

Large-scale synthesis of carbon nanofibers on Ni–Fe–Al hydrotalcite derived catalysts

I. Preparation and characterization of the Ni–Fe–Al hydrotalcites and their derived catalysts

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Abstract

A series of Ni²⁺–Fe²⁺–Al³⁺ hydrotalcite (HT) catalysts with varying compositions have been prepared by coprecipitation from Fe²⁺. The structure and properties of the catalysts were carefully characterized by various methods such as XRD, EXAFS, TGA, TPR, N₂ adsorption/desorption, XPS and H₂ chemisorption. It was shown that pure HT structures can only be prepared at low Fe²⁺ concentrations, while mixed oxide phases with spinel structure will form simultaneously at high Fe²⁺ concentrations. Pure HT structures are very important for small particle size, narrow size distribution and large surface area of the resulting catalysts. XPS study demonstrated Fe enrichment on the catalyst surfaces, which might have partly contributed to the low hydrogen chemisorption capacity for the Fe-containing catalysts.

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1. Introduction

Hydrotalcite (HT)-like materials, also known as layered double hydroxides, are a class of nanostructured anionic clay minerals. They have the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{n-}_{x/m}]^{x-}$, where M²⁺ and M³⁺ are divalent and trivalent cations and Aⁿ⁻ is the interlayer anion [1–3]. The HT-like compounds have received increasing attention in recent years. The industrial applications of HT are widespread, ranging from catalysts, precursors and supports of catalysts to anionic exchangers, sorbents, additives and precursors for composite materials [4,5]. Structurally, these materials consist of brucite-like (Mg(OH)₂) sheets wherein M²⁺ cations are octahedrally coordinated by six oxygen atoms belonging to hydroxyl ions, and partial substitution of M²⁺ by a trivalent cation M³⁺, such as Al³⁺, occurs. The partial substitution leads to a positive charge of the layer, which is

balanced by anions (usually CO₃²⁻). The anions occupy the interlayer space together with water molecules. The *x* value should be within a narrow range of 0.2–0.33 if a single phase material is desired [5–7].

What makes HTs interesting as catalyst precursors is that they can accommodate a large number of M²⁺, M³⁺ cation pairs [8,9]. Numerous HTs have been synthesized with divalent cations such as Mg, Mn, Co, Ni, Cu, Zn, etc., and trivalent cations such as Al, Cr, Fe, Co, V, etc. Furthermore, using HT as the precursor will, on subsequent calcination and reduction, result in the formation of a highly dispersed and homogeneous mixture of the cations on an atomic scale, with desirable properties such as high surface area and high thermal stability [10–12].

Catalysts consisting of nickel and iron have frequently attracted much attention. Supported Ni–Fe alloy catalysts have been studied in the Fisher–Tropsch synthesis [13,14], methanation [15], vapor phase oxidation of benzoic acid to phenol [16,17] and hydrogen peroxide decomposition [18]. More recently, the syntheses of CNFs and CNTs have attracted worldwide attention

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due to their distinct physical and chemical properties and many potential applications [19,20]. The syntheses have mainly involved Ni, Fe, Co or their alloy catalysts [21–23], which have been used either in the powder form or in the supported form. Metal powders will produce large amount of CNFs, but provide little or no control over the final CNF diameter or structure [24,25]. The supported catalysts normally have a low active metal loading, which results in a low productivity of CNFs per gram catalyst. In this study HT derived Ni–Fe–Al catalysts are proposed for the synthesis of CNFs because of their attractive properties such as high metal loadings, small particle sizes and high thermal stability. These properties will make them effective in producing CNFs with both high productivity and high quality. To be able to tune the structures of the CNFs, the Ni/Fe ratio of the bimetallic catalysts will be varied systematically.

The preparation of Fe-containing HT precursors has mainly involved Fe^{3+} [2,26–28]. Because of the narrow range of the x value for pure HT, Fe^{2+} cation should be used to be able to vary the Ni/Fe ratio systematically. Although the possibility of synthesizing HT structure from Fe^{2+} has been mentioned [1,29], study of the preparation of HT structures from Fe^{2+} is very limited. To the best of our knowledge, besides the two recent contributions of Auer et al. [30] and Li et al. [31], the preparation of HT from Fe^{2+} precursor has not been reported previously. In this paper we report a detailed study of the preparation and characterization of a series of Ni^{2+} – Fe^{2+} – Al^{3+} HT structures using Fe^{2+} precursor, and their derived Ni–Fe/ Al_2O_3 bimetallic catalysts. These HT derived catalysts will be employed in large-scale CNF synthesis in a subsequent study.

2. Experimental

2.1. Hydrotalcite preparation

The Ni^{2+} – Fe^{2+} – Al^{3+} HT catalysts were prepared by a method modified from Bhattacharyya et al. [32,33]. $\text{Ni}(\text{NO}_3)_2$, FeSO_4 and $\text{Al}(\text{NO}_3)_3$ were used as metal precursors, while Na_2CO_3 and NaOH acted as precipitates. For each preparation, stoichiometric amounts of Na_2CO_3 and NaOH were dissolved in 400 ml deionized water. A second solution containing $\text{Ni}(\text{NO}_3)_2$, FeSO_4 and $\text{Al}(\text{NO}_3)_3$ dissolved in 375 ml water was pumped slowly into the first solution under vigorous mechanical stirring. After the addition was complete, the gelatinous mixture was adjusted to pH 8.5 with nitric acid and aged at 80 °C for 15 h. The cooled sample was suction-filtered, washed repeatedly with large amount of water, and vacuum dried at 70 °C overnight. The whole preparation process was performed under N_2 protection, and the water used in all the preparations had been deoxygenated to prevent the oxidation of Fe^{2+} .

In all catalysts the Al^{3+} was maintained at a molar percentage of 0.25, which gives a (Ni + Fe)/Al molar ratio of 3/1. The Ni/Fe ratio was adjusted to 1:0, 8:2, 5:5, 2:8 and 0:1, respectively. The catalysts were accordingly denoted as Ni, NiFe (8:2), NiFe (5:5), NiFe (2:8) and Fe. The as-prepared HT precursors were calcined under 100 ml/min air at 480 °C for 15 h, while the temperature was raised to 480 °C at 5 °C/min. Finally, the calcined samples were sieved to a mesh size of 100–145 μm .

For the reduced samples, the calcined oxides were reduced to the metallic state in a 1:1 N_2/H_2 mixture (total flow 200 ml/min) for 15 h at 600 °C. After the reduction step, the samples were cooled down to room temperature under flowing N_2 and passivated in an air/ N_2 mixture (4% (v/v) air, total flow 100 ml/min) for 2 h to prevent bulk oxidation of the catalysts.

2.2. Catalyst characterization

X-ray diffraction (XRD) analysis was carried out with two different diffractometers. For phase identification, a Siemens D5005 X-ray diffractometer was used. Diffraction was performed with Cu K_α radiation and the peaks were identified by comparison with standards in a database. This was performed for as-prepared HTs, calcined and reduced catalysts.

For determining particle size distribution of the reduced samples, a Siemens D5000 X-ray diffractometer was used with $\text{Cu K}_{\alpha 1}$ radiation. The resulting peaks were analyzed with a profile fitting program (SIEMENS DIFFRAC^{plus} PROFILE), and crystal size and microstrain software (DIFFRAC^{plus} WIN-CRYSIZE). LaB_6 was used as the standard.

Transmission X-ray absorption spectroscopy (XAS) data were collected at the Swiss–Norwegian Beamlines (SNBL) at the European Synchrotron Radiation Facility (ESRF), France. Spectra were obtained at the Fe K-edge (7.112 keV) and Ni K-edge (8.333 keV) using a channel-cut Si (1 1 1) monochromator. Higher order harmonics were rejected by means of a chromium-coated mirror aligned with respect to the beam to give cut-off energy of approximately 15 keV. The software package WINXAS v3.1 [34] was used for near-edge region of the spectra (XANES) analysis to obtain qualitative and quantitative information on Ni and Fe. The XAS data were calibrated, pre-edge background subtracted (linear fit) and normalized. Extended X-ray absorption fine structure (EXAFS) model fitting was carried out with the program EXCURV98 using curved-wave theory and *ab initio* phase shifts [35]. EXAFS spectra were collected at the Fe and Ni K-edges for the sample NiFe (8:2) both as the oxide and in the reduced/passivated state. Ni and Fe metal foils, NiO, NiAl_2O_4 , $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 were used as model compounds to check the validity of the *ab initio* phase shifts and establish the general parameters for amplitude reduction and inelastic scattering of the photoelectrons. The model compounds were also used as references for the linear combination of XANES profiles.

Simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) were carried out using a PerkinElmer thermogravimetric analyzer (TGA) apparatus. The experiments were carried out in 40 ml/min air at a heating rate of 10 °C/min from 30 to 800 °C using 11–14 mg samples.

Temperature programmed reduction (TPR) study of the calcined catalysts was carried out with a CHEMBET-3000 TPD/TPR instrument. TPR was performed in 80 ml/min H_2/Ar mixture (7% (v/v) H_2) at a heating rate of 10 °C/min from 30 to 1000 °C using about 35 mg samples.

N_2 adsorption/desorption measurement was carried out with a Micromeritics TRiStar 3000 instrument using about 0.12 g samples at liquid nitrogen temperature. Before collecting the

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