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Catalytic conversion of biomass-derived levulinic acid into γ -valerolactone using iridium nanoparticles supported on carbon nanotubes

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ABSTRACT

A new method has been developed for the catalytic conversion of biomass-derived levulinic acid (LA) into γ -valerolactone (GVL) with molecular hydrogen (H_2) using a series of heterogeneous noble metal catalysts. Excellent yields of the GVL were obtained under mild reaction conditions of 50°C and 2 MPa of H_2 using iridium nanoparticles supported on carbon nanotubes (Ir/CNT). It is noteworthy that the reaction proceeded smoothly in the presence of formic acid (FA, co-produced with LA in equimolar amounts during the acid-mediated hydrolysis of lignocellulosic biomass). Furthermore, the FA remained intact, highlighting the practical advantages of this process for the convenient and cost-effective processing of a biomass-derived LA/FA solution. The method is effective for the simultaneous production of GVL and FA from a wide variety of renewable biomass resources.

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1. Introduction

Research into the effective utilization of renewable resources, such as biomass, has recently attracted considerable levels of attention because of the potential for these resources to be used as alternatives to petroleum for the production of chemicals and liquid fuels [1–5]. One strategy of particular interest involves the initial partial removal of oxygen from biomass to produce reactive intermediates, denoted as platform molecules, followed by the conversion of these molecules into the desired products [6,7]. γ -Valerolactone (GVL) has been suggested as a promising candidate molecule for this type of application because it possesses a variety of interesting

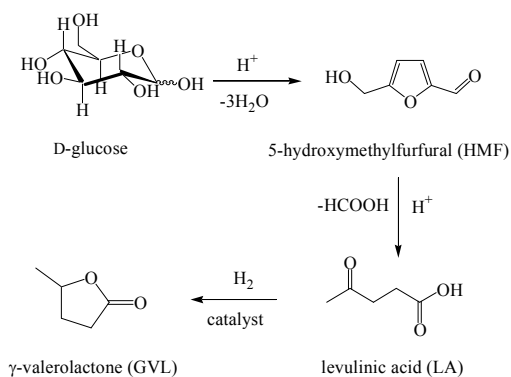
properties that make it suitable for use as a new platform molecule in next-generation biorefineries [8]. GVL has many potential applications, including its use as a solvent [9], food additive [10], and biofuel, where it could be used as a substitute for ethanol in gasoline-ethanol blends [11]. The hydrogenation of GVL provides access to methyltetrahydrofuran (MTHF), which is a potential fuel additive [1]. The selective formation of GVL from renewable resources therefore represents a highly desirable process and a promising move towards enhancing the sustainability of the chemical industry.

Extensive research efforts are currently being focused on the production of GVL from levulinic acid (LA), which can itself be produced at potentially low cost from the acid hydrolysis of

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Scheme 1. Acid catalyzed hydrolysis of D-glucose to LA and subsequent hydrogenation of LA to GVL.

lignocellulosic biomass [12,13], as outlined in Scheme 1. Of the variety of different synthetic protocols that could be used for this transformation, the catalytic hydrogenations of LA using molecular hydrogen (H₂) [14–17] or formic acid [18,19] (FA), which is co-produced in equimolar amounts to LA during the acidic hydrolysis of the lignocellulosic biomass, have attracted considerable levels of attention in recent years.

The synthesis of GVL via the hydrogenation of LA using a heterogeneous catalyst was first reported using platinum oxide as the catalyst [14], where the formation of GVL occurred in moderate yields of up to 87% in a diethyl ether solvent following 44 h of reaction. When Raney Ni was evaluated as a catalyst for the transformation, a higher yield of GVL (94%) was achieved at 220 °C under an initial hydrogen pressure of 48 atm (4.9 MPa) [15]. Recently, the hydrogenation of LA has been reported over a Ru/C catalyst, with a GVL yield of up to 91% in a methanol solvent at 130 °C and under 12 atm (1.2 MPa) of H₂ pressure [16]. In an attempt to reduce the temperature required of the transformation, Galletti et al. [17] reported the synthesis of GVL under milder conditions (50–70 °C and 0.5–3.0 MPa of H₂) using a ruthenium supported catalyst in conjunction with an acidic co-catalyst, such as Amberlyst-70, niobium oxide or niobium phosphate. Efforts have also been made towards the use of FA as a straightforward and highly convenient hydrogen source [19,21,22]. Most recently, we have shown that a simple gold catalyst system composed of particularly small Au nanoparticles (NPs of ca. 1.8 nm) deposited on ZrO₂ (Au/ZrO₂-VS; VS = very small) can successfully convert the biomass-derived LA and FA into GVL without the requirement for an external H₂ supply [23].

A number of homogeneous catalysts have also been reported for the hydrogenation of LA to GVL using molecular H₂ or FA as the reducing agents. Ruthenium-based complexes with phosphine ligands were typically applied in these cases. For example, Osakada et al. [24] reported the use of RuCl₂(PPh₃)₃ as an effective catalyst for the hydrogenation of LA to GVL. The yield of GVL was reported to be as high as 99% when a H₂ pressure of 11.8 atm (1.2 MPa) was used at 180 °C over a reaction period of 24 h. Recently, Mehdi et al. [18] reported the use of Ru(acac)₃ in combination with tri(3-sulfonatophenyl)phosphine (TPPTS) for the hydrogenation of LA to GVL in water at 140 °C and under 6.9 MPa of H₂ pressure. A GVL

yield of 95% was achieved in this case following a reaction period of 12 h. The transfer hydrogenation of LA with an excess of sodium formate (37 equiv.) catalyzed by [[η^6 -C₆Me₆]Ru(bpy)(H₂O)][SO₄] (bpy = 2,2'-bipyridine) was also examined. Both GVL and 1,4-pentanediol were obtained in 25% yield. Improved GVL yields (up to 95%) were reported when a RuCl₃/PPh₃ complex was used in conjunction with copious amounts of base (200 °C, 6 h) [25].

Taken together, all of this research effectively highlights the great incentives that are available for the development of new environmentally benign catalytic systems for the efficient synthesis of GVL from biomass-derived LA under mild conditions. Carbon nanotubes (CNT) have been identified as promising support materials for many metal catalysts, especially for catalysts used in liquid-phase hydrogenation reactions, because of their fascinating physical and chemical characteristics [26,27]. Herein, we report that iridium nanoparticles (Ir NPs) supported on CNT effectively facilitated the convenient conversion of LA to GVL in the presence of H₂ under mild aqueous conditions. Of particular significance is that the reaction even proceeded smoothly in the presence of FA, with the FA remaining intact and therefore offering practical advantages in terms of the potential for the direct processing of a biomass-derived LA/FA solution. The Ir-based metal catalysts, which had previously been established to be prominent for the chemoselective hydrogenation of a range of α,β -unsaturated carbonyl compounds [28,29], have been shown to be particularly useful for the hydrogenation of LA to produce GVL in an aqueous environment at temperatures as low as 50 °C.

2. Experimental

2.1. Catalyst preparation

The multi-walled CNTs were typically pre-treated in concentrated HNO₃ (68 wt%) at 120 °C under refluxing conditions to remove the remaining Ni catalyst and the amorphous carbon. Inductively coupled plasma (ICP) analysis showed that no Ni remained on the CNT following the treatment with HNO₃. Activated carbon (C) was also pre-treated with concentrated HNO₃ at 120 °C under refluxing conditions prior to its use. The deposition of Ir onto a variety of different supports (Ir loading, 4.5 wt%) was achieved via a classical impregnation method with an aqueous solution of H₂IrCl₆ (Sigma-Aldrich), followed by a period of drying at 100 °C. The resulting catalysts were then subjected to H₂/Ar (5 vol%) reduction at 300 °C for 2 h. Other noble metal catalysts (Ir loading, 4.5 wt%) were prepared using a similar impregnation method, except for Ir/MgO which was reduced at 450 °C for 2 h with H₂/Ar (5 vol%).

2.2. Catalyst characterization

The metal loadings of the catalysts were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer (Hitachi 4010). Powder X-ray diffraction (XRD) analyses of the catalysts were conducted on a Bruker D8 Advance

X-ray diffractometer (Bruker, Germany) using nickel filtered Cu K_{α} radiation ($\lambda = 0.15418$ nm). A tube voltage of 40 kV was used with a current of 40 mA. X-ray photoelectron spectroscopy (XPS) analyses were performed using a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The Mg K_{α} ($h\nu = 1253.6$ eV) was operated at 15 kV and 20 mA. The energy scale was internally calibrated by setting the C1s peak at 284.6 eV. Transmission electron microscopy (TEM) images of the supported catalysts were taken with a JEOL 2011 electron microscope operating at 200 kV. Prior to being transferred into the TEM chamber, the samples dispersed with ethanol were deposited onto a carbon-coated copper grid and then quickly transferred into the vacuum evaporator. The temperature-programmed desorption characterization process was conducted with using bespoke apparatus that had been constructed in-house. The sample (100 mg) was pretreated at 200 °C for 2 h and then cooled to 25 °C in flowing He. At this temperature, sufficient pulses of H₂ were injected until the occurrence of adsorption saturation. The system was then purged with He (30 ml/min) for about 2 h. The temperature was then raised from 25 to 650 °C at a ramp rate of 10°C/min to desorb the H₂. The desorbed H₂ was monitored using an OmniStar mass spectrometer (QMS-200) with an m/e signal of 2.

2.3. Catalytic activity measurements

2.3.1. General procedure for LA hydrogenation

The catalytic conversion of LA was performed in a stainless-steel autoclave (Parr Instrument, 25 ml) under 2.0 MPa of H₂ pressure at 50 °C for 1 h. For each reaction, 4.0 mmol LA (Sigma-Aldrich), 38.4 mg catalyst, 2.0 mmol 2-methoxyethyl ether (internal standard) and 10 ml solvent were charged into the reactor and stirred at 800 r/min. Upon completion of the reaction, the liquid products were analyzed on a Shimadzu GC-17A gas chromatograph equipped with a capillary column HP-FFAP (30 m × 0.25 mm) and an FID detector. The identification of the products was performed by using a GC-MS spectrometer via comparison with the commercially procured pure products.

2.3.2. Hydrogenation of LA in the presence of FA

The catalytic conversions of LA were typically performed with an equimolar amount of FA in a 25 ml Hastelloy-C high pressure Parr reactor under 4.0 MPa of H₂ pressure at 50 °C. For each reaction, 4.0 mmol of LA, 4.0 mmol of FA, an Ir/CNT catalyst (Ir 1 mol%), and 10 ml of water were charged into the reactor and the resulting mixture stirred at 800 r/min. Upon completion of the reaction, the liquid products were analyzed on a high performance liquid chromatography (HPLC) system (HP1100, Agilent) equipped with an refractive index detector (RID) and Platisil ODS C₁₈ column. H₂SO₄ (0.5 mmol/L) was then added to the mobile phase at flow rate of 1 ml/min. The column and detector temperatures were set at 40 °C.

2.3.3. Hydrogenation of biomass-derived LA/FA solution

Carbohydrate (1.8 g), consisting of cellulose, starch, sucrose, glucose, or fructose, was loaded into a teflon-lined stainless

steel autoclave (20 ml) followed by 10 ml of a 0.5 mol/L solution H₂SO₄. The autoclave was then rapidly heated to 170 °C and stirred vigorously for 1 h. Upon completion of the reaction, the pH of the mixture was adjusted to a pH of 2 via the addition of CaO and the mixture was subsequently filtered to remove any insoluble humins [23]. The CaO was added to remove any residual H₂SO₄ because the resulting CaSO₄ product could be used in the cement industry or as a soil conditioner. The carbohydrates-derived LA was then transferred to a 25 ml Hastelloy-C high pressure Parr reactor containing Ir/CNT and subjected to catalytic hydrogenation at 50 °C. The concentrations of the liquid products were determined using a HPLC system (HP1100, Agilent) equipped with an RID detector and a Platisil ODS C₁₈ column. H₂SO₄ (0.5 mmol/L) was added to the mobile phase at flow rate of 1 ml/min.

3. Results and discussion

3.1. Catalyst characterization

The multiwalled CNT support was synthesized according to procedures previously described in the literature via the catalytic decomposition of CH₄ over a MgO-supported Ni catalyst [30,31]. The resulting CNT was purified with boiling nitric acid (HNO₃), and subsequently rinsed with de-ionized water and ethanol before being dried under dry nitrogen. The supported iridium catalysts (Ir content ~4.5 wt%) were then prepared using a classical impregnation method followed by H₂ reduction at 300 °C for 2 h. The resulting Ir NPs were then deposited onto the CNT (denoted as Ir/CNT, see details in the experimental section). TEM analysis of the Ir/CNT catalyst reveals that the particles had an average diameter of about 1.9 nm (Fig. 1(a)). Figure 2 shows the XRD patterns of the Ir/CNT catalyst. The peak intensities and their 2 θ angles have been identified as characteristic of graphite. No diffraction lines assignable to metallic iridium could be detected for the Ir/CNT catalysts in Fig. 2(a), owing to the fact that the iridium particles were too small. All these results suggested that the iridium NPs were highly dispersed on the CNT surfaces. To identify the oxidation state of the Ir species on the CNTs, an XPS experiment was performed for the sample following the H₂ reduction. The Ir 4f peaks in the XPS spectra (Fig. 2(b)) showed that besides the main binding energy values at 60.8 and 63.9 eV, which were assigned to the 4f_{7/2} and 4f_{5/2} peaks of metallic iridium, binding energy values were also observed at 62.5 and 65.6 eV and were assigned to the 4f_{7/2} and 4f_{5/2} peaks of iridium dioxide, respectively [32]. The presence of IrO₂ was attributed to the aerial oxidation of nano-iridium particles and the incomplete reduction of IrO₂. Ir⁰ was the active species for the reaction because the catalyst was not active to catalyze the hydrogenation prior to the reduction.

3.2. General procedure for LA hydrogenation

The conversion of LA was initially studied in a variety of different media at 50 °C under 2.0 MPa of H₂ pressure in the presence of the Ir/CNT catalyst. As shown in Table 1, a high

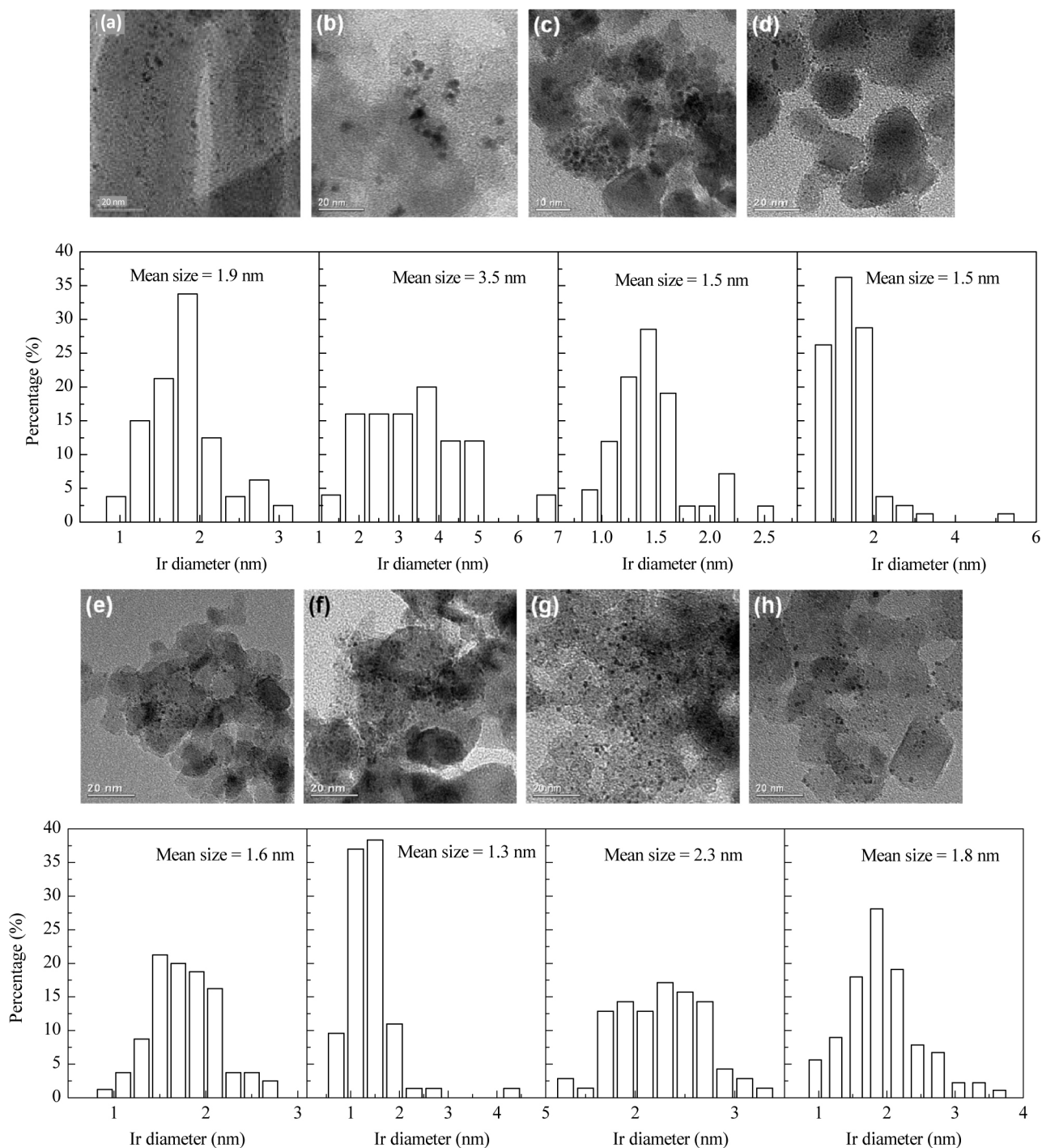


Fig. 1. Typical TEM micrographs and particle-size distributions for the supported iridium catalysts. (a) Ir/CNT; (b) Ir/C; (c) Ir/CeO₂; (d) Ir/TiO₂; (e) Ir/Al₂O₃; (f) Ir/ZnO; (g) Ir/SiO₂; (h) Ir/MgO.

yield of GVL was obtained when CHCl₃ was used as the reaction medium (Table 1, entry 1). In contrast, when toluene, methanol, acetone or dioxane were used as the solvent, the yield of GVL was lower (Table 1, entries 2–5). Surprisingly, water was found to be the best medium, providing an excellent yield of GVL after a reaction time of only 1 h (Table 1, entry 6). This discovery represented a highly desirable development, not only because water is a safe, economical, and environmentally benign solvent [33], but also because LA is typically prepared via

an acid-catalyzed hydrolysis process from an aqueous solution which provides the desired LA material in water [34]. The aqueous product solution of LA could therefore be telescoped directly into the current hydrogenation process to give GVL, representing an efficient sequence of transformations. Subsequent investigations revealed that the type of solid support used in the reduction process had a significant influence over the catalytic activity. Of the different supports tested, CNT was found to provide the best results. Activated carbon, CeO₂, TiO₂,

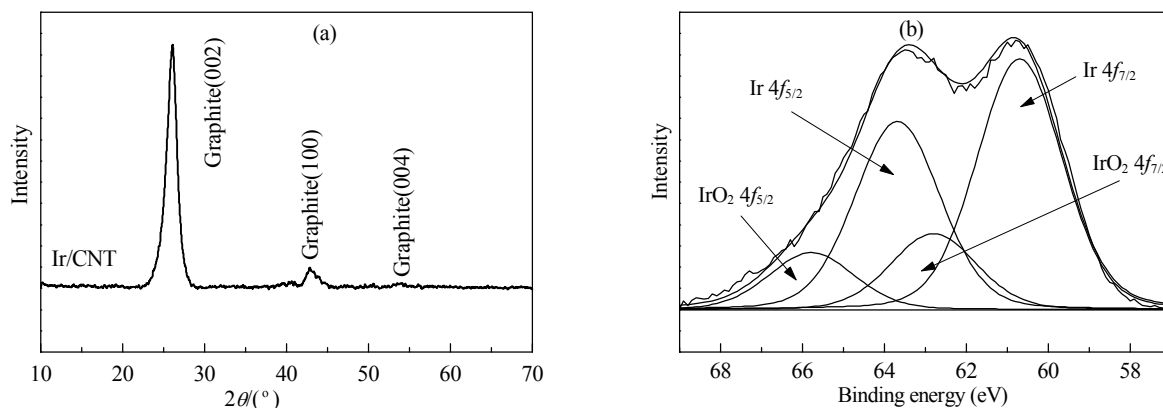


Fig. 2. XRD patterns (a) and XPS spectra (b) of the Ir/CNT catalyst reduced by H₂ at 300 °C.

Al₂O₃ and ZnO were also effective (Table 1, entries 7–11), whereas Ir/SiO₂ and Ir/MgO resulted in lower yields of the GVL (Table 1, entries 12 and 13). The use of other supported metals with catalytic potential, such as Ru, Pt, and Pd, resulted in significantly lower yields of GVL from the conversion of LA conversion under similar reaction conditions (Table 1, entries 15–19). The fact that all of these supported iridium catalysts possessed metal particles with similar mean sizes (1.5–3.5 nm, see Fig. 1(b)–(h)) effectively highlighted the roles played by both the noble metal and the nature of the underlying support in the catalytic activity observed during the current LA hydrogenation process. Our results clearly show that the Ir/CNT catalyst possesses an optimal level of activity for the hydrogenation of LA in water under mild conditions. It is noteworthy that

Table 1

Catalytic properties of the supported Ir catalysts in different media.

Entry	Solvent	Catalyst	Conversion ^a (%)	Selectivity ^b (%)	Yield (%)
1	CHCl ₃	Ir/CNT	93	98	91
2	Toluene	Ir/CNT	68	97	66
3 ^c	Methanol	Ir/CNT	20	90	18
4	Acetone	Ir/CNT	7	99	7
5	Dioxane	Ir/CNT	2	100	2
6	Water	Ir/CNT	100	99	99
7 ^d	Water	Ir/C	78	98	76
8	Water	Ir/CeO ₂	65	99	65
9	Water	Ir/TiO ₂	55	99	55
10	Water	Ir/Al ₂ O ₃	52	98	51
11	Water	Ir/ZnO	51	99	51
12	Water	Ir/SiO ₂	38	97	37
13	Water	Ir/MgO	20	99	20
14 ^e	Water	Ir/CNT	96	97	95.1
15	Water	Ru/CNT	65	100	65.0
16 ^f	Water	Ru/Al ₂ O ₃	22	98	21.5
17	Water	Pt/CNT	53	97	51.4
18	Water	Pd/CNT	19	97	18.4
19 ^g	Water	Pd/C	7	100	7.0

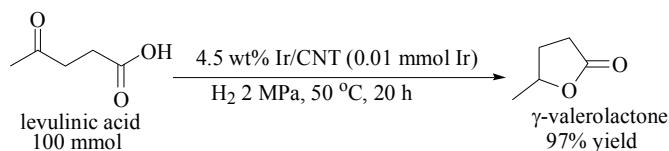
Reaction conditions: catalyst (Ir loading, 4.5 wt%), 4.0 mmol LA, Ir (0.23 mol%), 10 ml solvent, 50 °C, *p*(H₂) = 2.0 MPa, 1 h.

^aConversion and selectivity were determined by GC and GC-MS with bis(2-methoxyethyl) ether as the internal standard. ^bUnless otherwise stated, hydroxyvaleric acid was the only side-product. ^cMethyl levulinate was identified as an additional side-product. ^dC stands for activated carbon. ^eAfter four repeated uses. ^f5 wt% Ru/Al₂O₃ (stock # 11749), 5 wt% Pd/C (stock # 38300) provided by Alfa Aesar.

the reaction could proceed efficiently even under solvent-free conditions. As shown in Scheme 2, an almost quantitative GVL yield was achieved for a 100 mmol scale transformation of neat LA at 50 °C. Of particular practical significance was the observation that the reaction even proceeded smoothly at ambient pressure, although a longer reaction time was required, which permitted the use of standard glass reactor systems (see Fig. 3).

Iridium catalysts have been used as highly active catalysts in a variety of hydrogen-involving reactions, and the catalytic activity of Ir is well-known to be critically dependent on the nature of the support [3–37]. To clarify the origin of the enhanced activity of the catalyst towards LA conversion when CNT was used as a support, H₂ temperature-programmed desorption (H₂-TPD) measurements were conducted for the Ir NPs deposited on different supports. These measurements revealed that a significantly greater amount of H₂ was desorbed from the Ir/CNT relative to the other catalysts (Fig. 4), implying that the high adsorption capacity of H₂ associated with the Ir/CNT catalyst was responsible for its superior performance in the transformation of LA to GVL [38–42]. Furthermore, larger amounts of H₂ were adsorbed over the catalysts on the CNT, C, and TiO₂ supports, which highlighted the excellent correlation between this observation and their catalytic activity towards LA hydrogenation.

To better understand the GVL selectivity under different reaction conditions, the reaction pathway was considered. As shown in Scheme 3, there are two possible routes available for the production of GVL production, including (1) the hydrogenation of LA to hydroxyvaleric acid (HA) followed by dehydration to GVL (route a); or (2) the dehydration of LA to angelica lactone (AL) followed by hydrogenation to GVL (route b). It is known in the literature that LA dehydrates at moderate temperatures (300–450 °C) in the presence of strong mineral or solid acids to give the corresponding cyclic product, AL (Scheme 3) [43,44]. Considering our mild reaction conditions (< 100 °C) and the presence of HA (detected by GC-MS) as well as the absence of AL, route a was envisaged to be the most likely pathway for the production of GVL from LA. The selectivity to GVL was found to be less than 100% (ca. 96%) under very mild reaction conditions (< 50 °C, < 2 MPa of H₂) because of the formation of the HA intermediate. Although the HA in-



Scheme 2. Preparation of GVL from LA under solvent-free conditions.

intermediate was found to be particularly unstable, its intra-molecular lactonization to GVL occurred with considerable ease [19]. Increases in the reaction temperature and H₂ pressure allowed any HA formed to be readily dehydrated to form GVL and led to a higher level of GVL selectivity (Figs. 5 and 6). These results are consistent with the mechanism of GVL formation recently reported in the literature [17].

The reuse of the Ir/CNT catalyst was also studied. After each run, the catalyst was separated from the reaction mixture by filtration, thoroughly washed with water, and then reused as the catalyst for the next run under the same conditions. As shown in Table 1, the GVL yields remained high at 95% for the first four successive cycles (Table 1, entry 12), reflecting the high level of stability and reusability of the catalyst. The TEM and XPS results (Figs. 1 and 2) revealed no discernible changes in the mean diameters of the Ir NPs or in the metallic state of the Ir, respectively, following four successive runs. Further-

more, it was confirmed by ICP analysis that the Ir content of the used Ir/CNT catalyst was the same as that of the fresh catalyst and that no Ir was contained in the filtrate.

3.3. Hydrogenation of LA in the presence of FA

FA has recently attracted considerable interest from research focused on areas of green and sustainable chemistry because of its potential as a safe and convenient H₂ carrier [45–47]. FA is currently produced industrially by the hydration of carbon monoxide as well as the hydrogenation of carbon dioxide [48]. Given the fact that FA is produced in equimolar amounts to LA during the hydrolysis of lignocellulosic biomass, we also studied the effect of FA on the catalytic conversion of LA (Table 2). The deliberate addition of an equimolar amount of FA to the hydrogenation system led to significant retardation of the LA hydrogenation process (Table 2, entry 1). Under the

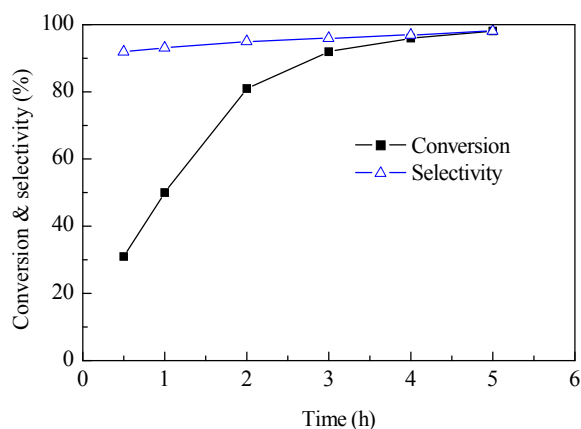


Fig. 3. Effect of reaction time on the catalytic performances of the 4.5 wt% Ir/CNT catalyst for the reduction of LA. Reaction conditions: 4.0 mmol LA, 0.23 mol% Ir, water 10 ml; $p(\text{H}_2) = 1 \times 10^5$ Pa, 50 °C. Note that the intermediate hydroxyvaleric acid was easily dehydration to GVL, affording a higher level of selectivity with extended reaction time.

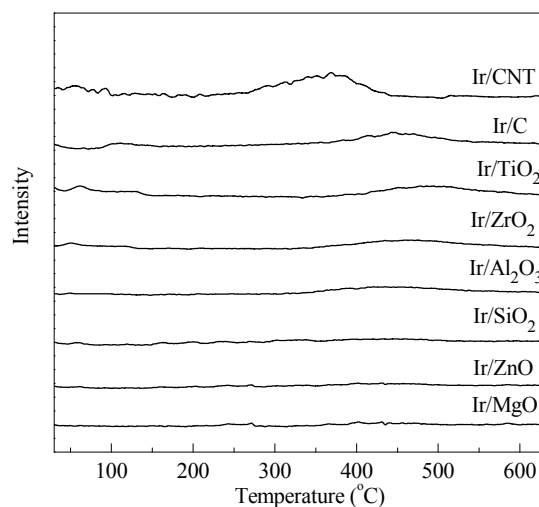
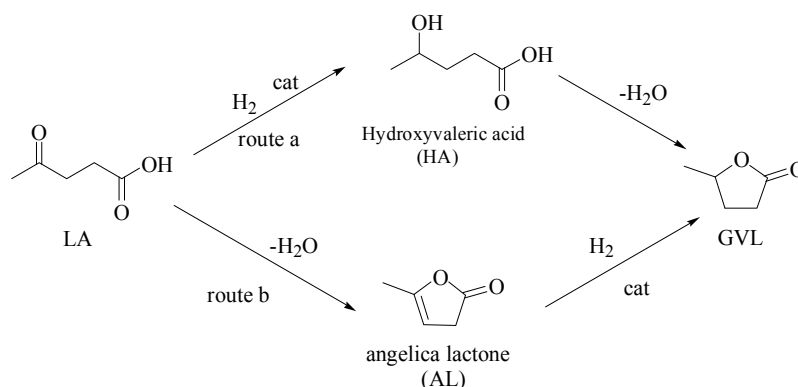


Fig. 4. H₂-TPD profiles for the Ir catalysts supported on different supports.



Scheme 3. Mechanisms for LA hydrogenation.

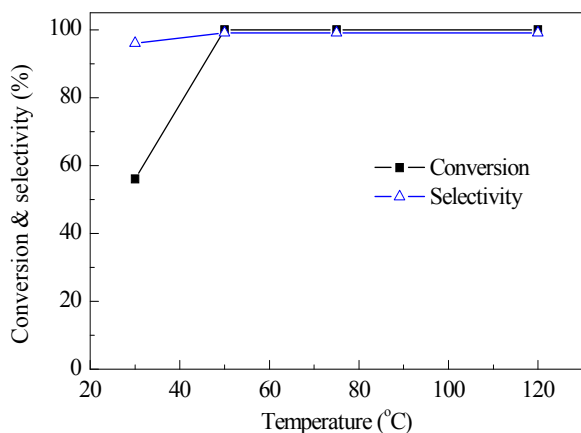


Fig. 5. Effect of reaction temperature on the catalytic performances of the 4.5 wt% Ir/CNT catalyst towards the reduction of LA. Reaction conditions: 4.0 mmol LA, 0.23 mol% Ir, 10 ml water, $p(\text{H}_2) = 2.0$ MPa, 1 h. Note that hydroxyvaleric acid was the only side-product.

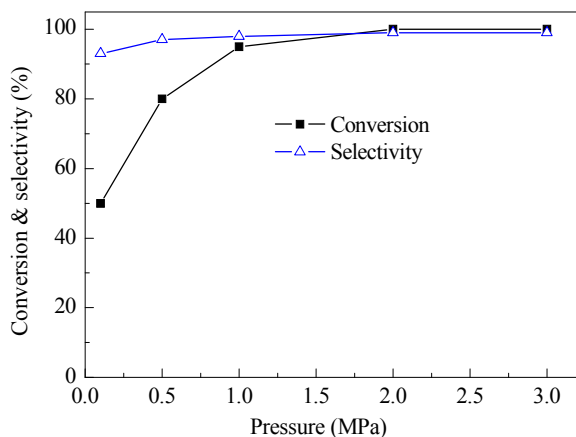


Fig. 6. Effect of H_2 pressure on the catalytic performance of the 4.5 wt% Ir/CNT catalyst towards the reduction of LA. Reaction conditions: 4.0 mmol LA, 0.23 mol% Ir, 10 ml water, 50 °C, 1 h. Note that hydroxyvaleric acid was the only side-product.

same conditions, an extension in the reaction time to 12 h led to an increase in the GVL yield up to 50% (Table 2, entry 3). In an attempt to improve the GVL yield, the reaction was carried out at higher temperatures. Unfortunately, however, the yield of GVL decreased from 50 to 31% when the reaction temperature was raised to 100°C (Table 2, entry 4). Furthermore, an even lower GVL yield was obtained at the elevated temperature of 150°C (Table 2, entry 5). Considering the notoriously low tolerance of platinum-group metals (PGM) toward CO in LA hydrogenation processes [23], the deactivation of the Ir/CNT catalyst in the current research was attributed to CO produced during the decomposition of FA at high reaction temperature. A separate control experiment was conducted to confirm the adverse impact of CO on the reaction. The experiment revealed that deliberate addition of small amount of CO (~1,000 ppm) to the direct hydrogenation system has a significant negative effect on the LA hydrogenation process. Such effect of CO on the hydrogenation of LA over Ir/CNT catalyst is similar to other Pt-group based catalyst [23]. In a separate series of reactions,

Table 2

Hydrogenation of LA over 4.5 wt% Ir/CNT catalyst by H_2 with an equimolar amount of FA.

Entry	Ir (μmol)	$T/^\circ\text{C}$	t/h	Conversion ^a (%)	Selectivity ^b (%)
1	9.2	50	1	9	98
2	9.2	50	6	32	99
3	9.2	50	12	50	99
4	9.2	100	12	31	99
5	9.2	150	12	8	99
6	40	50	12	80	99
7 ^d	40	50	12	96	99
8 ^e	40	50	12	0	—

Reaction conditions: 4.0 mmol LA, 4.0 mmol FA, 10 ml water, $p(\text{H}_2) = 2.0$ MPa. ^aConversion determined by HPLC. ^bHydroxyvaleric acid is the only side-product. ^c4.0 mmol LA, 4.0 mmol FA, 10 ml water, $p(\text{H}_2) = 4.0$ MPa. As monitored by HPLC, the concentration of FA remained constant during the reaction. ^d4.0 mmol LA, 4.0 mmol FA, 10 ml water, $P(\text{N}_2) = 2.0$ MPa.

the hydrogenation was conducted at lower temperatures but with elevated H_2 pressures to improve the reaction kinetics. Pleasingly, the yield of GVL could be significantly improved by an increase in the amount of catalyst or H_2 pressure (Table 2, entries 6 and 7). The highest GVL yield observed was 96% with 1 mol% Ir at 4 MPa of H_2 pressure in 12 h (Table 2, entry 7).

Importantly, the results revealed that the FA concentration remained constant (Table 2, entry 7) following the hydrogenation of LA with the Ir/CNT catalysts at 50°C over a period of 12 h. This lack of change was attributed to the reaction conditions being too mild to allow for the decomposition of FA in this particular case. A separate control experiment involving the application of the standard conditions to an equimolar mixture of LA and FA under a 2.0 MPa nitrogen (N_2) for 12 h confirmed that transfer hydrogenation of LA did not take place in the absence of H_2 (Table 2, entry 8). The fact that any unproductive decomposition of FA could be largely controlled by the careful choice of conditions made it possible to extract the GVL and FA with high levels of efficiency from water using the appropriate extraction solvents [22]. Given that both FA and LA are organic acids and have similar properties, it can be very difficult to separate these two products. However, given that GVL is more hydrophobic than LA and FA and that there is a significant difference in the boiling points of GVL and FA [22], a convenient and cost-effective separation of FA from GVL could be realized based on these properties.

3.4. Hydrogenation of biomass-derived LA/FA solution

To demonstrate the utility of the Ir/CNT catalyst in the context of biomass-derived substrates, we investigated the hydrogenation of LA obtained from the hydrolysis of D-glucose. A mixture of LA and FA was obtained the hydrolysis of D-glucose in the presence of H_2SO_4 (0.5 mol/L). Following the partial neutralization of the material and the subsequent removal of the insoluble humins by filtration (see experiment section for details), the hydrolyzed solution was transferred to an autoclave containing Ir/CNT and subjected to an reaction under 4.0 MPa of H_2 pressure at 50 °C for 12 h. It is important to note

Table 3

Dehydration of carbohydrates^a and subsequent hydrogenation of carbohydrate-derived LA using Ir/CNT as a catalyst^b.

Entry	Carbohydrate	Yield (%)		
		LA ^c	FA ^c	GVL ^d
1	Glucose	54	58	52 (96)
2	Fructose	61	67	60 (98)
3	Sucrose	58	65	56 (97)
4	Starch	52	60	50 (96)
5	Cellulose	34	40	32 (94)

^a Reaction conditions: 1.8 g carbohydrate, 20 ml water, 0.5 mol/L H₂SO₄, 180 °C, *p*(N₂) = 0.5 MPa, 1 h.

^b Reaction conditions: as-prepared dehydration solution, 0.43 g catalyst (Ir loading, 4.5 wt%), 50 °C, *p*(H₂) = 4.0 MPa.

^c Yield for the initial carbohydrate hydrolysis.

^d Overall yield for the two-stage conversion of the biomass-derived carbohydrate. The yield based on conversion of LA is given in parenthesis.

that, without isolation of the insoluble hydrolysis by-products, the subsequent LA hydrogenation is very slow under the as described reaction conditions, possibly due to a strong adsorption of humids to the iridium metal catalysts. Under these conditions, GVL was produced in 96% yield. The overall yield of GVL from glucose was approximately 52% (Table 3, entry 1). Further improvements to the GVL yield were achieved when D-fructose was used instead of D-glucose. The highest GVL yield was 60% following complete D-fructose conversion (Table 3, entry 2). Dimeric sugar (sucrose), a polymer (starch), and cellulose were also tested under the optimized conditions determined for D-glucose. In all three cases, near-complete conversion of the biomass-derived LA into GVL was observed (Table 3, entries 3–5), and the GVL was formed in 56%, 50%, and 32% overall yields, respectively. To the best of our knowledge, these results represent an unprecedented example of the simultaneous production of GVL and FA from renewable biomass resources via a simple and convenient catalytic hydrogenation under mild reaction conditions.

4. Conclusions

We have developed an efficient process for the hydrogenation of LA based on the use of CNT-supported Ir nanoparticles as a new heterogeneous catalyst. The method is highly effective and applicable to the hydrogenation of LA using H₂ even in the presence of FA under mild aqueous conditions, with the FA remaining unchanged. The method is effective for the simultaneous production of GVL and FA from a wide variety of renewable biomass resources. A convenient and cost-effective separation of FA from GVL can be realized because of the difference in the polarities and boiling points of GVL and LA.

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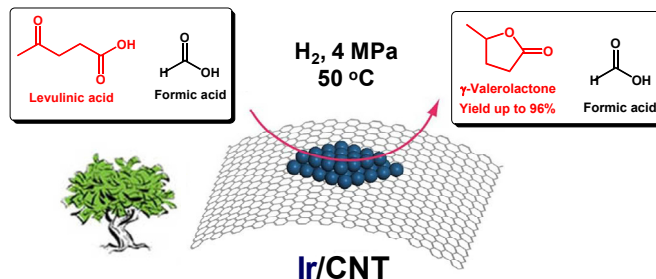
Graphical Abstract

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Catalytic conversion of biomass-derived levulinic acid into γ -valerolactone using iridium nanoparticles supported on carbon nanotubes

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Iridium nanoparticles supported on carbon nanotubes have been used as a highly efficient catalyst for the hydrogenation of biomass-derived levulinic acid to γ -valerolactone (GVL) in the presence of formic acid. The GVL was obtained in an excellent yield of 96% at an operating temperature of 50 °C.



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