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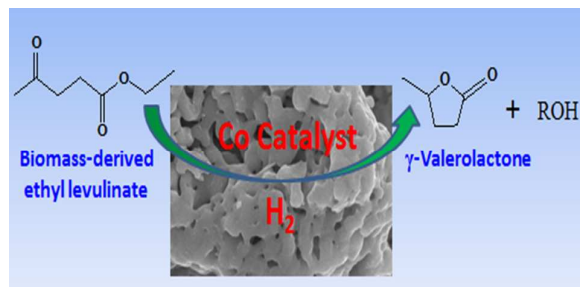


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Graphical abstract:

Cobalt catalyst is very efficient and stable for hydrogenation of biomass-derived ethyl levulinate to gamma-valerolactone at mild condition.

ARTICLE

Cobalt catalyst: Very efficient for hydrogenation of biomass-derived ethyl levulinate to gamma-valerolactone at mild condition

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Hydrogenation of ester levulinate to gamma-valerolactone (GVL) is an interesting reaction in biomass conversion to produce value-added chemicals. Exploration of efficient and robust catalysts is crucial for large-scale application. In this work, we conducted the reaction catalyzed by a Co catalyst, and it was found that commercially available Co_3O_4 was very efficient for this reaction under mild condition after reduction by H_2 . The effects of temperature, hydrogen pressure, amount of the catalyst used, and reaction time on the yield of GVL were studied. Under optimized conditions, the yield of GVL could reach 98%. The catalyst could be reused at least 10 times without notable loss of the activity and selectivity. The catalyst was characterized by scanning electron spectroscopy (SEM), transmission electron spectroscopy (TEM), X-ray photoelectron spectroscopy (XPS), and powder X-ray diffraction (XRD). It was demonstrated that the metallic Co^0 was the active species for the hydrogenation reaction. As far as we know, this was the first work to conduct the reaction using Co as the catalyst.

Introduction

Gradual depletion of fossil resources has stimulated the efforts for the sustainable production of fuels and chemicals. Lignocellulose, the main component of biomass, is an abundant and renewable carbon source for sustainable production of bulk chemicals and fuel additives.¹⁻³ Through biological or chemical approaches, lignocellulose and its derivatives can be converted into value-added chemicals, such as various alcohols,⁴⁻⁶ short chain hydrocarbons,^{7, 8} gluconic acid,⁹ 5-hydroxymethylfurfural (HMF),¹⁰⁻¹² lactic acid,¹³ pentanoic acid esters,¹⁴ 2,5-dimethylfuran,¹⁵ levulinic acid,¹⁶ gamma-valerolactone (GVL),^{17, 18} etc. Among these platform molecules, GVL is considered as one of the most appealing molecules as a fuel additive, solvent, liquid fuel, and ideal precursor for the production of more valuable chemicals.^{19,20}

Various biomass molecules have been reported for the production of GVL, such as cellulose,²¹ C6-sugars,^{22, 23} furfural alcohol,^{18, 24} etc. The hydrogenation of levulinic acid (LA) and its esters can generate GVL.^{18,25-27} Comparatively, the hydrogenation of ester levulinate to GVL is more attractive because the production of ester levulinate from lignocellulose has higher yield and facile separation process than the production of LA.²⁸⁻³⁰ In the process of hydrogenation, the H-donors can be H_2 ,¹⁹ formic acid,^{31,32} or isopropanol.¹⁸ Different

metal catalysts have been applied in the hydrogenation of LA and its esters, such as Ru, Rh, Pd, Pt, Ir, Re, Au, Cu, and Ni.^{20,33-36} Although many noble metal catalysts show excellent catalytic performances, the high cost and relatively low abundance limit their large-scale application to a certain degree.^{19,32} Furthermore, most of the reported catalysts often require a multi-step preparation or pretreatment process.^{20,37} Obviously, it is still highly desirable to develop non-precious, economically feasible, and easy-preparing catalysts using abundant metals for GVL production from biomass-derived platforms.^{19,38,39}

Several transition metal-based catalysts have been developed for the conversion of LA and its esters to GVL. RANEY® Ni, the representative of the Ni-based catalysts, has been applied in the hydrogenation of LA into GVL since 1947.⁴⁰ The application of Ni-based catalysts was also followed by other researchers.^{41,42} An efficient catalytic transfer hydrogenation (CTH) process with isopropanol as hydrogen source was developed using RANEY® Ni as the catalyst.¹⁸ ZrO_2 was also reported to be efficient catalyst in the CTH process for GVL production, but the reaction temperature was higher.³⁸ The catalysts of Cu/SiO_2 with tuneable Cu loadings was also applied to convert LA to GVL.³⁷ Up to now, most of the reported transition metal-based catalysts needed relatively high

reaction temperature, such as 150 ~ 220 °C for ZrO₂,³⁸ and 265 °C for Cu/SiO₂ catalysts.³⁷

Herein, we carried out the first work for hydrogenation of ethyl levulinate (EL) into GVL using Co catalyst. It was found that commercial Co₃O₄ could catalyze the reaction efficiently under mild reaction condition after being reduced in H₂ atmosphere. There are some obvious advantages of this catalyst for GVL production, such as relatively simple preparing process, high stability and efficiency, and use of abundant metal as catalyst.

Experimental

Materials

Ethyl levulinate (98%), gamma-valerolactone (98%), and dodecane (99%) were purchased from J&K Chemical. All the transition metal oxides were A. R. grade and provided by Sinopharm Chemical Reagent Co. Ltd. H₂ (99.99%) was provided by Beijing Analytical Instrument Company. All the chemicals were used as received.

Catalyst preparation

Before used, the Co₃O₄, NiO, and Fe₃O₄ were reduced to metallic state by H₂. For the reduction Co₃O₄ and NiO, a metal oxide was reduced in pure H₂ flow (15 mL/min) at atmospheric pressure by increasing temperature from 25 °C to 400 °C with a rate of 5 °C/min, and maintained at this temperature for 1 h before cooling to room temperature. For the reduction of Fe₃O₄, the metal oxide was reduced in pure H₂ flow (15 mL/min) at atmospheric pressure by increasing temperature from 25 °C to 500 °C with a rate of 5 °C/min, and maintained at this temperature for 1 h before cooling to room temperature.

Catalyst characterization

The structural properties of the catalysts were characterized by transmission electron microscopy (TEM, JEOL JEM-2100F) and scanning electron microscopy (SEM, HITACHI S-4800). Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 X-ray diffractometer using Cu K α radiation ($\lambda = 0.15406$ nm). The tube voltage was 40 kV and the current was 200 mA. X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab 250Xi using 200 W monochromated Al K α radiation. The 500 μ m X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about 3×10^{-10} mbar. Typically the hydrocarbon C1s line at 284.8 eV from adventitious carbon was used for energy referencing. The analysis of Co concentration in the reaction solution was conducted on ICP-AES (VISTA-MPX).

Reaction

The hydrogenation reaction was performed in a 10 mL Teflon-lined stainless steel autoclave equipped with a magnetic stirrer. In a typical experiment, 1 g ethyl levulinate (EL) and suitable amount of catalyst were introduced into the reactor. After

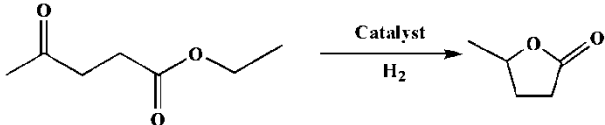
removing the air via vacuum pump, the reactor was placed in a constant temperature air bath. Hydrogen was charged into the reactor to a desired pressure, and then the stirrer was started. After reaction, the reactor was cooled in water to quench the reaction and the organic phase was extracted from the mixture by ethyl acetate. The sample was analyzed by gas chromatograph (GC, HP 4890) equipped with a flame ionization detector (FID), and dodecane was used as the internal standard. Identification of the products and reactant was done using a GC-MS (SHIMADZU-QP2010) as well as by comparing the retention times to respective standards in GC traces. In the reusability experiments, the catalyst was separated from the liquid by an external magnet, washed with ethanol and dried at room temperature under vacuum, and then reused for the next run without further reduction.

Results and Discussion

Screening and characterization of the catalysts

In our studies, Ni, Fe, and Co obtained from the metal oxides by hydrogen reduction were used as the catalysts for the hydrogenation of EL to GVL. The results are shown in Table 1. It can be seen that the Ni showed a moderate hydrogenation activity with a GVL yield of 35% (Entry 1). In contrast with the Ni catalyst, the Fe catalyst showed no activity for the hydrogenation reaction (Entry 2). Interestingly, the Co showed high activity with a GVL yield up to 94% (Entry 3). Different cobalt oxides, Co₃O₄ and CoO, were also attempted as catalysts in the hydrogenation of EL. It was found that both Co₃O₄ and CoO showed very low activity (Entries 4, 5). It can be deduced that the metallic Co⁰ was active for the reaction, which was verified in the following characterizations.

Table 1 Screening of catalysts for GVL production^a



Entry	Catalysts	Conversion/%	Selectivity/%	Yield/%
1	Ni	36	97	35
2	Fe	0	0	0
3	Co	99	95	94
4 ^b	CoO	2	50	1
5 ^b	Co ₃ O ₄	2	100	2

^aTypical reaction conditions were as follows until otherwise stated: EL, 1 g; catalyst, 0.1 g; reaction temperature, 130 °C; H₂ pressure, 3.3 MPa; reaction time, 3 h. ^b Commercial oxides were used directly without reduction.

In order to well understand the structure of the catalyst, some characterizations were conducted. Firstly, the morphology of the catalyst before and after reduction was characterized by SEM and TEM techniques (Fig. 1). From SEM images (Figs. 1a, 1b), the surface of the catalyst was rather smooth and

pyknotic before H₂ reduction, while it turned rough and porous after reduction. The TEM images further showed that the surface of the reduced catalyst had a loose and fibrous texture (Fig. 1c), which is favourable to enhancing the activity of the catalyst and the mass transfer of the reaction species.

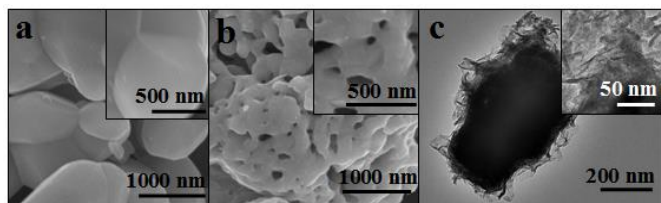


Fig. 1 SEM images of the Co₃O₄ before (a) and after (b) reduction, and TEM images of the catalyst after reduction (c). The insets show larger magnification.

XPS measurement was conducted to detect the chemical valence change of cobalt on the surface of the catalyst after reduction. The Co 2p spectra of the Co₃O₄ without reduction and reduced under typical conditions are given in Fig. 2. The decomposed spectrum of Co 2p could provide detailed information on the surface composition of Co₃O₄. On the basis of the published Co 2p spectra of Co₃O₄,^{43, 44} the peak at the binding energy (BE) of 779.5 eV could be assigned to a Co^{II/III} 2p_{3/2} configuration, while the peak at 794.6 eV could be attributed to the Co^{II/III} 2p_{1/2} configuration (Fig. 2a). The weak peaks at 788.1 eV and 804.7 eV represented the shake-up peaks for Co^{II/III} 2p_{3/2} and Co^{II/III} 2p_{1/2}, respectively. No peak for the metallic Co was observed in the Co 2p spectrum. These results indicated that it was the oxidation state of cobalt on the surface of Co₃O₄ without reduction. After Co₃O₄ was reduced by H₂, new peaks at 778.4 eV and 793.5 eV were observed (Fig. 2b). These two peaks could be assigned to Co⁰ 2p_{3/2} and Co⁰ 2p_{1/2}, respectively.⁴⁵ Thus, the metallic Co appeared on the surface of the catalyst after reduction, which verified our above speculation.

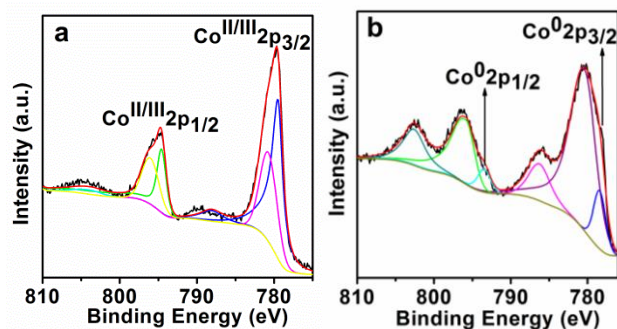


Fig. 2 Co 2p spectra of Co₃O₄ without reduction (a), and reduced by H₂ at 400 °C (b).

To give an insight into the bulk phase change of the catalyst after reduction, the XRD patterns of the catalysts were adopted (Fig. 3). It was found that the catalysts reduced under low temperatures (< 200 °C) remained the structures of the original

Co₃O₄ (JCPDS database PDF# 42-1617). When increasing the reduction temperature to 300 °C, new peaks appeared in the XRD patterns. The peaks at 36.4°, 42.5° and 61.5° corresponded to (111), (002) and (022) reflections of the CoO phase (PDF# 48-1719), while the peaks at 41.4°, 44.5° and 47.4° could be assigned to (010), (002) and (011) planes of the hcp-Co phase (PDF# 05-0727). This result was in agreement with the previous report that Co₃O₄ was reduced first to CoO and then to the metallic Co.⁴⁵ With partial reduction of Co₃O₄, the activity of the catalyst increased to a moderate level with a GVL yield of 52%. For the case of 400 °C, Co₃O₄ was totally reduced to the metallic Co because the peaks for Co₃O₄ disappeared. Besides the peaks for the hcp-Co phase, a new weak peak at 51.4° appeared, which could be assigned to fcc-Co phase (PDF# 15-0806).⁴⁶ The catalyst obtained at this reduction temperature exhibited the highest activity with a GVL yield up to 98%. These results verified further that the metallic Co⁰ was the active species for the hydrogenation process.

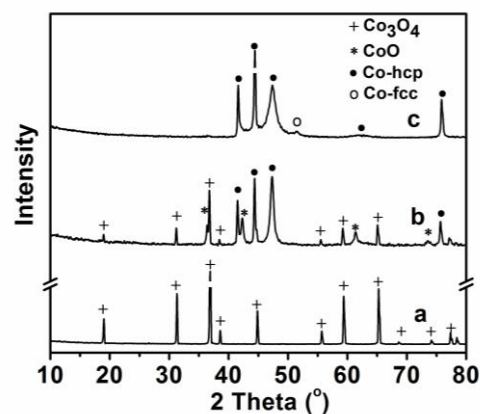


Fig. 3 XRD patterns of the catalysts reduced at different temperatures: (a) the original Co₃O₄; (b) 300 °C; (c) 400 °C.

The effect of catalyst dosage

The effect of catalyst dosage is given in Fig. 4. When the ratio of the catalyst to the substrate (EL) was 5 wt%, the GVL yield increased with the increasing of reaction time and reached up to 98% within 13 h. The reaction time could be shortened dramatically by increasing the catalyst dosage. Under a 15 wt% catalyst dosage, the reaction proceeded fast in the first two hours with a GVL yield of 89%, and the GVL yield increased to 97% within 8 h. Thus, a catalyst dosage of 15 wt% was adopted to obtain acceptable reaction rate and GVL yields.

We also studied whether the reaction could proceed under homogeneous catalysis. In the experiment, the solid Co catalyst was removed using an external magnet after a reaction time of 2 h under a 5 wt% dosage and the solution was allowed to react under the same reaction conditions (Fig. 4). It was found that no more GVL was produced after the removal of the catalyst, proving that the solid Co particles played the catalytic role.

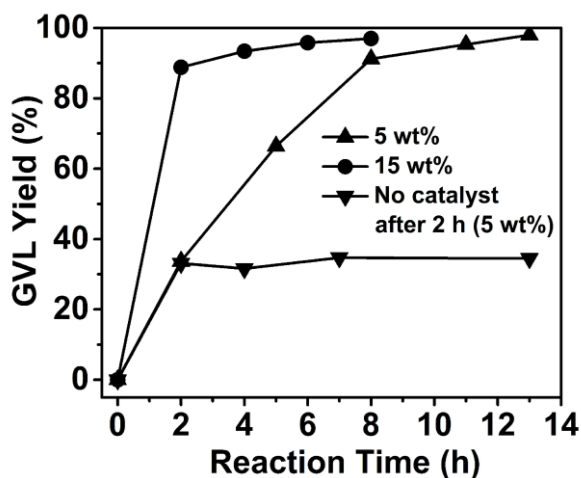


Fig. 4 Influence of the catalyst dosage on the yield of GVL. Reaction condition: EL, 1 g; 130 °C; H₂ pressure, 3 MPa.

The effect of reaction temperature

The effect of reaction temperature on GVL yield is shown in Fig. 5. It can be seen that reaction temperature affected the GVL yields dramatically. In the low temperature range (< 100 °C), the catalyst exhibited low activity with a GVL yield less than 21% within 2 h. Increasing the temperature could enhance the yield significantly. The GVL yield could reach 89% within 2 h at 130 °C. Thus, a temperature of 130 °C is high enough to obtain satisfactory reaction rate and GVL yields. This temperature is lower than that required for the reaction catalyzed by Ir/C (150 °C),⁴¹ ZrO₂ (150–220 °C),³⁸ and Cu/SiO₂ (265 °C).³⁷

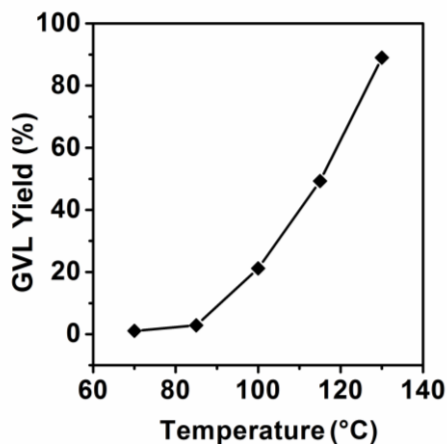


Fig. 5 Effect of reaction temperature on the yield of GVL. Reaction conditions: EL, 1 g; catalyst, 0.15 g; H₂ pressure, 3 MPa; reaction time, 2 h.

The effect of H₂ pressure

The effect of H₂ pressure on the yield of GVL is shown in Fig. 6. A moderate GVL yield (59%) was observed even under low H₂ pressure (1 MPa). Increasing the H₂ pressure could improve the reaction rate. The GVL yield could be as high as 96% within 2 h at a H₂ pressure of 4 MPa. The results showed that under similar conditions, the performance of the Co catalyst in

this study is comparable with or even better than those of the reported catalysts, such as ZrO₂, RANEY® Ni, Pd/C, Rh/C, Pt/C, and Re/C, etc.^{38,41,42}

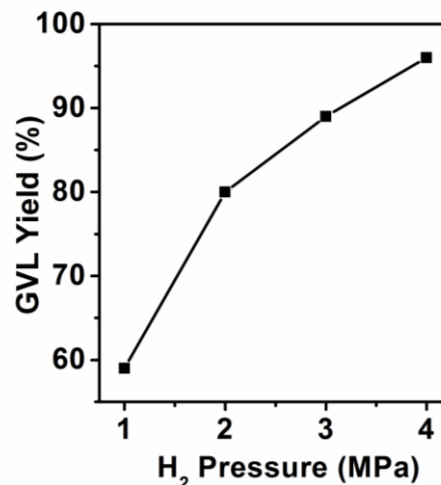


Fig. 6 Catalytic performances at different H₂ pressures. Reaction conditions: EL, 1 g; catalyst, 0.15 g; reaction temperature, 130 °C; reaction time, 2 h.

Reusability of the catalyst

The reusability of the catalyst was investigated under the experimental condition that the yield of GVL was controlled around 50%. After reaction, the catalyst could be separated by centrifugation or simply applying a magnet due to the catalyst could respond to external magnetic field (Fig. 7). The results are given in Fig. 8, for which the catalyst was recycled by an external magnetic field. The catalyst could be reused at least ten times without considerable change in GVL yields. The Co leaching during the reactions was investigated by determining the Co concentration in the reaction solutions via ICP, and the results were also given in Fig. 8. It can be seen that the Co concentrations in the reaction solutions were extremely low (< 0.42 ppm) during the ten recycling times. This may be attributed to solvent-free and weak polarity of the reactant and product. To investigate the morphology and structure change of the catalyst after reuse for 10 times, the recycled catalyst was characterized by SEM, XPS, and XRD (Fig. 9). From the SEM images (Figs. 9a and 9b), it can be seen that the porous structures of the catalyst were well maintained, and the particle size had no obvious change. The comparison of the XPS spectra of the virgin and recycled catalyst showed that the surface composition had no notable change and the Co⁰ still existed on the catalyst surface after reuse (Fig. 9c). The bulk structure of the recycled catalysts was detected by XRD (Fig. 9d). The results indicated that the bulk phase of the recycled catalyst was still Co⁰ and identical to the virgin catalyst. All the results are consistent with the fact that the catalytic performance of the Co catalyst was not changed after reused 10 times.

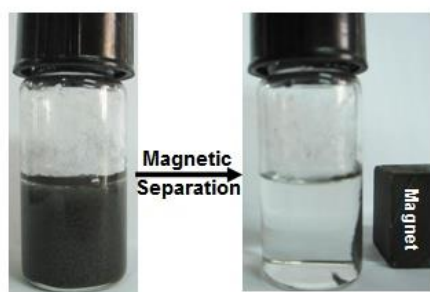


Fig. 7 Recycling of the catalysts using an external magnet.

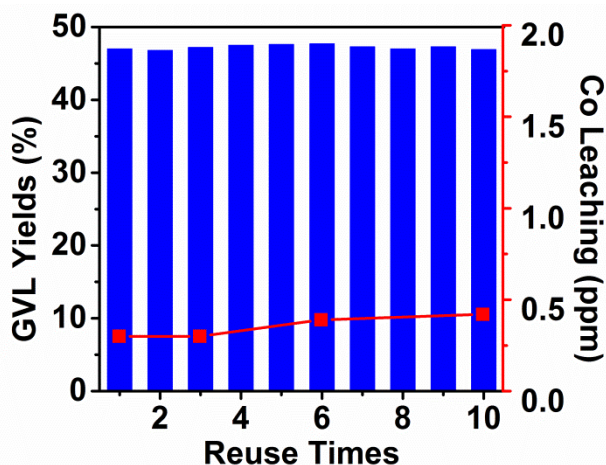


Fig. 8 The performance of the catalyst in the reuse experiments. Reaction conditions: EL, 1 g; catalyst, 0.05 g; 130 °C; H₂ pressure, 3 MPa; reaction time, 3 h.

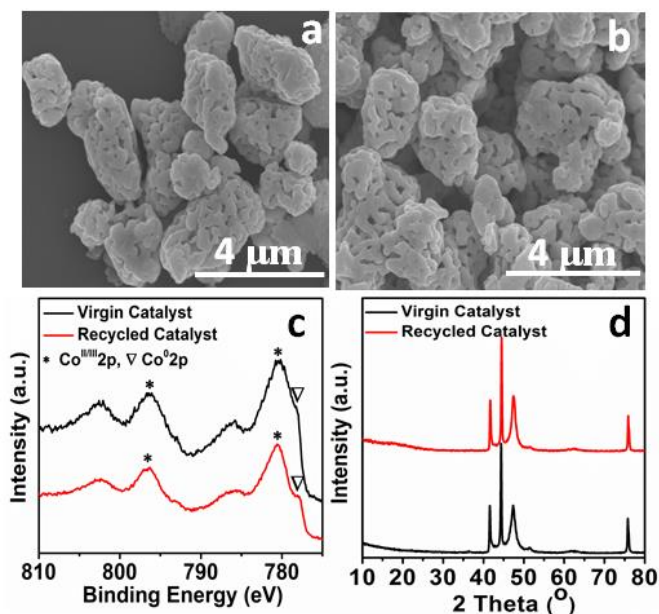


Fig. 9 Comparison of the virgin Co catalyst and the Co catalyst after reused 10 times. SEM images of the virgin (a) and recycled (b) catalysts, Co 2p spectra of the virgin and recycled catalysts (c), and XRD patterns of the virgin and recycled catalysts (d).

Conclusion

The hydrogen-reduced commercial Co₃O₄ has been found to be very active and selective in the hydrogenation of EL to GVL without using any solvent. Under the optimized conditions, EL could nearly be quantitatively converted into GVL with a high yield up to 98% under mild temperature and H₂ pressure. Further study has indicated that metallic Co⁰ is the active species in the hydrogenation reaction. The catalyst can be reused for at least four times without decreasing the yield of GVL considerably. We believe that the efficient and stable catalyst has great potential of application with obvious advantages.

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