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Hydrogenation of levulinic acid to γ-valerolactone in dioxane over mixed $MgO–Al_2O_3$ supported Ni catalyst

Kun Jiang[a,b], Dong Sheng[a], Zihao Zhang[a], Jie Fu[a,*], Zhaoyin Hou[c], Xiuyang Lu[a]

[a] Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China
[b] Department of Chemical Engineering, Huainan Union University, Huainan 232038, China
[c] Key Laboratory of Applied Chemistry of Zhejiang Province, Department of Chemistry, Zhejiang University, Hangzhou 310028, China

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ABSTRACT

Mixed $MgO–Al_2O_3$ (with different Mg/Al ratio) supported nickel catalysts were prepared via co-precipitation method and used for hydrogenation of levulinic acid to γ-valerolactone under mild condition. Characterization results indicated that mixed $MgO–Al_2O_3$ supported Ni catalysts possessed bigger surface area than that of Ni/MgO and Ni/Al_2O_3, and Ni dispersed highly on the surface of mixed $MgO–Al_2O_3$ support. It was found that mixed $MgO–Al_2O_3$ supported Ni catalysts were more active and selective for the hydrogenation of levulinic acid to γ-valerolactone than that of Ni/MgO and Ni/Al_2O_3, and the best yield of γ-valerolactone at 160 °C, 1 h and 3 MPa H_2 reached 99.7% over $Ni/MgAlO_{2.5}$, and $Ni/Mg_2Al_2O_5$ could be recycled without obvious loss of its initial activity.

1. Introduction

With the decrease of fossil reserves and increased demands for chemicals and fuels, there is an increasing emphasis on the utilization of renewable resources [1,2]. Biomass is a promising raw material that could satisfy society's requirements for chemicals and fuels, as it is abundant, inexpensive and renewable [3]. Cellulose, an important feedstock of biomass, has been studied to produce many platform chemicals, such as 5-hydroxymethylfurfural (HMF) [4], levulinic acid (LA) [5] and γ-valerolactone (GVL) [6]. Among of which, GVL can be used as a solvent, additive, and intermediate in the production of diverse value-added chemicals [7]. Recently, the importance of GVL received much attention all over the world since it was regarded as a bridge between biomass and liquid fuels [8,9].

GVL can be synthesized by the hydrogenation of bio-based LA. In the past decade, mainly noble metal catalysts, such as Ru, Ir, Rh, Pd, Re and Pt, were reported for the hydrogenation of LA to GVL [10–16], and Ru and Ir exhibited high activity. However, the high price and scarce resources of noble metals would limit their application in the industrial scale. Recently, more and more studies were focused on copper-based catalysts such as Cu/ZrO_2 [17,18], Cu/SiO_2 [19], Cu–Cr [20], and Cu–Fe [21]. Although LA hydrogenation proceeded efficiently over these Cu-based catalysts, high temperature (250 °C) and long reaction time (5 or 10 h) were needed in order to achieve a high conversion, and Cu catalysts deactivated easily under higher temperature. In order to overcome these problems, another type of non-noble metal catalysts, Ni-based catalysts, that have the advantages of relative higher stability during reaction and could be recycled easily due to its magnetism, were reported by several groups. Among of which, Ni/Al_2O_3, $Ni–Cu/Al_2O_3$, $Ni–MoO_x/C$ were tested for hydrogenation of LA to GVL under high temperature (250 °C) and/or hydrogen pressure (6.5–8.0 MPa) [22,23].

In this work, MgO, Al_2O_3 and mixed $MgO–Al_2O_3$ supported Ni catalysts were prepared via a co-precipitation method. The structure of these catalysts was characterized via N_2-adsorption, X-ray diffraction (XRD), and transmission electron microscopy (TEM). And the performance of these catalysts for hydrogenation of LA to GVL were tested under mild conditions (160 °C, 3 MPa) and compared with those published works.

* Corresponding author. Fax: +86 571 87952683.
E-mail address: jiefu@zju.edu.cn (J. Fu).

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2. Experimental

2.1. Materials

$Ni(NO_3)_2{\cdot}6H_2O$ (98%), $Mg(NO_3)_2{\cdot}6H_2O$ (99%), and $Al(NO_3)_3{\cdot}9H_2O$ (99%) were purchased from Aladdin Industrial Corporation, China. Levulinic acid (99%) was purchased from J&K Company Ltd., China. γ-Valerolactone (99%) was purchased from Sigma–Aldrich, USA. Dioxane (99.5%) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Hydrogen (99.999%) was purchased from Shanghai BaoQing Gases Industrial Co., Ltd. Deionized water was prepared in house.

2.2. Catalyst preparation

A series of MgO, Al_2O_3 and mixed MgO–Al_2O_3 supported Ni catalysts were prepared via a co-precipitation method. According to the component of the catalyst, $Ni(NO_3)_2{\cdot}6H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, and $Al(NO_3)_3{\cdot}9H_2O$ were dispersed in deionized water, and then precipitated with 0.2 M aqueous potassium carbonate under vigorous stirring at 30 °C of a pH value of 9.2. After aging the precipitate for 6 h at 30 °C, the precipitate was separated by filtration and washed with deionized water three times to remove the potassium. The precipitate was then dried in a forced air oven at 110 °C for 12 h and calcined at 400 °C (heating rate of 2 °C/min) for 4 h. Prior to the reaction, the calcined catalyst was reduced in a tube furnace with hydrogen (a flow rate of 0.1 L/min) at 650 °C (heating rate of 10 °C/min) for 3 h and identified as $Ni/Mg_xAl_yO_{(x+1.5y)}$ in which x, y refer to the amount of Mg and Al respectively.

2.3. Characterization

N_2 adsorption was performed at 77 K in a static volumetric apparatus (Micromeritics ASAP2020). Samples were degassed at 300 °C for 16 h before N_2 adsorption. Specific surface area was calculated using the Brunauer–Emmett–Teller (BET) equation, pore size and volume were calculated according to Barret–Joyner–Halenda (BJH) method. All calculations were based on the adsorption isothermals.

XRD patterns were recorded on a PANalytical Empyrean 200895, using Ni filtered Cu Kα radiation (λ = 0.154 nm) at 30 mA, 40 kV. The catalyst was reduced in a tube furnace with hydrogen (a flow rate of 0.1 L/min) at 650 °C for 1 h before XRD analysis.

The morphology of prepared catalysts was observed by the transmission electron microscope (JEM-2010). A small amount of samples were sonicated in acetone for 1 min, and then a drop of prepared suspension was deposited on a Cu grid coated with a carbon layer. The grid was dried at room temperature prior to analysis. The electron gun was operated at an accelerating voltage of 200 kV for the collection of TEM images.

2.4. Catalytic reaction

Hydrogenation of LA was carried out in a 100 mL custom designed stainless autoclave with Telfon interlayer. The typical reaction conditions used were listed as follows: 1 g LA in 40 mL dioxane with 0.1 g catalyst, and the reaction mixture was stirred at 1000 rpm at 160 °C, initial hydrogen pressure 3 MPa. After reaction, the mixture was filtered, washed, and diluted with deionized water into a volumetric flask of 250 mL. The compositions of the diluted samples were quantitatively determined by HPLC (Agilent 1100) equipped with a refractive index detector. 20 μL of a sample was injected into a Phenomenex Gemini 5u C18 110A column (250 × 4.60 mm, 5 μm) and eluted with a mixture (0.1 mM hydrochloric acid: acetonitrile = 99: 1) at a flow rate of 0.6 ml/min. The column was maintained at 35 °C and the calibration was carried out by commercial standards. For the recycle of catalyst, the filtered catalyst was washed in methanol with ultrasonic and dried at 60 °C for 12 h in a vacuum drying oven.

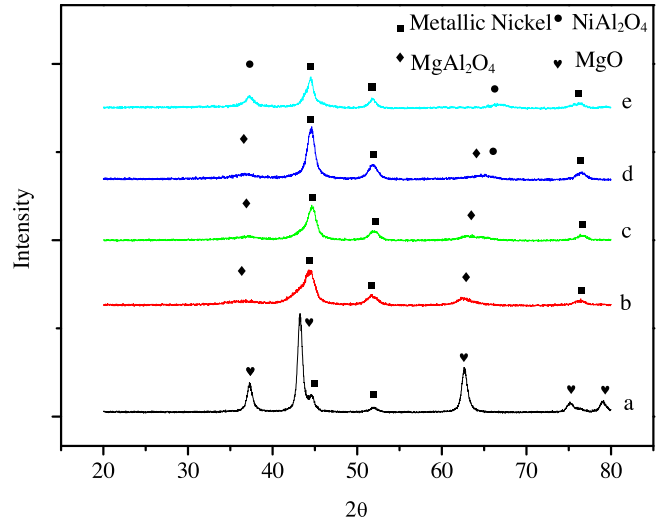

Fig. 1. XRD patterns of $Ni/Mg_xAl_yO_{(x+1.5y)}$ with different support compositions: (a) Ni/MgO; (b) $Ni/MgAl_{0.5}O_{1.75}$; (c) $Ni/MgAlO_{2.5}$; (d) $Ni/MgAl_2O_4$; (e) Ni/Al_2O_3.

3. Results and discussion

3.1. Characterization of catalyst

XRD patterns of Ni/MgO, Ni/Al_2O_3, and $Ni/Mg_xAl_yO_{(x+1.5y)}$ catalysts were shown in Fig. 1. A strong diffraction of the MgO phase was observed in the XRD pattern of Ni/MgO at $2\theta = 43.2°$ [24], while the intensity of metallic Ni was mild. Other patterns of $Ni/Mg_xAl_yO_{(x+1.5y)}$ with different support compositions were similar, A mild diffraction of $MgAl_2O_4$ phase was observed at $2\theta = 37.3$, 63.8°. The average crystalline size of metallic Ni was calculated Scherrer equation according to the half-width of Ni (1 1 1) at 44.3° and summarized in Table 1. It was found that the average crystalline size of metallic Ni of Ni/Al_2O_3 and Ni/MgO were 19.3 and 14.2 nm respectively, while it decreased to around 10 nm in $Ni/Mg_xAl_yO_{(x+1.5y)}$ catalysts. These results indicated that mixed MgO–Al_2O_3 supports were favorable for the dispersion of Ni.

The N_2 adsorption–desorption isotherms of these catalysts are shown in Fig. 2. It can be found that the isotherms of $Ni/MgAl_{0.5}O_{1.75}$ and $Ni/MgAlO_{2.5}$ exhibited different shapes compared to other catalysts. $Ni/MgAl_{0.5}O_{1.75}$ and $Ni/MgAlO_{2.5}$ showed type IV isotherms with steep H3 hysteresis loops, while $Ni/MgAl_2O_4$ was an obvious different isotherm with an increase in adsorption in the range of P/P0 = 0.5–0.7, which contributed to the smaller pore volume and pore size. The surface area, pore volume, and pore size of Ni/MgO, $Ni/MgAl_{0.5}O_{1.75}$, $Ni/MgAlO_{2.5}$, $Ni/MgAl_2O_4$, and Ni/Al_2O_3 that calculated via the N_2 adsorption thermals are summarized in Table 1. The surface areas of $Ni/MgAl_{0.5}O_{1.75}$, $Ni/MgAlO_{2.5}$, and $Ni/MgAl_2O_4$ were around 150 m^2/g, and this value was larger than that of Ni/MgO and Ni/Al_2O_3. And the higher surface area of mixed MgO–Al_2O_3 supported Ni catalysts could contribute to the higher dispersion of Ni.

The typical TEM images of $Ni/MgAlO_{2.5}$ are shown in Fig. 3. The laminar crystal was Al_2O_3 and the rods on the Al_2O_3 were MgO. The dark spot was metallic nickel, and the nickel particles (black spots) were well dispersed on the mixed MgO–Al_2O_3 support. The distribution of Ni particle size was obtained by the software of Nano Measurer based on Fig. 3a. The Ni particle sizes were mostly in the range of 5 to 13 nm, and the mean size of Ni was 9.6 nm. The average crystalline size obtained from XRD was the average size for all the