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Short Communication

Synthesis of a novel Ni/C catalyst derived from a composite precursor for hydrodechlorination

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ABSTRACT

Novel carbon supported nickel catalysts were successfully prepared by in situ reduction of Ni–Al layered double hydroxide/carbon hybrid composites (NiAl-LDH/C). The results indicated that the microstructure of supported Ni catalysts was profoundly affected by the composition of composite precursors. As-synthesized supported catalysts were found to show remarkably excellent catalytic performance in the liquid-phase hydrodechlorination of chlorobenzene. The presence of the highly dispersed metallic nickel nanoparticles with relatively small particle size over carbon matrix is proposed to be responsible for the excellent hydrodechlorination activity of the catalyst, on which a chlorobenzene conversion of 98.8% could be obtained.

1. Introduction

Nowadays, the development of effective procedure for hydrodechlorination (HDC) of chloroaromatic compounds is gaining increasing significance as a potential methodology for treating toxic halogenated waste. In the past decade, many efforts have been paid to the heterogeneous catalytic HDC of chlorobenzene (CB) and its derivatives with supported noble metal (e.g., Pt, Rh and Pd) catalysts [1–3]. However, the high cost of these catalysts greatly limits large-scale practical applications. More recently, supported nickel-based catalysts have been reported to exhibit good catalytic activity and high thermal stability in HDC [4–6].

Previously, we showed that high-surface-area NiO-based metal oxides could be obtained from Ni–Al layered double hydroxide/carbon composite (NiAl-LDH/C) by crystallization of NiAl-LDH and simultaneous carbonization of glucose under hydrothermal condition [7]. LDHs are known as a family of highly ordered two-dimensional layered materials [8]. They can be represented by the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A_{x/n}]^{n-}\cdot mH_2O$, where different M^{2+} and M^{3+} metal cations are uniformly distributed and orderly prearranged in the brucite-like sheets, and various charge-compensating anions (A^{n-}) are present in the interlayer space. According to the fact that LDHs can accommodate a large number of tunable M^{2+} and M^{3+} ions within the layers or in the interlayer space in the form of metal complexes, well-dispersed supported metal catalysts can be obtained by reducing calcined LDHs with desired active metal species [9–11]. This kind of structural transformation endows LDH materials with extraordinary capability as catalyst precursors in various metal-catalyzed reactions [12,13].

In this communication, we reported a synthesis of carbon supported Ni nanoparticle catalysts derived from NiAl-LDH/C composite. The carbon in the composite precursors serving as a reducing agent could in situ reduce Ni species upon heating in the absence of H_2 to form Ni nanoparticles highly dispersed on carbon matrix. The catalytic performance of as-synthesized carbon supported Ni catalysts was investigated in liquid-phase HDC of CB, and a correlation between the microstructure of the catalysts and their catalytic activities was discussed.

2. Experimental

2.1. Synthesis of NiAl-LDH/C hybrid composites

NiAl-LDH compounds were synthesized via a coprecipitation method. In this typical synthesis, $Ni(NO_3)_2\cdot 6H_2O$ and $Al(NO_3)_3\cdot 7H_2O$ (5.0 mmol) with different Ni^{2+}/Al^{3+} molar ratios (1, 1.5 and 2) were dissolved in 50 mL of deionized water. Subsequently, the solutions were titrated with an alkali solution of NaOH (0.8 M) and Na_2CO_3 (0.2 M) under vigorous stirring at room temperature until pH = 10.0. Then the suspension was aged at 65 °C for 24 h and denoted as LDH-x, where x is the initial Ni^{2+}/Al^{3+} molar ratio. After being washed in deionized water, the resulting LDH-x suspension was transferred and dispersed into Teflon-lined autoclave with 50 mL of glucose solution ($[C_6H_{12}O_6] = 2.5[Ni^{2+} + Al^{3+}]$) and aged at 150 °C for 10 h. The slurries were centrifuged and washed with deionized water and ethanol for

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three times, respectively. Finally, the precipitates were dried at 50 °C for 12 h, and denoted as LDH-x/C.

2.2. Synthesis of carbon supported Ni catalyst

The obtained LDH-x/C composites were placed in a tube-furnace reactor. The furnace was ramped from 30 to 500 °C at a rate of 5 °C/min under a nitrogen flow (40 mL/min), and held at 500 °C for 2 h. Then the furnace was naturally cooled to room temperature. Finally, the black products obtained were denoted as Ni-x/C. For comparison, LDH-1.5 sample without carbon deposition was reduced under a 10% v/v H_2/N_2 flow (40 mL/min) at 500 °C for 2 h with a ramping rate of 5 °C/min. The obtained catalyst was denoted as Ni-1.5.

2.3. Characterization

The in situ high-temperature XRD (HT-XRD) measurements were performed on a PANalytical X'Pert PRO MPD diffractometer (Cu Kα radiation, X'Celerator detector). Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vector 22 spectrometer. Elemental analysis was performed using a Shimadzu ICPS-7500 inductively coupled plasma atomic emission spectroscopy (ICP-AES). H_2 temperature programmed desorption (H_2-TPD) of the samples were characterized by using a Micromeritics ChemiSorb 2720. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were carried out on a JEOL 2100 operated at an accelerating voltage of 200 kV. The size distribution of particles was determined from more than 500 individual metal particles. The surface area-weighted diameter of particles (D) was calculated from the following equation:

$$D = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2},$$

where n_i is the number of particles of diameter d_i. X-ray photoelectron spectroscopy (XPS) was recorded on a VG ESCALAB 2201 XL spectrometer with a monochromatic Mg Kα X-ray radiation (1253.6 eV photons). Binding energies were calibrated based on the graphite C 1s peak at 284.6 eV.

2.4. Hydrodechlorination of CB

The liquid phase hydrodechlorination was carried out in a 100 mL stainless steel autoclave, which was charged with CB (24.6 mmol), the catalyst (0.1 g), ethanol solvent (50 mL) and NaOH (36.9 mmol). Air was flushed out of the reactor with nitrogen at room temperature. The reactor was then submerged into a water bath at 70 °C for 2 h under atmospheric pressure. Subsequently, H_2 was fed into the reactor at 1.0 MPa and the hydrodechlorination was initiated by starting stirring. Finally, the products were analyzed by an Agilent GC7890A gas chromatograph equipped with flame ionization detector and HP-5 capillary column.

3. Results and discussion

3.1. Characterization of hybrid composite precursors

The typical FT-IR spectra of NiAl-LDH and LDH-1.5/C samples are shown in Fig. 1. For NiAl-LDH, there are strong and broad absorption bands between 3600 and 3200 cm^{-1} associated with a superposition of hydroxyl stretching band (ν_{O-H}) arising from hydroxyl groups of the brucite-like layers and hydrogen-bonded of the interlayer water. The adsorption at 1636 cm^{-1} is assigned to the bending vibration of interlayer water (δ_{O-H}). The band observed at 2929 cm^{-1} is interpreted as the bridging mode of carbonate and water in the interlayer [14]. The absorption bands observed at 1384 and 783 cm^{-1}, which are assigned to stretching vibration mode of C–O (ν_{C-O}) and bending vibration (δ_{C-O}), respectively, show the existence of CO_3^{2-} in the interlayer [15]. The bands appearing below 600 cm^{-1} are interpreted as the M–O and M–OH lattice vibration modes. For LDH-1.5/C composite, except for the absorptions associated to LDH phase, the newly appeared band in the range of 1000 to 1200 cm^{-1} is mainly ascribed to C–OH stretching vibration, indicative of the presence of hydroxyl groups associated with carbon. Moreover, the band at about 1697 cm^{-1} attributed to asymmetric stretching vibration of C=C ($\nu_{C=C}$) confirms the aromatization and carbonization of glucose during hydrothermal treatment [16].

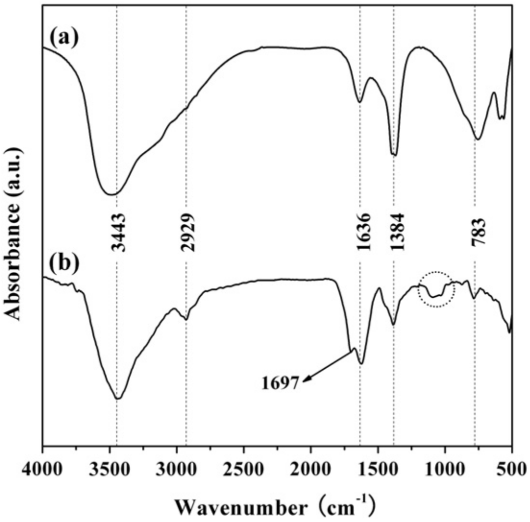

Fig. 1. FT-IR spectra of (a) LDH-1.5 and (b) LDH-1.5/C composites.

The in situ HT-XRD patterns of a representative LDH-1.5/C composite are shown in Fig. 2. The XRD pattern at room temperature depicts four broad characteristic reflections at 2θ angles below 40° attributed to (003), (006), (012) and (015) planes of hydrotalcite-like materials and a characteristic line at high 2θ of about 62° by the overlapped (110) and (113) planes (JCPDS No. 15-0087). However, no reflections related to graphite or other forms of carbon appear, indicative of the presence of carbon in noncrystalline form. It is believed that under the present hydrothermal treatment, the aromatization and carbonization of glucose lead to the formation of amorphous carbon, and thus the resultant carbon is further assembled with LDH

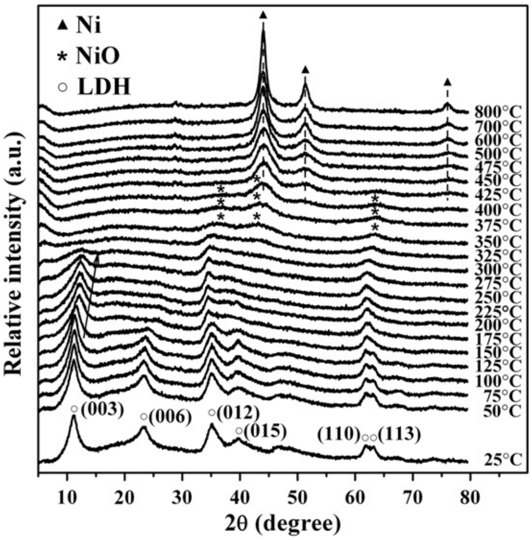

Fig. 2. In situ HT-XRD patterns of LDH-1.5/C hybrid composite in N_2 atmosphere at different temperature between 25 and 800 °C.