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A stable and effective Ru/polyethersulfone catalyst for levulinic acid hydrogenation to γ-valerolactone in aqueous solution

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ABSTRACT

A cross-linked sulfonated polyethersulfone supported Ru nanoparticle catalyst was prepared for highly hydrogenation of levulinic acid (LA) into γ-valerolactone (GVL) at mild conditions (3.0 MPa H_2 and 70 °C) in aqueous solution. X-ray diffraction (XRD) and transmission electron microscopy (TEM) characterizations show the formation of highly dispersed small (~3 nm) Ru clusters on the surface of polyethersulfone. Infrared spectroscopy (IR) and acid-base titration indicate the presence of sulfonic groups without the influence of the deposition of Ru species. Polyethersulfone consisted of cross-linked electron -withdrawing group —SO_2—, maintained its intrinsic thermal stability during the hydrogenating reaction process, and its swelling property promoted the adsorption of LA in aqueous solution. The synchronization of sulfonic groups as active sites for esterification process and metal sites for hydrogenation promoted the hydrogenation reactivity.

1. Introduction

Efficient conversion of biomass feedstocks to fuels and chemicals has been regarded as a promising strategy to maintain the sustainability in fuel supply and chemical production [1,2]. Levulinic acid (LA) is a well known product of hexose acid hydrolysis and it is inexpensively obtained by the decomposition of cellulose feedstock of glucose. Consequently, it is an attractive starting material for the production of many useful C_5 based compounds including γ-valerolactone (GVL) [2–20], methyltetrahydrofuran [21], δ-aminolevulinic acid and diphenolic acid [22]. Specially, GVL is widely applied as food additives, solvents or intermediates to produce useful chemicals, and a new platform molecule for gasoline and diesel fuels [23]. Thus, the production of GVL from LA hydrogenation represents a highly desirable process towards enhancing the sustainability of the chemical industry and earns much attention [2–21,24,25].

Since the reported catalytic hydrogenation of LA to GVL over Pt catalysts [24], the novel metal (Pd, Ru, Rh, Ir, etc) and transitional metal (Ni and Cu) based catalysts have been used [2–25]. Christian et al. [25] employed Raney Ni to hydrogenate LA at 220 °C, with 4.8 MPa of H_2 pressure to obtain 94% yield of GVL. Manzer et al. [26] investigated the activities of different metal catalysts supported on activated carbon such as Ir, Rh, Pd, Ru, Pt, Re and Ni at 150 °C, 5.5 MPa of H_2 using 1, 4-dioxane as solvent. The Ru/C catalyst was sieved to be the best choice with ~100% conversion and >97% selectivity of GVL after 4 h hydrogenation. Upare et al. [21] carried out the gas hydrogenation of LA over carbon supported Ru, Pt and Pd at 265 °C and 1–25 bar H_2, and also pointed out the best performance on Ru/C catalyst with ~100% conversion and ~100% selectivity. Liu [2] prepared Ru/C catalyst to conduct the hydrogenation reaction at a low temperature (130 °C, 1.2 MPa H_2) and obtain 92% conversion and 99% selectivity of GVL using 5 wt.% of LA in methanol. At present, LA hydrogenation is usually carried out in organic solvents [2–26], and the aqueous hydrogenation of LA over noble metal catalysts has been examined by Dumesic [27] and Pinel [28]. Surprisingly, in the green solvent (water), the yield of LA became low (<90%) in dilute solution (5 wt.%, 15 MPa H_2) [28] or concentrated aqueous solution (50 wt.%, 3.5 MPa H_2) [27]. Moreover, the Ru/C catalyst showed slow deactivation with time on stream (from 90 to 68% conversion after 106 h), and regeneration treatment of the

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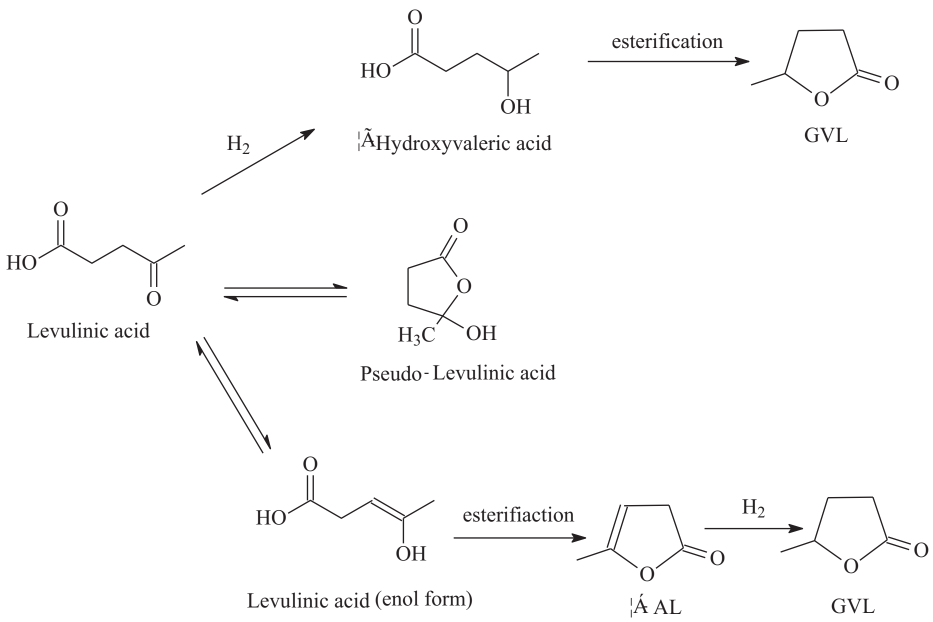

Scheme 1. Proposed reaction routes of LA hydrogenation.

catalyst under flowing H_2 at 673 K for 2 h only allowed for partial recovery of the initial catalytic activity (83% conversion) [27]. These literatures together show that there is still a challenge in developing a high active and stable Ru catalyst for the LA hydrogenation in aqueous solution.

Shown in Scheme 1 are the reaction pathways in LA hydrogenation based on the literature [2–27]. The formation of GVL required the reduction and esterification steps which require the metal sites and acid sites respectively [7–27]. Here, we propose a strategy of incorporation of acid sites into the Ru metal catalyst to promote the esterification reactivity and then the hydrogenation activity in LA hydrogenation. Galletti et al. [8] demonstrated that mixing acid catalysts with Ru metal catalysts promoted the hydrogenation of LA. Among the cationic exchange resins (Amberlyst 70 and 15), niobium phosphate and niobium oxides, Amberlyst A70 was shown to be the best acid catalyst with high yield of GVL (99%) using a lot of Ru metal catalyst (1 meq) at mild hydrogenation conditions (4.7 wt.% LA, 70 °C and 3.0 MPa H_2) and good recycling runs (5 times). Besides Amberlyst A70, they found the combination of Ru/C (0.01 meq) and niobium phosphate leads to a high yield (83%) of GVL at mild conditions (1.63 wt.% LA in products of giant reed hydrolysis, 70 °C and 0.5 MPa H_2) [29]. We expect that the use of acid catalysts as supports to disperse Ru metal should be a better strategy to synchronize the acid sites and metal sites as a bifunctional catalyst for the hydrogenation of LA because of the simultaneous access of both sites. Indeed, Luo et al. [16] used the metal oxides or zeolites as supports for Ru metal, and found the high promotion by ZSM-5 zeolites. However, the leaching of acid sites (Al atoms) of ZSM-5 occurred in the acidic conditions using organic solvent. Thus, the choice of acid support becomes challenge to the design of bifunctional catalysts. [30]

In our previous work [31], we have synthesized a new stable solid acid: sulfonated polyethersulfone (SPES), which showed high activity and good thermal stability in esterification process because of its swelling property and the introduction of —SO_2— group. After catalyst dwelling in reaction system, the volume of catalyst enlarged and pores in catalyst became loose, which increased contact area between reactants and catalytic active sites, thus improved the catalytic performance. The catalyst introduced pull-electron —SO_2— group, which increased the acid strength and the stability of sulfonic acid. Here, SPES was designed to disperse small Ru nanoparticles for the hydrogenation of LA in order to obtain a new bifunctional catalyst (Ru/SPES) with high activity and good stability.

2. Experimental

2.1. Chemicals and reagents

The cross-linked sulfonated polyethersulfone (SPES) were synthesized using *m*-trihydroxybenzene as a cross-linker as reference [31]. Amberlyst 15 was purchased from Alfa Aesar Company, Ltd. and used as received. Ruthenium trichloride (Ru > 37%), SiO_2 and carbon were purchased from KRS Fine Chemical Co. Ltd. (Tianjin, China) and used as received. Levulinic acid (98%, from GF Co., Tianjin, China) was employed without any purification.

2.2. Catalyst preparation

2.2.1. Synthesis of Ru/SPES

2.0 wt.% Ru/SPES was prepared by a modified impregnation method. Typically, 0.027 g $RuCl_3$ was firstly dispersed into 50 mL distilled water. After dissolved completely, 0.5 g polyethersulfone was added under constantly stirring. The mixed solution was kept at 70 °C for 6 h. The water was dried using rotary evaporator at 50 °C and then reduced at 130 °C for 6 h in H_2 flow ($100\ cm^{-3}\ g^{-1}\ min^{-1}$). The resulted Ru/SPES was directly re-dispersed into 20 mL water in a stainless steel autoclave for reaction.

2.2.2. Synthesis of Ru/SiO_2 and Ru/C

2.0 wt.% Ru/SiO_2 and Ru/C were prepared as referenced catalysts. In details, 0.5 g SiO_2 ($200\ cm^2\ g^{-1}$) or carbon ($1850\ cm^2\ g^{-1}$) was added to 50 mL 0.002 mol L^{-1} $RuCl_3$ aqueous solution. Then, the above solution kept stirring for 4 h at room temperature. After dried by rotary evaporator at 50 °C, the Ru/SiO_2 sample was obtained by calcination treatment at 500 °C in air for 3 h and then reduced at 500 °C under H_2 flow ($100\ cm^{-3}\ g^{-1}\ min^{-1}$) for 4 h, and Ru/C was directly reduction by H_2 at the same condition without calcination.

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2.3. Catalyst characterization

The structure of the catalysts was characterized by X-ray diffraction (XRD) on a Bruker D8 FOCUS (Bruker AXS GmbH, Cu Ka, $\lambda = 1.54178$ Å) instrument. The particle size distribution of Ru clusters was determined by transmission electron microscope (TEM, FEI Tecnai G2, operated at 200 kV) by counting at least 400 crystallites. The surface area weighted cluster diameters, d_{TEM}, were calculated using $d_{TEM} = \Sigma n_i d_i^3 / \Sigma n_i d_i^2$. The metal loading or metal and sulfur contents in reaction solution were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) on an IRIS Intrepid spectrometer. Infrared spectroscopy (IR, FTS6000Varian) was used to prove successful introduction of sulfonate group. The acidity of sample was determined by acid-base titration: 0.1 g samples were equilibrated in 20 mL of 0.1 mol L^{-1} NaOH solution for 12 h to neutralize acid, titrated excess NaOH with calibrated 0.02 mol L^{-1} HCl solution. The acidity density of Amberlyst 15 (6.9 mmol g^{-1}) was determined by acid-base titration.

2.4. Levulinic acid hydrogenation

LA hydrogenation reaction was carried out in a three-phase 30 mL glass tube in 50 mL stainless steel autoclave to avoid the effect of stainless steel on hydrogenation [32]. In a typical process, LA was diluted with distilled water (5.0 wt.% LA). The dosage of catalyst was 5.0 wt.% based on the quantity of LA. After that, the reactor was purified with hydrogen three times to eliminate air, then pressurized to 3.0 MPa and heated to 70 °C. After 2 h reaction, the reactor was quenched down to room temperature. The liquid-products were performed with a gas chromatograph (GC, FULI 9790) using a capillary column (40 m × 3 mm × 0.25 μm) with stationary phase of diethyl polysiloxane. The flame ionization detector (FID) was operated at 250 °C. The following temperature program was used in analysis: 60 °C for 1 min and increased to 220 °C (1.67 °C s^{-1}) for 5 min. Quantitative determination of Ru and sulfur leaching in liquid-products was measured by ICP-AES.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of supported Ru catalysts and the supports are shown in Fig. 1. Two broad peaks around $2\theta = 20°$ and 40° are found in SPES sample, indicating the amorphous structure of polymer the same as those of SiO$_2$ and carbon supports. After the deposition of Ru metal, a peak ascribed to (1 1 1) plane of Ru metal (PDF No. 06-0663) was observed on SiO$_2$ samples, suggesting the formation of large Ru metal crystals. However, no obvious peak corresponding Ru metal could be observed on Ru/SPES and Ru/C samples, suggesting the presence of highly dispersed tiny Ru clusters. Unlike SiO$_2$ support, the high dispersion of Ru on carbon should be benefited from a much higher surface area of carbon.

TEM images and particle size distribution graph of Ru/SPES were displayed in Fig. 2. Ru nanoparticle aggregates are randomly distributed over the surface of SPES (Fig. 2a). HRTEM image shows the irregular morphology (Fig. 2b) of aggregates. The average size of Ru particles (assuming spherical particles) was 3.0 nm, in agreement with the XRD pattern results.

It is well known that the activity of catalytic reactions was influenced by accessibility of reactants to active sites. Here the parameters of swelling support (SPES) could change in solvent, and affect of the adsorption capability of SPES in aqueous solution. The absorption of distilled water over Ru/SPES was investigated. Compared with initial state (volume: 0.5 mL; weight: 0.4 g), the volume and weight of catalyst (wet volume: 5.7 mL, wet weight: 5.6 g) enlarged about ten times after swelling in water at room temperature for 2 h. Based on equation of the swelling degree ($Q = (m - m_0)/m_0$, where m is the mass of swollen catalyst and m_0 is the initial mass of sample) [33], swelling degree of Ru/SPES in water was 13.2. This suggests that the pores in Ru/SPES catalyst would become loose after catalyst dwelling in reaction system [34], which increases contact area between reactants and catalytic active sites, thus improve the catalytic performance shown in the next Section below.

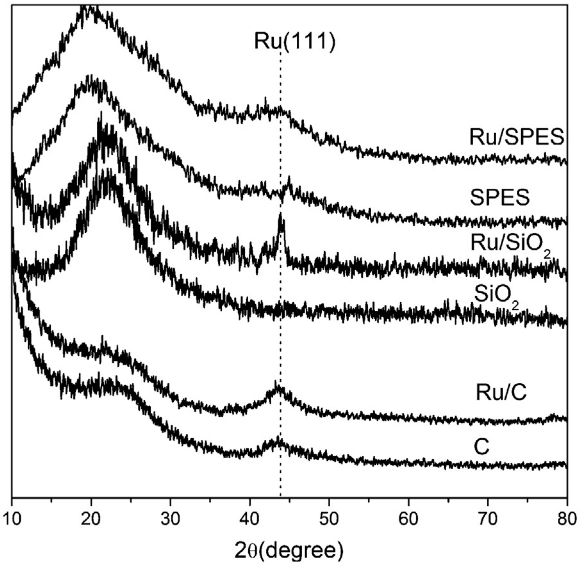

Fig. 1. XRD patterns of supports and their corresponding supported Ru samples.

Fig. 3 illustrates the infrared spectroscopy of Ru/SPES catalyst. The absorption bands at 1475 and 1600 cm^{-1} are attributed to the stretching vibration of C═C and that at 2940 cm^{-1} is assigned to C—H stretching vibration, which indicates the presence of aromatics [35]. The adsorption bands at 1088 and 1255 cm^{-1} are ascribed to the introduction of sulfonate group to the polymer [36]. The absorption band at 610 cm^{-1} assigned to —OH bending vibration bonding to —SO$_3$H groups [37]. The introduction of pull-electron —SO$_2$— increases the acid strength and the stability of sulfonic acid. The acidity density of catalyst was 3.8 mmol g^{-1} measured by acid-base titration.

The thermal stabilities of catalysts were investigated and shown in Fig. 4. It can be seen from the results that the Ru/SPES exhibited the weight loss at 45–130, 270–410 and 480–560 °C. These three peaks can be assigned to desorption of water, decomposition of sulfonic groups, and destruction of polymer framework, respectively. The sulfonic acid group in SPES began to decompose at 270 °C, and the rate reached the maximum at 345 °C. This suggests that Ru/SPES shows good thermal stability due to the chemical environment of the sulfonic group in main line of polymer (SPES contained electron withdrawing group —SO$_2$—) [31], and the deposition of Ru clusters on SPES did not change the stability.

3.2. Catalytic performance

For the LA hydrogenation, mild conditions (low temperature, low pressure, and short time, etc.) should be better to reduce the leach of active metal (i.e. Ru [16]) because of the high acidity of LA. Here, LA hydrogenation was carried in a stainless steel autoclave at 70 °C for 2 h with 2.0 wt.% Ru/SPES. The evaluation results of catalysts were summarized in Fig. 5. Ru/SiO$_2$ catalyst shows a low conversion (22.2%) of LA and a high selectivity (~98%) of GVL. The conversion increases to 54.5% using Ru/C with smaller Ru cluster

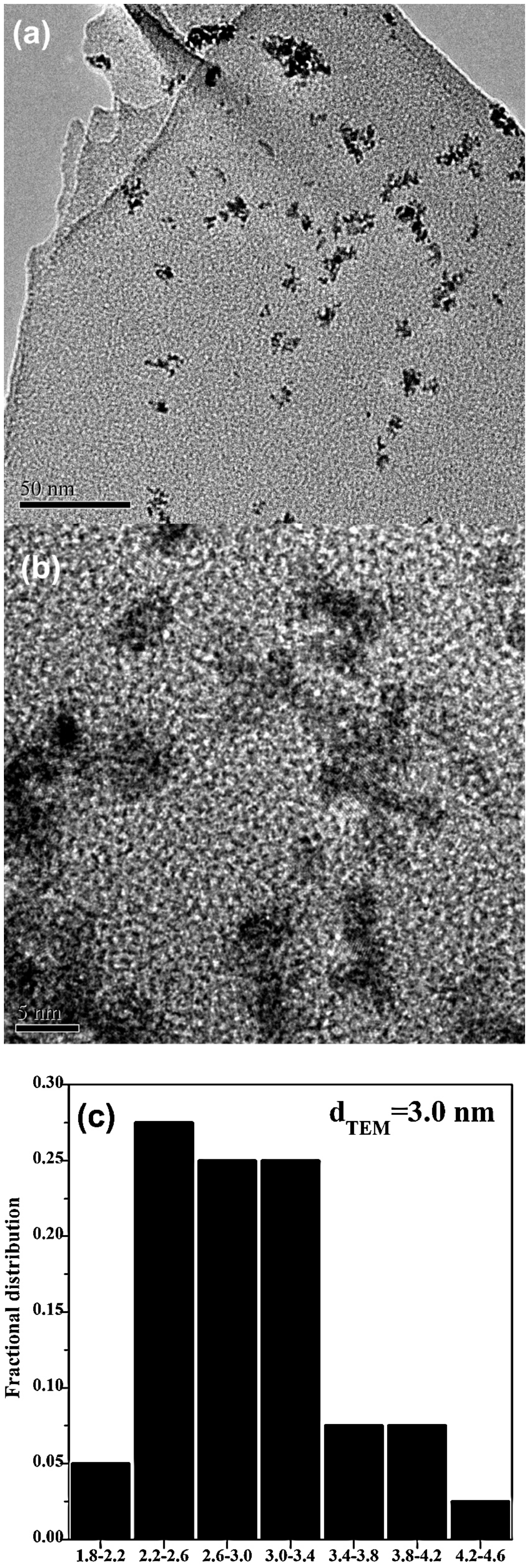

Fig. 2. (a) TEM images, (b) HRTEM images and (c) particle size distribution graph of Ru/SPES catalyst.

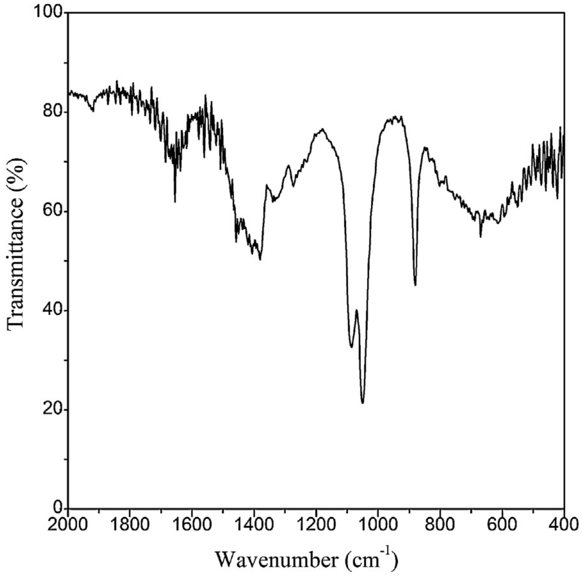

Fig. 3. Infrared spectra of Ru/SPES catalyst.

sizes and thus more surface active metal sites. Mixing the Ru/SiO$_2$ or Ru/C catalyst with Amberlyst 15 indeed increases the conversion of LA to 40.4% or 68.0% respectively, and the selectivity of GVL change little. This clearly confirms the promotion of hydrogenation reactivity of Ru metal using acid catalyst [8]. Unlike the Ru/SiO$_2$ and Ru/C catalysts, Ru/SPES has much higher conversion (87.9%) of LA, which should be benefited from the high dispersion of Ru clusters and the acidity of SPES.

In order to verify the process for LA hydrogenation in presence of acid catalyst, we collected products reacting for 0.5 h, 1 h and 2 h, respectively, to analysis contents by GC–MS. In all the reactions, LA and GVL were detected, but theoretical intermediates such as γ-hydroxyvaleric acid and angelicalactone (α-AL) were not determined (Scheme 1). γ-Hydroxyvaleric acid is very instable, which can react with alcohol to ester under acid condition shortly [2,5,38,39]. Therefore, we considered reaction processes as follows: LA hydrogenated to γ-hydroxyvaleric acid and then esterificated to GVL, which is in accordance with the research of Galletti [8].

A very low conversion (3.4%) of LA was observed on SPES supports, which confirms the facilitation of SPES for the hydrogenation of LA, the same as the work of Galletti [8]. This demonstrated the role of acid catalyst involving intermolecular lactonization and keto

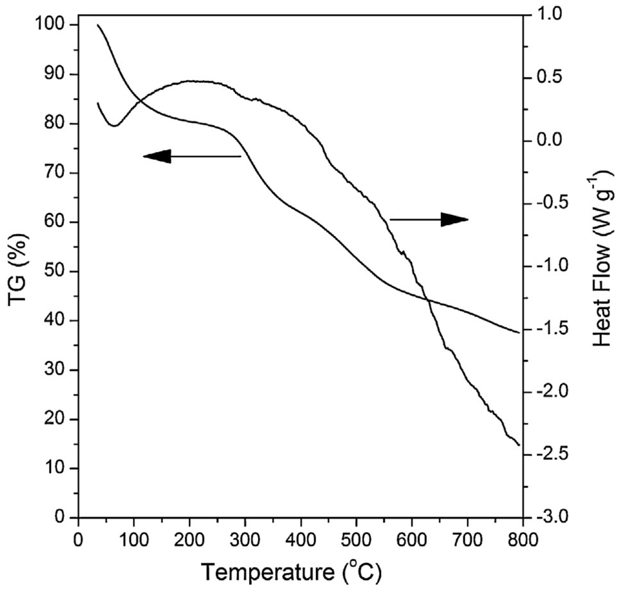

Fig. 4. Thermogravimetric (TG) curves of Ru/SPES.

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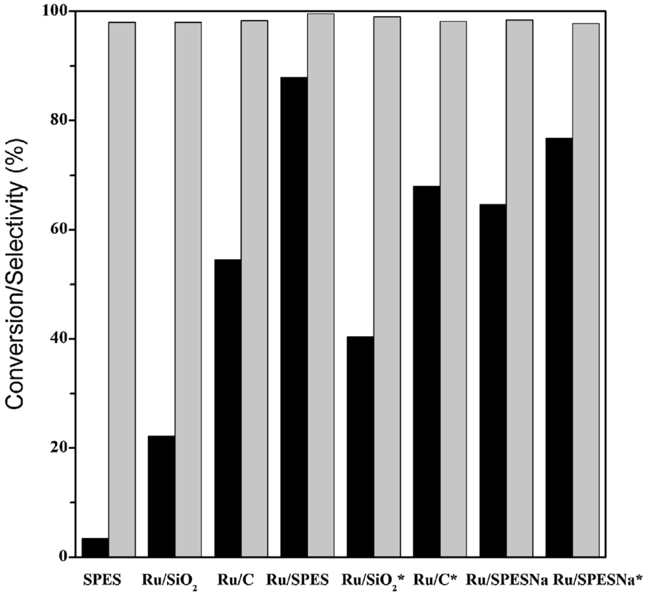

Fig. 5. LA conversion and GVL selectivity using different Ru supported catalysts. (Histogram in black: conversion of LA; Histogram in gray: selectivity of GVL. Ru/SiO$_2$*: Ru/SiO$_2$ and Amberlyst15 as co-catalysts; Ru/C*: Ru/C and Amberlyst15 as co-catalysts; Ru/SPESNa: Ru/SPES neutralized by NaOH aqueous solution; Ru/SPESNa*: Ru/SPESNa and Amberlyst15 as co-catalysts).

hydrogenation in LA hydrogenation. Here, we neutralized the acidic sites of Ru/SPES via ion-exchange using 0.1 mol L^{-1} NaOH aqueous solutions (Ru/SPESNa), the conversion decreases from 87.9% to 64.6%. Mixing the Ru/SPESNa with Amberlyst 15 led to 76.8% conversion, still lower than the Ru/SPES even the same acidity density of the catalyst were controlled. These data together show that deposition of metal clusters on acid supports is better than a mechanical mixture of metal and acid sites during the LA hydrogenation. Besides the acceleration esterification process (Scheme 1) by the acidic groups (—SO$_3$H) in SPES [40,41], the swelling property of SPES facilitates more LA reactants access to the acid sites and metal sites [34].

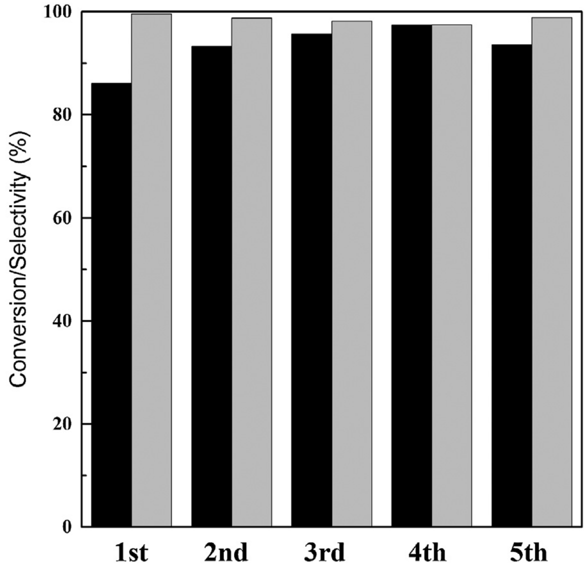

Fig. 6. LA conversion and GVL selectivity of Ru/SPES catalyst during recycling ((Histogram in black: conversion of LA; Histogram in gray: selectivity of GVL).

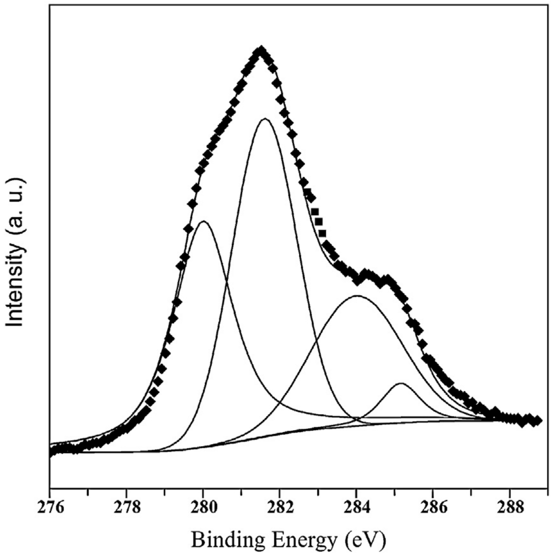

Fig. 7. XPS spectra of Ru/SPES catalyst.

Metal leaching is ascribed to the deactivation of catalyst in LA hydrogenation [16]. During the five recycles of catalysts, the Ru specials and sulfur species in the reaction solution could not be detected by ICP characterization, suggesting no leaching of Ru/SPES at mild reaction conditions. Interestingly, the conversion of LA increases from 87.9% to 92.1% after the first hydrogenation, and gradually to 97.2% at fourth run (Fig. 6). Moreover, the selectivity almost stays the same during recycling. The reason may be explained from the surface properties of small Ru clusters. Because of the high activity of Ru clusters in the air or oxygen atmosphere, the transfer of fresh Ru/SPES catalysts into the hydrogenation reaction inevitably contact oxygen to form some surface ruthenium oxides (Fig. 7). The binding energies of Ru were respectively 280.0, 281.5, 284.0 and 285.3 eV ascribed to Ru 3d$_{5/2}$ and Ru 3d$_{3/2}$. The values at 280.0 and 284.0 eV indicate the Ru^0 species on the surface of catalyst, while 281.5 and 285.3 eV suggest the formation for ruthenium oxychloride [42] from air exposition [43] during drying and storing process. These oxides could be reduced gradually during LA hydrogenation, and the conversion increases gradually. These data show the good stability of Ru/SPES in the hydrogenation of LA.

4. Conclusion

We reported a new bifunctional catalyst, cross-linked sulfonated polyethersulfone supported Ru nanoparticles, for the selective hydrogenation of levulinic acid to γ-valerolactone. High dispersed small (~3 nm) Ru clusters were formed over polyethersulfone via impregnation. The synchronization of surface acidic groups (SO$_3$H) of polyethersulfone for esterification process and metal sites for hydrogenation led to high reactivity, selectivity and stability. Compared with the metal catalysts mechanical mixing with acid catalysts, the swelling property of polyethersulfone promoted the adsorption capability of levulinic acid, and thus increased the accessibility of reactants to both metal sites and acid sites. The leaching of metal sites was avoided using polyethersulfone as supports, which improve the stability of catalyst.

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