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Levulinic acid hydrogenolysis on Al_2O_3 -based Ni-Cu bimetallic catalysts

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ABSTRACT

Inexpensive γ -alumina-based nickel-copper bimetallic catalysts were studied for the hydrogenolysis of levulinic acid, a key platform molecule for biomass conversion to biofuels and other valued chemicals, into γ -valerolactone as a first step towards the production of 2-methyltetrahydrofuran. The activities of both monometallic and bimetallic catalysts were tested. Their textural and chemical characteristics were determined by nitrogen physisorption, elemental analysis, temperature-programmed ammonia desorption, and temperature-programmed reduction. The monometallic nickel catalyst showed high activity but the highest by-product production and significant amounts of carbon deposited on the catalyst surface. The copper monometallic catalyst showed the lowest activity but the lowest carbon deposition. The incorporation of the two metals generated a bimetallic catalyst that displayed a similar activity to that of the Ni monometallic catalyst and significantly low by-product and carbon contents, indicating the occurrence of important synergetic effects. The influence of the preparation method was also examined by studying impregnated- and sol-gel-derived bimetallic catalysts. A strong dependency on the preparation procedure and calcination temperature was observed. The highest activity per metal atom was achieved using the sol-gel-derived catalyst that was calcined at 450 °C. High reaction rates were achieved; the total levulinic acid conversion was obtained in less than 2 h of reaction time, yielding up to 96% γ -valerolactone, at operating temperature and pressure of 250 °C and 6.5 MPa hydrogen, respectively.

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1. Introduction

Owing to diminishing oil reserves, increasing energy demands from emerging economies, and increasing global warming concerns, researchers have focused their attention on biomass-derived chemicals to replace non-renewable energy resources [1–5]. The suitability of biomass-derived products, such as liquid fuels, is being established by currently used first-generation biofuels (bioethanol and biodiesel) that are

easily produced from edible biomass [5,6]. However, this leads to expensive feedstocks and competition with the food market. In contrast, second-generation biofuels are derived from non-edible, inexpensive, and abundant lignocellulosic biomass. However, their production is more challenging than that of first-generation biofuels [6].

Levulinic acid (LA) is a key chemical towards the development of these new biofuels because it can be produced in good yields at both laboratory scale [7,8] and semi-industrial scale

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by acid hydrolysis of lignocellulosic materials and urban residues [6,9,10]. In 2004, the US Department of Energy classified LA as a “top ten” bio-based product obtained from biorefinery carbohydrates in accordance with characteristics such as potential as a platform chemical and building block, petrochemical replacement capability, and potential production scale-up [10].

LA can be converted into suitable and sustainable fuels such as γ -valerolactone (GVL) and 2-methyltetrahydrofuran (MTHF), as shown in Scheme 1. GVL possesses many of the properties of an ideal liquid both for energy and chemical product manufacture, as reported [11], and shows similar behavior to ethanol when added to gasoline. MTHF is a well-known fuel additive that can be added to gasoline in proportions of up to 70 vol% [12] in the absence of engine modification or used as part of new fuel formulations for flexible fuel engines, as reported by Paul [13] and the US Department of Energy [14]. However, direct production of MTHF from LA is rarely reported. To our knowledge only two published reports addressed this issue: Elliot and Frye [15] achieved an 89.8% MTHF yield using operating conditions of 242 °C and 10 MPa H_2 , and a Pd(5%)-Re(5%)/C catalyst. Upare and co-workers [16] reported a maximum MTHF yield of 89% using operating conditions of 265 °C and 2.5 MPa H_2 and a Cu(72%)-Ni(8%)/SiO₂ catalyst. In both cases, 1,4-dioxane was used as a solvent.

In contrast, GVL production is widely reported and carried out under milder conditions. Carbon-based ruthenium catalysts are used by many authors under reaction conditions that vary from 25 to 215 °C and from 1.2 to 5.5 MPa hydrogen [17–20] in solvents such as 1,4-dioxane or methanol. Temperatures of 70–150 °C and pressures of 0.5–3.5 MPa H_2 have been successfully used when water is employed as a solvent [21–23]. Other noble metals on different supports have also been reported to effectively activate the reaction process such as Pt over titania, silica, and zirconia [24–26], Au over zirconia [27], and Ir supported on carbon nanotubes [28]. However, reports using non-noble metals for LA hydrogenation are rare. GVL production in liquid phase [29,30] using copper supported on Cr₂O₃, Al₂O₃, or ZrO₂ has been reported but requires harsher conditions, i.e., temperatures of 200–265 °C, pressures of 3.0–7.0 MPa H_2 , and long reaction times of 5–10 h.

Non-noble metal catalysts are generally preferred owing to their higher availability and lower price that are more appropriate for large-scale operations such as biofuel production [29,30]. Hence, this work investigates the use of sustainable non-noble metal-based catalysts for the production of LA derivatives.

2. Experimental

2.1. Catalyst preparation

A series of catalysts were prepared by either the wet impregnation method (WI) or the sol-gel (SG) method. A commercial γ -Al₂O₃ support (Alfa Aesar) was used for the WI-based method. Nickel(II) nitrate hexahydrate (98.5%, Sigma-Aldrich) and copper(II) nitrate hemipentahydrate (98%, Alfa Aesar) were used as metal precursor salts, and aluminum isopropoxide (AIP, 98%, Aldrich) was used as an alumina precursor for the SG-based preparation.

The WI method consisted of mixing 1 g of the support with 9 mL water and calculated amounts of the precursor salt in a rotary vacuum evaporator. The mixture was stirred overnight at 90 r/min and heated to 65 °C, and the moisture was removed under vacuum.

To prepare the SG-based catalyst, the method previously described by Gandarias et al. [31] was employed. Briefly, the desired amount of AIP was dissolved in water at an AIP/water mass ratio of 1:9 at 40 °C while maintaining the pH of the solution between 3.8 and 4.2, adjusted with 1 mol/L HNO₃ solution. The metal precursor salt solutions were dissolved in an adequate amount of ethanol, and the resulting solution was added dropwise to the AIP solution. The mixture was stirred for 30 min at 40 °C and then sonicated for 30 min. The mixture was allowed to sit at 50 °C for 48 h, followed by overnight drying at 105 °C. The obtained products were ground (particle size: 0.42–0.50 mm) and calcined under air flow at the desired temperature (300 or 450 °C) for 1 h (heating rate: 2 °C/min). The methods are referred to as SG 300 and SG 450 based on the calcination temperature used.

Prior to conducting the activity tests, the catalysts underwent reduction in a tubular furnace at 650 °C for 1 h (heating rate: 10 °C/min) under 75 mL/min H_2 flow. Following cooling to room temperature, the catalysts were stored under isooctane to avoid contact with air.

2.2. Catalyst characterization

Elemental analysis of the catalysts was carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Perkin Elmer Optima 2000 OV. Samples were digested with a mixture of nitric, hydrochloric, and hydrofluoric acids using an ETHOS 1 Advanced Microwave Digestion System.

Surface area, pore volume, and pore size distribution were determined by N₂ physisorption at –196 °C on an Autosorb

Scheme 1. Levulinic acid conversion path into γ -valerolactone and 2-methyltetrahydrofuran.

1C-TCD (Quantachrome). Prior to analysis, all samples were degassed at 250 °C and 10 Pa for 3 h. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method, and pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method on the N₂ desorption curve.

Temperature-programmed reduction (TPR) of the samples was performed on an Autosorb 1C-TCD (Quantachrome). Reduction of the calcined catalyst samples was conducted under a gaseous mixture of 5 vol% hydrogen in argon (gas flow rate: 50 mL/min) at 1100 °C (heating rate: 10 °C/min). Hydrogen consumption was monitored on a thermal conductivity detector (TCD).

Thermogravimetric analyses (TGA) of the catalysts were performed on a Mettler Toledo TGA/SDTA851 using pure oxygen as an oxidizing agent. The catalysts were heated at 800 °C at a heating rate of 5 °C/min.

Ammonia temperature-programmed desorption (NH₃-TPD) analyses were performed on the same apparatus used for conducting the TPR analyses. The samples were placed in a U-shaped quartz reactor and reduced under a 50 mL/min H₂ flow at 650 °C for 1 h (heating rate: 10 °C/min). Then, the samples were cooled to 250 °C under He flow and maintained at this temperature for 30 min for degassing. The degassed samples were then cooled to 100 °C under flowing He prior to saturation with NH₃ in 10 vol% NH₃/He, followed by purging with He (50 mL/min) at 100 °C for 30 min. The temperature was then raised to 900 °C at a heating rate of 10 °C/min. The desorbed NH₃ was monitored on a TCD detector.

2.3. Activity tests

The experiments were carried out in stainless steel stirred autoclaves (Autoclave Engineers, 300 mL) at 250 °C for 6 h at 6.5 MPa H₂. The reactor was loaded with 1 g of the catalyst, heated to the reaction temperature under nitrogen, and purged with hydrogen. Then the feed mixture (200 mL, 5 wt% LA aqueous solution (98%, Aldrich)) was introduced from the feed cylinder. The reaction mixture was stirred at 600 r/min and samples were periodically extracted from the reactor to assess the reaction kinetics.

The samples were analyzed on an Agilent Technologies 6890N GC gas chromatograph equipped with a flame ionization detector and a thermal conductivity detector. The GC was equipped with a DB-1 column (60 m × 530 μm × 5 μm, Agilent Technologies), and helium was used as the carrier gas at 9.2 psi. The temperature program was set as follows: 40 °C for 5 min, 10 °C/min heating ramp for 16 min, and 250 °C for 5 min using a 30 °C/min ramp. Product identification and quantifica-

tion were performed by calibration against commercially available pure chemicals. The results were further confirmed by GC-MS analysis.

3. Results and discussion

3.1. Catalyst characterization

Table 1 presents the textural properties and the experimentally determined metal contents of the calcined catalysts. The experimentally determined metal contents of the WI-prepared catalysts were comparable with the theoretical metal contents. Ni contents were either higher or lower than the theoretical values, whereas Cu contents were consistently lower than the expected contents. The SG-based bimetallic catalysts featured a comparable Ni-to-Cu ratio with that of the WI-based bimetallic catalyst despite the lower metal contents of the SG-based bimetallic catalysts.

The monometallic and bimetallic catalysts supported on commercial alumina prepared by the metallic impregnation process featured lower surface areas (~150 m²/g) than that of the bare commercial alumina support (~230 m²/g) at a given metal loading. Pore volume was also lower, but the decrease was more significant for the Ni-containing catalyst by a factor of two. The addition of Cu only resulted in a pore volume loss of 25%, suggesting that i) Ni preferentially deposited onto the pores of the alumina support, whereas Cu deposited on the outer surface of the alumina support or ii) Cu obstructed smaller pores, whereas Ni deposited on larger pores. Considering the differences in the average pore radius between the WI-prepared catalysts and the alumina support, the first option is more likely because incorporation of Ni decreased the pore radius, whereas Cu addition enlarged the average pore size. Regardless, the effects associated with Ni deposition seem to prevail over the changes induced by Cu deposition.

Using the SG method, a higher surface area was achieved at a calcination temperature of 300 °C. However, a reduced surface area was obtained at a higher calcination temperature of 450 °C despite the lower metal loading of the corresponding catalyst. Calcination had a minimal effect on the pore volume of the final catalysts. However, at a higher calcination temperature, pore volume of the final bimetallic catalyst was approximately three times lower than that of the catalyst counterpart prepared by the impregnation method. Also, a higher calcination temperature enlarged the average pore size.

Figure 1 shows the results of the TPR analysis of the three bimetallic catalysts. Important differences are highlighted regarding the composition and reducibility of the surface metallic

Table 1
Elemental and textural characterization of the calcined catalysts.

Catalyst	Ni (wt%)	Cu (wt%)	Ni + Cu (wt%)	Ni/Cu ratio	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore radius (nm)
γ-Al ₂ O ₃	0	0	0	0	227.2	0.81	6.81
Ni/Al ₂ O ₃ (WI)	36.11	0	36.11	∞	146.9	0.35	4.64
Cu/Al ₂ O ₃ (WI)	0	30.01	30.01	0	152.9	0.58	7.55
Ni-Cu/Al ₂ O ₃ (WI)	19.62	12.86	32.48	1.53	151.0	0.36	4.76
Ni-Cu/Al ₂ O ₃ (SG 300)	13.26	8.88	22.14	1.49	186.1	0.20	2.06
Ni-Cu/Al ₂ O ₃ (SG 450)	8.56	5.5	14.06	1.56	132.4	0.16	4.87

Fig. 1. TPR profiles of the calcined bimetallic catalysts Ni-Cu/Al₂O₃ prepared by different methods and associated peak decomposition.

species. The strong nickel-alumina interactions, corresponding to peaks observed above 600 °C in the SG 450 catalyst, forming nickel aluminates, were absent in the SG 300 catalyst. This indicates that these interactions are strongly dependent on the temperature [32]. However, the WI bimetallic catalyst features reduction peaks above 600 °C that are associated with these nickel species [31] even at a calcination temperature of 300 °C. This discrepancy may be attributed to the higher nickel content in the WI catalyst (as opposed to that in the SG catalyst) and the different types of alumina support; the sol-gel-derived alumina calcined at 300 °C is not fully converted to γ -alumina [33]. Thus, the differences between the supports can instigate the formation of different species [32].

Copper species are reduced at temperatures ranging from 245 to 340 °C. The increase in the reduction peak's maximum temperature is related to the copper loading of the catalyst. Higher metal loadings promote agglomeration and formation of larger crystallites that require higher temperatures for reduction [34]. Additionally, copper addition induces a shift to lower temperatures in the reduction peaks ascribed to weakly interacting nickel by hydrogen spillover effects [34] that facilitate the reduction reaction of Ni²⁺ to Ni⁰ and nucleate the formation of metallic Ni particles. This reduction took place at the low temperatures in the SG catalyst calcined at 300 °C, as indicated by the overlapping peaks because fewer nickel aluminates were formed.

The catalysts prepared by impregnation and the bare alumina support were further characterized by NH₃-TPD to determine the acidity of the catalysts. The profiles are presented in Fig. 2.

As observed in Fig. 2, the bare γ -Al₂O₃ support exhibits the highest acidity, displaying a small peak centered at 200 °C and a broad peak between 300 and 700 °C with its maximum at 410 °C. The incorporation of Ni resulted in a minor acidity loss in the low-temperature region. Considerable reduction in acidity was observed in the high-temperature region. However, important desorption peaks centered at 400 °C were also observed. In general, Cu monometallic catalyst showed high acid-

Fig. 2. NH₃-TPD profiles of γ -Al₂O₃, Ni/Al₂O₃, Cu/Al₂O₃, and Ni-Cu/Al₂O₃ catalysts prepared by WI.

ity loss across the temperature range studied. The bimetallic catalyst featured an intermediate acidity profile. However, it displayed a higher acidity loss in the low-temperature region when compared with that of other catalysts. In the high-temperature region, the bimetallic catalyst showed two small peaks with an appreciable shift to higher temperatures when compared with the peak of the monometallic Ni catalyst. These observations were attributed to the co-existence of the Cu and Ni species.

3.2. Catalyst activity

The hydrogenolysis activities of the five catalysts were measured towards the conversion of LA into α -angelicolactone (AL), GVL, and MTHF in an aqueous medium under 6.5 MPa hydrogen. First, a series of experiments were performed, employing the monometallic and bimetallic catalysts prepared by the WI method to determine the most hydrogenating active phase for this reaction and evaluate the synergetic effect arising from the co-existence of the Cu and Ni metals in the bimetallic catalyst. These results are summarized in Fig. 3.

Figure 3 shows that the Ni and Ni-Cu catalysts are the most active systems and produced a maximum GVL yield of

Fig. 3. GVL yield as a function of reaction time plots of the Ni/Al₂O₃, Cu/Al₂O₃, and Ni-Cu/Al₂O₃ catalysts prepared by WI.

91%–92% after 2 h of reaction, corresponding to an LA conversion of $\sim 100\%$. In contrast, Cu catalyst exhibited a significantly lower activity, achieving a non-asymptotic maximum GVL yield of 66% after 6 h of reaction time, corresponding to an LA conversion of 75%. Despite the lower activity of the copper catalyst, the presence of copper seems to inhibit catalyst deactivation based on the low AL yields obtained with the Cu-containing catalysts. AL yields of ~ 0 , 1.6%, and 4.1% were obtained with the Cu monometallic, bimetallic, and Ni monometallic catalysts, respectively. Because AL is produced by acid-catalyzed dehydration of LA, AL detection indicates the onset of activity loss because active catalysts easily convert LA into GVL. AL is a well-known coke precursor [35]; hence, AL detection can be related to the production of coke on the used catalysts. AL concentration became significant at reaction times greater than 3 h. At these reaction times, LA concentration was negligible because complete conversion of LA was achieved at reaction times shorter than 2 h. Hence, the detected AL is believed to be due to the previously formed GVL or AL desorbed from the catalyst surface. To date, the reversible $\text{AL} \leftrightarrow \text{GVL}$ reaction has not been reported in the literature.

The influence of the preparation method on the catalytic activity of the bimetallic catalysts was then investigated. The activity of the two bimetallic catalysts prepared by the SG method and calcined at two different temperatures (300 and 450 °C) was examined. Figure 4 shows the results.

As observed in Fig. 4, all studied catalysts achieved complete LA conversion in less than 2 h with comparable GVL yields ($\sim 90\%$). The catalyst prepared by WI displayed the highest activity at the early stages of the reaction. However, both SG-prepared catalysts calcined at different temperatures achieved superior GVL yields (SG 450 catalyst: 92%; SG 300 catalyst: 96%; WI catalyst: 91%) at the later stages of the reaction. Moreover, the SG catalysts achieved a slightly higher AL production (2.4%) when compared with that of the WI catalyst (1.6%)—these yields were considerably lower than that ob-

Fig. 4. GVL yield as a function of reaction time plots of the Ni-Cu/Al₂O₃ bimetallic catalysts prepared by SG and WI.

tained for the Ni/Al₂O₃(WI) catalyst. Considering the large differences in the total metal loading between these three catalysts, the different yields obtained are attributed to the higher dispersion obtained by the SG method when compared with that achieved by the WI method [36]. The higher dispersion enables a more intimate contact between the acidic and hydrogenating active sites, which results in a faster hydrogenation of the intermediate product AL, consequently reducing carbon deposition on the catalyst surface. The latter processes were further investigated by thermogravimetric analysis of the calcined and the used catalysts. The results are presented in Fig. 5.

The fresh catalysts (Fig. 5(a–c)) show a water desorption peak between 50 and 100 °C and additional peaks at higher temperatures depending on the type of catalyst studied. The additional peaks can be associated with the decomposition of the metal precursor salts. It is worth noting that these peaks are shifted to lower temperatures for the SG catalyst, which

Fig. 5. TGA curves of fresh catalysts (a) Cu/Al₂O₃(WI), (b) Ni/Al₂O₃(WI) and (c) Ni-Cu/Al₂O₃(SG 300) and (d–f) corresponding to used catalysts.

may indicate a greater extent of dispersion and/or exposure of the metal particles.

The profiles of the used catalysts differ significantly among themselves and from those of the fresh catalysts. The thermogram (Fig. 5(d)) of the spent Cu monometallic catalyst featured a water desorption peak at 50 °C, a reaction product (LA and/or GVL) desorption peak at 220 °C, and a large weight gain peak at ~450 °C that is due to oxidation of metallic Cu to CuO. At higher temperatures (500 °C), a sharp and considerable weight loss peak is observed due to the combustion of carbon deposited on the surface of the catalyst [36,37]. The profile (Fig. 5(e)) of the Ni monometallic catalyst is comparable with the thermogram of the Cu monometallic catalyst, except for the sharp weight loss at 300 °C. Also, the Ni monometallic catalyst showed a lower weight increase at 450 °C because Ni forms species that are more difficult to reduce, such as nickel aluminates, which are not reduced upon activation of the catalyst prior to the activity test and hence these species cannot be oxidized further.

The profile (Fig. 5(f)) of the SG-prepared catalyst exhibits the same desorption peaks; however, they differ from those of the WI-prepared catalysts in regards to the weight increase features associated with metal oxidation. Metal oxidation is not evidenced in the profile of the SG-prepared catalyst, suggesting the high dispersion of the particles and consequently the existence of smaller particles and greater particle exposure. The used SG catalysts were stored in the presence of air. Hence, oxidation of the SG catalysts is expected to occur prior to the TGA treatment. The carbon contents of the catalysts were estimated based on two assumptions owing to the interfering presence of the metal oxidation peak. The first estimation is based on the area of the peak associated with carbon combustion, whereas the second estimation is based on the weight difference between the pre- and post-combustion states where the metal oxidation peak is unaccounted for. The results, presented in Table 2, are consistent with the previously discussed hypothesis that correlates the deposited carbon amount with the increased AL yields observed in the WI-prepared catalysts. Because the carbon contents estimated for the three bimetallic catalysts are similar, the estimation method can be extended to the SG catalysts.

The measured deposited carbon contents are in good agreement with the previously discussed catalyst acidity profiles. The deposited carbon amount is clearly related to the previously discussed high-temperature acidity shown in Fig. 2; the Ni monometallic catalyst showed the highest amount of strong acid sites, whereas Cu monometallic catalyst showed

Fig. 6. Metal-normalized reaction rates of the catalysts. (1) Cu/Al₂O₃(WI); (2) Ni/Al₂O₃(WI); (3) Ni-Cu/Al₂O₃(WI); (4) Ni-Cu/Al₂O₃(SG 300); (5) Ni-Cu/Al₂O₃(SG 450).

negligible amounts of these type of acid sites and the bimetallic catalyst featured an intermediate level of acidity.

To further compare the activities of the five prepared catalysts, the initial reaction rate of LA conversion per mole of metal was calculated. This parameter was estimated using the LA conversion obtained at the first sampling time (30 min) and the total metal content of each catalyst, as measured by ICP-AES (Table 1). The results are displayed in Fig. 6.

The metal-normalized initial reaction rates of the different catalysts differ significantly. However, the trend is comparable. First, the WI-based Cu monometallic catalyst was the least active, displaying $< 0.05 \text{ mol}_{\text{LA}} \text{mol}_{\text{metal}}^{-1} \text{min}^{-1}$, whereas the WI-based Ni monometallic catalyst was five times more active. In terms of activity per total metal content, only a small increase was noticed between the WI Ni monometallic and Ni-Cu bimetallic catalysts. However, the differences in the individual metal contents were significantly larger in the presence of the two metals. For instance, the activity related to Ni increased by 50% and the activity related to Cu was more than 14 times higher when compared with that of the WI mono- and bimetallic catalysts. In regards to the SG catalysts, the calcination temperature plays an important role. SG 300 catalyst achieved a lower activity than that of the WI bimetallic catalyst. In contrast, SG 450 catalyst showed the highest activity, achieving up to $0.67 \text{ mol}_{\text{LA}} \text{mol}_{\text{Ni}}^{-1} \text{min}^{-1}$ and $1.14 \text{ mol}_{\text{LA}} \text{mol}_{\text{Cu}}^{-1} \text{min}^{-1}$. This activity increase is clear evidence of the synergetic effects exerted by Cu and Ni, affording a highly efficient catalyst in terms of metal loading—similar conversion and selectivity are achieved with significantly low metal contents.

4. Conclusions

Inexpensive alumina-based Ni-Cu catalysts were successfully prepared for the hydrogenolysis of levulinic acid to form γ-valerolactone, achieving high yields of up to 96%. The activities of the monometallic and bimetallic catalysts were tested. The co-existence of the metals supported on alumina afforded enhanced positive effects. Additionally, a higher activity per metal atom was observed for the sol-gel-prepared catalyst

Table 2

Carbon content of the used catalysts estimated from TGA.

Catalyst	Carbon content (%)	
	Based on peak area	Based on weight difference
Ni/Al ₂ O ₃ (WI)	5.7	4.5
Cu/Al ₂ O ₃ (WI)	4.1	2.0
Ni-Cu/Al ₂ O ₃ (WI)	5.1	3.7
Ni-Cu/Al ₂ O ₃ (SG 300)	4.8	4.7
Ni-Cu/Al ₂ O ₃ (SG 450)	3.6	4.0

Graphical Abstract

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Levulinic acid hydrogenolysis on Al_2O_3 -based Ni-Cu bimetallic catalysts

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The influence of the metallic phase and preparation methods of alumina-based copper-nickel catalysts on the hydrogenolysis of levulinic acid to produce γ -valerolactone was studied. High yields of up to 96% were achieved.

when compared with that of the catalysts prepared by a wet impregnation procedure. This difference can be attributed to the balanced amounts of acid and metallic sites. TGA assessment of the carbon deposition on the catalytic surfaces revealed that copper plays a key role in inhibiting carbon deposition on the catalyst despite the lower activity of Cu compared with that of Ni. Cu-Ni/ Al_2O_3 catalysts are promising candidates for hydrogenolysis reactions in the biorefinery industry.

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