Influence of pH tuning at the precursor-preparation process on the structural characteristics and catalytic performance of hydrothermally synthesized ZnAl$_2$O$_4$ nanoparticles

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1. Introduction

Zinc aluminate (ZnAl$_2$O$_4$) is a stable material with a wide bandgap, and extensive research has been conducted regarding its use in photocatalysis [1,2] and as an ultraviolet laser source [1,3–7]. In particular, nanoscale ZnAl$_2$O$_4$ can potentially catalyze the degradation of NO$_x$ species [8] and dyes [1,2], as well as the steam reforming of ethanol [9,10]. For these applications, establishing a suitable chemical synthesis process is an important issue from an industrial viewpoint. A common problem in the chemical synthesis of ZnAl$_2$O$_4$ nanoparticles is the generation of ZnO as an impurity. Even in samples judged to be single-phase based on X-ray diffraction (XRD), absorption peaks due to ZnO are frequently observed in the ultraviolet-visible (UV-Vis) spectra of such products. However, we recently succeeded in fabricating high-purity ZnAl$_2$O$_4$ nanoparticles by hydrothermal synthesis [11], where the key aspect of this synthesis was controlling the pH of the source solution during precursor preparation. This technique enables us to easily synthesize pure ZnAl$_2$O$_4$ nanoparticles. However, the lattice constants of our ZnAl$_2$O$_4$ nanoparticles are obviously larger than those of samples sintered by typical solid-state reactions. This difference in lattice constants is attributed to the site exchange phenomenon in the crystals as we have previously verified [11]. The crystal structure of ZnAl$_2$O$_4$ is a normal spinel structure, in which the Zn$^{2+}$ and Al$^{3+}$ cations form tetrahedral and octahedral structures with coordinated O$^{2-}$ anions, respectively. This site-exchange phenomenon refers to the cation substitution between these Zn$^{2+}$ and Al$^{3+}$ hydroxides in the source solution change at pH 9. Additionally, we compared the catalytic performance with regards to the decomposition of methylene blue for the nanoparticles made from source solution with pH 7 (NP7) and 10.5 (NP10.5). The smaller-sized NP7 did not show any catalytic performance; whereas, the larger NP10.5 accelerated the decomposition of methylene blue. The critical difference between NP7 and NP10.5 is the Zn$^{2+}$ deficiency, rather than the particle size. This result is important for future investigations in order to improve the catalytic properties of ZnAl$_2$O$_4$ nanoparticles.
from finely pH-controlled source solutions (pH = 7–10.5) and verified the structural characteristics of the products. Moreover, the catalytic performances were checked for some of these obtained ZnAl$_2$O$_4$ nanoparticles.

2. Materials and methods

Zinc aluminate nanoparticles were synthesized by a hydrothermal reaction based on the two-liquid route described in our previous study [11]. Briefly, Al(NO$_3$)$_3$·9H$_2$O (0.066 M) and Zn(NO$_3$)$_2$·6H$_2$O (0.333 M) were dissolved separately in 100 mL of deionized water, and an appropriate amount of NaOH was added to these solutions and stirred for 1 h. The two solutions were then mixed and stirred for 2 h, and the pH of the solution was adjusted by adding nitric acid. In this study, the pH value of this source solution was systematically controlled to be 7, 8, 8.5, 9, 9.5, 10, and 10.5. The pH-controlled source solutions were centrifuged, and the precursor powder was obtained by drying the precipitate under vacuum at 70°C. Hydrothermal synthesis was conducted by heating the aqueous precursor solution loaded in a 100 mL polytetrafluoroethylene (PTFE) container inside a stainless steel pressure vessel. The inner pressure of the container was controlled to be 10 MPa at 200°C, and the synthesis was performed for 10 h. After the hydrothermal reaction, the materials within the PTFE container were centrifuged, and the nanoparticles were extracted by drying the precipitate under vacuum at 70°C. The obtained nanoparticles were examined by powder XRD using an RINT-2200H spectrometer (Rigaku) with Cu Kα ($\lambda$ = 1.542 Å) radiation to elucidate their phase contents, lattice parameters and crystallite sizes via the Scherrer equation [12]. In addition, the amount of ZnO impurity phase was verified based on UV-Vis absorption spectra. UV-Vis reflectance spectra were measured with a V570DS spectrometer (JASCO) and converted into absorption spectra using the Kubelka-Munk equation [13]. Compositional analysis was performed on the fabricated nanoparticles using energy-dispersive X-ray (EDX) analysis with a JSM-6010 PLUS/LA instrument (JEOL). The morphology and particle sizes of the nanoparticles were also observed by transmission electron microscopy (TEM) with an accelerating voltage of 200 kV on a JEM-2100 instrument (JEOL). The catalytic performance was determined for characteristic ZnAl$_2$O$_4$ nanoparticles synthesized in this study from precursor source solutions of pH 7 and 10.5, using the ZnAl$_2$O$_4$ powder sintered via solid-state reaction as a reference. For this, 0.1 g of each powder sample was put separately into 20 mL of methylene blue solution (2.65 × 10^{-6} M). These methylene blue solutions were then exposed to sunlight, along with a solution without nanoparticles. UV-Vis measurements were carried out for these solutions before and after 1, 3, 5, and 10 h of sunlight exposure, and the time dependence of the methylene blue signals is discussed.

This manuscript denotes the ZnAl$_2$O$_4$ samples as NP$_X$, where $X$ indicates the pH value of the source solution used. For instance, NP7 denotes the sample made from pH-controlled source solutions of pH = 7. In addition, the sintered polycrystalline powder reference is denoted as SP.

3. Results and discussion

ZnAl$_2$O$_4$ nanoparticles were successfully synthesized using a hydrothermal reaction with precursors made from pH-controlled source solutions. Figure 1 shows the XRD patterns of these samples from source solutions of different pH values and of the sintered reference powder. According to the XRD patterns, all samples were single-phase spinel oxides. Our previous study indicated that a peak shift related to lattice expansion was observed for the hydrothermal samples relative to the reference signal [11]. This difference indicates that site exchange between Zn$^{2+}$ and Al$^{3+}$ ions is promoted by the hydrothermal process. The lattice constants of the samples shown in Figure 1 were plotted against the pH values of their respective pH-controlled solutions, as shown in Figure 2. Although the pH dependence of the lattice constant could not be seen for the hydrothermally-synthesized samples, these samples had larger lattice...
constants than the reference sintered sample. These trends match well with those in our previous report [11]. We also observed a new trend for the full-width at half maximum (FWHM) of the XRD peaks in Figure 1. A prominent difference in the FWHM of the XRD peaks was observed between the samples made from high pH source solutions (NP9.5, NP10, and NP10.5) and those made from low pH solutions (NP7, NP8, NP8.5, and NP9).

Figure 3 shows the crystallite size calculated from the FWHM of the XRD peaks for these samples. The average crystallite size is approximately 13 nm for samples made from lower pH source solutions (pH < 9). This is apparently smaller than the average size for samples made from higher pH source solutions (40 nm). Figure 4 shows the TEM images for NP7 (a,b), NP10.5 (c,d), and SP (e). Nanocrystals are clearly observed for NP7 and NP10.5, even though they tend to agglomerate on the dried microgrids during TEM observation. On the other hand, Figure 4(e) shows irregularly shaped polycrystals.

Moreover, the average crystalline size of NP7 appears to be smaller than 20 nm, and that of NP10.5 appears to be larger than 20 nm. These trends are consistent with the result shown in Figure 3. We
speculated from these results that there is some inflection point between samples made from higher- and lower-pH source solutions, and that this point exists around pH = 9–9.5. The UV-Vis spectra for the samples are shown in Figure 5. The NP9 and NP9.5 signals are more intense than those of the other samples. Only the NP9 shows a clear shoulder at approximately 350 nm, which may be attributed to ZnO. These data also show abnormalities in the NP9 and NP9.5 samples. Additionally, there were differences in the absorption edge between nanoparticles made from higher- and lower-pH source solutions. The nanoparticles made from higher-pH source solutions show a similar absorption edge to that of SP. However, the absorption edges of the nanoparticles made from lower-pH source solutions are red-shifted, implying that their bandgaps are narrower than that of the sintered sample. This indicates that there are differences in the formation of ZnAl$_2$O$_4$ in precursors made using higher- and lower-pH source solutions, and that the cutoff pH value is 9–9.5.

In order to clarify these differences, the Zn/Al composition ratio was evaluated for all samples.

Figure 6 shows the Zn/Al ratios as determined from EDX spectral intensities. This study observed the Zn/Al ratio numerous times in order to exclude the influence of measurement deviations from this discussion. In addition, the Zn/Al ratio of the sintered sample was previously confirmed to be 0.5 based on inductively coupled plasma mass spectrometry (ICP-MS) [14,15]. Thus, the dashed line in Figure 6 is the value calibrated for the stoichiometric composition of ZnAl$_2$O$_4$. Variations in the Zn/Al ratio from this stoichiometric value can be clearly seen for the samples made from low-pH source solutions; such variations indicate aluminum-rich or zinc-poor compositions. However, the structural characteristics and charge neutrality of ZnAl$_2$O$_4$ tolerate neither aluminum-rich nor oxygen-rich conditions, such as ZnAl$_{2+x}$O$_{4+3x/2}$. Hence, the decrease in the Zn/Al ratio observed for the low-pH samples indicates a zinc deficiency, i.e., Zn$_{1-x}$Al$_2$O$_4$. This may be related to the appearance of trace ZnO impurities for these samples, as previously shown in Figure 5. Considering the preparation process of the pH-controlled source solutions in this study, the chemical equilibrium of the possible precipitates, such as zinc–aluminum layered double hydroxide [Zn$_{1-x}$Al$_x$(OH)$_2$(NO$_3$)$_x$], aluminum oxyhydroxide [AlO(OH)], and zinc hydroxide [Zn(OH)$_2$], should change at very low pH conditions. Under such conditions, the amount of Zn$^{2+}$ in solution is considered to be higher than that of Al$^{3+}$, because the solubility product of Zn$^{2+}$ is much larger than that of Al$^{3+}$ [16]. Thus, the overall composition of the precipitate seems to become aluminum-rich rather than stoichiometric after centrifugation. Accordingly, the low pH source solution tends to yield an aluminum-rich precursor, and the hydrothermal synthesis using it produces Zn$_{1-x}$Al$_2$O$_4$ with $x \neq 0$. Based on the above results, three categories of ZnAl$_2$O$_4$ samples emerge: hydrothermally-synthesized nanoparticles made from pH-controlled source solutions at pH = 7 (Zn-deficient nanoparticles with high site exchange: NP7) and at 10.5 (stoichiometric nanoparticles with high site exchange: NP10.5), and sintered polycrystalline powder (stoichiometric particles with low site exchange: SP).

As part of this study, we compared the catalytic properties of these ZnAl$_2$O$_4$ nanoparticles [14,15]. Figure 7 shows the typical UV-Vis spectra of methylene blue solution measured after exposure to sunlight. The UV-Vis spectra in Figure 7(a) correspond to the solution without ZnAl$_2$O$_4$ nanoparticles as reference data; whereas, Figure 7(b) shows data for ZnAl$_2$O$_4$ nanoparticles (NP10.5). Initially, the spectra are nearly identical as those just after addition (0 h), and then both methylene blue solutions are degraded by sunlight radiation over time. Once photodegradation began however, the catalytic effect
of NP10.5 was clearly observed in the spectra shown in Figure 7(b).

The intensities of the absorption peaks for all samples are plotted against time in Figure 8, where the intensities are normalized against those before addition of the ZnAl$_2$O$_4$ samples. From these data, the catalytic effect could be observed for NP10.5 and SP, but we could not identify such an effect for NP7. The decomposition rate of methylene blue with NP7 was comparable to that of the reference data without ZnAl$_2$O$_4$, even though NP7 had a positive factor originating from its larger specific surface area (due to its smaller crystallite size). Some negative factors can be considered present in the catalytic properties of our ZnAl$_2$O$_4$ samples, namely, the higher site exchange of NP7 and NP10.5, smaller specific surface of SP and NP10.5, and the nonstoichiometric Zn$^{2+}$ deficiency of NP7. However, NP10.5 has the highest catalytic performance in our study; thus, Zn$^{2+}$ deficiency is substantially the key factor for the catalytic properties of ZnAl$_2$O$_4$, rather than site exchange and specific surface area. Zn$^{2+}$ deficiency should change the bandgap of ZnAl$_2$O$_4$, and can be identified by UV-Vis (Figure 5); here, the bandgaps of NP10.5 and SP are nearly identical. As such, deactivation in the catalytic performance of NP7 is considered to correlate with the red-shift of the bandgap due to Zn$^{2+}$ deficiency. Additionally, the NP7 particles are expected to have a similar structure to γ-Al$_2$O$_3$, which has a porous structure [17], because both particles can be regarded as spinel aluminates with high zinc deficiency. In this case, the adsorption ability of NP7 for organic materials is thought to be higher than those of NP10.5 and SP. From these results, we conclude that the higher Zn$^{2+}$ deficiency and adsorption ability degrade the catalytic performance of NP7 ZnAl$_2$O$_4$; whereas, NP10.5 and SP retain their catalytic properties in the absence of these negative factors.

4. Conclusions

We fabricated ZnAl$_2$O$_4$ nanoparticles by hydrothermal synthesis, using precursor materials made from pH-controlled source solutions. The produced ZnAl$_2$O$_4$ nanoparticles showed obvious structural differences based on the pH values of their respective source solutions, and the dividing line between these different structures exists at pH = 9–9.5. The particle size of ZnAl$_2$O$_4$ made from solutions of pH > 9 was clearly greater than for the nanoparticle made from solutions at pH ≤ 9; the latter also contained zinc deficiency. These structural characteristics directly influence the bandgap, and thereby the catalytic properties of ZnAl$_2$O$_4$ for the decomposition of methylene blue. Thus, catalytic behavior was observed for NP10.5 and SP, but not for NP7. The higher site exchange, smaller specific surface area, and greater Zn$^{2+}$ deficiency can be considered negative factors for the catalytic performance of our ZnAl$_2$O$_4$ samples. Our experimental results reveal that Zn$^{2+}$ deficiency is the most influential factor among them. Therefore, future investigations for improving the
catalytic properties of ZnAl$_2$O$_4$ should pay considerable attention to controlling the stoichiometric composition, rather than focusing on nanoparticulation or inhibiting the site exchange. This is important not only for hydrothermal synthesis, but also for all chemical approaches to the fabrication of ZnAl$_2$O$_4$ nanoparticles with an end goal of catalysis application.

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Disclosure statement

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