Highly stable Ru nanoparticles incorporated in mesoporous carbon catalysts for production of γ -valerolactone

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Graphical abstract

Highlights

- Ruthenium nanoparticles incorporated in mesoporous carbon catalysts for the production of γ -valerolactone from levulinic acid in water are reported.
- Ruthenium nanoparticles incorporated in mesoporous carbon catalysts showed excellent reusability and thermal stability.
- Leaching could be minimised by changing to incorporated structure.
- The mechanism of high reusability and thermal stability for incorporated ruthenium catalysts are studied.

Abstract

The hydrogenation of levulinic acid to γ -valerolactone with water as solvent is a crucial reaction for producing fine chemicals. However, the development of highly stable catalysts is still a major challenge. Here, we prepared a Ru nanoparticles incorporated in mesoporous-carbon (Ru-MC) catalyst to achieve high stability in acidic aqueous medium. The Ru-MC showed excellent catalytic performance (12024h⁻¹ turnover frequency) in the hydrogenation of LA-to-

GVL. Compared with Ru supported on mesoporous carbon catalyst (Ru/MC) prepared by conventional wet impregnation method, the Ru-MC showed excellent reusability (more than 6 times) and thermal stability (up to 600 °C). Based on H₂-TPR-MS characterization, it was proposed that the incorporated structure significantly increased the interaction between Ru nanoparticles and carbon support, which effectively prevent the leaching and sintering of Ru nanoparticles and contributed to increased high reusability and thermal stability of the Ru-MC.

Keywords: Mesoporous carbon, Ru nanoparticles, hydrogenation, biomass, stability

1. Introduction

With the depletion of fossil resources and concern for environment, the conversion of biomass to chemicals and liquid fuels has attracted interest worldwide. γ -valerolactone (GVL), a naturally occurring chemical in fruits, is a safe and value-added product that can be widely used as liquid fuel, renewable solvent, food additives, and intermediate in the synthesis of fine chemicals[1-3]. In the past few years, attention was highly focused on GVL obtained by hydrogenation of levulinic acid (LA). LA also has been of interest for many years because it can be produced cost effectively and in high yield from renewable feedstock in a new industrial process, *via* tandem dehydration and hydrolysis reactions of C₅ and C₆carbohydrates [4-9].However, the production of GVL from LA still use traditional and corrosive homogeneous acid catalysis that are limited by a low yield of GVL, high energy consumption, and severe pollution. To overcome these problems and due to heterogeneous catalysts' easy recycling and eco-friendly properties, numerous heterogeneous catalysts have been explored and designed for the conversion of LA. Ruthenium appears as the most active and selective metal for the conversion of LA to GVL compared with the other metals (Ir, Rh, Pd, Pt...) [10-15]. From a

very detailed kinetic investigation of solvent effects in hydrogenation of LA on Ru/C catalyst, Wang [16] pointed out the highest hydrogenation activity was observed in protic solvents. Therefore water is the best 'green' option for its polar protic properties and vast reserves around the world. Actually, it is well recognized that the nature of supports have an obvious influence on the catalytic performance of the catalysts. Carbon materials, including active carbon, graphite, etc., are excellent catalyst supports due to their inertness, non-toxicity, good water resistant, textural and mechanical properties [17, 18].

While most studies focused on the activity and selectivity of the catalyst, the third critical parameter of the catalytic performance, i.e. stability, has been much less investigated [19]. LA is generally produced from lignocellulose, with a mineral acid employed as catalyst [20]. The presence of mineral acid in LA product streams creates additional challenges to the catalyst stability. Although supported Ru on carbon (Ru/C) catalysts have excellent initial catalytic performance, their activity decreases sharply in a batch hydrogenation process. Wei [21] pointed out that at least four factors were reported to be responsible for Ru/C catalysts deactivation in water: (I) Ru leaching into the reaction bulk; (II) Ru aggregation on the carbon surface; (III) carbon deposition on Ru nanoparticles and (IV) the phase transformation of Ru nanoparticles and support. To improve stability, many different strategies are applied in recent studies. Jamal [22] and Wen [20] used metallic oxide supports to increase the interaction between Ru NPs and supports to gain higher stability. Wei [21] used embedding method to decelerate the deactivation of Ru catalyst in methanol system. The embedded structure could prevent the Ru NPs from migration, aggregation, and leaching during reaction process. Similarly, Wang's group [23] encapsulated metal nanoparticles in porous graphene layers, enhancing the stability of the catalyst. Tan [24] prepared a stable catalyst by modifying the supports with 3-

aminopropyltriethoxysilane and hence enhancing the Ru-support interaction. As a result, the ruthenium metal was bound to support's surface *via* coordination with the amino ligands and valid gain stability. Li [25] and Liu [26] also found that bimetal catalyst obtained much higher stability, mainly due to the second metal change the geometric and electronic structures thus preventing the agglomeration and sintering of metal particles. From the above-mentioned studies it can be concluded that there are at least three methods to enhance the catalysts' stability: (i) by modifying the supports with organic groups or metal oxide; (ii) by changing the catalysts' structure and (iii) by introducing other metals to form alloy.

In recent reports, we have developed a Ru-Carbon catalyst with uniform Ru NPs incorporated on the mesoporous carbon supports (Ru-MC)[27, 28]. And the Ru-MC catalyst exhibited excellent catalytic performance and stability for the hydrogenation of benzoic acid with water as solvent. The first key point of high stability of Ru-MC is that the special incorporated structure can prevent the Ru NPs aggregation due to the confinement of the carbon matrix, on the other hand, Ru NPs incorporated in the carbon can significantly enhance the interaction between Ru NPs and carbon supports. Herein, we demonstrate that the Ru-MC catalyst has a significant, positive impact on stability in the hydrogenation of LA to GVL in acidic aqueous medium. The catalytic performance of the incorporated Ru-MC catalyst was compared to the supported Ru/MC catalyst prepared by traditional wet impregnation method. We then propose further insights into the enhanced stability of Ru-MC compared with Ru/MC *via* a series of characterization techniques.

2. Experimental

2.1. Materials

Ruthenium chloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$) was purchased from Sino-Platinum Metals Co. Ltd. A commercialized Nano-silica with particle size of 15 ± 5 nm and surface area of 250 ± 30 $\text{m}^2 \text{g}^{-1}$ was provided by Hangzhou Wanjing New Material Co. Ltd. Levulinic acid was purchased from Aladdin Co.Ltd. Other reagents were obtained from Shanghai Chemical Reagent Inc. of Chinese Medicine Group. All materials were analytical grade and used without any further purification.

2.2. Preparation of incorporated Ru-MC

A typical process for preparation of the Ru-MC catalyst was described as in the reference [27]: Firstly, 6.00 g of SiO_2 was loaded with 0.18 g of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ aqueous solution by an impregnation method for 12h. Then, 12.54 g of sucrose, 0.99 g of oxalic acid and $\text{SiO}_2 @ \text{RuCl}_3 \cdot x\text{H}_2\text{O}$ powder were added into an agate pot with several different sizes iron balls, and ground for 60 minutes at 150 rpm, until the solid powder turned gray. The mixed composite was dried at 100 °C for 6 h and at 160 °C for 6 h, respectively. After that, the composite was carbonized at 850 °C for 3 h under N_2 flow (50 mL min^{-1}). The Ru-carbon-silica composite was then washed with sodium hydroxide solution at 70 °C twice to remove the silica template completely. The template-free product was thus obtained (denominated as Ru-MC). It should be noted that the Ru^{3+} ions can be reduced into Ru NPs during the carbonization process. For clarity, the preparation methods for the above samples are summarized in Scheme 1.

2.3. Preparation of supported Ru/MC

The supported ruthenium catalyst on mesoporous carbon (MC) (denominated as Ru/MC) was prepared by a wet impregnation method. The process for preparation of the MC was similar

with the Ru-MC except without addition of the $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ at the first step. Then Ru/MC was reduced at 400 °C for 2 h under high purity H_2 flow (30 mL min^{-1}) before being tested in levulinic acid hydrogenation. The synthesized MC was used as support without any additional treatment.

2.4. Characterization of Catalysts

N_2 physisorption isotherms were recorded with a Quantachrome Autosorb-IQ apparatus setup operating at -196 °C. Prior to performing the measurements, the samples were outgassed for 8 h at 300 °C. Surface areas were determined using the Brunauer–Emmett–Teller (BET) theory, while total pore volumes were determined from the aggregation of N_2 vapor adsorbed at a relative pressure of 0.99. The pore size distribution was acquired from the desorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) model. Powder X-ray diffraction (XRD) patterns were measured with a Rigaku D/Max-2500/pc powder X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) in a 2θ range from 10 to 80° and a scan speed of 4° min^{-1} . TEM images were recorded on a JEOL JEM-1200EX instrument and particle size distribution of Ru nanoparticles was performed from the TEM images using ImageJ software.

The metal loading of fresh and used Ru catalysts was analyzed by ultraviolet spectrophotometry with an ultraviolet spectrophotometer (model 7600) from Shanghai Jinghua Instruments Co. Ltd. A typical process was described: First, 0.10 g catalyst was calcined with 2.5 g Na_2O_2 under 680 °C for 20 min in a muffle furnace to oxidize the Ru^0 completely. The product was then dissolved with a mixed 40 mL concentrated HCl-Ethanol solution (volume ratio=1: 1) then 10 mL thiourea aqueous solution (0.1 g mL^{-1}) was added at 80 °C for 10 min to get a blue, clear solution. Last, the absorbance of as-prepared solution was measured with 620 nm excitation wavelength. With external standard method, the Ru content of catalyst could be calculated.

CO chemisorption was carried out on a Quantachrome Autosorb-IQ Chemisorb apparatus. Prior to measurements, the pre-reduced catalysts were further reduced in situ for 2 h at 400 °C in high purity H_2 . Then vacuum 2 hours, and static adsorption of CO molecule at 40 °C. The metal dispersion was estimated based on the assumption of a spherical geometry of the particles and an adsorption stoichiometry of one CO molecule on one Ru surface atom [27]. The dispersion (D) of Ru NPs was calculated based on following equations:

$$D = \frac{V_{NTP}M}{V_M m C P} * 100$$

Here, V_{NTP} refers to the adsorption volume of CO at normal temperature and pressure and $V_M = 22.414 \text{ L mol}^{-1}$. M is the atomic mass of Ru ($101.07 \text{ g mol}^{-1}$). And m is the weight of catalyst. C is the stoichiometry between Ru and CO chemisorption (CO:Ru=1:1). P is the amount of Ru loading.

The incorporating degree of the Ru nanoparticles was estimated via an equation based on the particle size measured via CO chemisorption and TEM characterization. $D_{\text{incorporating}} = 100 \times (1 - N_s/N_c)\%$ in which N_s is the number of metal atoms present on the surface measured by using the CO chemisorption technique and N_c is the number of metal atoms present on the surface based on the average crystallite size determined by using TEM characterization.

Hydrogen-temperature-programmed-reduction (H_2 -TPR-MS) of Ru catalysts were carried out with a self-made TPD/TPR instrument. The sample (50 mg) was heated in a fixed bed U-shaped quartz tubular reactor located inside an electrical furnace under 5 % H_2 /Ar flow (30 mL min^{-1}) and the mass spectra were collected by an on-line Hiden gas analyzer (QIC 20). The temperature was raised at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ from 100 to 850 °C. The following mass signals of H_2 , CH_3 and H_2O were monitored simultaneously by a quadrupole mass spectrometer: $m/e = 2$ (H_2), 15 (CH_3) and 18 (H_2O) amu.

Argon-Temperature-programmed-desorption (Ar-TPD-MS) of Ru catalysts were also carried out with the same instrument but under high purity argon. The temperature program was raised from 100 °C up to 850 °C at a rate of 10 °C min⁻¹ under a flow of high purity Ar (30 mL min⁻¹) during the whole test program. The following mass signals of H₂O and CO₂ were monitored simultaneously by the quadrupole mass spectrometer: m/e = 18 (H₂O) and 44 (CO₂) amu.

2.5. Evaluation of Catalytic Activity and Reusability

The evaluation of the catalytic performance of the Ru catalysts for LA hydrogenation was carried out in a 50 mL stainless-steel stirred pressure reactor. 18 mg of Ru catalysts and 17.8 mmol of LA, were placed in the sealed reactor loaded with 20 mL of deionized water. Prior to the liquid-phase reaction, the whole reactor was purged with H₂ three times to drain air. Next, the reaction mixture was heated to the desired temperature, and then charged with H₂. The stirring speed was 1000 rpm to remove the effects of mass transfer resistance. At the end of the reaction, the reactor was cooled rapidly to room temperature in an ice bath, after which the remaining H₂ was released. The product mixtures were identified and quantified by a SHIMADZU GC-2014 gas chromatography apparatus equipped with a AT-FFAP chromatographic column (30 m×0.32 mm×0.5 µm) and a flame ionizing detector, using authentic samples for calibration.

The reusability of the catalysts under the applied batch conditions was assessed by multiple recycling tests. Considering that the catalysts will be lost during the recovery process, three-fold mass (54 mg) of catalyst and levulinic acid (53.4 mmol) were placed in the reactor. The solid was recovered after reaction by centrifugation followed by drying for 6 h at 80 °C in vacuum oven. Finally, the catalyst was transferred back to the reactor and a new catalytic run was performed with the addition of a new batch of substrate under standard reaction conditions.

The turnover frequency (TOF) was calculated based on the following equations:

$$TOF = \frac{n_{LA}^{conv.LA}}{n_{Ru}Dt}$$

Here, n_{LA} and n_{Ru} refer to the LA and Ru moles. $Conv_{LA}$ is the conversion of LA after reaction. D is the dispersion of Ru from CO chemisorption and t is the reaction time in hour.

3. Results and discussion

3.1. Catalytic performance, reusability and Thermal stability

As reported previously, the conversion of LA to GVL can be conducted at moderate reaction temperature in the range of 20 to 230 °C. With the above concern, reaction temperature was in the range of 30 to 110 °C and H_2 pressure was set at 4 MPa. Yield of GVL as a function of various catalysts are shown in Table 1. There is nearly no LA conversion at 110 °C after 1 h without catalyst (entry 1). Similar results were obtained when the support MC was used as catalyst (entry 2). Compared Ru/MC with Ru-MC, Ru-MC clearly displayed higher catalytic activity than Ru/MC under identical conditions (entries 3 and 4), with a LA conversion of 64% and a GVL yield of 64% at 70 °C after 1 h ($12024h^{-1}$ turnover frequency). Conversely, the turnover frequency of Ru/MC was $3348h^{-1}$, which was one third of Ru-MC. When the reaction temperature changed from 30 to 110 °C, the LA conversion and GVL yield quickly improved from 15% and 15% to 100% and 99%, respectively (entries 5 to 8). Clearly, the Ru-MC significantly enhanced the catalytic activity.

The reusability of Ru-MC and Ru/MC were examined by performing multiple recycling runs. As shown in Figure 1, a clear, continuous deactivation was observed with Ru/MC catalyst, with a decrease in LA conversion from initial 73% to 22% after five consecutive runs, with a reduction level of 70%. Under the same conditions, the Ru-MC showed only a small drop in

GVL yield from 98 to 90% after six cycles, with a reduction level of only 8% indicating the superiority of the new type of Ru-MC catalyst for multiple runs.

To study the thermal stability of Ru-MC, the catalyst was treated at 400 °C and 600 °C under high purity nitrogen for 2 h before evaluation (10 °C min⁻¹, 50 mL min⁻¹). As shown in Table 1, for Ru-MC-400 and Ru-MC-600, the catalytic performances did not decrease after calcination (entries 9-10). These results demonstrate the high thermal stability of Ru-MC catalyst. The above results revealed the obvious advantages of Ru-MC over a conventional Ru/MC catalyst in terms of catalytic performance and stability.

3.2. Physicochemical properties of catalysts

The porous structures of Ru-MC and Ru/MC catalysts are analyzed with N₂ sorption techniques. For both Ru-MC and Ru/MC, the isotherms are typical type IV with an H₁ hysteresis loop (Fig. 2a), which is typical for mesoporous materials. From Figure 2b, the pore size of Ru-MC and Ru/MC are 9.6 nm (calculated from desorption branch of the isotherm). The specific surfaces area of Ru-MC is 961 m² g⁻¹ and pore volume is 1.72 cm³ g⁻¹, while Ru/MC is 956 m² g⁻¹ and the pore volume is 1.78 cm³ g⁻¹, both catalysts present high specific surfaces areas and pore volumes (Table 1). The similarity in textural properties among both catalysts indicates that their different catalytic performance is not directly associated to their porous structure.

The XRD patterns of MC, Ru-MC, Ru/MC, Ru-MC-400, Ru-MC-600, Ru/MC-400 and Ru/MC-600 catalysts are given in Figure 3 (the black lines). Two broad peaks appeared at 22° and 43° for all catalysts, corresponding to (002) and (001) crystal planes from the graphitic structure of the carbon supports [29, 30], which indicates that MC, Ru-MC and Ru/MC have amorphous carbon framework. One weak peak appeared at 44.0° for Ru/MC catalyst which correspond to (101) diffractions of bulk hexagonal Ru (Ru PDF#65-1863), because during the

high temperature reduction process (400 °C for 2 h), the Ru nanoparticles are easily sintering. Using Scherrer equation, we calculated the Ru particle size in Ru/MC to be 9.2 nm. No peak appeared for Ru-MC of bulk hexagonal, indicating the high dispersion and small particle size of Ru NPs in this sample. In fact these observations are consistent with our previous study [27]. It should be pointed out that despite the thermal treatment at 400 °C and 600 °C, respectively; no signs of sintering were detected in the Ru-MC catalyst. But for Ru/MC-600, an obvious peak at 44.0° for Ru could be observed which indicates that the loaded Ru NPs were sintered during heat treatment at 600 °C. These results clearly show the Ru-MC has the successful incorporation of Ru particles in the MC matrix and has excellent thermal stability.

The status of Ru nanoparticles was characterized by CO chemisorption and TEM, the data and figures are given in Table 2 and Figure 4, respectively. For Ru-MC, the level of CO chemisorption and dispersion of Ru nanoparticles were 52.0 $\mu\text{mol gcat}^{-1}$ and 26.6%, respectively. The dispersion of Ru nanoparticles was lower than that for Ru/MC (59.2%). Such a level of Ru dispersion for Ru-MC is relatively low. From Table 2, the amount of CO chemisorbed on the Ru-MC catalyst was lower by one-fold compared with Ru/MC catalyst but the particle size obtained from TEM shows was 2.7 nm (Fig. 4a). Very likely the underestimation in the dispersion value for Ru-MC compared with Ru/MC is due to the shielding effect of the support; i.e. part of the ruthenium particles are buried in the framework of carbon for Ru-MC and cannot be reached by CO molecules [27]. The estimated incorporating degree was 58.7% for Ru-MC. This indicates that the synthesis method for preparing Ru-MC could successfully incorporate part of the Ru nanoparticles within the framework of the carbon. As shown in Figure 4, the high dispersion and uniform size of Ru NPs can be observed. This result is consistent with the XRD characterization (Fig. 3).

During hard-template SiO_2 etching by NaOH-water-ethanol solution process, $-\text{COOH}$ groups could be introduced to the surface of catalyst. Argon-temperature-programmed-desorption detected by mass spectroscopy (Ar-TPD-MS) was used to investigate the surface environment of Ru-MC and Ru/MC. The results are shown in Figure 5. Three main CO_2 ($m/e=44$) desorption peaks were observed at 265, 325 and 490 $^\circ\text{C}$ for Ru-MC (Figure 5a) and two CO_2 desorption peaks are observed at 388 and 515 $^\circ\text{C}$ for Ru/MC (Figure 5b). The first peak at 265 $^\circ\text{C}$ for Ru-MC could be assigned to the decomposition of $-\text{COOH}$, because a H_2O ($m/e=18$) peak could be observed at the same temperature [31]. The $-\text{COOH}$ of Ru/MC decomposed during the reduction process at 400 $^\circ\text{C}$. The other two CO_2 peaks of Ru-MC and Ru/MC were both ascribed to the decomposition of lactone groups and anhydride groups. Combining the catalytic performance of Ru-MC, Ru-MC-400, Ru-MC-600 and Ru/MC with TPD-MS, there was no direct relationship between surface groups and catalytic performance. As a result, the high activity of Ru-MC was not caused by the organic groups present on the surface of catalysts.

To identify the metal-support interaction between Ru NPs and the carbon framework, hydrogen-temperature-programmed-reduction detected by mass spectroscopy (H_2 -TPR-MS) of Ru-MC and Ru/MC catalysts were performed under 5% H_2/Ar . The results are shown in Figure 6. There are two H_2 ($m/e=2$) consumption peaks observed at 290 and 411 $^\circ\text{C}$ for Ru-MC from Fig. 6a. These two peaks corresponded to methane since CH_3 ($m/e=15$) peaks were observed at similar temperatures while no H_2O ($m/e=18$) signal was observed within the range investigated. Therefore, both peaks could be assigned to the methanation of carbon species with hydrogen in presence of metallic Ru. For Ru/MC (Figure 6b), three H_2 consumption peaks were observed at 185, 284 and 528 $^\circ\text{C}$. Combined with the signal of H_2O ($m/e=18$) and CH_3 ($m/e=15$) (magnified

5 times), the first peak at 185 °C was assigned to the reduction of Ru^{3+} due to the signal of water appearing at the same temperature. The peaks at 284 and 528 °C were attributed to the methanation of carbon. One H_2O peak was observed at 528 °C, which could be assigned to the reaction between H_2 and lactone group. Compared to the methanation temperature and signal strength of Ru-MC and Ru/MC catalysts, the Ru-MC have relatively lower temperature for occurring methanation, and higher methanation strength. This observation can be explained by an easier methanation of the carbon support for incorporated Ru-MC catalyst than for supported Ru/MC catalyst owing to the strong interaction between Ru NPs on the carbon support.

The strong interaction between Ru NPs and carbon matrix for Ru-MC could enhance the catalyst's activity during reaction process. The H_2 molecules can be adsorbed dissociatively on the Ru surface and spilled over from Ru NPs onto the support [28], in addition, LA molecules are often found to be adsorbed on the surface of the support next to the metal-support interface [32]. It has been reported that the hydrogenation of LA molecules occurs partly through the co-adsorption of dissociative H atoms and LA molecules on the carbon support sites [33]. The strong interaction between Ru NPs and carbon support acts as a bridge which can facilitate the migration of dissociative H atoms from the active metal to the support, which could effectively increase the concentration of dissociative H atoms on carbon support [28], thus greatly improves the specific activity of the Ru-MC catalysts.

As a result, Ru-MC catalyst possessed useful characteristics such as large surface area, highly dispersed Ru nanoparticles, strong interaction between Ru NPs and carbon support and enhanced hydrogenation capacity. Overall, the excellent catalytic performance and stability of Ru-MC was due to its engineered structure, which promotes metal-support interaction and results in small and well dispersed Ru clusters with outstanding hydrogenation capacity.

3.3. Insight into stability and deactivation mechanism

To get insight into the deactivation mechanism, the fresh and used Ru-MC and Ru/MC catalysts were characterized by N₂physisorption, TEM, XRD and TPD-MS. The N₂physisorption measurements showed a slight (Table 3), drop in surface area and pore volume from 961 to 839 m² g⁻¹ and 1.72 to 1.54 cm³ g⁻¹, respectively for Ru-MC after recycling. On the other hand, the surface area and pore volume from Ru/MC dropped from 956 to 850 m² g⁻¹ and 1.78 to 1.65 cm³ g⁻¹, respectively. But the pore diameter of the used Ru-MC and Ru/MC catalysts were both 9.6 nm. That means the decrease in surface area was due to the organic molecules be absorbed to the catalysts. The reduction in surface area was 12.7% and 11.1%, respectively for Ru-MC and Ru/MC (calculated from $[(S_{\text{fresh}} - S_{\text{used}})/S_{\text{fresh}}] \cdot 100$). In light of these results we can point out that the discrepancy on the reusability is not correlated to the decreased in surface area of the studied materials.

To study the surface properties of used catalysts, an Ar-TPD-MS experiment was performed, as shown in Figure 7. The surface oxygenic functional groups of used Ru-MC did not change significantly (Fig. 5a and Fig. 7a). However, comparing Figure 5b and Figure 7b, it was found that a peak of CO₂ appeared at 218 °C for used Ru/MC. This indicates that carboxyl groups present on the catalyst surface after reaction. However, as we demonstrated that changes in surface carboxyl groups did not affect the activity and stability of the catalysts. The results suggest that the deactivation of the catalysts was not caused by the change of organic groups on surface of catalyst.

The distribution of Ru nanoparticles on fresh and used Ru-MC (recycled five times) was characterized by high resolution TEM techniques, as shown in Figure 8. It can be observed that

after recycling, no obvious particle aggregation occurred (Figure 8a). The size distribution of used Ru-MC (recycled five times) was still around 3.0 nm. Therefore, TEM measurements performed on both fresh and used Ru-MC exclude sintering and corroborates the robustness of Ru NPs of incorporated in the porous carbon framework.

The XRD patterns of used Ru-MC and Ru/MC are shown in Figure 3 (red lines). No obvious diffraction peak assigned to Ru is observed for used Ru-MC, indicating absence of large Ru NPs after reaction. This result suggests that the incorporated structure can prevent the sintering of Ru NPs, which was also confirmed by the high resolution TEM results as shown in Fig 8. However, the peak intensity at 44.0° for bulk Ru NPs decreased for used Ru/MC compared to the fresh sample. This might be due to the leaching of bigger Ru NPs from the support. This is discussed further in the next section.

The leaching of Ru catalysts can be monitored by determining either the Ru concentration in the reaction bulk after hydrogenation or the Ru content difference between the fresh and used Ru catalysts. In our work, the leaching of Ru was determined from the Ru content between the fresh and used catalysts (been used one time) by spectrophotometric method. Results on Table 3 reveal that the maximum discrepancies of fresh and used catalysts, with the incorporated Ru-MC catalyst Ru content dropping from 1.96 to 1.76% after been used, the ratio of loss Ru was 10.2%. This loss could be attributed to Ru leaching from NPs that were not properly incorporated in the framework of the carbon supports. Despite of the loss of Ru, the catalyst still displayed remarkable reusability levels. The Ru content of supported Ru/MC catalyst dropped from 2.24 to 1.40% after one-time use representing an overall Ru loss of 37.5%. As shown in Figure 1, the decline in LA conversion for Ru/MC is apparent after one-time use. Due to the large decrease in conversion for Ru/MC after recycling five times, the reasonable conjecture can be made that the

Ru content in Ru/MC decreased from 2.24% to barely any. Hence, the deactivation of the Ru/MC catalysts were caused by leaching of Ru, and the incorporated Ru-MC could effectively prevent the leaching of Ru NPs due to the confinement of Ru NPs by carbon supports and the strong interaction between Ru NPs and carbon supports.

4. Conclusion

A new generation of Ru stabilized on porous carbon structures with promising applications in bio-resources hydrogenation reactions has been developed in this work. The comparison of the catalytic performance of the incorporated Ru catalysts (Ru-MC) vs traditional Ru supported catalysts (Ru/MC) in LA hydrogenation reveals remarkable differences. The incorporated Ru-MC catalyst performed much better than supported Ru/MC catalysts. The Ru-MC catalyst displayed high reusability upon recycling for six times with the LA conversion above 90%. In addition, the Ru-MC also exhibited excellent thermal stability, maintaining high dispersion of Ru NPs after calcination at 600 °C for 2 h in nitrogen, no sintering and deactivation occurred. However, the Ru/MC catalyst showed clear deactivation after recycling for five times with the LA conversion dropping from 73% to 22%. Extensive characterization of the catalysts showed that the deactivation of the Ru/MC catalyst was mainly due to the weak interaction between Ru and carbon support, resulting in significant leaching of Ru NPs during recycling. As a result, the incorporated structure of Ru-MC catalyst showed high stability for LA hydrogenation in water system. The excellent catalytic performance achieved with the Ru-MC material is due to its incorporated structure, which enhanced the interaction between Ru nanoparticles and carbon support and promotes metal-support interaction resulting in small and stable Ru NPs with outstanding hydrogenation capacity. Overall this work provides a novel strategy to design highly efficient hydrogenation catalysts with potential impact in biomass upgrading processes.

‘Declarations of interest: none’.

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Figure Captions:

Scheme 1. Schematic illustration of the preparation of incorporated Ru-MC catalyst.

Fig. 1. Reusability results of Ru-MC and Ru/MC. Reaction conditions: LA (53.4 mmol), water (20 mL), catalyst dosage 5000 with respect to LA (molar ratio), 110 °C, 4 MPa, 1000 rpm, and 1 h.

Fig. 2. (a) N₂ adsorption-desorption isotherm and (b) pore size distribution of Ru-MC and Ru/MC catalysts.

Fig. 3. XRD patterns of MC, fresh Ru-MC, fresh Ru/MC, fresh Ru-MC-400, fresh Ru-MC-600, fresh Ru/MC-400, fresh Ru/MC-600, used Ru-MC and used Ru/MC.

Fig. 4. The TEM (a) (inset is particle size distribution of Ru NPs) and HRTEM (b) images for fresh Ru-MC catalysts. White circles points Ru NPs.

Fig. 5. Ar-TPD-MS profiles of fresh Ru-MC (a) and Ru/MC (b) catalysts.

Fig. 6. H₂-TPR-MS profiles of fresh Ru-MC (a) and Ru/MC (b) catalysts.

Fig. 7. Ar-TPD-MS profiles of used Ru-MC (a) and used Ru/MC (b) catalyst.

Fig. 8. The TEM (a) (inset is particle size distribution of Ru NPs) and HRTEM images (b) for used Ru-MC catalysts. White circles points Ru NPs.

Scheme 1.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Table 1. Texture and catalytic properties of Ru-MC and Ru/MC catalysts in the hydrogenation of LA.^[a]

Entry	catalysts	S.A. (m ² g ⁻¹) ^[b]	P.V. (cm ³ g ⁻¹) ^[c]	P.D. (nm) ^[d]	Ru content (wt %)	T (°C)	Conv. LA (%)	Yield. GVL (%)	TOF [e] (h ⁻¹)
1	No catalyst	-	-	-	-	110	1	1	-
2	MC	935	1.74	9.6	-	110	3	3	-
3	Ru/MC	956	1.72	9.6	2.24	70	39	39	3348
4	Ru-MC	961	1.78	9.6	1.96	70	64	63	12024
5						30	15	15	-
6						50	37	37	-
7						90	93	92	-
8						110	100	99	-
9	Ru-MC-400	977	1.83	9.6	1.96	70	64	63	11988
10	Ru-MC-600	964	1.80	9.6	1.96	70	63	62	11916

[a] Reaction conditions: LA (17.8 mmol), H₂O (20 mL), 1000 rpm, PH₂ 4MPa, reaction time 1 h, the catalyst dosage was defined as the molar ratio (5000) between LA and Ru.

[b] BET surface area.

[c] Total pore volume.

[d] Pore diameter calculated from desorption branch of the isotherm.

[e] The turnover frequency in our work was calculated based on the surface Ru determined by CO chemisorption.

Table 2. Dispersion of ruthenium NPs determined by CO chemisorption of Ru-MC and Ru/MC.

Catalysts	CO-chemisorption		TEM			
	CO Uptake ($\mu\text{mol g}^{-1}$)	Ru S. A. (m^2g^{-1})	Dispersion (%)	Dispersion (%)	Particle Size (nm) ^a	D _{incorporating} (%)
Ru-MC	52	97	26.6	49.3	2.7	58.7
Ru/MC	116	215	59.2	-	-	-

Table 3. Texture properties and Ru content of used Ru-MC and used Ru/MC catalysts.

Used Catalysts	S.A. (m ² g ⁻¹) [a]	P.V. (cm ³ g ⁻¹) [b]	P.D (nm) [c]	Ru (wt.%)	Used Ru (wt.%)	Ru loss ratio (%)
Ru-MC	839	1.54	9.6	1.96	1.76	10.2
Ru/MC	850	1.65	9.6	2.24	1.40	37.5

[a] BET surface area.

[b] Total pore volume.

[c] Pore diameter calculated from desorption branch of the isotherm.