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Article

Nano-sized $NiLa_2O_4$ spinel–$NaBH_4$-mediated reduction of imines to secondary amines

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ABSTRACT

Nano-sized $NiLa_2O_4$ spinel was produced by thermal decomposition of Ni–La compounds via a sol-gel method. The well-crystallized spinel structure was formed after calcination at 750 °C. The physicochemical properties of the spinel were investigated using differential thermal analysis, X-ray diffraction, transmission electron microscopy, scanning electron microscopy, and particle size distribution analysis. The results show that the nanoparticles have regular shapes with well-defined crystal faces and consist of uniform quasi-spherical crystallites of average size 40 nm. The refined unit cell parameters are a = 3.861205 Å and c = 12.6793 Å. This new nano-sized $NiLa_2O_4$ spinel is an efficient heterogeneous catalyst for the selective conversion of imines to the corresponding secondary amines in the presence of $NaBH_4$ as a reducing agent, in good to excellent yields. All the reactions were completely chemoselective at room temperature and had relatively short reaction times. Secondary amines with different aryl groups, including those bearing electron-withdrawing or electron-donating groups, were obtained under the optimum reaction conditions. The catalyst was readily recovered and was recycled four times with no significant loss of catalytic activity.

1. Introduction

Imine reduction to the corresponding amine is a widely used and important functional group transformation reaction in synthetic organic chemistry. Many amines are used in the pharmaceutical and agricultural industries [1–7]. Two approaches are commonly used to convert imines to amines. One is catalytic hydrogenation, which requires high pressure. The other is hydride reduction, which uses metal hydrides such as $LiAlH_4$ or $NaBH_4$ [8]. $LiAlH_4$ is normally used in a dry organic solvent in a protective inert atmosphere [9,10]; in contrast, $NaBH_4$ is an inexpensive, safe, and environmentally friendly reducing agent. Various Lewis acids such as LiCl [11], $TiCl_4$ [12], $TiCl_3$ [13], Ni_2B [14], I_2 [15], $ZrCl_4$ [16], and $CoCl_2$ [17] have been used to reduce C=N bonds in the presence of $NaBH_4$, but they are not always effective.

Spinel oxides play important roles in various catalytic applications, e.g., gaseous pollutant decomposition [18] and the water-gas-shift reaction [19]. In normal spinels, AB_2O_4, A is generally a divalent cation occupying tetrahedral sites, and B is a trivalent cation occupying octahedral sites. In inverse spinels, half of the B cations occupy tetrahedral sites, and the formula is $B(AB)O_4$.

Spinels are prepared using various methods, including hydrothermal synthesis [20], modified oxidation processes [21], forced hydrolysis [22], and ball-milling [23], solid-state [24], and microemulsion methods [25]. Sol-gel methods are preferred because they are effective and convenient techniques and use less energy and materials [26].

In this study, as part of our research on organic transfor-

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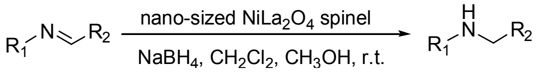

Scheme 1. Imines to the corresponding secondary amines by $NaBH_4$ and $NiLa_2O_4$.

mations using simple reagents, catalysts, and reaction media [27], we investigated the direct reduction of imines to the corresponding secondary amines by $NaBH_4$ in the presence of a catalytic amount of nano-sized $NiLa_2O_4$ spinel (Scheme 1).

2. Experimental

2.1. Preparation of $NiLa_2O_4$ powders

Citric acid (18 mmol, 3.50 g) was gradually added to a solution of $LaCl_3$ (4 mmol, 1.48 g) and $Ni(NO_3)_2\cdot 4H_2O$ (2 mmol, 0.58 g) in deionized water (10 mL), with constant magnetic stirring. The gel was heated at 80 °C for 3 h and dried at 120 °C for 24 h. It was then ground to a powder in an agate mortar and fired at 750 °C in air for 4 h.

2.2. Characterization

Decomposition of the dried polymeric gel precursor was investigated using differential thermal analysis (DTA; NETZSCH, Germany) at a heating rate of 10 °C/min in the range 25–1000 °C. Crystal structures were examined by X-ray diffraction (XRD; Xpert 200, Philips, Cu K_α radiation) at a scanning rate of 0.02°/s in the 2θ range 0° to 70°. The morphologies and dimensions of the nanoparticles were examined using transmission electron microscopy (TEM; LEO 912AB, accelerating voltage 120 kV). The morphologies of the calcined powders were examined using scanning electron microscopy (SEM; LEO 1450VP, accelerating voltage 120 kV).

2.3. General procedure for imine reduction to amines

$NaBH_4$ (0.37 mmol, 0.014 g) was added at room temperature to a stirred mixture of the appropriate imine (0.5 mmol) and nano-sized spinel $NiLa_2O_4$ (0.3 mol%, 6.0 mg) in CH_2Cl_2 (1 mL). Methanol (1 mL) was added slowly under constant magnetic stirring. On completion of the reaction, which was monitored using thin-layer chromatography (TLC; *n*-hexane:ethyl acetate = 8:2), the catalyst was removed by centrifugation and the solvent was evaporated under reduced pressure. Addition of water (10 mL) gave an oily liquid; the mixture was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure to afford the product. The sample purity was confirmed using TLC and ^1H nuclear magnetic resonance (NMR) spectroscopy.

3. Results and discussion

3.1. Thermal analysis

Figure 1 shows the DTA curve of the $NiLa_2O_4$ gel precursor obtained using the sol-gel method. The DTA curve has a large endothermic peak at around 100 °C, which is related to the evaporation of water. The combustion of organic compounds such as citric acid causes the exothermic peak at around 200 °C. The small exothermic peak at 350 °C is attributed to the decomposition of nitrate, which decomposes completely at around 420 °C, giving a large exothermic peak [28]. The exothermic peak at 750 °C corresponds to crystallization of the $NiLa_2O_4$ phase. No obvious change is observed above 800 °C. It is therefore concluded that the optimum calcination temperature is 750 °C.

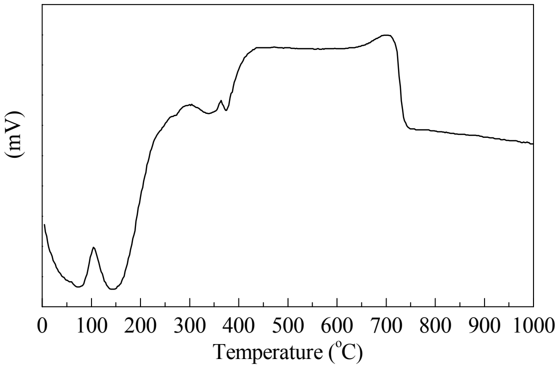

Fig. 1. DTA curve of $NiLa_2O_4$ gel precursor obtained using the sol-gel method.

3.2. XRD analysis

Figure 2 shows the XRD pattern of spinel-type $NiLa_2O_4$, which was formed when the gel was calcined at 750 °C for 4 h. No secondary phase is observed. The good agreement between the experimental and calculated data confirms that the sample consists of a single phase. Rietveld refinement showed that the material had a tetragonal unit cell with the I_4/mmm space group. The refined unit cell parameters were a = 3.861205 Å and c = 12.6793 Å. The unit cell volume was 189.035 $Å^3$, which is in close agreement with the results reported in the literature [29].

3.3. Powder morphology

Figure 3 shows a TEM image of the $NiLa_2O_4$ nanoparticles prepared at 750 °C. It shows that nanoparticles were homogeneous and consisted of uniform quasi-spherical crystallites of

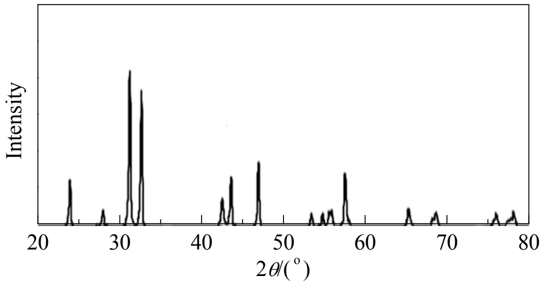

Fig. 2. XRD pattern of $NiLa_2O_4$ nanopowder sintered at 750 °C.