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Article

An efficient and reusable bimetallic Ni₃Fe NPs@C catalyst for selective hydrogenation of biomass-derived levulinic acid to γ -valerolactone

Haojie Wang^{a,b}, Chun Chen^{a,#}, Haimin Zhang^a, Guozhong Wang^a, Huijun Zhao^{a,c,*}^a Key Laboratory of Materials Physics, Centre for Environmental and Energy Nanomaterials, Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, Anhui, China^b University of Science and Technology of China, Hefei 230026, Anhui, China^c Centre for Clean Environment and Energy, Griffith University, Queensland 4222, Australia

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ABSTRACT

Bimetallic nanostructures have attracted great interest as efficient catalyst to enhance activity, selectivity and stability in catalytical conversion. Herein, we report a facile one-pot carbothermal route to in-situ controllable synthesize heterogeneous bimetallic Ni₃Fe NPs@C nanocatalyst. The X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy and N₂ adsorption-desorption results reveal that the Ni₃Fe alloy nanoparticles are evenly embedded in carbon matrix. The as-prepared Ni₃Fe NPs@C catalyst shows excellent selective hydrogenation catalytic performance toward the conversion of levulinic acid (LA) to γ -valerolactone (GVL) via both direct hydrogenation (DH) and transfer hydrogenation (TH). In DH of LA, the bimetallic catalyst achieved a 93.8% LA conversion efficiency with a 95.5% GVL selectivity and 38.2 mmol g⁻¹ h⁻¹ GVL productivity (under 130 °C, 2MPa H₂ within 2 h), which are 6 and 40 times in comparison with monometallic Ni NPs@C and Fe NPs@C catalysts, respectively. In addition, the identical catalyst displayed a full conversion of LA with almost 100% GVL selectivity and 167.1 mmol g⁻¹ h⁻¹ GVL productivity at 180 °C within 0.5 h in TH of LA. Under optimal reaction conditions, the DH and TH catalytic performance of 500-Ni₃Fe NPs@C(3:1) catalyst for converting LA to GVL is comparable to the state-of-the-art noble-based catalysts. The demonstrated capability of bimetallic catalyst design approach to introduce dual-catalytic functionality for DH and TH reactions could be adoptable for other catalysis processes.

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1. Introduction

The ever increased demand for fuels and chemicals adding to the rapidly diminished fossil resources call for renewable resource to secure sustainable economic development [1]. In this regard, the effectively utilizing biomass to produce fuels

and value-added chemicals has proven to be a suitable solution because biomass is the most abundant non-fossil carbon-neutral and renewable resource on earth [2]. To date, extensive effort has been devoted to convert biomass and its derivatives into fuels, fine chemicals and commodity materials [3]. For example, the massively produced levulinic acid (LA) via

^{*} Corresponding author. Tel: +86-551-65591263; Fax: +86-551-65591434; E-mail: h.zhao@griffith.edu.au[#] Corresponding author. Tel: +86-551-65591263; Fax: +86-551-65591434; E-mail: chenchun2013@issp.ac.cn

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cellulose hydrolysis and dehydration biorefinery processes is one of the Top 10 most promising biomass derived platform molecules [4–6]. It can be converted, through selective hydrogenation, into valuable-added chemicals such as γ -valerolactone (GVL), which can be directly utilized as gasoline blender, food additive or solvent, and used as precursors for the production of plastics, polymers, hydrocarbons (aromatics, alkenes and alkanes) and other valuable chemicals [7–11].

LA can be converted into GVL by homogeneous and heterogeneous catalysis. However, heterogeneous catalysis is preferred because homogeneous catalysis suffers from shortcomings of requiring catalyst separation and recovery [12]. To date, a variety of heterogeneous catalysts (e.g., PtO₂, Raney-Ni, Ni/MoO_x/C, Cu/ZrO₂, CuB₂₃/graphene, Au-Pd/TiO₂, Ru/C, Ir/CNT, NiCu/Al₂O₃, RuSn/C and Mo₂C) have been reported for selective hydrogenation of LA to produce GVL [13–22]. Among the reported heterogeneous catalysts, the activated carbon supported ruthenium catalyst (Ru/C) has been deemed as one of the best performed catalysts, capable of achieving a 97.5% GVL yield at room temperature, but suffered critical drawbacks of aggregation and metal leaching [18]. Although precious metals-based catalysts generally possess high LA conversion efficiency, their expensive and scarcity nature adding to poor stability greatly limit the large-scale applications of precious metals-based catalysts. Development of high performance nonprecious catalysts is therefore vitally important to achieve economically viable large-scale conversion of LA, but highly challenging [23].

The activation and hydriding of carbonyl group in LA molecule is an important elemental step to selectively convert LA to GVL. Gallezot et al. [24] demonstrated that incorporating a secondary metal into Ni-based catalysts could promote the activation of C=O bonds and increase catalytic activity. Yang et al. [25] confirmed the promotional effect of bimetal catalyst by density function theory (DFT) calculations of Ni₃Fe alloy. To this end, various Ni-Fe bimetallic heterogeneous catalysts, especially those supported on carbon, have been reported for hydrogen generation and biomass conversion [26–28]. Based on these reported findings, the nanostructure bimetallic Ni₃Fe alloy could possess superior selective hydrogenation activity to efficiently convert LA into GVL, which has not yet been fully exploited.

Various methods have been used to synthesis Ni₃Fe bimetallic nanocrystals, including chemical reduction, co-reduction, hydrothermal, thermal decomposition, electrochemical reduction, sol-gel method, mechanical alloying, microwave plasma method and the nano-templating approach [29–38]. Nevertheless, these methods exhibit drawbacks of low yield of alloy nanoparticles (NPs), containing impurity phases and large grain sizes, and involving complex procedures, unsuitable for controllable synthesis. As a solid-state metathesis reaction, the carbothermal reduction has been widely utilized to obtain carbon supported metallic materials due to its simplicity, controllability, low-cost and environmentally friendly nature [39]. Inspired by this and based on our previous works [40,41], we envisage that carbothermal reduction could be an effective

approach to synthesize desirable nanostructured bimetallic Ni₃Fe catalyst on carbon support.

Herein, we report a facile one-pot carbothermal approach to *in-situ* controllable synthesize highly stable bimetallic Ni₃Fe alloy NPs evenly embedded in active carbon support (denoted as Ni₃Fe NPs@C). Importantly, the resultant Ni₃Fe NPs@C catalyst exhibit excellent selective hydrogenation catalytic activities toward the conversion of LA to GVL via both direct hydrogenation (DH) and transfer hydrogenation (TH) under moderate reaction conditions. The best performed Ni₃Fe NPs@C catalysts can achieve 6 and 40 times enhanced GVL productivity when compared to its monometallic counterparts (e.g., Ni NPs@C and Fe NPs@C). The finding of this work paves a way to developing high performance and low-cost nonprecious catalysts for effective biomass utilization.

2. Experimental

2.1. Chemicals

All reagents and starting materials are commercially supplied and used as received without further purification. The commercial activated carbon and levulinic acid (chromatography purity) are purchased from Aladdin Industrial Corporation. Ni(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, methanol, ethanol, isopropanol, formic acid are of analytically purity and purchased from Sinopharm Chemical Reagent Co. Ltd.

2.2. Catalyst synthesis

A typical Ni₃Fe NPs@C catalyst contains 20 wt% of Ni₃Fe NPs. In a typical carbothermal synthesis procedure, 1.0 g of activated carbon was immersed with 1.0 mL solution containing 2.58 mmol Ni(NO₃)₂·6H₂O and 0.86 mmol Fe(NO₃)₃·9H₂O (Ni:Fe = 3:1), respectively, and subjected to an incipient-wetness impregnation treatment for 0.5 h. The treated material was dried at 60 °C overnight in a vacuum oven and used as the precursor. The ready to used Ni₃Fe NPs@C catalyst with 20 wt% of Ni₃Fe NPs was obtained by calcining the precursor in a tubular furnace at 500 °C (with a ramp rate of 5 °C min⁻¹) for 2 h under nitrogen atmosphere (150 mL min⁻¹).

For comparison purposes, the monometallic Ni NPs@C, Fe NPs@C and a series of bimetallic NiFe NPs@C catalysts were synthesized using similar experimental procedures under different carbothermal temperatures (400 to 700 °C) and with different Ni:Fe molar ratios (denoted as T-NiFe NPs@C(*x*:*y*)), where *T* referred to the treatment temperature and *x*:*y* indicate the precursor Ni:Fe molar ratios.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded with Philips X-Pert Pro X-ray diffractometer using a Cu K α radiation (λ = 0.15406 nm) at 40 kV and 40 mA. Samples were scanned from 5° to 85° with a scanning rate of 2.67° min⁻¹ and a step size of 0.033°. High resolution TEM (HRTEM) and transmission electron microscopy (TEM) images were obtained us-

ing a Tecnai G2 F30 S-TWIN instrument (FEI Co., USA) operated at an accelerating voltage of 200 kV. BET specific surface area and pore structures were measured by a pulsed N₂ adsorption-desorption method at -196 °C using a surface area and porosity analyzer (Autosorb iQ Station 2). X-ray photoelectron spectroscopy (XPS) were obtained using an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, USA) with Al K_{α1,2} monochromatized radiation at 1486.6 eV X-ray source. The measure XPS energies were corrected using the C 1s peak of the pollutant carbon at 284.6 eV. The metal elements content were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICP-6300, Thermo Fisher Scientific) after microwave digestion of the samples.

2.4. Catalyst performance evaluation

DH of LA experiments were performed in a 25-mL stainless steel autoclave equipped with a mechanical stirrer, a pressure gauge and an automatic temperature control apparatus. In a typical catalyst evaluation procedure, 30 mg catalyst was dispersed into a mixture solution of 0.5 mmol LA and 10 mL isopropanol in the reactor. The reactor was sealed, purged three times with N₂, followed by pressurizing with 2 MPa H₂ and heating to a target temperature with mechanical stirred at 500 r/min⁻¹. Likewise, the TH of LA experiments was conducted under the same procedure, except for that N₂ was used to replace H₂ as the pressurized gas. When the reaction was over, the autoclave was rapidly cooled down to the room temperature and the product was separated from the catalyst by a magnet. Where needed, the recovered catalyst was reused after washed with water, acetone, and ethanol in turns and dried under flowing nitrogen at 60 °C. The resultant supernatant was sampled and analyzed by GC-FID (Shimadzu, GC-2010 Plus) equipped with a KB-WAX capillary column (30 m × 0.25 mm × 0.25 μm). GVL and LA were quantified using n-octanol as an internal standard. The product was also confirmed by a GC-MS system (Thermo Fisher Scientific-TXQ Quantum XLS, column-TG-WAXMS, 30 m × 0.25 mm × 0.25 μm).

LA conversion, GVL selectivity and productivity were calculated according to Eqs. (1) to (3):

$$\text{LA conversion (\%)} = \left(1 - \frac{\text{Remaining amount of LA}}{\text{Initial amount of LA}}\right) \times 100\% \quad (1)$$

$$\text{GVL selectivity (\%)} = \frac{\text{Amount of GVL}}{\text{Sum amount of products}} \times 100\% \quad (2)$$

$$\text{GVL productivity} = \frac{\text{Amount of GVL}}{\text{Metal weight in catalyst (g)} \times \text{Reaction time (h)}} \quad (3)$$

3. Results and discussion

3.1. Material characteristics of bimetallic Ni₃Fe NPs@C catalyst

Fig. 1 summarizes the synthesis procedure and the morphology, chemical composition, electronic structure properties of 500-Ni₃Fe NPs@C(3:1) catalyst. Fig. 1(a) schematically illustrates the carbothermal synthetic procedure, where the acti-

vated carbon acts synchronously as the reducing agent, stabilizer and support matrix. As shown in Fig. 1(b), the XRD peaks of the as-synthesized 500-Ni₃Fe NPs@C(3:1) at 44.1°, 51.4° and 75.7° can be assigned to (111), (200) and (220) reflections of Ni₃Fe (JCPDS-ICDD card No. 65-3244) [42]. TEM images (Fig. 1(c) and (d)) confirm that the Ni₃Fe NPs with uniform particle sizes are homogeneously embedded in the sheet-like carbon support. The HRTEM (Fig. 1(e)) shows lattice fringes with a spacing of 2.05 Å corresponding to (111) planes of Ni₃Fe [42]. The corresponding fast Fourier transform (FFT) pattern further confirm the existence of (111) facets (insert in Fig. 1(e)). The selected area electron diffraction (SAED) image (Fig. 1(f)) reveals the presence of polycrystalline components, the observed rings correspond to (111), (220), (311), (331), and (551) planes of Ni₃Fe, respectively. The elemental mapping images indicate that Ni and Fe are uniformly distributed over the entire carbon support matrix (Fig. 1(g)). The Ni₃Fe bimetallic structure was further confirmed by the compositional line scanning profiles (Fig. S1). It reveals a uniform alloy composition of Ni₃Fe NPs without significant segregation of each component. A Ni:Fe molar ratio of 75.9:24.1 in the catalyst can be obtained from the EDX spectrum (Fig. 1(h)), while an almost precisely 3:1 Ni:Fe molar ratio was determined by ICP. The N₂ adsorption-desorption isotherms (Fig. 1(i)) display a typical type-I isotherms with a high BET surface area of 854.6 m² g⁻¹ and a pore size distribution centralized around 4 nm (insert in Fig. 1(i)). The XPS spectra of Ni 2p_{3/2} and 2p_{1/2} features with energy peaks at 853.1 and 870.5 eV, attributing to Ni⁰ species (Fig. 1(j)), while the Fe 2p_{3/2} and 2p_{1/2} spectra reveal the characteristic energy peaks of Fe⁰ at 707.2 and 720.3 eV, respectively [26,43]. Based on the above characterization results, it can be concluded that the synthesized 500-Ni₃Fe NPs@C(3:1) catalyst is a Ni₃Fe alloy form of NPs and homogeneously embedded in carbon supporting matrix.

3.2. Catalytic performance

The hydrogenation performances of 500-Ni₃Fe NPs@C(3:1) catalyst were systematically evaluated for conversion of LA to GVL via DH and TH reaction routes, respectively.

Fig. 2 shows the DH performance of the 500-Ni₃Fe NPs@C(3:1) catalyst in isopropanol. The effect of reaction time was firstly investigated under 130 °C reaction temperature of and 2 MPa H₂ pressure (Fig. 2(a)). The results revealed that both LA conversion efficiency and GVL selectivity increased as the reaction proceeded. A 93.8% LA conversion efficiency with a 95.5% GVL selectivity and 38.2 mmol g⁻¹ h⁻¹ GVL productivity can be achieved within 2 h of reaction (Table S1, entry 9). The effect of reaction time under 150 °C reaction temperature was also investigated (Fig. S2). When reaction time is less than 2 h, the obtained LA conversion efficiency and GVL selectivity under 150 °C are significantly higher than that obtained from the corresponding reaction time under 130 °C. Almost 100% GVL selectivity and full LA conversion can be readily attained within 2 h reaction. These key DH performance indicators surpass the performance of most reported high-performance DH catalysts, including noble metal-based catalysts such as Ru/C, Ir/C, Re/C,

Fig. 1. (a) The preparation scheme of bimetallic $\text{Ni}_3\text{Fe NPs@C}$; XRD pattern (b), TEM (c, d) images (inset: particle size distribution diagram), HRTEM (e) image (inset: corresponding FFT pattern), SAED (f) image, elemental mappings (g), EDS spectrum (h), nitrogen adsorption-desorption isotherm and Pore size distribution (i) (inset), Ni 2p and Fe 2p XPS spectra (j, k) of the as-prepared 500- $\text{Ni}_3\text{Fe NPs@C}(3:1)$.

Pt/C and Pd/C (Table S1, entries 1–6). The DH performance of the monometallic catalysts of Ni NPs@C and Fe NPs@C synthesized with the same procedure as that of bimetallic counterparts were also investigated. Under the same reaction conditions (2 MPa H_2 , 130 °C, 2 h), the achieved LA conversion efficiency, GVL selectivity and productivity by Ni NPs@C and Fe NPs@C are 23.9%, 60.1%, 6.1 $\text{mmol g}^{-1} \text{h}^{-1}$, and 10.9%, 19.7%, 0.9 $\text{mmol g}^{-1} \text{h}^{-1}$, respectively (Table S1, entries 7 and 8). These monometallic catalysts performance results confirm the effectiveness of enhancing DH performance via bimetallic catalyst design.

The reaction temperature and H_2 pressure are important reaction parameters and their effect on DH performance of 500- $\text{Ni}_3\text{Fe NPs@C}(3:1)$ were investigated. Fig. 2(b) shows the

effect of reaction temperature on LA conversion efficiency and GVL selectivity under 2 MPa H_2 with 2 h reaction time. An increase in temperature from 90 to 130 °C leads to rapid increases in both conversion efficiency and selectivity. A full conversion of LA with almost 100% GVL selectivity can be achieved when the reaction temperatures ≥ 150 °C. It should be noted that beside the targeted GVL, a portion of LA was converted to 4-hydroxypentanoic acid (denoted as H1) via the reduction of C=O bonds at lower reaction temperature (e.g., <150 °C) (Fig. S3(a)). However, no observable side reactions occurred at high reaction temperatures (e.g., >150 °C) (Fig. S3(a)), suggesting the synthesized bimetallic catalyst only possesses catalytic activity toward DH of LA to GVL at high temperature. This is because the produced 4-hydroxypentanoic

Fig. 2. DH performance of 500-Ni₃Fe NPs@C(3:1) catalyst. (a) Effect of reaction time under 130 °C and 2 MPa H₂; (b) Effect of reaction temperature under 2 MPa H₂ with 2 h reaction time; (c) Effect of H₂ pressure under 130 °C with 2 h reaction time; (d) Recyclability test under 130 °C, 2 MPa H₂ and 1 h reaction time.

acid can be further transformed into GVL at high temperature via intramolecular lactonization [8]. Fig. 2(c) shows the effect of H₂ pressure on LA conversion efficiency and GVL selectivity under 130 °C reaction temperature and 2 h reaction time. As expected, the LA conversion efficiency increased with the H₂ pressure. Interestingly, the GVL selectivity is almost independent of the H₂ pressure when varied from 0.5 to 2 MPa. As shown in Figs. 2 and S3(a), the DH of LA to produce GVL will undergo two steps: LA transformation to form 4-hydroxypentanoic acid (H1) through hydrogenation and the conversion of intermediate H1 to form GVL via intramolecular lactonization. The first step involves active H⁺ release and adsorption on the catalytically active site, which is highly correlated to the reaction temperature, time and H₂ pressure. As such, the LA conversion can be greatly enhanced by these parameters. However, the intramolecular lactonization in the second step is independent of the active H⁺ but associated with reaction temperature and time. In addition, the generated intermediate H1 is unstable. Therefore, the GVL selectivity depends obviously on the reaction time and temperature rather than hydrogen pressure.

For practical applications, the catalyst reuse is highly desirable. Fig. 2(d) shows the recyclability test result. It was found that no noticeable decay in both LA conversion efficiency and

GVL selectivity can be observed after four reuse cycles, signifying an excellent stability and reusability of the bimetallic catalyst. To further confirm this, the catalyst after four cycles of reuse was characterized by XRD, TEM, EDS, XPS (Fig. S4). Comparing to the as-synthesized 500-Ni₃Fe NPs@C(3:1) (Fig. 1(b)–(k)), the reused catalyst showed insignificant changes in particle size, morphology, crystal structure and composition. Only worth mentioning changes resulting from the reuse are the slightly decreased Fe³⁺ and increased Fe²⁺ and Fe⁰ contents due to the reductive reaction environment. The leaching catalyst materials were also examined by ICP analysis. Less than 1% metal contents loss was determined from the catalyst after four reuse cycles (Table S2, entry 6).

Comparing to DH, TH possesses a distinctive advantage of not requiring the use of high pressure H₂. In this work, the application of 500-Ni₃Fe NPs@C(3:1) catalyst was also extended to convert LA to GVL via TH reaction route using isopropanol as the H-donor. The effect of the reaction time on LA conversion efficiency and GVL selectivity was firstly investigated under 180 °C reaction temperature (Fig. 3(a)). A full conversion of LA with almost 100% GVL selectivity can be attained within 0.5 h. Under the reaction conditions, a GVL productivity of 167.1 mmol g⁻¹ h⁻¹ can also be obtained (Table S1, entry 15). The

Fig. 3. Catalytic performance of 500-Ni₃Fe NPs@C(3:1) catalyst in TH of LA. (a) Effect of reaction time, at 180 °C, and 2 MPa N₂; (b) Effect of reaction temperature, at 2 MPa N₂, 2 h; (c) Effect of solvent, at 180 °C, 2 MPa N₂, within 2 h.

effect of the reaction temperature on LA conversion efficiency and GVL selectivity was then investigated (Fig. 3(b)). When the reaction time was fixed at 2 h, both LA conversion efficiency and GVL selectivity are increased almost linearly with reaction temperature. A full conversion of LA with almost 100% GVL selectivity can be obtained when 180 °C reaction temperatures was employed. The GVL selectivity increase with reaction temperature implies that the esterification of LA and isopropanol are dominant reactions at lower reaction temperatures, which can be evidenced by the detected esterification products (T1 and T2, which are isopropyl levulinate and isopropyl 4-hydroxypentate) under lower reaction temperature (Fig. S3(b)). When the reaction temperature reaches 180 °C, the dehydrogenation activity is greatly enhanced as evidenced by the formation of large amount of acetone (Fig. S3(b)). Under the circumstance, a sufficient amount of active H can be realized to facilitate the formation of GVL, leading to a high GVL selectivity. The above results also suggest that the release of active H from isopropanol is a control step of GVL formation reaction. In this regard, the chemical nature of H-donor could strongly affect the rate of active H release. The effect of H-donors on LA conversion efficiency and GVL selectivity was subsequently investigated using different H-donors including isopropanol, methanol, ethanol and formic acid (Fig. 3(c)). The results reveal a conversion efficiency performance trend of isopropanol > primary alcohols > formic acid. However, the primary alcohols such as methanol and ethanol could not lead to the production of GVL due to the formation of stable T1 (e.g., methyl-levulinate or ethyl-levulinate), a type of esterification products that are difficult to be further converted to GVL. Comparing to alcohols, formic acid possesses low LA conversion efficiency but exhibits ~23% GVL selectivity, indicating it can be used as H-donor for converting LA to GVL. However, formic acid exhibits stronger corrosion effect of on Ni₃Fe NPs@C catalyst, leading to a poor catalyst stability (Table S2, entry 4). The above results suggest that under the optimal reaction conditions, the TH performance of 500-Ni₃Fe NPs@C(3:1) catalyst for converting LA to GVL is comparable to the state-of-the-art Ru-based catalysts (Table S1, entries 10–12). The TH performance of the monometallic catalysts of Ni NPs@C and Fe NPs@C were also investigated. Under the

reaction temperature of 180 °C and within 2 h, the achieved LA conversion efficient, GVL selectivity and productivity by Ni NPs@C and Fe NPs@C are 82.3%, 98.9%, 34.3 mmol g⁻¹ h⁻¹, and 77.1%, 15.6%, 5.1 mmol g⁻¹ h⁻¹, respectively (Table S1, entries 13 and 14). These monometallic catalysts performance results confirm the effectiveness of enhancing TH performance via bimetallic catalyst design.

The above results demonstrate superior DH and TH catalytic performances of 500-Ni₃Fe NPs@C(3:1) catalyst. To acquire an in-depth understanding on the catalyst structure and catalytic activity relationship, different Ni-Fe based catalysts were synthesized and evaluated for their DH and TH performance for converting LA to GVL (Table 1, Figs. 4, and S5). For a given carbothermal temperature of 500 °C, a change in Ni:Fe ratio used during synthesis leads to compositional and structural changes of the resultant materials. When a Ni:Fe ratio of 1:1 was used, the resultant material (500-NiFe NPs@C(1:1)) was found to be composed by Fe₃O₄ and metallic NiFe alloy (Figs. 4(a) and S5(a)). While a Ni:Fe ratio of 1:3 used during synthesis (500-NiFe NPs@C(1:3)) leads to the formation of Fe₃O₄, metallic NiFe alloy and Ni (Figs. 4(a) and S5(b)). With increased ratio of Ni:Fe, the chemical states of the resultant catalysts changed from the Ni/Fe₃O₄ hybrid to the bimetallic Ni₃Fe alloy, leading to the catalytic performance improvement for both DH and TH reactions (Table 1). When the Ni:Fe ratio used during the synthesis was fixed at 3:1, changes in carbothermal temperatures can also lead to compositional, structural and particle size changes of the resultant materials. A low carbothermal temperature of 400 °C results in the formation of NiO and Fe₂O₃ (400-NiFe NPs@C(3:1)) (Figs. 4(b) and S5(c)), while higher carbothermal temperatures of 600 and 700 °C (600-NiFe NPs@C(3:1) and 700-NiFe NPs@C(3:1)) lead to the formation of NiFe alloy (Figs. 4(b), S5(d), and S5(e)), which coincides with the phase diagram of Ni-Fe shown in Fig. S6. Also, the size of NPs increased obviously with increased carbothermal temperatures. The formation of NiFe alloy and increased NPs size under high carbothermal temperatures result in a decrease in the catalytic activity for both DH and TH reactions.

The effects of these structural and compositional changes are directly reflected in their catalytic performances (Table 1). The 500-Ni₃Fe NPs@C(3:1) possesses the best performance

Table 1Catalytic performance and structural information of 500-Ni₃Fe NPs@C and other related catalysts in DH and TH of LA.

Entry	Catalyst	Phase	Average NPs size ^a (nm)	DH of LA ^b		TH of LA ^c	
				LA	GVL	LA	GVL
				Conversion efficiency (%)	Selectivity (%)	Conversion efficiency (%)	Selectivity (%)
1	500-NiFe NPs@C(1:3)	Fe ₃ O ₄ /NiFe/Ni	6.7	49.4	80.2	68.0	15.3
2	500-NiFe NPs@C(1:1)	Fe ₃ O ₄ /NiFe	8.7	60.6	95.1	81.4	57.2
3	500-Ni ₃ Fe NPs@C(3:1)	Ni ₃ Fe	9.8	93.8	95.5	99.7	99.5
4	400-NiFe NPs@C(3:1)	NiO/Fe ₂ O ₃	6.6	13.9	29.9	79.7	25.8
5	600-NiFe NPs@C(3:1)	NiFe	24.1	62.5	84.2	99.1	86.5
6	700-NiFe NPs@C(3:1)	NiFe	33.5	23.9	69.1	58.3	71.8

^aThe average NPs size derived from the particle size distribution diagram in Fig. 1(d) and Fig. S5;^bDH reaction condition: 0.5 mmol LA, 30 mg catalyst, 10 mL isopropanol, 130 °C, 2 MPa H₂, 2 h;^cTH reaction condition: 0.5 mmol LA, 30 mg catalyst, 10 mL isopropanol, 180 °C, 2 MPa N₂, 2 h. **Fig. 4.** XRD patterns of the catalyst samples with variation of Ni:Fe molar ratio (a) and variation of carbothermal temperature (b).

among all catalysts investigated. These results suggest that all bimetallic Ni-Fe containing catalysts possess a certain degree of catalytic activity towards DH and TH transformation of LA to GVL. Their catalytic activities depend on the Ni:Fe ratio and particle size.

3.3. Possible mechanistic pathways of DH and TH reaction routes

Possible mechanistic pathways for DH and TH reaction routes to convert LA to GVL with bimetallic Ni-Fe catalyst is proposed based on the determined intermediates (Fig. 5).

With DH reaction route, the active H* is provided by the dissociation of molecule hydrogen (H₂). The carbonyl group in LA and H* are specifically absorbed onto and activated by the catalyst to form 4-hydroxypentanoic acid (H1) as an intermediate product. This can be evidenced by the fact that H1 was the only detectable intermediate during DH process (Fig. S3(a)). The produced 4-hydroxypentanoic acid intermediate is unstable and can be easily converted to GVL via intramolecular lactonization [8,44], especially under a relative high temperature.

With TH reaction route, the esterification reaction between the hydroxyl group of isopropanol and carboxyl group of LA

can readily occur to form an intermediate of isopropyl levulinate (T1) [10]. When the reaction temperature reaches a key point (ca. 180 °C), the catalyst promotes the 2-propanol dissociation to release active H*. The carbonyl group of T1 and H* are

Fig. 5. Proposed mechanistic pathway for DH and TH of LA to GVL over Ni₃Fe NPs@C catalyst.

catalyzed by the catalyst to convert T1 into T2 (isopropyl 4-hydroxypentate), which is unstable and inclined to take the intramolecular lactonization reaction to generate target product of GVL.

4. Conclusions

We have demonstrated superior catalytic performance of bimetallic Ni-Fe NPs supported on activated carbon catalysts to convert LA to GVL via both DH and TH reaction routes. The bimetallic Ni-Fe catalysts in a form of Ni₃Fe NPs@C possesses the best catalytic performance that can be synthesized under a 500 °C carbothermal temperature using a Ni:Fe molar ratio of 3:1. Under the optimal reaction conditions, Ni₃Fe NPs@C catalyst can respectively achieve LA conversion and GVL selectivity of 93.8% and 95.5% via DH reaction route and 99.7% and 99.5% via TH reaction route. Such superior DH and TH catalytic performances surpass the performance of most reported catalysts including precious metal based catalysts. The demonstrated capability of bimetallic catalyst design approach to introduce dual-catalytic functionality for DH and TH reactions could be adoptable for other catalysis processes.

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Graphical Abstract

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An efficient and reusable bimetallic Ni₃Fe NPs@C catalyst for selective hydrogenation of biomass-derived levulinic acid to γ-valerolactone

Haojie Wang, Chun Chen *, Haimin Zhang, Guozhong Wang, Huijun Zhao *
Institute of Solid State Physics, Chinese Academy of Sciences, China;
University of Science and Technology of China, China;
Griffith University, Australia

A controllable carbothermal synthesized bimetallic Ni-Fe NPs supported on activated carbon catalyst (Ni₃Fe NPs@C) possesses superior dual catalytic functionality towards both direct hydrogenation (DH) and transfer hydrogenation (TH) of Levulinic Acid (LA) into value-added γ-Valerolactone (GVL).

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乙酰丙酸选择性加氢合成 γ -戊内酯中高效和可循环使用的Ni₃Fe NPs@C双金属催化剂

王豪杰^{a,b}, 陈 春^{a,#}, 张海民^a, 汪国忠^a, 赵惠军^{a,c,*}

^a中国科学院固体物理研究所, 环境与能源纳米材料中心, 安徽合肥230031, 中国

^b中国科学技术大学, 安徽合肥230026, 中国

^c格里菲斯大学, 清洁环境与能源中心, 昆士兰4222, 澳大利亚

摘要: 生物质经催化转化合成燃料及化学品是当前研究的热点。目前, 生物质的催化转化主要聚焦于纤维素、半纤维素和木质素的解聚及其下游产物合成。其中, 乙酰丙酸(LA)作为纤维素解聚的主要产物之一, 是一种极具竞争力的平台化合物和重要的生物质转化中间体。LA通过催化转化可以合成各类高附加值的化学品, 例如, 通过催化加氢LA可选择性合成 γ -戊内酯(GVL)。所合成的GVL用途广泛, 可作为绿色溶剂、食品、燃料添加剂、(塑料、高分子、烃类或者其它高附加值化学品)前驱体等。目前, LA-to-GVL的研究主要着眼于非均相催化体系, 包括负载型贵金属和非贵金属催化体系。其中, 贵金属催化剂主要有Ru, Au, Pd, Rh, Ir和Pt, 虽然催化效率高, 条件温和, 但是成本高, 难以实现工业化。此外对于广泛使用的Ru/C催化剂, 存在金属-载体间相互作用不强、活性组分易流失、导致催化剂稳定性差等问题; 而非贵金属则普遍存在催化活性不佳及反应条件苛刻等缺点。因此, 开发高效、稳定、反应条件温和且具有工业化应用前景的非贵金属催化剂具有显著的研究意义, 这也是当前的研究趋势。

在特定温度下, 金属离子与碳基底存在较强的相互作用。鉴于此, 本文通过一步碳热还原法合成了活性炭负载的Ni₃Fe双金属催化剂(Ni₃Fe NPs@C)。该催化剂在LA-to-GVL转化体系中展现了直接加氢(DH)和转移加氢(TH)双功能催化特性。首先, 考察了其在DH体系中的反应特性: 在130 °C和2 MPa氢压反应条件下经2 h反应, LA转化率达到93.8%, GVL选择性为95.5 %, GVL产率是相应的单金属Ni/C和Fe/C催化剂的6倍和40倍。此外, 在TH催化反应体系中, 在180 °C, 0.5 h和无外加氢源的反应条件下, 以异丙醇为反应溶剂和供氢体, LA几乎完全转化为GVL, 其反应效率同样相较于单金属Ni/C和Fe/C催化剂大幅度提高。所合成的Ni₃Fe NPs@C双金属催化剂DH和TH催化性能优于绝大多数报道的LA加氢贵金属和非贵金属催化剂。而且, 该催化剂具有良好的循环利用性能, 经过四次循环, 其结构和化学状态没有发生明显的改变, 稳定性明显优于商业化的Ru/C催化剂。此外, 通过系统分析其催化性能以及材料结构, 明确了该催化剂在LA的DH和TH反应体系中的活性位点, 并提出了可能的反应路径。该研究为其它类型的DH和TH反应体系以及生物质高效转化过程提供了新的催化剂设计思路。并且这种催化剂及其制备方法简单、绿色, 易于工业化推广和应用。

关键词: 乙酰丙酸; γ -戊内酯; 双金属催化剂; 氢化; 双催化功能

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*通讯联系人. 电话: (0551)65591263; 传真: (0551) 65591434; 电子邮箱: h.zhao@griffith.edu.au

#通讯联系人. 电话: (0551)65591263; 传真: (0551) 65591434; 电子邮箱: chenchun2013@issp.ac.cn

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