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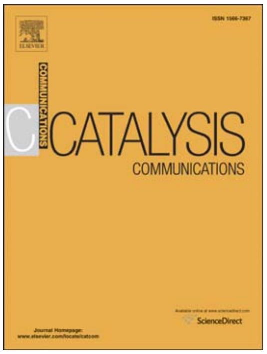

Ruthenium Nanoparticles on Colloidal Carbon Spheres: An Efficient Catalyst for Hydrogenation of Ethyl Lactate in aqueous phase

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Ruthenium Nanoparticles on Colloidal Carbon Spheres: An Efficient Catalyst for Hydrogenation of Ethyl Lactate in aqueous phase

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Abstract

A ruthenium catalyst supported on glucose-derived carbon spheres was prepared and characterized by TEM, XPS, FTIR TG-DTG and XRD. The Ru /CSP catalyst showed an excellent catalytic performance for the hydrogenation of ethyl lactate to 1, 2-propanediol in water. The catalyst was recycled for six times without the marked loss in both the activity and selectivity. The steric hindrance and electronic effects of substrates on the hydrogenation were tested. It is postulated that the high performance of this novel catalyst system is related to the cooperation between the hydroxyl groups of support surface and water as a solvent.

Keywords: Ruthenium; Aqueous-phase hydrogenation; Ethyl lactate; Carbon spheres

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1. Introduction

1，2-propanediol (1,2-PDO) is an important industrial chemical, which is widely used as solvent or a raw material to produce polymers, resins, and functional fluids [1]. A commercial route to synthesize 1, 2-PDO is the hydration of propylene oxide derived from propylene by either a chlorohydrin process or a hydroperoxide process, which is unfavorable from green chemistry point of view [2, 3]. Thus, to develop a clean and economical synthetic approach of 1, 2-PDO is necessary. Ethyl lactate can be easily obtained by the fermentation of renewable sources such as agricultural crops and biomass streams. The hydrogenation of ethyl lactates would lead to the formation of 1, 2-PDO [4-8], which provides an eco-friendly alternative to the petroleum-based process for 1, 2-PDO production. Hydrogenation of carboxylic acids and esters to the

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corresponding alcohols is often carried out under a high hydrogen pressure (20-30MPa) and reaction temperature (473-573K) [9, 10]. Therefore, various attempts have been paid to developing some highly efficient catalyst systems that can work under the mild conditions [11-13]. Louessard et al. [11] first reported that Ru-Sn/SiO_2 was effective for the hydrogenation of ethyl acetate to ethanol. In addition, Luo et al. [4, 5] discovered that the introduction of tin to ruthenium catalyst was an effective method to improve the activity and selectivity for the hydrogenation of ethyl lactate to 1, 2-PDO. Feng et al. [14] investigated the effect of supports, and Ru/SiO_2 showed the highest activity for the hydrogenation of ethyl lactate to 1, 2-PDO. Hwang et al. [15] studied the vapor-phase hydrogenation of ethyl lactate over copper-silica nanocomposites and discovered the dispersion of Cu on silica was a major factor affecting the catalytic activity in the reaction. In our previous study [6], it was found that the hydrogenation of ethyl lactate was easy to achieve over RuB/TiO_2 in aqueous solution, but the amorphous RuB particles were liable to crystallization to lose catalytic activity. Furthermore, we found that the synergic effect between surface hydroxyl groups of AlOOH and water could drastically promote the catalytic behavior of the Ru-Pt/AlOOH catalyst in the hydrogenation of methyl propionate to propanol [16]. Unfortunately, the quick crystal growth of the carrier AlOOH in water resulted in dropping of the catalyst’s activity, causing a poor reusable catalyst.

Recently, a new carbon material, prepared by the hydrothermal treatment of low-cost glucose, has aroused many interests [17]. The preparative process belongs to “green chemistry” because it does not cause contamination to the environment and the

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reactant is safe. Moreover, according to the research about glucose-based carbon spheres (CSP), the outer layer offers numerous functional groups, such as carboxylic, aldehyde, and hydroxyl groups. Therefore, the noble metal nanoparticles can be easily loaded on the carbon sphere and stabilized by the surface groups [17, 18]. And they were used for Suzuki-Miyaura reactions [19] and the reduction of methyl orange [20]. We herein report the carbon spheres supported ruthenium nanoparticles to catalyze the hydrogenation of ethyl lactate in water. The as-obtained Ru/CSP catalyst exhibits the highly catalytic activity and selectivity. The recycling potential of the Ru/CSP catalyst is also assessed.

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2. Experimental Section

2.1. Materials and methods

All the reagents (A.R.) were commercially available and used as received. The procedure for preparing carbon spheres was in accordance with the reported method by Sun et.al. [17].

The loading of ruthenium was analyzed by inductively coupled plasma (ICP, IRIS Intrepid). Transmission electron microscopy (TEM) was carried out in Tecnai G^2 F20 S-TWIN. The X-ray photoelectron spectra (XPS) were recorded with a Kratos XSAM800 spectrometer. And the IR spectra were recorded on a NEXUS 670. All liquid samples were analyzed by gas chromatography (Agilent 6890) equipped with a capillary column PEG -20 M (30 m × 0.25 mm). n-Decane was used as internal standard. Reactants and products were identified by comparison with the standard

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samples and GC-MS.

2.2. Catalytic test

The hydrogenation was carried out in a 60 ml steel autoclave equipped with a magnetic stirrer and electric temperature controller. In a typical experiment, the catalyst (88.0 mg), ethyl lactate (0.5 ml), and distilled water (3 ml) were added to the autoclave. It was purged with H_2 three times, pressurized with H_2 to the designed pressure. After the autoclave was heated to the designed temperature, the stirring rate was set at a constant of 1500 rpm.

The conversion of ethyl lactate and selectivity of 1, 2-PDO is defined as following:

$$\text{Conversion of ethyl lactate (\%)} = \frac{\text{ethyl lactate consumed}}{\text{ethyl lactate initially charged}} \times 100\%$$

$$\text{Selectivity (\%)} = \frac{\text{carbon in specific product}}{\text{carbon in all detected products}} \times 100\%$$

3. Results and discussion

3.1 Catalyst characterization

The TEM images of Ru /CSP catalyst were shown in **Fig.1**. The synthesized Ru nanoparticles had an average diameter of ~3 nm and the size of carbon spheres was typically ~500 nm. It was indicated that the highly dispersed Ru nanoparticles have been supported on the surface of carbon spheres through an *in-situ* reduction process in ethanol, and no aggregation was observed.

The carbon spheres were prepared from glucose under hydrothermal condition at 180℃, leading to aromatization and carbonization [21-23]. To confirm the existence

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and kinds of these surface groups, FTIR spectra of carbon spheres, Ru /CSP and Ru /CSP after catalysis were showed in **Fig.2**. As shown, the samples exhibited the absorption peaks at 1710 and 1620 cm^{-1}, which were attributed to C=O and C=C vibrations, respectively, supporting the concept of aromatization of glucose during hydrothermal treatment. Moreover, the strong band at 3450 cm^{-1} implies the existence of a large number of residual hydroxyl groups on their surface before and after catalysis.

The binding energy of Ru/CSP is at 280.5 eV in XPS spectra (**Fig.3)**, which is close to the binding energies of Ru^0, clearly indicating the formation of zero valent ruthenium [24]. The binding energies at 284.6 eV, 286.3 eV and 288.5 eV, corresponding to C-C、C-H, C-O、O-H and C=O of carbon spheres further indicated the existence of carboxylic, aldehyde, and hydroxyl groups on the surface of carbon spheres.

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3.2 Effect of solvent

The effect of solvents on the hydrogenation of ethyl lactate was shown in **Table 1**. It can be seen that the catalysts reduced in ethanol, 2-propanol, or 1-butanol show little difference in both activity and selectivity when the reaction was carried out in water (Table, entries 2-4), 91.8%~93.7% conversions of ethyl lactate were obtained with excellent selectivity towards 1,2-PDO (ranging from 92.3%~95.4%). However, the conversion obviously decreased to 74.9% when using Ru/CSP pretreated by H_2 as catalyst under identical condition (Table 1, entry 1). In our previous study [16], the

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carrier (γ-Al_2O_3) of catalyst (Ru-Pt/γ-Al_2O_3) could be transformed into OH-rich boehmite (AlOOH) under hydrothermal condition to obtain a highly active catalyst for the hydrogenation of methyl propionate. Since carbon spheres are hydroxyl-rich carbonaceous materials, there was no need to generate hydroxyl groups through hydrothermal treatment. So the reduction of Ru/CSP with H_2 in water was not an optimum process. When the hydrogenation was performed in alcohols (Table 1, entries 5 to 8), both the conversion and the selectivity to 1, 2-propanediol were reduced due to the serious transesterification reaction between substrate and solvent alcohols. Beside the transesterification product, the desired 1, 2-PDO was rare. Therefore, the best catalytic result was obtained in water as solvent. In this case, 93.7% of ethyl lactate was converted with selectivity of 95.4% to 1, 2-PDO (Table 1, entry 2), which was better than the reported Ru-Sn bimetallic catalysts for the hydrogenation of ethyl lactate [4, 5]. In addition, for Ru/charcoal, moderate conversion of ethyl lactate (70.9%) and selectivity to 1, 2-PDO (85.4%) were observed. The colloidal ruthenium nanoparticles exhibited markedly high selectivity (97.8%), whereas the conversion of ethyl lactate was conservative (80.5%). These results clearly demonstrated that the prepared Ru/CSP exhibited high catalytic performance in the presence of both water and support.

ICP-AES analysis showed that 9.2 ug of Ru was found in the filtrate. In order to understand whether it is the ruthenium species leached into the solution that catalyzed the reaction, a filtrate was used in the hydrogenation of ethyl lactate (entry 10^e). As low as 5% conversion testified that the Ru/CSP played the catalytic role.

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3.3 Effect of steric and electronic factors

The effect of the steric and electronic factor of substrates for the hydrogenation of carboxylic ester was investigated on Ru/CSPs. The results were shown in **Table 2**.

Firstly, several alkyl propionates were hydrogenated with 5.0 MPa H_2 at 453K for 8h (Table 2, entries 1-4). As can be seen, increasing the bulkiness of the alkyl group obviously decreased the conversion, possibly due to the larger alkyl group, which is no favorable for the adsorption of the substrate on the catalyst. On the other hand, it also slowed down the hydrogenolysis of alkyl group. Therefore, the hydride species selectively attacked the carbonyl group (Table 2, entries 1-4). And the selectivity towards desired propanol increased from 62.1% to 91.5% when the alkyl changing from methyl to isopropyl group. Then, ethyl acetate and ethyl trifluoroacetate were also subject to the identical condition (Table 2, entries 5, 6). It was found that the strong electron-withdrawing $–CF_3$ attached to the carbonyl group greatly increased the conversion and the selectivity toward 2,2,2-trifluroethanol to ›99% and 94.7%, respectively. These results implied that the electronic property on carbonyl carbon of esters was the key factor for both the activity and the selectivity of hydrogenation.

It is noteworthy that a significant amount of acid was also produced besides the desired product propanol. In order to clarify the reason for the formation of acid, N_2 was introduced to replace H_2 during the reaction of methyl propionate. In this case, propionic acid was still detected in the product, possibly resulted from the hydrolysis pathway. Furthermore, after the initial hydrogenation reaction, we detected methane, ethane and propane for different hydrogenated substrate in the vent gas. These results

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proved the occurrence of hydrogenolysis during the hydrogenation process.

Therefore, we speculated that there were three possible reaction routes for the substrate esters (**Schem1**). Firstly, ruthenium species activated hydrogen. Meanwhile, the basic oxygen atom in water molecule was easy to combine with the activated hydrogen molecule through hydrogen bond and promotes the heterolytic splitting of the activated hydrogen molecule to give a ruthenium-hydride species [25, 26]. The hydrogen bond between carbon sphere and substrate molecule promoted not only the adsorption of substrate, but also the activation of C=O bonds. Afterwards, the hydride on ruthenium attacked the positively charged carbon on carbonyl group （C_{I}） to form the intermediate aldehyde (Route ①), which was quickly hydrogenated to give both the alcohol and the regeneration of the active catalyst. Meanwhile, the hydride might also attack the carbon in alcohol (C_{II}) to form acid and alkane (Route ②). The hydrolysis of ester occurs inevitably on the account of the fact that the hydrogenation is carried out in the aqueous solvent (Route ③). The acid could be further hydrogenated.

When the reaction was completed, the product was separated from the catalyst by a simple centrifugation. The catalyst was reused after washing with distilled water three times. The data, showed in **Figure.4**, indicated that the activity of the catalyst and the selectivity to 1, 2-PDO decreased slightly after six catalytic cycles. The results reflected that the Ru nanoparticles could be stabilized by the surface groups on the carbon spheres. Probable reasons for the loss of activity and selectivity were leaching of ruthenium active species in each cycle or somewhat aggregation of Ru

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nanoparticles（**Fig.1** c, d）.

4. Conclusions

The Ru /CSP catalyst prepared by a simple *in-situ* reduction route exhibits good activity and selectivity in water for hydrogenation of ethyl lactate without a second metal or any additive. The selectivity of 95.4% to 1, 2-PDO could be obtained with conversion of 93.7% of ethyl lactate over Ru /CSP at 423K under 5 MPa of H_2 for 8h. It can be concluded that the surface groups presented on the carbon spheres are effective for preventing the aggregation of the ruthenium nanoparticles during the reaction. Both the surface groups on the carbon spheres and water as the solvent are important to this catalytic system. The increase of the steric hindrance disfavored the reaction, and the electron-withdrawing group on the substrate was beneficial to the reaction. Meanwhile, there may be three pathways for hydrogenation of ester in aqueous solvent: hydrogenation, hydrogenolysis and hydrolysis. This environmentally friendly catalyst could be reused for up to six times with a slight decrease in activity and selectivity.

Acknowledgements

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The list of Table, Figure, and Scheme captions

Fig.1. TEM and HRTEM images of the Ru/CSP

Fig.2. FTIR spectra of carbon spheres

Fig.3. XPS spectra of fresh Ru/CSP

Table 1 Effect of solvent on the hydrogenation of ethyl lactate over Ru/CSP

Table 2 The hydrogenation performance of the Ru/CSP for different substrates

Schem1.The proposed mechanism

Fig.4. Recycling experiments for the hydrogenation of ethyl lactate

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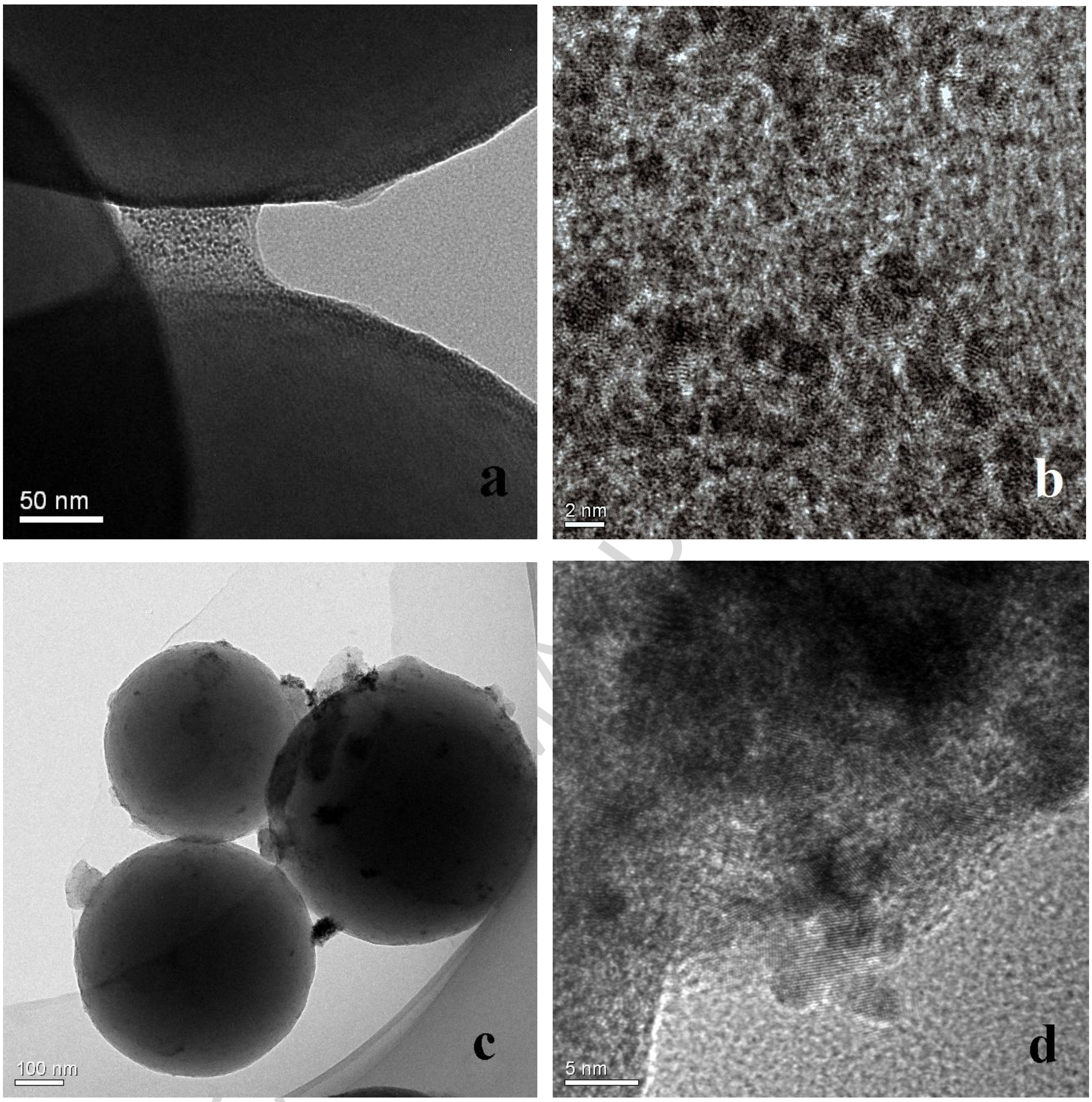

Fig.1. TEM and HRTEM images of the Ru/CSP catalyst before used (a,b), after six catalytic cycles(c,d).

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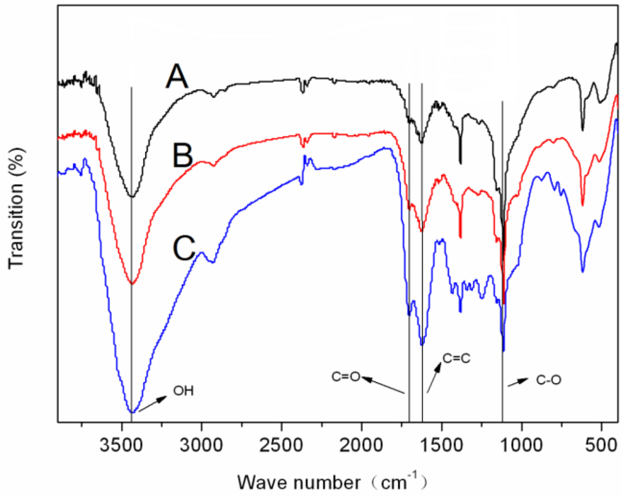

Fig.2. FTIR spectra of carbon spheres: A) sample unloaded with metal, B) Ru/CSP catalyst, and C)Ru/CSP catalyst after catalysis

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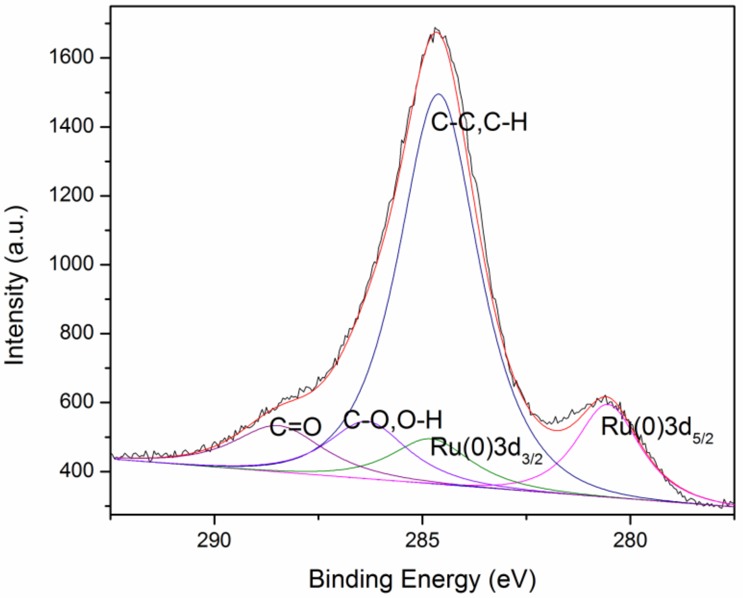

Fig.3. XPS spectra of fresh Ru/CSP

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Table 1 Effect of solvent on the hydrogenation of ethyl lactate over Ru/CSP Catalyst .[a]

Entry	Reductant	Solvent in hydrogenation	Conversion%	Selectivity		
				1,2-PDO[b]	TREF[c]	PA[d]
1	H_2	Water	74.9	91.2	-	8.7
2	Ethanol	Water	93.7	95.4	-	4.6
3	2-Propanol	Water	93.7	92.5	-	7.5
4	1-Butanol	Water	91.8	92.3	-	7.8
5	Ethanol	Methanol	51.1	6.2	93.6	0.2
6	Ethanol	Ethanol	2.4	98.7	-	1.2
7	Ethanol	2-Propanol	10.6	49.3	45.8	4.9
8	Ethanol	1-Butanol	27.0	9.8	83.1	7.2
9	Ethanol	1,4-Dioxane	0.8	77.9	-	22.0
10[e]	Ethanol	Water	5.0	94.5	-	5.5

Reaction condition: [a] 423 K; 5.0 MPa H_2; 8 h; 3 ml H_2O; 1% Ru catalyst;

[b]1,2-propanediol; [c] Transesterification; [d] propionic acid; [e] reused filtrate.

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Table 2 The hydrogenation performance of the Ru/CSP for different substrates. [a]

Entry	Substrates	Conversion (%)	Selectivity (%)	
			n-propanol	PA [e]
1	Methyl propionate	51.2	62.1[b]	37.8
2	Ethyl propionate	31.0	80.7[b]	19.3
3	n-propyl propionate	24.5	87.6[b]	11.5
4	Isopropyl propionate	13.8	91.5[b]	8.5
5	Ethyl acetate	42.9	84.0[c]	16.0
6	Ethyl trifluoroacetate	＞99%	94.7[d]	5.2

Reaction condition: [a] 453 K, 5.0 MPa H_2, 8 h, 3.0 ml H_2O, 2% Ru catalyst; [b] selectivity to propanol; [c] selectivity to ethanol; [d] selectivity to 2,2,2-trifluoroethanol; [e] propionic acid.

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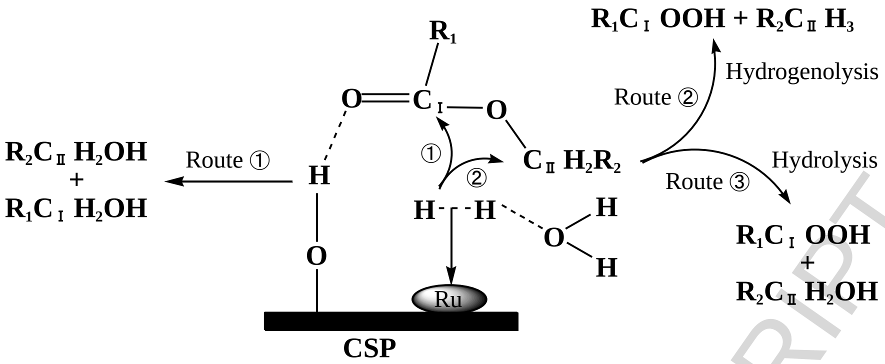

Schem1.The proposed pathway in the hydrogenation of ester in aqueous-phase.

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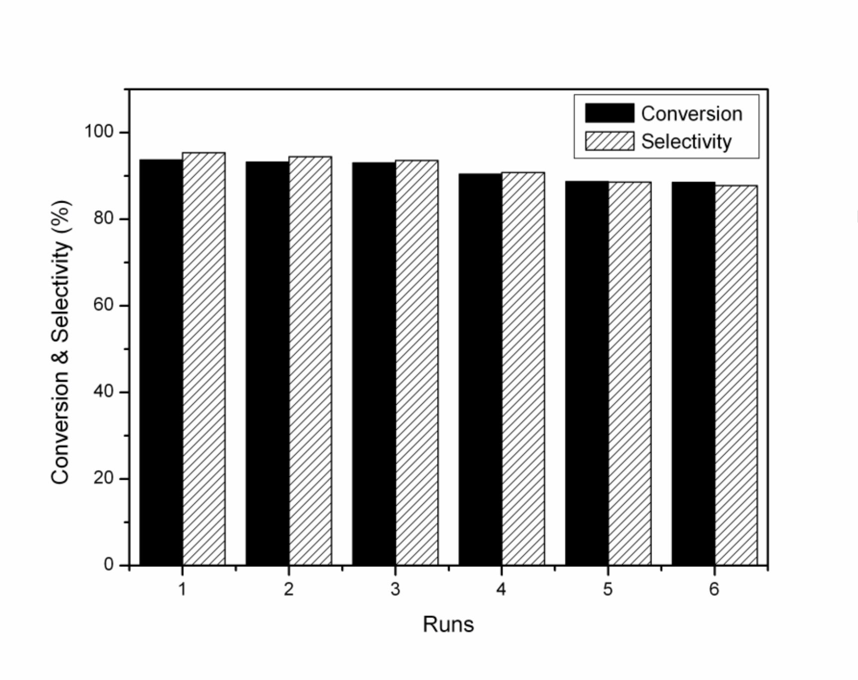

Fig.4. Recycling experiments for the hydrogenation of ethyl lactate

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Highlights:

1 Ethyl lactate was efficiently hydrogenated to 1, 2-PDO in H_2O over Ru/CSP catalyst.

2 The catalyst was recycled for six times without marked activity loss.

3 The possible hydrogenation pathway was suggested.

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