Nano-size MZnAl (M = Cu, Co, Ni) metal oxides obtained by combining hydrothermal synthesis with urea homogeneous precipitation procedures

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ABSTRACT

The well-crystallized MZnAl (M = Cu, Co, Ni) layered-double hydroxides (LDHs) were synthesized by combining hydrothermal synthesis with urea homogeneous processes. The LDH precursors were calcined at 450 °C to obtain the nanoscale mixed metal oxides. Characterization techniques including XRD, TG–DTG, TPR, N_2 adsorption/desorption, HRTEM and SEM were carried out to investigate the LDH precursors, thermal decomposition behavior and reducibility, porosity and morphology of the calcined samples. For the LDHs containing Cu, the thermal decomposition process became more complex because of its Jahn–Teller effect, and the phases of the calcined samples were different as a result of preparation conditions. Hydrothermal synthesis led to easy generation of the spinel phase at lower thermal treatment temperature (450 °C). Further, the reducibility and texture properties were influenced.

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1. Introduction

Layered-double hydroxides (LDHs), also called anionic clays and hydrotalcite-like compounds, are attracting much research interests because of their wide application (Rives and Ulibarri, 1999). Their structure consists of positively charged metal hydroxides with interlayer anions and water (Cavani et al., 1991; Valente et al., 2008). The formula of LDHs is generally described as $M_y^{2+}M_x^{3+}(OH)_2(A^{n-})_{x/n} \cdot m\,H_2O$, where M^{2+} is a bivalent cation, M^{3+} is a trivalent cation, A^{n-} is an anion with the charge of n and m is the number of interlayer water. Although LDH materials are easily prepared by co-precipitation method, some properties such as crystallinity, particle-size distribution and specific surface area are not easy to control. Costantino et al. (1998) synthesized well-crystallized LDHs using "homogeneous precipitation" method in the presence of urea, but the process usually took long time to prepare pure LDHs at ambient conditions. Hydrothermal synthesis is a well-known and established method for preparing microporous crystals, complex oxides and inorganic–organic hybrid materials (Feng and Xu, 2001). It can shorten the preparation time of LDH materials and obtain the much smaller particle size (Benito et al., 2006; Benito et al., 2008).

In addition to their intrinsic interest, one of the most important applications of LDHs is as catalyst precursors or support. The metal cations were homogeneously distributed in hydrotalcites, and heterogeneous catalysts with a high dispersion of metal sites could be obtained through thermal treatment (Rives and Ulibarri, 1999). On the other hand, the transition metal oxides such as Cu-based, Co-based and Ni-based catalysts are widely used for oxidative steam reforming methanol (Velu et al., 2000b; Murcia-Mascaros et al., 2001; Turco et al., 2007), Fischer–Tropsch synthesis (Khodakov et al., 2003; Herrero et al., 2007; Chu et al., 2008) and hydrogenation of acetylene reaction (Rives et al., 1998; Monzon et al., 1999), respectively. Generally, the redox catalyst was firstly obtained as metal oxides after calcination treatment, then, the mixed metal oxides were reduced in reductive gas such as hydrogen gas to generate the active sites: metallic atoms. The particle size of the active phase, mostly decided by the preparation techniques, had a significant influence on the reducibility of the catalyst (Khodakov et al., 2002). As a result, the catalytic reaction was profoundly effected. Thus, to obtain high dispersion catalyst, it is necessary to improve the conventional preparation techniques.

In our present work, the objective was to prepare high dispersion mixed metal oxides. LDH materials containing Cu/Co/Ni, Zn and Al were prepared by combining hydrothermal synthesis and urea homogeneous precipitation method. Further, the nano-size composite metal oxides were prepared by thermal treatment. XRD, TG–DTG, TPR, etc. measurements were employed for characterizing the LDH precursors and the calcined samples.

2. Experimental

2.1. Preparation

The layered-double hydroxide (LDH) precursors were prepared by urea homogeneous precipitation method (Costantino et al., 1998; Atake

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et al., 2007). Appropriate amounts of $CuCl_2 \cdot 2H_2O$ (or $CoCl_2 \cdot 6H_2O$ or $NiCl_2 \cdot 6H_2O$), $ZnCl_2$ and anhydrous $AlCl_3$ were dissolved in deionized water to obtain 0.5 M aqueous solution, respectively. The urea was added until the molar ratio of urea to Al^{3+} is equal to 10. The $CuCl_2$ (or $CoCl_2$ or $NiCl_2$) solution was added into the mixture solution containing Zn^{2+} and Al^{3+} drop by drop at the boiling temperature. A green solution appeared and then refluxed under vigorous stirring for 24 h. The precipitates were recovered by separating the mother solution, washed with deionized water at least 3 times, and then socked in 0.05 M Na_2CO_3 aqueous for 24 h in order to exchange the chloride ions, eventually present in the materials, with carbonate ions. After equilibration with Na_2CO_3 aqueous solution, the suspension was filtered, washed with deionized water and dried at 110 °C overnight. The obtained samples were denoted as MZnAl-U.

The hydrothermal synthesis for LDH precursors was that the urea precipitation process took place under the hydrothermal conditions (Rao et al., 2005; Xu and Lu, 2005). There were some differences in hydrothermal synthesis process compared with the above method. The appropriate amounts of metal chloride were together dissolved in deionized water firstly, then the urea was added under vigorous stirring until the ratio of urea/Al^{3+} is equal to 10. Then the mixture was transferred into Teflon bottle, which was kept in a stainless steel autoclave. After the autoclave was sealed tightly, it was placed in the temperature-controlled electric oven and subjected to the hydrothermal treatment at 120 °C for 24 h. The following steps such as precipitate recovery, washing with deionized water, socking in Na_2CO_3 aqueous and drying were the same as that of urea homogeneous precipitation method. The obtained samples were denoted as MZnAl-HT.

The LDH precursors were heated from room temperature to 450 °C and held on the temperature for 5 h. The heating rate used in this study was 3 °C/min from room temperature to 300 °C and 2 °C/min above 300 °C. The obtained samples were abbreviated as MZnAl-Uc and MZnAl-HTc for the samples prepared under ambient and hydrothermal conditions, respectively.

2.2. Characterization techniques

X-ray powder diffraction (XRD) measurements were employed to determine the properties of the LDH precursors and the crystalline phase of the calcined catalysts, which were performed on DX-100 diffractometer with CuKα radiation, scanning 2θ angles in the range of 5–80°.

The thermal decomposition behavior of the catalyst precursors was tested using TGA Q500 (TA Co., USA) instrument at a heating rate of 10 °C/min from room temperature to 800 °C. The thermogravimetric (TG) and the differential thermogravimetric (DTG) curves were recorded by a personal computer.

The surface area, total pore volume and average pore diameter were measured by the N_2 adsorption/desorption, using a Quantachrome Nova 1000e apparatus at liquid nitrogen temperature. Samples were degassed at 300 °C for 3 h prior to analysis.

Temperature-programmed reduction (TPR) measurements were carried out at atmospheric pressure in a fixed-bed. 25 mg sample was loaded in a quartz reactor with N_2 at 100 °C for 30 min. Then the nitrogen was replaced by the reductive gas (5% H_2/N_2) at a flow rate of 30 mL/min. The temperature of the reactor was increased linearly from 100 to 550 °C at a rate of 10 °C/min by a temperature-programmed controller. The effluent stream was analyzed by a thermal conductivity detector (TCD).

The high resolution transmission electron microscopy (HRTEM, JEOL 2010F, 200.0 kV) and scanning electron microscopy (SEM, JSM 7401E, 1.0 kV) were used to study the morphology of the calcined samples.

3. Results and discussion

3.1. Crystalline phase test for LDHs

XRD test was carried out to confirm the hydrotalcite-like structure of the LDH materials. The patterns are reported in Fig. 1. The patterns of
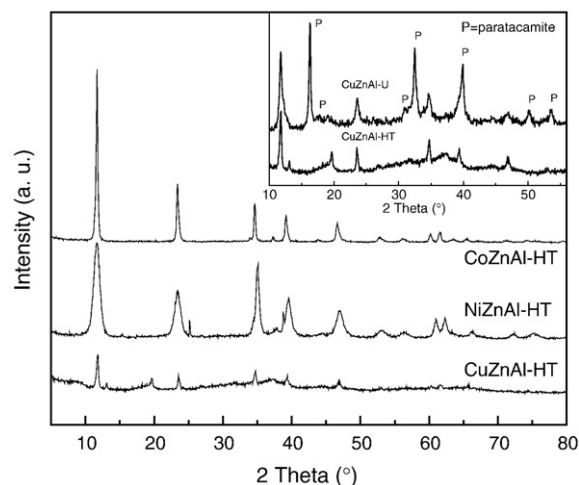

Fig. 1. XRD patterns of MZnAl (M = Co, Ni, Cu) layered-double hydroxides prepared under hydrothermal conditions.

CoZnAl-HT and NiZnAl-HT samples had typical characteristic reflections for hydrotalcite phase with well-crystallized, showing sharp and symmetric reflections around $2\theta = 11.7$, 23.4 and 35.1°, corresponding to the basal spacing close to 0.75, 0.38 and 0.26 nm, respectively, ascribed to the diffraction plane (003), (006) and (009) (Cavani et al., 1991; Rives and Kannan, 2000). From the inlet figure, the XRD pattern of CuZnAl-U, except the characteristic reflection of hydrotalcite-like phase as described above, displayed impurity phase around $2\theta = 16.2$, 18.8, 32.5, 39.8, 50.2 and 53.6°, which were assigned to the characteristic reflection of paratacamite, $Cu_{2-x}Zn_x(OH)_3Cl$ (Turco et al., 2007). In the CuZnAl-HT sample prepared under hydrothermal conditions, the paratacamite still existed, but the intensity obviously weakened. Maybe two reasons are responsible for it, firstly, Cu^{2+} ions showed Jahn–Teller effect that favored the formation of distorted octahedral structure (Khan and O'Hare, 2002), secondly, Cu^{2+} ions could be depleted by ammonia originated from urea hydrolysis, which made the synthetic procedure more complex. The thickness of the brucite-like layer is ca. 0.48 nm, thus the interlayer spacing is close to 0.27 nm, which suggests that carbonate anions could be located with molecular planes parallel to the brucite-like layer. The reflection around $2\theta = 61.0$° was assigned to the reflection of (110) plane. From that the crystallographic parameter a can be calculated. The parameter c could be calculated from (003), (006) and (009) reflection according to the equation $c = d(003) + 2d(006) + 3d(009)$, which depended on the size of interlayer anions and electrostatic forces between interlayer anions and the layers (Rives and Kannan, 2000). The results were gathered in Table 1. The decrease in both variables was observed in the following order: CuZnAl-HT > CoZnAl-HT > NiZnAl-HT. The decrease in parameter a could be attributed to their octahedral radius ($r_{Cu} > r_{Co} > r_{Ni}$), while the decrease in parameter c resulted from the differences of electrostatic forces between interlayer anions and the brucite-like layer containing CO_3^{2-} interlayer anion LDH materials.

3.2. Thermal decomposition behavior of LDH materials

Thermogravimetric (TG) analysis was performed to investigate the thermal decomposition behavior of MZnAl (M = Co, Ni, Cu) layered-

Table 1
Chemical formula of LDH materials.

Sample	Formula[a]	a (nm)	c (nm)
CuZnAl-HT	$Cu_{0.335}Zn_{0.335}Al_{0.33}(OH)_2(CO_3)_{0.165} \cdot 0.52\,H_2O$	0.3072	2.262
CoZnAl-HT	$Co_{0.335}Zn_{0.335}Al_{0.33}(OH)_2(CO_3)_{0.165} \cdot 0.38\,H_2O$	0.3059	2.259
NiZnAl-HT	$Ni_{0.335}Zn_{0.335}Al_{0.33}(OH)_2(CO_3)_{0.165} \cdot 0.53\,H_2O$	0.3025	2.254

[a] The interlayer water content was calculated from TG test.