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Effect of Surface Modification with Layered Double Hydroxide on Reduction of Nitrate to Nitrogen over $BaLa_4Ti_4O_{15}$ Photocatalyst

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$BaLa_4Ti_4O_{15}$ photocatalyst, one of the most active UV light responsive photocatalyst for water splitting, was modified with MgAl–LDH (layered double hydroxide) of an anion adsorbent to improve photocatalytic activity for reduction of nitrate to nitrogen. The activity of the $Ni/BaLa_4Ti_4O_{15}$ photocatalyst was significantly improved by this surface modification with MgAl–LDH deposited by homogeneous precipitation using urea hydrolysis.

Recently, reductive decomposition of nitrate with H_2 has been studied on the basis of bimetallic catalysts of precious and base metals,[1] for example, Pd–Cu catalyst supported on activated carbon.[2,3] These hydrogenation catalysts have also been investigated by using hydrotalcite as a support.[4–6] Hydrotalcite was found to be effective to keep nitrite near active sites due to its anion adsorption properties.[5,7] However, these catalysts can work only using hydrogen gas for the reductive nitrate decomposition, which consumes fossil fuels and energy. From this point of view, photocatalytic processes have recently been expected to be a new water treatment method,[8] that enables the use of light as energy and water as a reducing reagent. Some metal oxide photocatalysts (i.e., TiO_2, $Ba_5Nb_4O_{15}$, $SrTiO_3$, $K_3Ta_3B_2O_{12}$, $NaTaO_3$, $KTaO_3$, and $BaLa_4Ti_4O_{15}$)[9–12] have been developed to reduce nitrate to nitrite and then to nitrogen gas without any sacrificial reagents. Among them, $BaLa_4Ti_4O_{15}$ photocatalyst with layered perovskite structure shows high activity for water splitting and reduction of nitrate to nitrogen.[9] The affinity between $BaLa_4Ti_4O_{15}$ and LDH should be good because of the opposite surface charges of these materials in a neutral medium. It is expected that the photocatalytic activity of the reduction of nitrate to nitrogen is improved by the surface modification with MgAl–LDH to enhance adsorption of nitrate and nitrite ions.

In the present study, effect of surface modification with LDH on reduction of nitrate to nitrogen over $BaLa_4Ti_4O_{15}$ photocatalyst was examined without any sacrificial reagents.

$BaLa_4Ti_4O_{15}$ photocatalyst (BLT) was prepared by a polymerizable complex method.[13] It was then modified with MgAl–LDH by urea homogeneous precipitation.[14] 120 mL of deionized water, $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ (Wako, purity: 99.0%, 98.0%, respectively; $Mg^{2+} + Al^{3+} = 2.0$ mmol), and urea (Wako, purity: 99.0%; urea/($Mg^{2+} + Al^{3+}$) ratio in mol = 100) were added into a beaker and stirred at 298 K. The BLT (0.7 g) was added and dispersed by using ultrasound around pH 3.5. The suspension was stirred at 363 K for 5 h. The pH increased to about 8.5 by hydrolysis of urea resulting in precipitation of LDH. The resulting powder consisting of BLT and MgAl–LDH was recovered by filtration, washed with deionized water, and dried. Ni cocatalyst (0.5 wt %) was loaded by impregnation using an aqueous solution of $Ni(NO_3)_2$. The impregnated powder was calcined in air at 543 K for 1 h and reduced under hydrogen at 773 K for 2 h. The obtained powder was characterized by powder X-ray diffraction (Rigaku; RINT2500), UV–visible diffuse reflectance spectroscopy (Jasco; UbestV-570), SEM-EDX (Jeol; JSM-6700), and elemental analysis by ICP (SII; SPS3100). Photocatalytic reactions were carried out in a closed gas circulation system with a vacuum line. 0.5 g of photocatalyst was dispersed in an aqueous solution (350 mL) of 10 mmol L^{-1} $NaNO_3$ and 10 mmol L^{-1} H_3BO_3 as a buffer for pH control.[9] The suspension was stirred in a quartz reaction cell under irradiation with a 400-W high-pressure mercury lamp (USHIO). Amounts of evolved gases were determined by gas chromatography (Shimadzu; MS-5A column, Ar carrier), and remaining nitrate ions and reaction products in the aqueous solution were measured by ion chromatograpy (TOA DKK; ICA-2000).

The LDH was identified by ICP elementary analyses and SEM-EDX. The ratio of Mg^{2+} to Al^{3+} of the LDH in the prepared photocatalyst was 1.8 when that in the starting material was 9. Thin plate-like crystals of LDH were observed with a dimension of about 1 µm, in contact with BLT crystal particles as shown in Figure 1. SEM-EDX analysis revealed that Ni cocatalyst was loaded preferentially on BLT rather than LDH. DRS measurement showed that the surface modification with LDH did not change the absorption edge wavelength, indicating that the band gap (3.8 eV) of the bulk property did not change (Figure S1[16]).

Figures 2 and S2[16] show X-ray diffraction patterns of Ni (0.5 wt %)/LDH (12 wt %)/BLT photocatalyst before and after photocatalytic reaction. The peaks corresponding to LDH

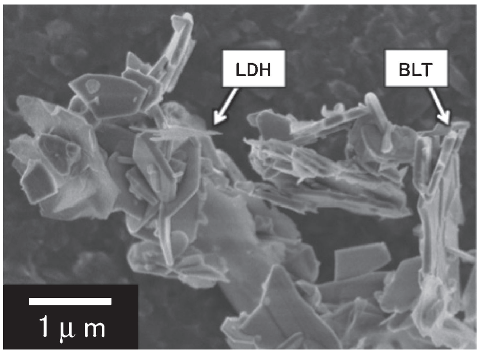

Figure 1. SEM image of Ni/LDH/BLT photocatalyst.

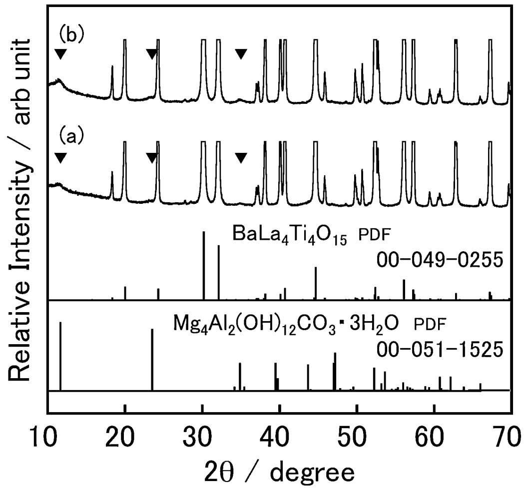

Figure 2. X-ray diffraction patterns of Ni/LDH/BLT photocatalyst (a) before and (b) after photocatalytic reaction. ▼ indicates LDH pattern.

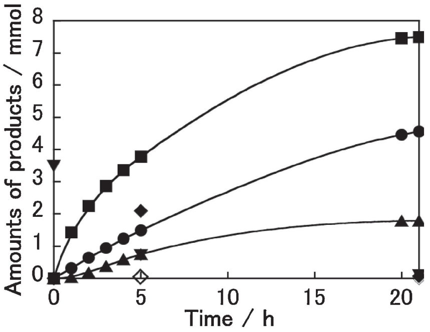

Figure 3. Reduction of nitrate over Ni/LDH/BLT photocatalysts in an aqueous medium. ■: O_2, ●: H_2, ▲: N_2, ◆: NO_2^-, ◇: NH_4^+, ▼: NO_3^-.

Table 1. Effect of starting Mg^{2+}/Al^{3+} ratio of LDH supported on BLT photocatalyst on reduction of nitrate[a]

Photo catalyst	LDH /wt %	Mg^{2+}/Al^{3+} ratio	NO_3^- (21 h) /µmol	Amounts of products (21 h) /µmol				
				H_2	O_2	N_2	NO_2^-	NH_4^+
Ni/BLT	0	—	440	270	3270	810	1630	0
Ni/LDH/BLT	12	3	50	1590	5950	1720	20	50
Ni/LDH/BLT	9	9	90	4560	7490	1790	70	10
LDH/BLT	11	3	580	0	1640	0	2790	0
none	0	—	520	0	1470	0	2930	0

[a] Catalyst: 0.5 g, cocatalyst: Ni (0.5 wt %), solution: 10 mM $NaNO_3$, 10 mM H_3BO_3 (350 mL), inner irradiation cell made of quartz, 400-W high-pressure mercury lamp.

slightly increased after the photocatalytic reaction, suggesting that the LDH structure was reconstructed in the aqueous solution during the reaction. It indicates that the LDH structure can be maintained even after thermal treatments up to 773 K for the photocatalyst preparation as reported by Miyata.[15]

Figure 3 and Table 1 show products of nitrate reduction on Ni/LDH/BLT photocatalysts in comparison with those on Ni/BLT, LDH/BLT, and without photocatalyst. The LDHs were prepared with 3 and 9 of the Mg^{2+}/Al^{3+} ratios. It was demonstrated that the addition of LDH on photocatalyst surface resulted in improvement of NO_3^- conversion to N_2, accompanied by a decrease in NO_2^- and an increase in H_2 evolution. The higher Mg^{2+}/Al^{3+} ratio (= 9) in the starting material resulted in a significant increase in the H_2 evolution. The photocatalytic reaction did not proceed without Ni cocatalyst. NO_2^- and O_2 were produced not only by photocatalytic reaction but also by photochemical decomposition.[12] The e^-/h^+ and the mass balance values calculated from the data in Table 1 were close to 1 within the allowable experimental error. The N_2 yield reached almost 100%. It can be supposed that the adsorption of produced NO_2^- on LDH promotes further reduction to nitrogen by concentrating NO_x^- ions near the photocatalyst surface. Moreover, it should be noted that the modification with LDH enhanced H_2 evolution compared with unmodified Ni/BLT photocatalyst. This phenomenon was considered to be due to the promoting of water splitting by surface LDH as shown in Table S1.[16]

In conclusion, the modification of BLT photocatalyst with MgAl–LDH enhanced reductive decomposition of nitrate into N_2 and also water splitting. It will be due to formation of active hydrogen generation sites on the catalyst surface. This surface modification method will also be applicable for other photocatalysts.

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16 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.