distilled water (300 cm^3) in the cell by use of a magnetic stirrer. The reaction mixture was deaerated by flushing it with Ar gas before the reaction. The reaction was carried out by irradiating the mixture using an Hg lamp. Gas that evolved during irradiation was analyzed by an on-line gas chromatograph (DS6200, TCD, Ar carrier and MS-5A).

Temperature Programmed Reduction (TPR)

TPR was carried out in order to study the chemical nature of the oxidic Ni component according to the pretreatment condition. Each sample (200 mg) was first heated at 150 °C for 2 hrs in an He flow followed by cooling to room temperature. Then, the sample was heated in a 4 vol% H_2/Ar flow (30 cm^3/min) from 50 °C to 900 °C at 10 °C/min. Water produced during the reduction was removed with a cold trap consisting of ethanol and ice (down to -30 °C). The consumption of H_2 was measured with a thermal conductivity detector.

Characterization

The surface areas of the oxides were measured by the BET method using N_2 adsorption in a constant volume adsorption apparatus (ASAP2010, Micrometrics, USA). The distribution of a particle size was measured by Centrifugal particle size analyzer (SA-CP3, SHIMADZU). Before the measurement of particle size distribution, the oxide was dispersed in methanol and then treated in an ultrasonic bath for 10 min. The crystal structures of the oxides were determined by a powder X-ray diffractometer (XRD, Regaku D/MAX-III) with Cu-*K* radiation.

The transmission electron microscopy (TEM) was performed with a Model EM912 Omega manufactured by Carl Zeiss, Germany. The band gap energy was measured by UV/VIS/NIR spectrometer (V-570, JASCO)

Results and Discussion

Reaction of oxides and carbonates corresponding to the composition $CsLa_2Ti_2NbO_{10}$ in air at 1150 °C readily yields single-phase materials confirmed by XRD analysis. The peaks at $2\Theta = 5.751°$ and $23.129°$ could be assigned to (001) and (100) planes, respectively. The unit cell parameters of the A axis and C axis of $CsLa_2Ti_2NbO_{10}$ were 3.8423 Å and 15.3550 Å, respectively. The measured surface area of $CsLa_2Ti_2NbO_{10}$ is 1.8 m^2/g.

The diffuse reflectance spectra of the $CsLa_2Ti_2NbO_{10}$ and Ni/$CsLa_2Ti_2NbO_{10}$ treated under different conditions are compared in Fig. 1. The band gap of $CsLa_2Ti_2NbO_{10}$ was estimated to be about 3.4 eV from the onset of the absorption spectra (a).

Figure 2 showed the H_2 production rate. All catalysts produce H_2 and O_2 from the photodecomposition reaction of pure water. The maximum photocatalytic activity is obtained over 1 wt% Ni/$CsLa_2Ti_2NbO_{10}$ reoxidized for 2 hr. The photocatalytic activity was increased as the time course of reoxiation within 2 hrs. Reoxidation for 4 hrs decreased the photocatalytic hydrogen production which evolved the 38.9 mol/hrg-cat of hydrogen. It is observed that the activity of a 1 wt% Ni/$CsLa_2Ti_2NbO_{10}$ reoxidized for 2 hrs was 20 times higher than that of 1 wt% Ni/$CsLa_2Ti_2NbO_{10}$ reoxidized for 1 hr. The average hydrogen production rate of 1 wt% Ni/$CsLa_2Ti_2NbO_{10}$ reoxidized for 2 hrs was 212 mol/hrg-cat. For 1 wt% Ni/$CsLa_2Ti_2NbO_{10}$ reoxidized for 1 hr and 2 hrs, it is observed that hydrogen evolved at a constant rate of 11.7 mol/hrg-cat and 212 mol/hrg-cat, respectively. In case of reoxidation for 1.5 hrs, the highest production rate was obtained after irradiation for 3 hrs. After that, the activity gradually decreased and did not reach the constant production rate. In contrast with a case of reoxidation for 1.5 hrs, the hydrogen evolution rate increased but the differential slope decreased as increasing the irradiation time for the sampled reoxidized for 4 hrs.

Figure 3 shows the TEM photographs of 1 wt% Ni/$CsLa_2Ti_2NbO_{10}$ reoxidized for various times. Figure 3(a) is a micrograph of a sample reduced at 500 °C. Ni metal particles of 7-20 nm are observed. It should be noted that such Ni particles were not so homogeneously dispersed over $CsLa_2Ti_2NbO_{10}$ support. However, it is difficult to infer from a TEM photograph whether the Ni particles are located at the surface or between layers. When the reduced sample was reoxidized at 200 °C for 1 hr, the growth of particles was observed in Fig. 3(b). Ni particles of 10-40 nm were observed. Reoxidation for 2 hrs caused the reduction of particle size to about 10 nm and the Ni particles were hardly observed over the surface of support as shown in Fig. 3(c). the longer reoxidation time of 4 hrs made a marked change in the loaded nickel compared to the sample reoxidized for 2 hrs as shown in Fig. 3(c) and (d). Long reoxidation resulted in a decrease of photocatalytic activity of hydrogen evolution. Large particles of 30-50 nm, which can from aggregation of Ni particles is observed in the sample.

The TPR profiles of our samples are shown in Fig. 4. The 1 wt% $Ni/CsLa_2Ti_2NbO_{10}$ calcined at 300 °C shows two peaks with maxima at 340 °C and 580 °C. Most of H_2 consumption was observed between 450 °C and 700 °C. The consumption at 340 °C is attributed to the reduction of bulk NiO particles. The main reduction H_2 at 580 °C was reported in case of alumina supported Ni catalyst[3], which is arising from the reduction of dispersed nickel oxide. This two distinct reduction profiles indicate that poorly dispersed nickel oxide like bulk oxide and highly dispersed NiO exist together on the surface of $CsLa_2Ti_2NbO_{10}$ support. After reduction at 500 °C, no H_2 consumption was observed, indicative of full transformation of NiO species into Ni metal. After reoxidation at 200 °C for 1 hr, the peak with a maximum at near 380 °C was observed. The reduction temperature is lowered by about 200 °C compared with that of a sample calcined at 300 °C. This result shows that the reoxidized Ni phase differs very much in properties from the same sample calcined at 300 °C. After reoxidation for 1.5 hrs, the relative ratio of the two species in the sample changed. The intensity at higher temperatures increased. After reoxidation for 2 hrs, a relatively narrower peak was observed near 380 °C, indicative of the existence of homogeneous nickel species compared to previous ones. Since the initial point (300 °C) and final point (550 °C) of three peaks (curve c, d and e) were similar to each other, it could be concluded that the nickel species were almost similar. Unlike previous results, the sample reoxidized for 4 hrs shows a very different consumption profile. The TPR profile of a sample reoxidized for 4 hrs displays a broad consumption between 290 °C and 620 °C. From this profile, it is suggested that various nickel species might exist but the clear distinction of nickel species could not be explained yet.

Conclusions

The reduction followed by reoxidation treatment of $Ni/CsLa_2Ti_2NbO_{10}$ should be necessary because of its lower conduction potential over that of NiO. Reoxidized samples showed the photocatalytic activities for H_2 evolution. The maximum photocatalytic activity was observed when reoxidized for 2 hrs. With the increase in the reoxidation time interval, the Ni species became the homogeneous dispersion of NiO on Ni metal. However, the formation of the NiO phase and the growth of a particles size was observed after reoxidation for 4 hrs, resulting in the drastic decrease of photocatalytic activity. Therefore, photocatalytic decomposition of water was dependent on the reoxidation time interval, which affected the particle size of the Ni species and the distribution of Ni/NiO.

References

1. Takata, T., Furumi, Y., Shinohara, K., Tanaka, A., Hara, M., Kondo, J.N. and Domen, K.: *Chem. Mater.,* **9**, 1063(1997).
2. Kudo, A., Satama, K., Tanaka, A., Askura, K., Domen, K., Maruya, K. and Onishi, T.: *J. Catal.*, **120**, 337(1989).
3. Molina, R. and Poncelet, G.: *J. Catal.*, **173**, 257(1998).

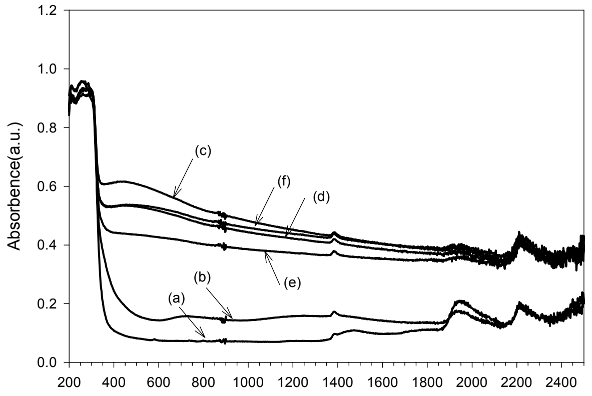

Fig. 1. UV-vis absorption spectra
(a) $CsLa_2Ti_2NbO_{10}$ as prepared
(b) 1 wt% $Ni/CsLa_2Ti_2NbO_{10}$ calcined at 300 °C and then (c) reduced at 500 °C for 2 hrs followed by oxidation at 200 °C for (d) 1hr (e) 2 hrs and (f) 4 hrs.

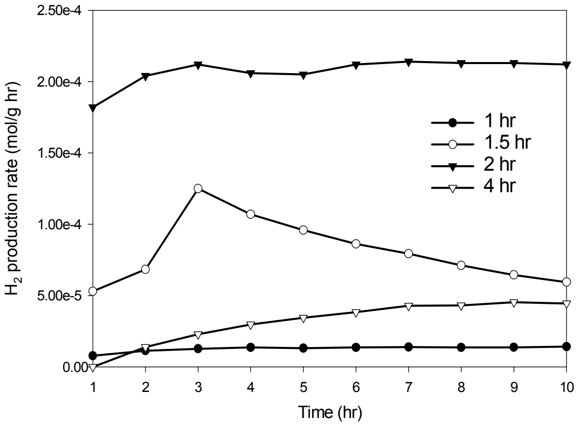

Fig. 2. H_2 production rate (mol/g hr) after reduction at 500 °C for 2hr followed by oxidation at 200 °C for different time intervals

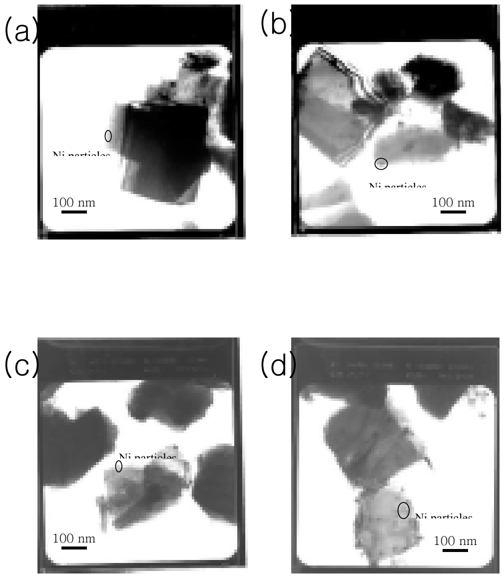

Fig. 3. TEM micrographs(x100,000magnitude) of (a) 1 wt% $Ni/CsLa_2Ti_2NbO_{10}$ reduced at 500 °C followed by reoxidation at 200 °C for (b) 1hr (c) 2 hrs and (d) 4 hrs.

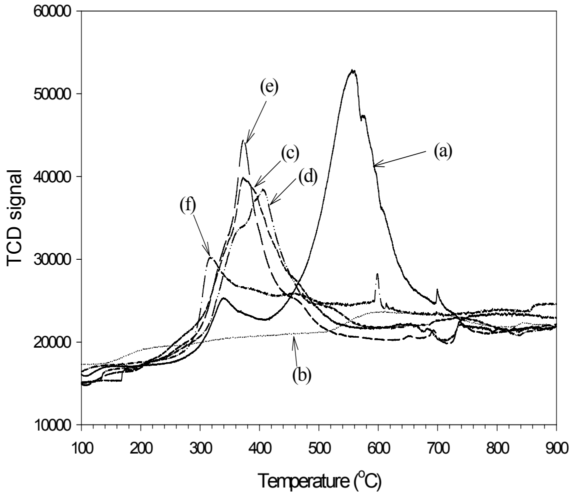

Fig. 4. TPR profiles of (a) 1 wt% $Ni/CsLa_2Ti_2NbO_{10}$ calcined at 300 °C and then (b) reduced at 500 °C for 2 hrs followed by reoxidation at 200 °C for (c) 1hr (d) 1.5 hrs (e) 2 hrs and (f) 4 hrs.