Nickel-promoted copper–silica nanocomposite catalysts for hydrogenation of levulinic acid to lactones using formic acid as a hydrogen feeder

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ABSTRACT

Highly active, thermally stable nickel-promoted copper–silica nanocomposite catalysts were prepared via a deposition–precipitation method and used for hydrogenation of levulinic acid (LA) using formic acid (FA) as H_2 feeder. Ni(20)Cu(60)-SiO$_2$ (3:1 weight ratio of Cu to Ni, 80 wt% metal content) showed better activity for vapor-phase formation of γ-valerolactone (GVL) from LA with FA as a hydrogen source. The catalyst selectively converts 99% of LA into 96% of GVL; the remaining 4% is angelica-lactone (AL). The effect of different concentrations of Ni promoted on Cu-silica and different LA to FA molar ratios on the catalyst activity affecting the hydrogen-free hydrogenation of LA was studied. The catalyst Ni(20)Cu(60)-SiO$_2$ exhibited long-term stability (200 h) without loss in activity. Characterization using TEM, XPS, TPR, XRD and N$_2$O titration was performed to find the most active phase for LA hydrogenation to GVL and the reason for the long-term stability. It was found that Ni-promoted well-dispersed metallic Cu species were the most active phases in hydrogenation, and the nanocomposite nature of the catalyst helped in providing long-term stability to the active phase.

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1. Introduction

For over half a century, most chemical industries have depended on fossil resources for major feed stocks; however, most of the fossil-fuel reservoirs are in the mature stages of their economic life spans. Hence, it is crucial to develop integrated systems that can produce valuable chemicals from alternative biomass [1–4]. Safe and economic production of bio-based chemicals and biofuels is a major challenge of today [1–4]. Among the bio-based chemicals, levulinic acid (LA) is a well-known product developed by the hydrolysis of hexoses (six-carbon sugars, C6 sugars), and it can be obtained inexpensively from the decomposition of cellulosic materials [3]. Alternatively, formic acid (FA) may be coproduced with LA via acid-catalyzed conversion of C6 sugars [4]. Very

recently, Upare et al. successfully demonstrated the BrØnsted-acid-catalyzed chemical conversion of C6 sugars and cellulose to LA [4a]. Consequently, LA is an attractive starting material for the production of many useful C5-based compounds such as γ-valerolactone (GVL), 2-methyltetrahydrofuran (MTHF) and other derivatives. GVL can be utilized as a versatile platform chemical for various valuable products [5]; it is also useful in the industry as a solvent for lacquers, insecticides and adhesives. It also has some uses in cutting oil, brake fluid and as a coupling agent in dye baths [5].

Recently, Dumesic and co-workers reported an integrated process for the production of liquid alkenes from GVL and suggested an inexpensive method to produce GVL from biomass [6]. Catalytic approaches to the hydrogenation of LA to form GVL have been reported in the literature [3,7,8]. Most researchers used batch-type reactors and high-pressure hydrogen [3,7] or supercritical CO$_2$ for their studies [8]. Recently, Fu and co-workers reported an economically viable hydrogen-free (H$_2$-free) synthesis of GVL from LA, using FA as a hydrogen source, in a batch-type reactor over ruthenium-based homogenous and heterogeneous catalytic systems [9]. They also reported the selective synthesis of LA and FA in a molar ratio of approximately 1:1.

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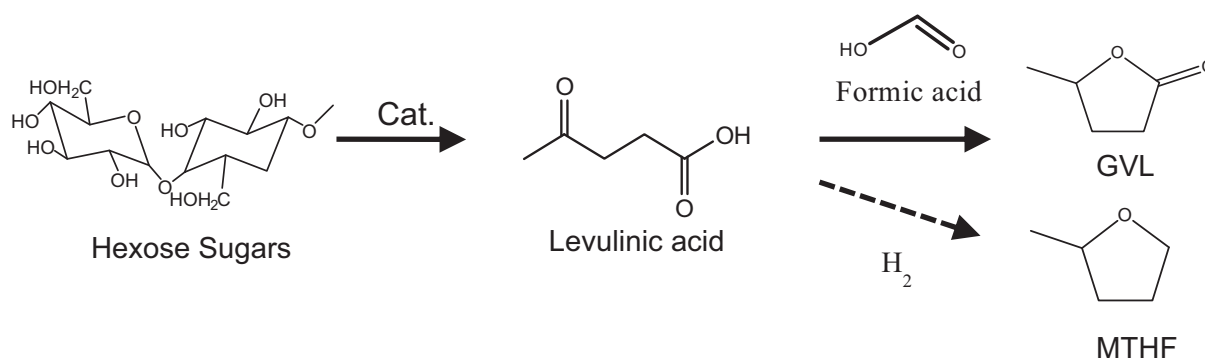
Scheme 1. Synthesis of lactones from biomass-derived levulinic acid and formic acid.

There are a few recent reports involving the use of heterogeneous catalysts for the direct synthesis of GVL from LA and FA as a hydrogen source using gold [10] and ruthenium-based catalysts [9–11]. Very recently, Dumesic and co-workers reported the continuous production of GVL from LA and FA using H_2SO_4 over a noble-metal-supported catalyst at 35 bar [12]. It is worthwhile to mention that continuous vapor-phase processes have advantages over batch-type processes, such as easy recovery of both the catalyst and products. As reported elsewhere, the noble metals Ru, Pt and Pd are frequently considered good hydrogenation catalysts at high temperatures [7]. Transitions metals can also be utilized as catalysts for hydrogenation [13]. However, copper and nickel are rarely considered effective hydrogenation catalysts at high temperatures because of their leaching in the liquid phase and sintering of copper particles at high temperatures [14]. Recently, Upare et al. reported Ni promoted Cu/SiO_2 nanocomposite catalysts, which provide a sustainable catalyst life in continuous hydrocyclization of biomass-derived carboxylic acids to corresponding hydrofurans and lactones under vapor-phase conditions in hydrogen [15]. The nanocomposite nature of copper–silica catalysts helps in preventing metallic sintering and in avoiding significant deactivation. Therefore, it seemed worthwhile to investigate the evolution of the active metal surface in catalysts. Herein, we report a continuous process for selective synthesis of GVL from LA using FA as a hydrogen source over an inexpensive highly stable Ni-promoted $Cu-SiO_2$ nanocomposite catalyst system under atmospheric pressure. Scheme 1 represents the continuous production of GVL from biomass via hydrogenation of LA using FA as a hydrogen source.

2. Experimental

2.1. Materials

$Cu(NO_3)_2 \cdot 3H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were supplied by Wako, and NaOH (AR grade) was obtained from local suppliers at Daejeon, South Korea, and were used as received. The SiO_2 source was Ludox SM-30 colloidal silica supplied by Aldrich. It had a surface area of $345\,m^2/g$ and was used as received. LA (98%, Alfa Aser), FA (99%, Aldrich), and 1,4-dioxane (99.5%, Alfa Aser) were used for hydrogenation of LA to GVL.

2.2. Catalyst preparation

In a typical catalyst-preparation procedure, known amounts of $Cu(NO_3)_2 \cdot 3H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ are dissolved in doubled-distilled water, and the desired amount of silica solution (Ludox SM-30, $S_{BET} = 345\,m^2/g$) comprising 7 nm silica nanoparticles was added dropwise to the water at 4 °C. For precipitation, a solution of 0.1 N NaOH was added to the above suspension until the pH became 9.2. The suspension was then stirred for 12 h at room temperature,

followed by stirring at 85 °C for 5 h. The resulting suspension was filtered and washed with distilled water repeatedly until sodium was no longer detected in the filtrate. The solid was then dried in air at 120 °C for 12 h, pressed into pellets, crushed, sieved (No. 20–40 mesh), and finally calcined in air at 600 °C for 8 h. Before the reaction, catalyst samples were reduced at 290 °C with a mixture of 5% H_2 in N_2 (30 ml/min) for 2 h. The metal composition with silica will be described hereinafter as $Ni(x)Cu(y)$-SiO_2, $x + y = 80$ wt% based on metal oxides, NiO and CuO. Prior to the characterization of catalysts, the reduced and used materials were stabilized in N_2 atmosphere after their reduction at 290 °C or after reaction at 265 °C, by which we could somehow able to prevent the significant oxidation of reduced metallic species before characterizations of catalysts.

2.3. Catalyst characterization

The structure and crystallinity of the catalyst samples were determined by X-ray diffraction analysis on Rigaku Ultima IV Diffractometer (40 kV, 40 mA), which is equipped with Cu tube in Graphite-Monochromatic for Cu Kα radiation. XRD results were recorded by using PDXL software program in the 2θ range between 5 and 80° using slower 1° per min scanning rate. H_2-TPR experiments were carried out in Micromeritics model Pulse Chemisorb 2705 equipped with a thermal conductivity detector (TCD) to monitor H_2 consumption is in the temperature range of 100–800 °C in 5%H_2/He. XPS analysis of the catalysts was carried out to identify the chemical state of the surfaces before and after reduction. The XPS system consisted of a preparation and main chamber, connected via a gate valve. Reduced catalysts were treated under 1 atm of 5% H_2/N_2 at 350 °C for 4 h. The reduction step was advanced into the preparation chamber, and then XPS spectra of each catalyst were obtained in the main chamber (base pressure ~$3.0 \times 10^{-1\circ}$ Torr) without exposing the samples to air. XPS spectra were collected using Mg Kα (1253.6 eV) as a monochromatic energy source and with a concentric hemispherical analyzer (CHA, PHOIBOS-Has 2500, SPECS). Charging effects were calibrated with Ag $3d_{5/2}$ (368.3 eV) and $3d_{3/2}$ (374.3 eV) spectra. For detailed analysis, Cu and Ni $2p_{3/2}$ spectra were deconvoluted using CASA-XPS software. Background subtraction was processed by Shireley method. Each spectrum was fitted with a linearly combined Gaussian/Lorenzian functions. Specific surface areas of catalysts were measured by N_2 physisorption at liquid nitrogen temperature using Micromeritics Tristar 3000 surface area analyzer and standard multipoint BET analysis method. Samples were degassed in flowing N_2 for 12 h at 200 °C before N_2 physisorption measurements. The specific surface areas were evaluated using the Brunauer–Emmett–Teller (BET) method in the p/p_0 range of 0.05–0.2. The particle morphology and crystal size of catalysts were examined using a transmission electron microscope (TEM; Technai