Priority Communication

Novel layered double hydroxide/oxide-coated nickel-based core–shell nanocomposites for benzonitrile selective hydrogenation: An interesting water switch

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ARTICLE INFO

ABSTRACT

Two novel layered double hydroxide (LDH)/layered double oxide (LDO)-coated nickel-based core–shell nanocomposites were first prepared from a hydrotalcite-like precursor. Water was found to act as a switch to tune the structures and acid–base properties between Ni@mSiO$_2$@LDO and Ni@mSiO$_2$@LDH, as demonstrated by transmission electron microscopy and temperature-programmed desorption of ammonia, resulting in chemoselective hydrogenation of benzonitrile to afford N-benzylidenebenzylamine (selectivity 92.3%) and benzylamine (selectivity 76.1%), respectively.

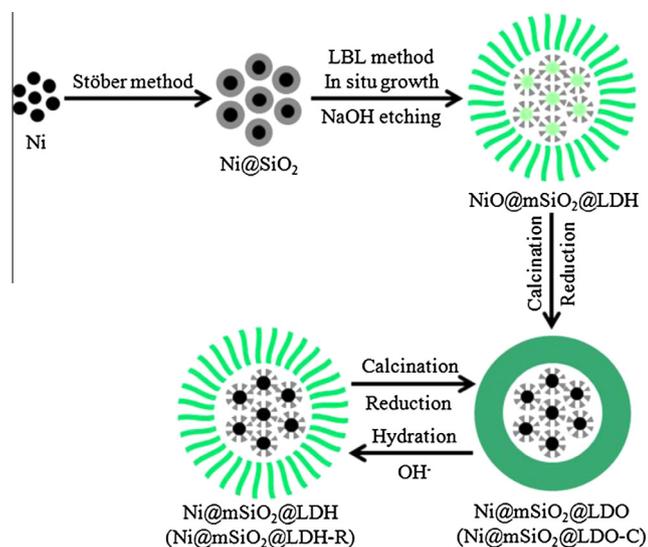© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Catalytic hydrogenation of unsaturated compounds has attracted much interest due to the green nature of this process and the ready availability of suitable substrates [1]. Selectivity control is one of the most important issues in catalytic hydrogenation [2]. Imines are important intermediates due to their wide applications in the synthesis of pharmaceuticals, fungicides, agricultural chemicals, dyes, and fragrances [3]. Thus, a series of methods have been developed to construct imines, including condensation of amines with ketones or aldehydes [4], oxidative self-coupling of amines [5], and oxidative coupling of amines with alcohols [6]. However, all of these methods use amines as starting materials and usually generate large amounts of by-products [7]. The relatively high prices of amines, as well as increasing demands for green synthesis, have limited the widespread application of these approaches. Alternatively, condensation reactions between the highly reactive imine intermediate and amines in the hydrogenation of nitriles can produce imines [8]. Furthermore, nitriles are usually cheaper than amines and the catalytic hydrogenation of

nitriles represents an atom-economic process [9]. However, most of the research regarding the hydrogenation of nitriles has focused on their transformation into primary amines, which can be subsequently applied as useful intermediates in the pharmaceutical, agrochemical, and plastics industries [10–15]. There are only a few reports on the direct hydrogenation of nitriles to imines [9,16–19]. Moreover, although a few methods have been developed to produce primary amines over supported nickel-based catalysts [20,21], most of the reported methods have used homogeneous organometallic complexes or supported noble metals as catalysts. Difficulties in the efficient separation and recycling of the homogeneous catalysts and the high prices of the noble metals limit further applications of such catalysts in industry. Thus, there is still a great need for the development of efficient and cheap catalysts for the selective hydrogenation of nitriles to imines or primary amines.

Recently, core–shell nanocomposites have attracted increasing attention in the field of catalysis [22]. This is largely due to the fact that good catalytic activity, selectivity, and stability of core–shell nanocatalysts can easily be achieved by tuning the size and shape of the core as well as the composition and thickness of the shell [23,24]. One common core–shell nanocatalyst uses the active species as cores and mesoporous materials as shells [25]. The outer

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Scheme 1. Schematic illustrating the preparation of nanocomposites.

mesoporous shells can modify the structure of the catalysts and improve their catalytic performance. Noble metals are usually selected as the cores of the core–shell nanocatalysts due to their high activities. For example, Ikeda et al. fabricated a core–shell structured catalyst comprising a platinum nanoparticle in the core and hollow porous carbon in the shell (Pt@hmC), that exhibited high activity and recyclability in the hydrogenation of olefins [26]. In contrast, there are few reports on the preparation and application of nanocomposites using transition metals as cores [27,28]. In the work reported here, we designed and prepared two novel layered double hydroxide (LDH)/layered double oxide (LDO)-coated nickel-based core–shell nanocomposites (Ni@mSiO$_2$@LDO and Ni@mSiO$_2$@LDH, Scheme 1). We found that water can act as a switch to tune their structures and acid–base properties, resulting in chemoselective hydrogenation of benzonitrile to afford N-benzylidenebenzylamine (DBI) and benzylamine (BA), respectively. To the best of our knowledge, this is the first report on the preparation of tunable LDH/LDO-coated nickel-based core–shell nanocomposites and their application in the selective hydrogenation of benzonitrile.

2. Materials and methods

2.1. Materials preparation

Materials preparation is displayed in the Supplementary Information (SI).

2.2. Characterization

X-ray diffraction (XRD) patterns were acquired with a Bruker D8 diffractometer using a Cu Kα radiation source at 40 kV and 100 mA with a step size of 0.02° over the range 10°–80°. Transmission electron microscopy (TEM), selected area electron diffraction (SAED), and X-ray energy dispersive spectroscopy (EDS) were performed on a FEI Tecnai G^2 F20 S-TWIN microscope at an extraction voltage of 3950 V, gun lens 1, and spot size 1. Brunauer–Emmet–Teller (BET) surface areas and pore volumes of the nanocomposites were measured by nitrogen physisorption at 77 K using a Micromeritics Tristar II 3020 apparatus. Before the measurements, the samples were dried at 393 K for 2 h. Temperature-programmed desorption of NH$_3$ (NH$_3$ TPD) and H$_2$ chemisorption were carried
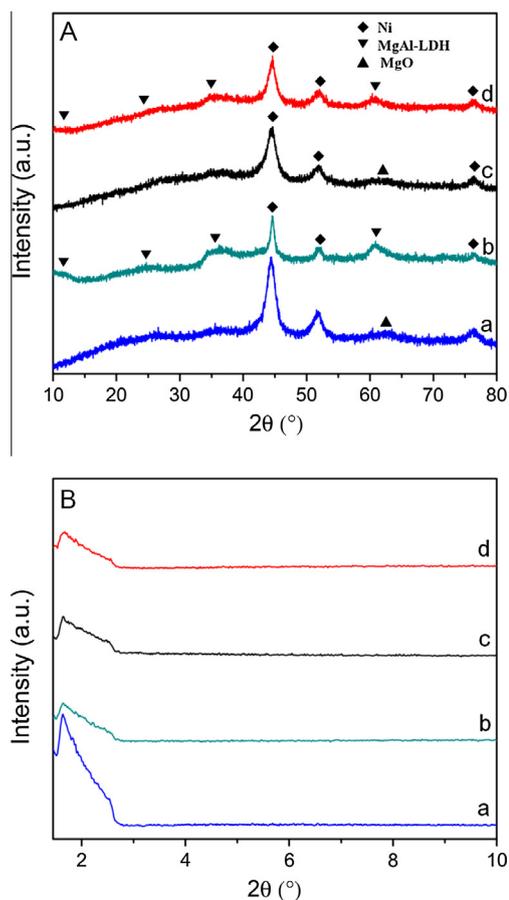
out on a TP-5000 instrument equipped with a thermal conductivity detector.

2.3. Catalytic tests

Selective hydrogenation of benzonitrile was performed as follows: benzonitrile (3.0 mL), catalyst (0.12 g), and water (60 mL) were mixed in a 100 mL stainless steel autoclave equipped with a mechanical stirrer and an electric heating system. The autoclave was first filled three times with H$_2$ to exclude residual air and then pressurized to 2.0 MPa with H$_2$. After it was heated to the requisite temperature, hydrogenation was started by stirring the reaction mixture vigorously and allowed to proceed for 3 h. Reaction mixtures were analyzed by gas chromatography using a 30 m SE-30 capillary column and the product structures were identified using gas chromatography–mass spectrometry (GC–MS) on an Agilent 5975C spectrometer.

3. Results and discussion

Fig. 1A shows the wide-angle X-ray diffraction (XRD) patterns of the prepared core–shell nanocomposites. In contrast NiO@mSiO$_2$@LDH (Fig. S1 in the SI), Ni@mSiO$_2$@LDO (Fig. 1A, curve a) exhibits the characteristic peaks of metallic Ni and poorly crystalline MgO at 2θ = 60°–65°, indicating the transformation of LDH to amorphous LDO [29,30] and the reduction of NiO to Ni during the calcination and reduction process. In contrast, Ni@mSiO$_2$@LDH (Fig. 1A, curve b) shows characteristic diffraction peaks at about 11.3°, 23.7°, 34.6°, and 60.5°, just like those of MgAl-LDH [31]. In

Fig. 1. Wide-angle (A) and small-angle (B) XRD patterns of the prepared core–shell nanocomposites. Ni@mSiO$_2$@LDO (a), Ni@mSiO$_2$@LDH (b), Ni@mSiO$_2$@LDO-C (c), and Ni@mSiO$_2$@LDH-R (d).