



Simple preparation method for Mg–Al hydrotalcites as base catalysts



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ABSTRACT

In this paper, we report a very simple preparation method for Mg–Al hydrotalcites (HTs) as base catalysts via the hydration of their corresponding metal oxides (MgO and Al₂O₃) without any particular controlled variables. We also propose a reasonable explanation for a series of reaction pathways in which Mg–Al HTs are formed from their metal oxides. The Mg–Al HTs were formed by the reaction of Mg²⁺ and Al(OH)₄[−], which resulted from the hydration of both metal oxides. The prepared Mg–Al HTs retained their unique properties, including their layered hydroxide structure and memory effect and showed considerable catalytic activity in the isomerization of glucose to fructose. Consequently, this simple hydration of both metal oxides successfully synthesized Mg–Al HTs, which can be used as base catalysts or as catalyst precursors for calcined HTs in various base-catalyzed reactions.

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1. Introduction

Hydrotalcites (HTs) are well-known layered double hydroxides (LDH) that have the general formula [M²⁺_{1-x}M³⁺_x(OH)₂][A^{n−}_{x/n}·mH₂O], where M²⁺ and M³⁺ represents metal components with divalent and trivalent cations, respectively. For the divalent metal component, magnesium is the most common, although many other metal species with a cation size similar to that of Mg are also available, such as Co, Cu, Ni, Ca, Zn, and Mn. Al generally occupies the positions of the trivalent metal component, although Fe and Cr can be also employed [1–5]. The isomorphous substitution of M²⁺ by M³⁺ leads to a brucite-like (Mg(OH)₂) layered structure and excessive positive charges. Accordingly, some available anions, such as CO₃^{2−}, NO₃[−], Cl[−], SO₄^{2−}, and OH[−] are located in the interlayer along with water molecules to compensate for the excessive positive charges. As a result, HTs have a unique layered structure with positively charged brucite-like layers and compensating anions [6–10].

Due to their unique structures, HTs have two representative and prominent properties: the ability to capture and exchange organic and inorganic anions and memory effect. These unique properties have resulted in these compounds having a wide range of applications as anion exchangers, absorbing agents, stabilizers for

polymers, catalysts, electroactive materials, and pharmaceuticals [11–13]. As such, many attempts have been made to synthesize HTs with unique properties to meet the specific requirements of various application areas. Accordingly, various preparation techniques have been extensively investigated, including the co-precipitation method, sol-gel method, hydrothermal synthesis, microwave irradiation, and electrochemical methods. The preparation techniques of HTs were well reviewed by M.R. Othman et al. [14].

Although the co-precipitation method has been widely employed in previous studies, in the preparation of HTs it has a severe drawback in the excessive number of parameters that must be considered during the co-precipitation step, which affects the successful formation of HTs. These parameters include pH value, temperature, metal precursor, and aging time. Moreover, keeping the pH value of solution constant throughout the entire precipitation procedure is very difficult even when high-speed stirring is employed, which leads to the low crystallinity of HT. Moreover, the urea method, which uses urea as a precipitating and pH-control agent, is very sensitive to temperature during preparation. As such, temperature control is a key factor in obtaining HT by the urea method. In addition to the above two typical preparation methods, sol-gel, hydrothermal, combustion, and steam activation methods can be applied in the preparation of HTs. However, most preparation methods have rather complex preparation processes with inherent problems, such as too many synthetic parameters to achieve precise control, low reproducibility, high preparation cost, and difficulty in mass production [14].

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To overcome these problems, here we report a simple method for the preparation of Mg–Al HTs, which are the most representative HTs, using their corresponding metal oxides. Of course, there have been a number of previous attempts to prepare Mg–Al HTs via the hydration of metal oxides [15–18]. G.Q. Lu et al. demonstrated that Mg–Al HTs could be prepared in three steps: dissociation, deposition, and diffusion. Although interesting results regarding the preparation of Mg–Al HTs from their corresponding metal oxides were already reported, there has been a lack of clear discussion about the reaction pathway, or, in particular, its uncommon deposition and diffusion [15]. Furthermore, a slight change in the initial pH value of the precursor solution greatly affects the final product, leading to difficulty in obtaining single-phase Mg–Al HTs. Therefore, the main aim of this paper is to present a very simple preparation method for obtaining single-phase Mg–Al HTs using their metal oxides without any particular controlled variables, and to provide a reasonable explanation for a series of reaction pathways in which Mg–Al HTs are formed from their metal oxides. We hope this paper will contribute to making the preparation process of HTs easy and simple to achieve using commercially available materials.

Researchers in the field of heterogeneous catalysts have exhibited great interest in the utilization of the memory effect of HTs for various base-catalyzed reactions, which is a property unique to HTs. In the memory effect of HTs, as-synthesized HTs can be transformed into their corresponding mixed metal oxides by thermal treatment in air, and in turn, the original structure of HTs with layered double hydroxides can be successfully recovered by immersing the mixed metal oxides in water, which is known as the reconstruction process. Our group has consistently studied the tuning of the basic catalytic properties of Mg–Al HTs using this memory effect [19,20]. Accordingly, in addition to preparing Mg–Al HTs using a simple method, in this study we also focused on their memory effect and base catalytic properties. We employed glucose isomerization as a model reaction to explore the catalytic base properties of Mg–Al HTs.

2. Experimental

2.1. Material preparation

All chemicals were used without further purification. We used two different types of metal oxides as sources of magnesium and aluminum. We purchased commercial metal oxides (MC: MgO commercially provided, AC: Al₂O₃ commercially provided) from Sigma-Aldrich, and we prepared as-synthesized metal oxides (MS: MgO synthesized in the laboratory, AS: Al₂O₃ synthesized in the laboratory) by calcining corresponding metal nitrates at 450 °C for 10 h in air. In a typical procedure, we simultaneously added known amounts of magnesium oxide (1.6 g) and aluminum oxide (0.68 g) to 100 ml of distilled water in a wide-mouth bottle. Then, we sealed the bottle with its cap, and aged the resulting solution containing the magnesium and aluminum sources while vigorously stirring at different temperatures (60 and 80 °C) and for different periods of times (6 h, 12 h, 1 d, 3 d, 5 d, and 7 d). Thereafter, we collected the white precipitate through filtration, and dried it overnight at 80 °C in an oven. We denoted the prepared samples as XY.Z, where XY and Z represent the sources of the metal oxides and the aging time, respectively. For example, MSAC.5 d indicates a sample prepared via hydration for 5 d using MgO that was synthesized in the laboratory (MS) and commercially provided Al₂O₃ (AC). For comparison, we also prepared a Mg–Al hydrotalcite (HT.C) with a ratio of Mg/Al = 3 by a co-precipitation method using the procedure reported in our previous work [19].

2.2. Reconstruction process

To confirm the memory effect of the prepared sample, we also conducted a reconstruction process according to the method reported in our previous work [19]. The prepared sample was calcined at 450 °C for 10 h in air to obtain the calcined Mg–Al HT. Next, we added the calcined Mg–Al HT (approximately 2 g) to 100 ml of distilled water, and then stirred the resulting solution vigorously in an inert atmosphere at 60 °C for 24 h. We then filtered the solution to obtain a solid product, and lastly, dried it overnight at 80 °C to yield the reconstructed Mg–Al HT.

2.3. Characterization

We characterized the crystalline structure of the prepared samples by powder X-ray diffraction (XRD) measurement, and recorded the XRD spectra on an X'pert-Pro PANalytical diffractometer using Cu–K α radiation ($\lambda = 1.54056 \text{ \AA}$). We recorded diffraction patterns within a 2θ range of 5–80°. We analyzed the morphological features of the sample by scanning electron microscopy (SEM), and obtained SEM images on a JSM-6700F field emission (FE) microscope operating at 15 kV. We immobilized the samples on a copper holder using conducting resin and coated them with platinum prior to characterization. We also conducted ICP-AES analysis (PerkinElmer, OPTIMA 4300DV) in order to confirm the metal contents of the samples. The specific surface areas of the samples were determined by the Brunauer-Emmett-Teller (BET) method using N₂ adsorption and desorption measurements conducted at –196 °C with a constant-volume adsorption apparatus (BEL Japan, BELSORP-mini II). In order to confirm the chemical bonds in the samples, infrared spectra were also recorded on a Jasco FT-IR-460 spectrometer in range of 4500–900 cm^{–1} using the KBr pellet technique. Using a mass spectrometer (MS), we carried out thermogravimetric (TG) analysis (NETZSCH, TG209F1) to confirm the thermal behavior of the samples. The TG analyses were carried out in a temperature range of 25–900 °C at a heating rate of 10 °C/min in an air stream, and recorded MS traces of $m/z = 18$ and 44 for the evolved water and CO₂, respectively.

2.4. Procedure for glucose isomerization and product analysis

We conducted the isomerization of glucose to fructose in a batch-type glass reactor. In a typical reaction, we used 0.3 g of glucose, 0.1 g of catalyst, and 10 ml of dimethylformamide. The reaction was performed at 100 °C for 5 h. After the reaction was complete, we cooled the reactor in an ice bath. We then filtered off the catalysts using a syringe filter and analyzed the filtrate by high performance liquid chromatography (Young Lin instrument, YL9100) using an ultraviolet-visible (UV–vis) detector and a refractive index (RI) detector. The mobile phase was 0.005 M H₂SO₄ at a flow rate of 0.5 mL/min and we separated the reaction products using a Biorad Aminex HPX87 H column at 50 °C. We plotted the calibration curves using a series of standard solutions to quantify the glucose and fructose. We determined the glucose conversion and fructose selectivity using the following equations, and calculated the fructose yield by multiplying the conversion and selectivity.

$$\text{Conversion of glucose(\%)} = \frac{\text{moles of glucose reacted}}{\text{moles of glucose supplied}} \times 100$$

$$\text{Selectivity for fructose(\%)} = \frac{\text{moles of fructose formed}}{\text{moles of glucose reacted}} \times 100$$

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