



Synthesis and highly efficient photocatalytic activity of mixed oxides derived from ZnNiAl layered double hydroxides



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Received 21 September 2015; accepted 13 January 2016

Abstract: ZnO/NiO/ZnAl₂O₄ mixed-metal oxides were successfully synthesized through a hydrotalcite-like precursor route, in which appropriate amounts of metal salts solutions were mixed to obtain a new series of ZnNiAl layered double hydroxides (LDHs) as precursors, followed by calcination under different temperatures. The as-obtained samples were characterized by SEM, HRTEM, TEM, XRD, BET, TG-DTA, and UV-Vis spectra techniques. The photocatalytic activities of the samples were evaluated by degradation of methyl orange (MO) under the simulated sunlight irradiation. The effects of Zn/Ni/Al mole ratio and calcination temperature on the composition, morphology and photocatalytic activity of the samples were investigated in detail. The results indicated that compared with ZnNiAl-LDHs, the mixed-metal oxide showed superior photocatalytic performance for the degradation of MO. A maximum of 97.3% photocatalytic decoloration rate within 60 min was achieved from the LDH with the Zn/Ni/Al mole ratio of 2:1:1 and the calcination temperature of 500 °C, which much exceeded that of Degussa P25 under the same conditions. The possible mechanism of photocatalytic degradation over ZnO/NiO/ZnAl₂O₄ was discussed.

Key words: ZnNiAl layered double hydroxide; mixed oxide; photocatalytic degradation; photocatalytic activity

1 Introduction

For environmental remediation and pollution control, the effective removal of cationic dyes from the textile industry has always been a challenging issue. With the rapid development of nanostructured semiconductors for efficient harvesting abundant solar light, photocatalysis has received extensive attention for the removal of organic dyestuffs [1,2]. In particular, the mixed metal oxides prepared by thermal treatment of layered double hydroxides (LDHs), acted as photocatalysts, have been the focus of attention due to their versatility of chemical composition and high dispersion [3–5]. Different metals and proportion in LDHs can be controlled, which could tune the semiconductor properties of the layered-structure LDH materials and facilitate the transfer of the photogenerated electrons to the surface of photocatalysts, and this might

provide great potential for their application in dye degradation [6,7]. ZHAO et al [8] have recently conducted studies on the thermal treatment of ZnAl-LDH at 800 °C with different Zn²⁺/Al³⁺ mole ratios, which showed an enhanced photocatalytic activity with an increase in the mole ratio. CARRIAZO et al [9] also reported that the photocatalytic activity and crystallinity of the metal oxide produced from Zn–Al–CO₃–LDH are improved with proper control of calcination temperature and Zn²⁺/Al³⁺ mole ratio. Furthermore, there are reports on the introduction of In [10,11] and Ce [12] integrated on LDH materials as efficient photocatalysts. However, to the best of our knowledge, the use of earth-abundant metals such as Ni and Cu for the generation of LDH precursors is rare, especially for the degradation of MO. It is of great significance to employ the cheap metals for the synthesis of high-performance photocatalysts. On the other hand, although it is known that the replacement of M²⁺ by a higher-valence metal ion of similar radius is

Foundation item: Project (21306041) supported by the National Natural Science Young Foundation of China; Project (21271071) supported by the National Natural Science Foundation of China; Project (15A076) supported by the Scientific Research Foundation of Hunan Provincial Education Department of China

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DOI: 10.1016/S1003-6326(16)64360-1

beneficial for the improvement of photocatalytic properties of LDHs [13–15], it has been scarcely reported about the partial substitution of M^{2+} by another type of M^{2+} .

In this work, we synthesized a series of ZnO/NiO/ZnAl₂O₄ mixed-metal oxides with large specific area and studied their physicochemical properties. Especially, the incorporation of Ni²⁺ cation contributes to the enhanced photocatalytic activities for the degradation of high-concentration MO compared with ZnAl-LDHs under simulated sunlight irradiation. Besides providing new highly efficient sun-light-induced photocatalysts, the present work has further implications to photocatalytic degradation of organic pollutants.

2 Experimental

2.1 Synthesis of precursor

We followed the synthetic procedure described by ZHAO et al [8]. Typically, keeping the total concentration of metal ions fixed at 1.0 mol/L, Zn(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O with different Zn²⁺/Ni²⁺/Al³⁺ mole ratios were dissolved in deionized water to form a clear solution at room temperature. NaOH and Na₂CO₃ were mixed in deionized water to form an alkali solution ($[OH^-] = 1.6[Zn^{2+}] + [Ni^{2+}] + [Al^{3+}]$ and $[CO_3^{2-}] = 2.0[Al^{3+}]$), which was subsequently added drop-wise into the above salt solution under vigorous stirring at room temperature. The pH value of the solution was adjusted to 8–9. The mixture was transferred into a teflon-lined autoclave and thermally treated at 150 °C for 10 h, and then filtered and washed with distilled water until pH=7. The solid was oven-dried at 60 °C overnight to obtain ZnNiAl-LDHs precursors with different Zn²⁺/Ni²⁺/Al³⁺ mole ratios (i.e., 1:1:1, 2:1:1, 3:1:1, 1:2:1, 1:3:1, 2:1:1, 3:1:1). The one with Zn²⁺/Ni²⁺/Al³⁺ mole ratio of 2:1:1 is specifically denoted herein as ZNA-2-LDH.

2.2 Synthesis of mixed-metal oxides

The precursors were calcined in air at 400, 500, 600, 700, and 800 °C for 4 h, respectively, and allowed to cool down to room temperature. These obtained mixed-metal oxides with the Zn/Ni/Al mole ratio of 2:1:1 were denoted as ZNA-2-400, ZNA-2-500, ZNA-2-600, ZNA-2-700 and ZNA-2-800, respectively, where the first number refers to the mole ratio of Zn²⁺/Ni²⁺/Al³⁺ and the second number refers to the calcination temperature. In comparison, the ZnAl-LDH with mole ratio of Zn²⁺/Al³⁺ being 3:1 was prepared in the similar way without Ni addition.

2.3 Characterization

The crystal phase and size of samples were

identified by powder X-ray diffraction (XRD, Bruker D8) using Cu K_α radiation ($\lambda=1.5418 \text{ \AA}$) at a scan speed of 0.05 (°)/s, a voltage of 40 kV, and a current of 300 mA. The surface morphologies of samples were observed by scanning electron microscopy (SEM, Nova Nano 230) operated at 30 kV and transmission electron microscopy (TEM, JEOL JEM-2010) operated at 200 kV. UV-Vis diffused reflectance spectra (DRS) of the samples were obtained using a UV-Vis spectro photometer (UV-2550, Shimadzu, Japan). Brunauer-Emmett-Teller (BET) surface areas were determined over the nitrogen adsorption isotherms apparatus (ST-08 analyzer), and all samples were degassed at 200 °C overnight before measurements.

2.4 Photocatalytic activity evaluation

The photocatalytic activity of the samples was evaluated by degradation of MO (100 mg/L solution). A 150 W xenon lamp with $\lambda=200-900 \text{ nm}$ was used as the simulated sunlight source. For each run, 0.3 g of catalyst was added into 600 mL MO solution and stirred for 30 min in the dark to establish an adsorption/desorption equilibrium. Then, the solution was exposed to simulated sunlight for photocatalytic reaction. The luminous intensity was measured at 100 mW/m² by the auto-range ST-85 optical radiometer (Photoelectric Instrument Factory of Beijing Normal University, China). During irradiation, the catalyst was kept in suspension state by a magnetic stirrer. Samples for analysis were extracted through pipette every 10 min and centrifuged immediately. Using a 752 UV-Vis spectrophotometer at the maximum absorption wavelength of $\lambda_{\text{max}}=465 \text{ nm}$ of MO, the absorbance of the suspension and initial solution was determined, respectively. Decoloration rates are presented as c/c_0 , where c_0 and c are the initial concentration of MO at adsorption/desorption equilibrium and the concentration of MO at a specified irradiation time, respectively. Blank experiments, i.e., without catalyst or in the dark, were carried out under the same condition. Each set of measurements was repeated three times, and the experimental error was within $\pm 5\%$.

3 Results and discussion

3.1 Characterization

As shown in Fig. 1, almost the same typical structures are observed in the XRD patterns of ZnAl-LDH ($n(\text{Zn}^{2+})/n(\text{Al}^{3+})=3:1$) and ZnNiAl-LDH ($n(\text{Zn}^{2+})/n(\text{Ni}^{2+})/n(\text{Al}^{3+})=2:1:1$) precursors. The diffraction peaks at $2\theta=11.7^\circ$, 23.5° , 34.6° , 39.2° , 46.7° , 52.9° , 56.3° , 60.2° and 61.5° can be assigned to (003), (006), (009), (015), (018), (1010), (0111), (110) and (113) reflections of LDH, respectively, characteristic of a layered structure [16,17]. Besides, the reflections at $2\theta=32^\circ$ and

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