Contents lists available at ScienceDirect

# Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

# MIL-53-NH<sub>2</sub>-derived carbon-Al<sub>2</sub>O<sub>3</sub> composites supported Ru catalyst for effective hydrogenation of levulinic acid to $\gamma$ -valerolactone under ambient conditions

Chi Van Nguyen<sup>a</sup>, Babasaheb M. Matsagar<sup>b</sup>, Jyun-Yi Yeh<sup>b</sup>, Wei-Hung Chiang<sup>a,\*\*</sup>, Kevin C.-W. Wu<sup>b,c,d,\*</sup>

<sup>a</sup> Department of Chemical Engineering, National Taiwan University of Science and Technology, No. 43, Sec. 4, Keelung Road, Taipei, 10607, Taiwan

<sup>b</sup> Department of Chemical Engineering, National Taiwan University, No. 1, Sec. 4, Roosevelt Road, Taipei, 10617, Taiwan

<sup>c</sup> Center of Atomic Initiative for New Materials (AI-MAT), National Taiwan University, Taiwan

<sup>d</sup> International Graduate Program of Molecular Science and Technology, National Taiwan University (NTU-MST), Taiwan

#### ARTICLE INFO

Keywords: Metal-Organic frameworks (MOFs) Ru@C-Al\_2O<sub>3</sub>composites Levulinic acid Hydrogenation γ-valerolactone

#### ABSTRACT

Herein, we report the synthesis of stable and efficient novel Ru-embedded C-Al<sub>2</sub>O<sub>3</sub> catalyst for the hydrogenation of levulinic acid (LA) to  $\gamma$ -valerolactone (GVL) in water under ambient condition. The prepared Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst is characterized in detail using various physicochemical characterization techniques (XRD, XPS, Raman spectroscopy, TEM, TGA, and ICP-OES). The Ru nanoparticles confined within MIL-53-NH<sub>2</sub>-derived C-Al<sub>2</sub>O<sub>3</sub> (denoted as Ru@C-Al<sub>2</sub>O<sub>3</sub>) show remarkable efficiency for the hydrogenation of LA into GVL (99.9% yield) under ambient reaction condition (hydrogen pressure 1 atm, 25 °C). The ultra-small particles size (1 nm) and high electron density surrounding Ru NPs resulted in excellent catalytic performance for the hydrogenation of LA. The Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst is stable under reaction condition and exhibits consistent catalytic activity during recycle experiments. Furthermore, this catalyst shows lower activation energy (Ea = 34.66 kJ mol<sup>-1</sup>) compared to the reported methods for the hydrogenation of LA to GVL.

# 1. Introduction

Increasing energy consumption together with decreasing fossil fuel reserves is one of the most concerned issues of future energy security. Searching for alternative carbon resources is being an urgent demand [1–3]. Lignocellulosic biomass is considered as a promising candidate for replacing fossil carbon resources since it is a renewable and sustainable carbon feedstock [4]. Moreover, lignocellulose biomass is non-edible and abundant in the world [5,6]. Hence, in recent years, the conversion of lignocellulose biomass into highly-valued products has become an attractive research field [7,8].

Among the various transformations of lignocellulose biomass into value-added chemicals, the hydrogenation of levulinic acid (LA) to  $\gamma$ -valerolactone (GVL) is extensively studied using both homogeneous and heterogeneous catalysts [9–13]. Because LA is one of the top biomass-derived platform chemicals, which was easily produced from biomass such as cellulose and xylose, with low cost and high efficiency [8,14,15]. On the other hand, (GVL) is a promising intermediate

product, used for the production of transportation fuel, polymeric materials, and other fine chemicals [16,17]. In addition, it can be used as a green solvent, liquid fuel additive, and flavouring agent [18,19].

Recently, various catalysts and reaction conditions have been investigated for the hydrogenation of LA into GVL efficiently [13,20,21]. For example, the homogeneous catalytic systems including metal salts and Pd complex in combination with organic ligands were employed to hydrogenate LA into GVL with more than 95% GVL yield under the presence of pure hydrogen or formic acid as a hydrogen source [9,22]. However, these homogeneous catalysts are facing some critical problems including the instability of metal complex, a complication of preparing catalyst ligands, and difficulty in the product purification [22,23]. While some heterogeneous catalysts such as metallic catalysts and metal-supported catalysts have been used for converting LA to GLV to solve the above-mentioned problems [24–27], it is required to use the harsh reaction conditions including high temperatures (100–270 °C) and high pressure (4–15 MPa) to achieve a high yield of GVL [13,25,27]. Moreover, organic solvents were used in some cases, which

https://doi.org/10.1016/j.mcat.2019.110478 Received 12 April 2019; Received in revised form 3 June 2019; Accepted 13 June 2019 2468-8231/ © 2019 Elsevier B.V. All rights reserved.





<sup>\*</sup> Corresponding author at: Department of Chemical Engineering, National Taiwan University, No. 1, Sec. 4, Roosevelt Road, Taipei, 10617, Taiwan. \*\* Corresponding author.

E-mail addresses: whchiang@mail.ntust.edu.tw (W.-H. Chiang), kevinwu@ntu.edu.tw (K.C.-W. Wu).

are not environmental friendly and also not cost-effective for industrial applications [2,13,27]. Besides, the metal leaching in the reaction environment and the catalyst deactivation after reaction are the most concerned issues. Therefore, the catalytic conversion of LA into GVL in water under mild reaction condition is challenging [26].

The hydroxyapatite supported ruthenium (Ru) has been reported as the efficient catalyst for LA hydrogenation into GVL, compared to other hydroxyapatite supported metals such as Pd, Pt, Cu, and Ni [21,28]. In addition, the commercial Ru/C catalyst exhibited the high catalytic activity for converting LA into GVL [29], nevertheless, the catalyst is not reusable due to its deactivation and metal leaching during the reaction [29-31]. Recently, the use of metal oxides (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, and SiO<sub>2</sub>) and functionalized metal oxides (NH<sub>2</sub>-y-Al<sub>2</sub>O<sub>3</sub>) were reported for stabilization of Ru nanoparticles (NPs) during LA hydrogenation reaction at 70 °C and 4 MPa H<sub>2</sub> pressure [25,32]. On the other hand, Yulei Zhu et al. have demonstrated that Ru NPs supported on reduced graphene oxide (RGO) promoted the LA hydrogenation to GVL with 99.9% yield at low temperature (40 °C, 4 MPa hydrogen pressure) [24]. However, the stability of Ru-supported catalysts under reaction and their reusability is the major issue in many reactions. Thus, the development of a stable and efficient catalyst for LA hydrogenation to GVL at ambient reaction condition is of great significance.

Metal-Organic Framework (MOF)-derived nanomaterials including porous carbons (PC) and metal oxides (MO) have shown extensive studies for catalysis applications due to its diverse active sites, welldefined structures, facile modified functions, large surface area, and good thermal stability [33-35]. In addition, the introduction of second metal into the structure of MOF-derived nanomaterial could create a superior catalyst, which could involve both the benefits of foreign metal and advantages of MOF-derived nanomaterials [36-38]. Here, we describe the synthesis of novel Ru embedded in MIL-53-NH<sub>2</sub>-derived C-Al<sub>2</sub>O<sub>3</sub> catalyst and its use for the LA hydrogenation into GVL in water under mild reaction conditions (1 atm, 25 °C). As shown in Scheme 1, the RuCl<sub>3</sub>@MIL-53-NH<sub>2</sub> is first prepared via de novo synthesis method, which was reduced to form Ru nanoparticles inside C-Al<sub>2</sub>O<sub>3</sub> honeycomb-like structure (named as Ru@C-Al2O3). The detailed catalyst characterization was determined by using XRD, XPS, Raman spectroscopy, TEM, TGA, and ICP-OES, indicating that ultra-small Ru nanoparticles size (1 nm) are well-dispersed inside the C-Al<sub>2</sub>O<sub>3</sub> honeycomblike structure. The prepared Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst is highly active for the hydrogenation of LA to GVL at ambient hydrogen pressure (1 atm) in aqueous solution. In addition, the kinetic parameters including the activation energy and reaction rate constant for LA hydrogenation over Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst were studied and calculated. We find that the small Ru NPs and high electron density around to Ru<sup>0</sup> play an important role for LA conversion. Furthermore, the C-Al2O3 honeycomb-like structure can stabilize Ru during reaction condition.

#### 2. Materials and methods

# 2.1. Chemicals

Levulinic acid (LA, 98%), Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, and  $\gamma$ -valerolactone (GVL, 98%) were purchased from Acros Organics. 2-aminoterephthalic

acid (99%),  $Al_2O_3$  powder,  $TiO_2$  powder, activated carbon (AC),  $RuCl_3:3H_2O$  were purchased from Sigma-Aldrich. All chemicals were directly used without any further purification.

# 2.2. Synthesis of MIL-53-NH<sub>2</sub>

The MIL-53-NH<sub>2</sub> as synthesized by modification from the previous report [39]. Typically, 2-aminoterephthalic acid (7.5 g) was added into 10 mL aqueous solution of 1 M NaOH (mixture A). Then, 5 mL of Al  $(NO_3)_3$ ·9H<sub>2</sub>O (1.5 g) solution was dropped into the mixture A. The obtained reaction mixture was magnetically stirred at RT for 1 day. The yellow powder was centrifuged and washed with deionized water for several times to remove NaOH and unreacted linker. Finally, the resulting solid was dried under vacuum at RT to obtain MIL-53-NH<sub>2</sub>.

#### 2.3. Synthesis of RuCl<sub>3</sub>@MIL-53-NH<sub>2</sub> and Ru@C-Al<sub>2</sub>O<sub>3</sub>

The RuCl<sub>3</sub>@MIL-53-NH<sub>2</sub> was synthesized using a similar method which was used for the synthesis of MIL-53-NH<sub>2</sub>. Initially, 2-aminoterephthalic acid (7.5 g) was added into 10 mL NaOH solution (1 M) (mixture A). Next, the mixture B containing 5 mL of  $Al(NO_3)_3$ '9H<sub>2</sub>O solution (1.5 g) and 5 mL RuCl<sub>3</sub> (0.1 M) was added dropwise into the mixture A. The mixture was then magnetically stirred at RT for 24 h. After 24 h, the resulting solid was centrifuged and washed with deionized water for several times. Subsequently, the solid product was dried under vacuum at RT to obtain a RuCl<sub>3</sub>@MIL-53-NH<sub>2</sub>.

### 2.3.1. Synthesis of Ru@C-Al<sub>2</sub>O<sub>3</sub> composite

The Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by reducing the RuCl<sub>3</sub>@ MIL-53-NH<sub>2</sub> powder at 500 °C for 5 h, with a heating rate of 5 °C min<sup>-1</sup> under H<sub>2</sub>/N<sub>2</sub> mixed gas flow (80 mL min<sup>-1</sup>). After completion of reduction, the resulting solid was denoted as Ru@C-Al<sub>2</sub>O<sub>3</sub>.

#### 2.4. Catalytic levulinic acid (LA) hydrogenation into $\gamma$ -valerolactone

All experiments were performed in a three-neck round bottom flask connected with the condenser. Typically, 10 mL water was added to the three-neck round bottom flask followed by 20 mg Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst and LA (1 mmol). When the reaction temperature reached to 60 °C, the hydrogen gas was passed through the mixture with a flow rate of 50 mL min<sup>-1</sup> at 1 atm. The reaction take place under continuous stirring for 2 h. After 2 h reaction time, the reaction mixture was cooled to room temperature and diluted to 25 ml with deionized water. The reaction solution was filtered with a 0.22 µm syringe filter for high-pressure liquid chromatography (HPLC) analysis.

#### 2.5. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Cu K $\alpha$  radiation source on a Rigaku-Ultima IV instrument. The chemical state of elements (Ru 3d and Cl 2p) present in prepared samples was studied using X-ray photoelectron spectrometer (XPS, Thermo Scientific, Theta Probe). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM)



Scheme 1. Illustration for the synthesis of Ru@C-Al<sub>2</sub>O<sub>3</sub> and catalytic LA hydrogenation into GVL.

measurements were performed with a field-emission transmission electron microscopy (FETEM, JEM-2011 F) operating at 200 kV voltages. The Ru loading on the Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst and the leaching of Ru in the reaction solution was determined using induced coupled plasma-optical emission spectrometry (ICP-OES). Raman spectroscopy was performed on a Renishaw-UV–vis Raman System 1000 using a CCD detector at room temperature.

#### 2.6. Analysis of products

HPLC equipped with a refractive index detector (HPLC-RI) and ICE-Coregel 87H3 column (operated at 35 °C) was employed for the analysis. The sulfuric acid aqueous solution (8 mM) used as mobile phase with a flow rate of  $0.6 \text{ mL min}^{-1}$ . The conversion of LA and product yield were calculated by the following formula.

Conversion (%) = 
$$\frac{initial mole of LA - fianl mole of LA}{initial mole of LA} \times 100\%$$
  
product yield (%) =  $\frac{mole of GVL (HPLC)}{initial mole of LA} \times 100\%$ 

#### 3. Results and discussion

#### 3.1. Characteristics of as-synthesized catalyst

The structure of synthesized RuCl<sub>3</sub>@MIL-53-NH<sub>2</sub> was first determined using XRD (Fig. 1a). The diffraction peaks of RuCl<sub>3</sub>@MIL-53-NH<sub>2</sub> were in good agreement with that of the as-synthesized MIL-53-NH<sub>2</sub> and the previously reported XRD pattern for MIL-53-NH<sub>2</sub> [39], indicating the formation of MIL-53-NH<sub>2</sub> framework. The thermogravimetric analysis (TGA) result shows that an unchanged weight of RuCl<sub>3</sub>@MIL-53-NH<sub>2</sub> remains 22.64 wt % (above 420 °C) which is larger than a 20.1 wt% of MIL-53-NH<sub>2</sub> (above 550 °C) (Fig. 1b). In addition, the XPS analysis of RuCl<sub>3</sub>@MIL-53-NH<sub>2</sub> reveals the presence of Ru  $3d_{5/2}$  and Cl 2p peaks at the binding energy of 280.75 eV and 198.3 eV, respectively (Fig. 1c-d). These results indicate that the RuCl<sub>3</sub> species

are successfully loaded within MIL-53-NH<sub>2</sub> framework.

After performing thermal treatment at 500 °C under H<sub>2</sub>/N<sub>2</sub> atmosphere for RuCl<sub>3</sub>@MIL-53-NH<sub>2</sub>, the MIL-53-NH<sub>2</sub> was transformed into C-Al<sub>2</sub>O<sub>3</sub>, at the same time the RuCl<sub>3</sub> present inside the framework of MIL-53-NH2 was reduced to Ru nanoparticles (NPs) confined within C-Al<sub>2</sub>O<sub>3</sub>. The XRD pattern Ru@C-Al<sub>2</sub>O<sub>3</sub> shows that the RuCl<sub>3</sub>@MIL-53-NH<sub>2</sub> was completely decomposed under thermal reduction (Fig. 1a). Moreover, the Raman spectrum of Ru@C-Al<sub>2</sub>O<sub>3</sub> exhibited two peaks at 1353 cm<sup>-1</sup> and 1596 cm<sup>-1</sup> (Figure S1), corresponding to D band and G band of graphitic carbon, respectively [40]. The disorder of carbon structure is determined based on the intensity ratio of D band over G band ( $I_D/I_G$ ). The  $I_D/I_G$  of Ru@C-Al<sub>2</sub>O<sub>3</sub> is 1.02, which is much larger than the calculated value in the MIL-53-NH<sub>2</sub>-derived C-Al<sub>2</sub>O<sub>3</sub> (I<sub>D</sub>/  $I_{G} = 0.61$ ) (Figure S1). The increased  $I_{D}/I_{G}$  ratio in Ru@C-Al<sub>2</sub>O<sub>3</sub> indicates more defects in the Ru@C-Al<sub>2</sub>O<sub>3</sub> substrate which could be due to the presence of Ru NPs. Furthermore, TGA result showed that a 43.6 wt % weight loss in case of Ru@C-Al2O3 is observed at 355 °C, which could be due to the removal of adsorbed water and amorphous carbon (Fig. 1b), and the remaining components above 400 °C may be Ru and Al<sub>2</sub>O<sub>3</sub> components

The XPS spectrum of Ru@C-Al<sub>2</sub>O<sub>3</sub> showed the binding energy of Ru  $3d_{5/2}$  at 280.3 eV (Fig. 1c) which is lower than the value of Ru  $3d_{5/2}$  in RuCl<sub>3</sub>, showing that RuCl<sub>3</sub> was reduced to metallic Ru. In addition, the elements including carbon, oxygen, aluminum, and nitrogen were determined by means of XPS, with the concentration of 24 at.%, 48 at.% 20 at.%, and 3 at.%, respectively. It is noteworthy that these elements in the material play a crucial role for catalytic performance. The nitrogen atoms and chemical configurations of C1s including C–O (286.0 eV), C = O (287.1 eV), and O-C = O (289.6 eV) (Figure S2) were demonstrated as important anchoring sites for Ru species [24,41]. Moreover, the Al<sub>2</sub>O<sub>3</sub> host is a solid acid catalyst for accelerating dehydration reaction [42] which is one of intermediate steps in the LA-to-GVL hydrogenation. Therefore, we suggest that the Ru@C-Al<sub>2</sub>O<sub>3</sub> material can act as novel catalyst for LA hydrogenation into GVL.

The ICP-OES analysis of  $Ru@C-Al_2O_3$  showed 3.1 wt % Ru concentration. However, there are no obviously X-ray diffraction peaks of Ru nanoparticles (Fig. 1a), suggesting that the particles size of Ru could



Fig. 1. Characteristics of as-synthesized materials. a) X-ray diffraction (XRD), b) TGA results, XPS spectra of c) Ru 3d<sub>5/2</sub> and d) Cl 2p.



Fig. 2. a-b) TEM and HRTEM images of Ru@C-Al<sub>2</sub>O<sub>3</sub>, c) Ru nanoparticles size distribution in Ru@C-Al<sub>2</sub>O<sub>3</sub>.

be smaller than 5 nm which is below the detection limit of XRD [26]. Additional TEM analysis was performed to determine the particles size of Ru NPs. As shown in Fig. 2a-c, the Ru NPs have a uniform distribution within the C-Al<sub>2</sub>O<sub>3</sub> host, with an averaged particles size of 1 nm which is also consistent with the XRD result. Small particle size of Ru NPs suggests that Ru@C-Al<sub>2</sub>O<sub>3</sub> may have high catalytic activity. We suggest that such a uniform distribution of Ru nanoparticles was contributed from the MIL-53-NH<sub>2</sub> material because it provides an ordered nanospace that can serve as an ideal location for stabilizing and preventing the aggregation of Ru NPs during reduction.

#### 3.2. Catalytic studies

The prepared Ru@C-Al2O3 catalyst was further used for the hydrogenation of LA to GVL in the water environment at 60 °C under ambient hydrogen pressure (1 atm). The reaction is carried out in water environment at 60 °C under ambient pressure of hydrogen gas (1 atm). Initially, C-Al<sub>2</sub>O<sub>3</sub> and Ru@C-Al<sub>2</sub>O<sub>3</sub> catalysts were investigated for LA hydrogenation to GVL to understand the effect of Ru in C-Al<sub>2</sub>O<sub>3</sub> (Table 1). The result shows that the C-Al<sub>2</sub>O<sub>3</sub> catalyst is not active for the LA conversion (Table 1, entry 1). In contrast, a high LA conversion of 91% was observed in the presence of Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst (3.1 wt% Ru) within 2 h (Table 1, entry 2), indicating that the presence of Ru played an important role for the hydrogenation of LA to GVL. The amount of Ru@C-Al2O3 catalyst and reaction time has a substantial effect on the LA conversion and GVL yield (Table 1, entry 2-6). The Ru@C-Al<sub>2</sub>O<sub>3</sub> (20 mg) catalyst shows complete conversion of LA into GVL at 60 °C within 2 h. Moreover, Ru@C-Al<sub>2</sub>O<sub>3</sub> also exhibits high activity at RT and 45 °C with 99.9% GVL yield for 3 h and 5 h reaction time, respectively (Table 1, 7-8). It is noticed that LA hydrogenation to GVL at ambient hydrogen pressure and temperature has not reported yet (Table S1). In our present report, the Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst shows

#### Table 1

Levulinic acid (LA) hydrogenation into  $\gamma$ -valerolactone (GVL) using various catalysts at ambient hydrogen pressure.

Entry	Catalysts	Amount of catalyst (mg)	T (°C)	Time (h)	LA Conversion (%)	GVL Yield (%)
1	C-Al <sub>2</sub> O <sub>3</sub>	10	60	2	0	0
2	Ru@C-Al <sub>2</sub> O <sub>3</sub>	10	60	2	91	91
3	Ru@C-Al <sub>2</sub> O <sub>3</sub>	15	60	2	95	95
4	Ru@C-Al <sub>2</sub> O <sub>3</sub>	20	60	2	100	> 99.9
5	Ru@C-Al <sub>2</sub> O <sub>3</sub>	20	60	1	95	95
6	Ru@C-Al <sub>2</sub> O <sub>3</sub>	20	60	0.5	70	70
7	Ru@C-Al <sub>2</sub> O <sub>3</sub>	20	45	3	100	> 99.9
8	Ru@C-Al <sub>2</sub> O <sub>3</sub>	20	RT	5	100	> 99.9
9	Ru/Al <sub>2</sub> O <sub>3</sub>	20	60	2	87	87
10	Ru/TiO <sub>2</sub>	20	60	2	88	88
11	Ru/AC	20	60	2	60	60

Reaction condition: LA (1 mmol), H<sub>2</sub>O (10 mL), hydrogen gas (50 mL min $^{-1}$ ) at 1 atm.

excellent performance for the hydrogenation of LA into GVL at ambient reaction condition.

To compare the catalytic activity of Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst with other Ru-supported catalysts, we synthesized various Ru-supported catalysts such as Ru/Al<sub>2</sub>O<sub>3</sub> (3.2 wt% Ru), Ru/TiO<sub>2</sub> (3.23 wt% Ru), and Ru/AC (3.3 wt% Ru). Further, these catalysts were used for LA hydrogenation to GVL under desired reaction condition (Table 1, entry 9-11). The Ru/ Al<sub>2</sub>O<sub>3</sub>, Ru/TiO<sub>2</sub>, and Ru/AC catalysts exhibited lower activity for LA conversion (Ru/Al<sub>2</sub>O<sub>3</sub> 87%, Ru/TiO<sub>2</sub> 88%, and Ru/AC 60%) at 60 °C for 2 h. Although these catalysts show better efficiency for the hydrogenation of LA into GVL, it is required to use higher temperature and pressure [24,25,29,43]. These results reveal that the Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst is highly active for LA hydrogenation to GVL at ambient reaction condition.

The reaction kinetics of LA hydrogenation into GLV is studied to calculate reaction rate constant (k) and activation energy (Ea). The LA hydrogenation was carried out at different temperatures and reaction time using Ru@C-Al<sub>2</sub>O<sub>3</sub> as a catalyst under ambient hydrogen pressure (Fig. 3a). It was reported that the reaction pathway for hydrogenation of LA into GVL proceeds via the formation either angelia lactone or 4hydroxyl pentanoic acid as an intermediate product (Scheme S1), which is subsequently converted to GVL [16]. However, we have not observed these intermediate products in all of our experimented reaction conditions (Fig. 3a), suggesting that the formation of the intermediate products is an instantaneous step. In addition, the only GVL product was detected by HPLC, suggesting that further hydrogenation of GVL to side products does not proceed (Fig. 3a). Thus, we assume that the catalytic hydrogenation of LA to GVL should obey the firstorder reaction kinetics which can be expressed as the following equation;

$$-\mathbf{r}(LA) = -\frac{d[LA]}{dt} = k^*[LA]$$

where [LA] means molar concentrations of LA, and k is the rate constant of LA hydrogenation at a certain temperature. After the subsequent integral calculation, the original equation will become.

$$-\ln(1-X) = kt$$

where t and X are the reaction time and LA conversion, respectively. As shown in Fig. 3b, the linear relationship between  $-\ln(1-x)$  and reaction time is well-established, indicating that the hydrogenation of LA into GVL is the first-order reaction [24,26], with a high reaction rate constant (k) of  $0.654 h^{-1}$ ,  $1.404 h^{-1}$ , and  $2.532 h^{-1}$  at temperatures of 25 °C, 45 °C, and 60 °C, respectively (Table 2). Moreover, the activation energy (E<sub>a</sub>) over Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst was determined to be Ea = 34.66 kJ mol<sup>-1</sup>, which is lower than the reported Ea values for the hydrogenation LA into GVL (Table 2). This demonstrates that Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst exhibits an excellent catalytic reactivity for the LA hydrogenation to GVL at ambient temperature and hydrogen pressure. Further, the reaction rate constant (k) of the LA hydrogenation over various amounts of Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst was also determined. As



Fig. 3. a) LA concentration and GVL yield at varing reaction time and temperature using  $Ru@C-Al_2O_3$  catalyst, b) plots of -ln(1-x) vs reaction time. Reaction condition: LA (1 mmol),  $Ru@C-Al_2O_3$  (20 mg),  $H_2O$  (10 mL), hydrogen gas (50 mL min<sup>-1</sup>).

 Table 2

 Reaction rate constant (k) and activation energy (Ea) of LA hydrogenation over various Ru-supported catalysts.

Entry	Catalysts	T (°C)	H <sub>2</sub> gas (MPa)	k (h <sup>-1</sup> )	Ea (kJ mol <sup>-1</sup> )	Ref.
1	Ru/C-Al <sub>2</sub> O <sub>3</sub>	RT	Ambient (~0.1)	0.654	34.66	This work
		45		1.404		
		60		2.532		
2	Ru/RGO	40	4	2.092	66.01	24
3	Ru/AC	40	4	0.338	87.66	24
4	Ru-TPPTS	50-90	4.5	1.5	61.0	35
5	Ni-NIO	110-140	2	-	93.7	14
5	111-1110	110-140	4	-	93.7	14

Reaction condition: LA (1 mmol), H<sub>2</sub>O (10 mL), hydrogen gas (50 mL min $^{-1}$ ) at 1 atm.

shown in **Figure S3**, the reaction rate constant increased from  $1.878\,h^{-1}$  to  $2.526\,h^{-1}$  corresponding to the increase of  $Ru@C-Al_2O_3$  catalyst amount from 10 mg to 20 mg, indicating that the  $Ru@C-Al_2O_3$  catalyst played inportant role for the hydrogenation of LA into GVL.

We speculate that the extraordinary properties of Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst resulted in the superior performance for LA hydrogenation at ambient reaction condition. We find that the binding energy of Ru  $3d_{5/2}$ in Ru@C-Al<sub>2</sub>O<sub>3</sub> is 280.3 eV (Fig. 1b), which is lower than the previously reported values of Ru supported on the other substrates [24]. A lower binding energy of Ru<sup>0</sup> NPs in Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst indicates the higher electron density surrounding to Ru<sup>0</sup> NPs, leading to the highly active catalyst, which was demonstrated by Yulei Zhu's group [24]. Moreover, the small particle size of Ru<sup>0</sup> NPs within Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst could induce more active surface for catalyzing LA hydrogenation. Thus, we suppose that high electron density on Ru<sup>0</sup> NPs and small average particle size could be the important factors for high catalytic activity of Ru@C-Al<sub>2</sub>O<sub>3</sub>. Another possible reason resulted in the excellent catalytic performance of Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst is based on the Al<sub>2</sub>O<sub>3</sub> species which could promote the dehydration step, consequently, the reaction rate of LA hydrogenation enhanced. The acidic Al<sub>2</sub>O<sub>3</sub> support bearing the strongly active sites of Ru<sup>0</sup> NPs lead to low activation energy.

It is noticed that the hydrogen gas plays a crucial role for LA hydrogenation [10,44], thus, a variable flow rate of hydrogen gas was considered for investigating the effect of hydrogen flow rate on the hydrogenation of LA (Fig. 4). In case of LA hydrogenation, LA does not consume in the absence of hydrogen. As expected, LA concentration significantly decreased using 10 mL min<sup>-1</sup> hydrogen flow rate, confirming the importance of hydrogen gas. Subsequently, the increase of hydrogen flow rate from 30 mL min<sup>-1</sup> to 60 mL min<sup>-1</sup> resulted in complete conversion of LA, suggesting that the optimum flow rate of



Fig. 4. Influence of hydrogen flow rate on LA hydrogenation over  $Ru@Al_2O_3$  catalyst (20 mg) at 60  $^\circ C$  for 1 h.

hydrogen is  $50 \text{ mL min}^{-1}$ . On the other hand, The increasing trend of GVL yield over time is similar to the increasing trend of LA conversion, since the side products were not observed in this reaction.

The stability and reusability of Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst were further investigated for the hydrogenation of LA. The catalyst was recycled as described by the following procedure. At the end of the LA hydrogenation run, the catalyst was separated from the reaction mixture using high-speed centrifugation. The obtained catalyst was thoroughly washed five times with water to remove the adsorbed species. Then the recycled catalyst was dried and used for the next run under identical reaction conditions. For product analysis, after the complete reaction, the reaction mixture was cooled to room temperature and then diluted to 25 mL using water. It was filtered with a 0.22  $\mu$ m syringe filter for HPLC analysis. As shown in Fig. 5, the Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst was highly active after seven runs. In addition, ICP-OES measurement shows that there are no Ru leaching during the reaction, indicating that Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst is highly stable.

# 4. Conclusion

We synthesized a stable and recyclable catalyst for efficient LA hydrogenation to GVL at ambient reaction condition. The RuCl<sub>3</sub>@MIL-53-NH<sub>2</sub> was prepared *via de novo* synthesis method, which was reduced under H<sub>2</sub>/N<sub>2</sub> pressure to obtain Ru nanoparticles confined within C-Al<sub>2</sub>O<sub>3</sub>. The Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst exhibits remarkable efficiency for hydrogenation of the LA into GVL at ambient hydrogen pressure. GVL was significantly obtained over the catalyst with a high yield of 99.9% and low activation energy of 34.66 kJ mol<sup>-1</sup> at ambient reaction



Fig. 5. Recyclability of Ru@C-Al<sub>2</sub>O<sub>3</sub> catalyst. Reaction condition: LA (1 mmol,), (20 mg), H<sub>2</sub>O (10 mL), hydrogen gas (50 mL min<sup>-1</sup>), 60 °C, 2 h.

condition. The apparent activation energy value over  $\rm Ru@C-Al_2O_3$  catalyst is the lowest compared to other Ru-supported catalysts. In addition, the catalyst can be reused seven times without any significant loss in catalytic activity. Our study offers a novel Ru-supported catalyst, which would be useful in various catalytic applications for biomass conversion.

#### Acknowledgments

The authors would like to thank the Ministry of Science and Technology (MOST), Taiwan (104-2628-E-002-008-MY3;105-2211-E-002-227-MY3;105-2218-E-155-007;105-2221-E-002-003-MY3;105-2622-E155-003-CC2) and the Aim for Top University Project at National Taiwan University (105R7706; 107L2033-32; 107L891204; 107L7703; 107L104312; 107L7828) for the funding support. We thank the Mass Spectrometry and Transmission Electron Microcopy (JEOL-JEM-2100) Core Facility at Department of Chemistry, National Taiwan University.

# Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110478.

#### References

- [1] R. Gounder, Catal. Sci. Technol. 4 (2014) 2887-2886.
- [2] M.J. Climent, A. Corma, S. Iborra, Green Chem. 16 (2014) 516-547.
- [3] R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sa'dabaa, M.L. Granados, Energy Environ. Sci. 9 (2016) 1144–1189.
- [4] P. Gallezot, Chem. Soc. Rev. 41 (2012) 1538–1558.
- [5] B.M. Matsagar, S.A. Hossain, T. Islam, H.R. Alamri, Z.A. Alothman, Y. Yamauchi, P.L. Dhepe, Kevin C.-W. Wu, Sci. Rep. 7 (2017) 13508.
- [6] Y.-T. Liao, B.M. Matsagar, Kevin C.-W. Wu, ACS Sustainable Chem. Eng. 6 (2018) 13628–13643.
- [7] B. Sang, J. Li, X. Tian, F. Yuan, Y. Zhu, Mol. Catal. 470 (2018) 67-74.
- [8] B.M. Matsagar, M.K. Munshi, A.A. Kelkar, P.L. Dhepe, Catal. Sci. Technol. 5 (2015)

5086-5090.

- [9] C. Ortiz-Cervantes, M. Flores-Alamo, J.J. García, ACS Catal. 5 (2015) 1424–1431.
- [10] S. Zhu, Y. Xue, J. Guo, Y. Cen, J. Wang, W. Fan, ACS Catal. 6 (2016) 3035-3042.
- [11] L. Bui, H. Luo, W.R. Gunther, Y.R. Leshkov, Angew. Chem. Int. Ed. 52 (2013) 8022–8025.
- [12] L. Deng, J. Li, D.-M. Lai, Y. Fu, Q.-X. Guo, Angew. Chem. Int. Ed. 48 (2009) 6529–6532.
- [13] W.R.H. Wright, R. Palkovits, ChemSusChem 5 (2012) 1657–1667.
- [14] T. Werpy, G. Persen, The national revewable energy laboratory (NREL), 1 (2004) 1–13.
- [15] B.M. Matsagar, C.V. Nguyen, M.S.A. Hossain, M.T. Islam, Y. Yamauchi, P.L. Dhepe, Kevin C.-W. Wu, Sustain. Energy Fuels 2 (2018) 2148–2153.
- [16] Z. Zhang, ChemSusChem 9 (2016) 156-171.
- [17] E.I. Gurbuz, D.M. Alonso, J.Q. Bond, J.A. Dumesic, ChemSusChem 4 (2011) 357–361.
- [18] S. Song, S. Yao, J. Cao, L. Di, G. Wu, N. Guan, L. Li, Appl. Catal. B: Environ. 217 (2017) 115–124.
- [19] E.I. Gurbuz, J.M.R. Gallo, D.M. Alonso, S.G. Wettstein, W.Y. Lim, J.A. Dumesic, Angew. Chem. Int. Ed. 52 (2013) 1270–1274.
- [20] K. Hengst, M. Schubert, H.W.P. Carvalho, C. Lu, W. Kleist, J.-D. Grunwaldt, Appl. Catal. A: General 502 (2015) 18–26.
- [21] Y. Kuwahara, Y. Magatani, H. Yamashita, Catal. Today 258 (2015) 262-269.
- [22] Vr. Fábos, Ls.T. Mika, I.N.T. Horváth, Organometallics 33 (2014) 181-187.
- [23] C. Delhomme, L.-A. Schaper, M. Zhang-Preße, G. Raudaschl-Sieber, D. Weuster-Botz, F.E. Kühn, J. Organomet. Chem. 724 (2013) 297–299.
- [24] J. Tan, J. Cui, X. Cui, T. Deng, X. Li, Y. Zhu, Y. Li, ACS Catal. 5 (2015) 7379–7384.
   [25] J. Tan, J. Cui, T. Deng, X. Cui, G. Ding, Y. Zhu, Y. Li, ChemCatChem 7 (2015) 508–512.
- [26] C. Xiao, T.-W. Goh, Z. Qi, S. Goes, K. Brashler, C. Perez, W. Huang, ACS Catal. 6 (2016) 593–599.
- [27] A. Villa, M. Schiavoni, C.E. Chan-Thaw, P.F. Fulvio, R.T. Mayes, S. Dai, K.L. More, G.M. Veith, L. Prati, ChemSusChem 8 (2015) 2520–2528.
- [28] M. Sudhakara, V.V. Kumara, G. Naresh, M.L. Kantam, S.K. Bhargava, A. Venugopala, Appl. Catal. B: Environ. 180 (2016) 113–120.
- [29] M.G. Al-Shaal, M. Calin, I. Delidovich, R. Palkovits, Catalan J. Commun. Cult. Stud. 75 (2016) 65–68.
- [30] M.G. Al-Shaal, W.R.H. Wright, R. Palkovits, Green Chem. 14 (2012) 1260–1263.
  [31] J. Ftouni, A. Muñoz-Murillo, A. Goryachev, J.P. Hofmann, E.J.M. Hensen, L. Lu,
- C.J. Kiely, P.C.A. Bruijnincx, B.M. Weckhuysen, ACS Catal. 6 (2016) 5462–5472.
   J. Tan, J. Cui, G. Ding, T. Deng, Y. Zhu, Y.W. Li, Catal. Sci. Technol. 6 (2016) 1469–1475.
- [33] J.-K. Sun, Q. Xu, Energy Environ. Sci. 7 (2014) 2071–2100.
- [34] S. Dang, Q.L. Zhu, Q. Xu, Nat. Rev. Mater. 3 (2017) 1-7075.
- [35] X. Fang, Q. Shang, Y. Wang, L. Jiao, T. Yao, Y. Li, Q. Zhang, Y. Luo, H.-L. Jiang, Adv. Mater. 30 (2018) 1705112.
- [36] W. Cao, W. Luo, H. Ge, Y. Su, A. Wang, T. Zhanga, Green Chem. 19 (2017) 2201–2211.
- [37] A.H. Valekar, K.-H. Cho, S.K. Chitale, D.-Y. Hong, G.-Y. Cha, U.-H. Lee, D.W. Hwang, C. Serre, J.-S. Chang, Y.K. Hwang, Green Chem. 18 (2016) 4542–4552.
- [38] Y. Kuwahara, H. Kango, H. Yamashita, ACS Sustainable Chem. Eng. 5 (2017) 1141–1152.
- [39] M. Sánchez-Sánchez, N. Getachew, K. Díaz, M. Díaz-García, Y. Chebude, I. Día, Green Chem. 17 (2015) 1500–1509.
- [40] Y. Zheng, Y. Jiao, L. Ge, M. Jaroniec, S.Z. Qiao, Angew. Chem. Int. Ed. 52 (2013) 3110–3116.
- [41] S. Ji, Y. Chen, Q. Fu, Y. Chen, J. Dong, W. Chen, Z. Li, Y. Wang, L. Gu, W. He, C. Chen, Q. Peng, Y. Huang, X. Duan, D. Wang, C. Draxl, Y. Li, J. Am. Chem. Soc. 139 (2017) 9795–9798.
- [42] H. Yan, Y. Yang, D. Tong, X. Xiang, C. Hu, Catalan J. Commun. Cult. Stud. 10 (2009) 1558–1563.
- [43] A.S. Piskuna, J. Ftounib, Z. Tanga, B.M. Weckhuysen, P.C.A. Bruijnincx, H.J. Heeres, Appl. Catal. A: General 549 (2018) 197–206.
- [44] M. Chalid, A.A. Broekhuis, H.J. Heeres, J. Mol. Catal. A: Chemical 341 (2011) 14–21.