

# Efficient Conversion of D-Glucose into D-Sorbitol over Carbonized Cassava Dregs-Supported Ruthenium Nanoparticles Catalyst

Zengyong Li, Ying Liu,\* and Shubin Wu \*

A carbonized cassava dregs-supported ruthenium nanoparticles catalyst (Ru/CCD) was prepared by a simple impregnation-chemical reduction method. The synthesized Ru/CCD catalysts were characterized by X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The catalytic performances of the Ru/CCD catalysts were evaluated in the conversion of D-glucose into D-sorbitol under hydrogen atmosphere. Moreover, the effects of various parameters on glucose hydrogenation and the recyclability of the catalysts were investigated in detail. The optimized D-sorbitol yield reached up to 98.6% at 120 °C for 1.5 h with D-glucose conversion of 99.7%. The Ru nanoparticles played an important role in the hydrogenation of D-glucose into D-sorbitol, and the Ru particle was widely dispersed all over the support surface. In addition, the Ru/CCD catalyst was stable during the reaction and was reused for up to five successive runs with a slight decrease in D-sorbitol yield.

*Keywords:* Cassava dregs; Ruthenium; D-Glucose; D-Sorbitol

*Contact information:* State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, Guangdong, 510640, China;

\* *Corresponding authors:* amyliu@scut.edu.cn, shubinwu@scut.edu.cn

## INTRODUCTION

With the gradual depletion of fossil feedstock and the deteriorating pollution situation, new renewable alternatives to fossil feedstock are being explored (Zhang *et al.* 2012; Xi *et al.* 2013; Dabbawala *et al.* 2016). Biomass, a sustainable resource for the energy and carbon cycles in nature, has aroused worldwide attention (Kobayashi *et al.* 2011; Han and Lee 2012; Liao *et al.* 2014; Zhu *et al.* 2014). Cassava dregs, a waste byproduct with a large lignocellulosic component, are generated during the cassava-based bioethanol production (He *et al.* 2014; Kristensen *et al.* 2014; Nguyen *et al.* 2014). D-Sorbitol is an important chemical intermediate and a new energy chemical that has significant applications in food, medicine, textiles, and cosmetics, as well as in the chemical industry (Deng *et al.* 2010; Zheng *et al.* 2010; Liu *et al.* 2011; Chen *et al.* 2013; Negoi *et al.* 2014; Ribeiro *et al.* 2017).

Recently, D-sorbitol has been produced by catalytic hydrogenation of D-glucose in industrial production. A Raney-type Ni catalyst has been developed for the production of D-sorbitol. However, the Ni in the Raney-type Ni catalyst easily leaches into the solution (Zhang *et al.* 2013). In addition, the easy deactivation of the catalyst is an important issue with Raney-type Ni catalysts (Dabbawala *et al.* 2016). To overcome the drawbacks of the Raney-type Ni catalysts, several catalysts have been applied in the hydrogenation of D-glucose, especially Ru-based catalysts (Mishra *et al.* 2014; Lazaridis *et al.* 2015). The Ru-based catalysts have higher activity than Raney-type Ni catalysts. Furthermore, the Ru-

based catalysts have shown good stability in this reaction (Romero *et al.* 2016). The activity of Ru-based catalysts partially depends on supports such as activated carbon (Lazaridis *et al.* 2015), MCM-41 (Zhang *et al.* 2011), ZSM-5 (Guo *et al.* 2014), silica (Wang *et al.* 2015), and NiO-modified TiO<sub>2</sub> (Mishra *et al.* 2012). Therefore, it is very important to study the preparation and application of carbonized cassava dregs-supported ruthenium nanoparticles catalysts.

Inappropriate disposal of cassava dregs has led to pollution and a wastage of resources. In an effort to solve this problem, in the present work a solid catalyst was prepared using carbonized cassava dregs as the support and ruthenium as the active metal. The pollution problem of cassava dregs burning was solved by using cassava dregs as a raw material as the carbon support. The catalytic performance of the obtained catalysts in the hydrogenation of D-glucose was thoroughly investigated. The effects of various parameters and reaction conditions on the catalytic performance of the prepared catalysts were examined.

## EXPERIMENTAL

### Materials

RuCl<sub>3</sub>·3H<sub>2</sub>O, PtCl<sub>3</sub>·3H<sub>2</sub>O, NaBH<sub>4</sub>, AgNO<sub>3</sub>, activated carbon (AC), D-glucose, and D-sorbitol were purchased from Shanghai Jingchun Reagent (Shanghai, China). All chemicals used were of analytical grade.

### Catalyst Preparation

The carbonized cassava dregs-supported ruthenium nanoparticle catalyst was prepared by a simple impregnation-chemical reduction method (Dabbawala *et al.* 2016). The cassava dregs powder was carbonized in an N<sub>2</sub> atmosphere at 450 °C for 1.5 h to yield carbonized cassava dregs (CCD). The carbonized cassava dregs-supported ruthenium nanoparticle catalyst (Ru/CCD) was prepared by treating 0.8 g of CCD, 0.1089 g of RuCl<sub>3</sub>·3H<sub>2</sub>O, and 60 mL of deionized water in a flask with vigorous stirring. After 2 h, the 100 mL of 1 wt.% NaBH<sub>4</sub> solution was added drop by drop to the flask, and the mixture was vigorously stirred for 4 h. After completion of the reduction, the obtained product was filtered and washed with deionized water until the chloride was washed out as detected by AgNO<sub>3</sub>. The product was dried overnight in a vacuum oven at 50 °C. The loading of Ru was kept at 5 wt.%. The Ru/AC catalyst and Pt/CCD catalyst were prepared using the same method.

### Catalyst Characterization

The specific surface area (BET) and volume of the catalysts were determined by the standard nitrogen adsorption method using an ASAP 2460 instrument (Micromeritics Instrument Corporation, Shanghai, China). The specific surface areas of the samples were calculated using the BET equation. The element composition of the catalysts was determined by the use of a Vario EL cube element analysis instrument (Elementar Analysensysteme GmbH, Langenselbold, Germany). Powder X-ray powder diffraction (XRD) was performed in a Bruker D8 Advance diffractometer (Karlsruhe, Germany) using Cu K $\alpha$  radiation. The operating voltage and current were 40 kV and 40 mA, respectively. The step length was 0.02°, with a scanning rate of 2°/min. The oxidation state of Ru on the catalyst was analyzed by X-ray photoelectron spectroscopy (XPS) using a Kratos Ultra system (Manchester, UK) and an Al K $\alpha$  radiation source. The binding energies for each

spectrum were calibrated with a C1s value of 284.6 eV. The surface morphology and structure of the samples were determined using a scanning electron microscope (SEM, Merlin, Heidenheim, Germany). The distribution of Ru particles in the catalysts was analyzed with a transmission electron microscope (TEM, JEOL JEM-2100F, Tokyo, Japan). The catalyst samples for TEM were ultrasonically dispersed in ethanol and then deposited on carbon-coated copper grids using a capillary and air-dried for 30 min. The Ru content in the catalyst and the reaction solution was determined by inductive coupled plasma-atomic emission spectroscopy (ICP-AES, Shanghai, China).

### Catalytic Reaction

The conversion of D-glucose into D-sorbitol is described in Fig. 1. All reactions were performed in a 50 mL high-pressure reactor (PARR 5500). A total of 25 mL of 10 wt.% D-glucose solution was prepared in water at approximately 65 °C. Next, 1.0 wt.% of the prepared catalyst was introduced into the reactor, and the reactor was purged with 3 MPa of hydrogen gas. The reaction was carried out at 120 °C with a stirring rate of 600 rpm for 1.5 h. The reactor was cooled to room temperature, and the products were separated by filtration. The solid catalyst was dried at 50 °C overnight. The liquid products were analyzed by high-performance liquid chromatography (HPLC; Agilent 1200 Series, Palo Alto, CA, USA) equipped with an RI detector and a Shodex SUGAR SC1011 column (8 × 300 mm). The eluent was water with a flow rate of 1 cm<sup>3</sup> min<sup>-1</sup>. The column was maintained at 80 °C by a column heater. The sampling loop had a volume of 5 μL.

The D-glucose conversion, yield of D-sorbitol, and corresponding D-sorbitol selectivity were calculated using the equations (Negoi *et al.* 2014) below.

$$\text{D-glucose conversion (\%)} = [(\text{mass of starting D-glucose} - \text{mass of D-glucose after reaction}) / \text{mass of starting D-glucose}] * 100 \quad (1)$$

$$\text{D-sorbitol yield (\%)} = (\text{mass of D-sorbitol} / \text{mass of starting D-glucose}) * 100 \quad (2)$$

$$\text{D-mannitol yield (\%)} = (\text{mass of D-mannitol} / \text{mass of starting D-glucose}) * 100 \% \quad (3)$$

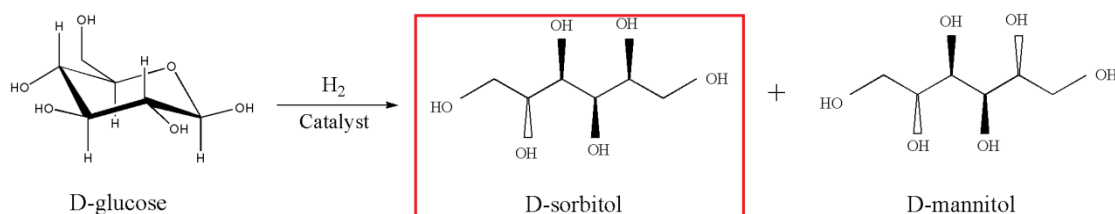


Fig. 1. Hydrogenation of D-glucose to D-sorbitol with possible side product

## RESULTS AND DISCUSSION

### Catalyst Characterization

#### *Textural and physicochemical properties analysis*

The specific surface area (BET), volume, and element composition of the catalysts were determined. As shown in Table 1, the BET surface area of the cassava dregs, CCD, and Ru/CCD were 9.251 m<sup>2</sup>g<sup>-1</sup>, 10.502 m<sup>2</sup>g<sup>-1</sup>, and 9.688 m<sup>2</sup>g<sup>-1</sup>, respectively. After the treatment with carbonization and the deposition of the Ru nanoparticles, the surface area

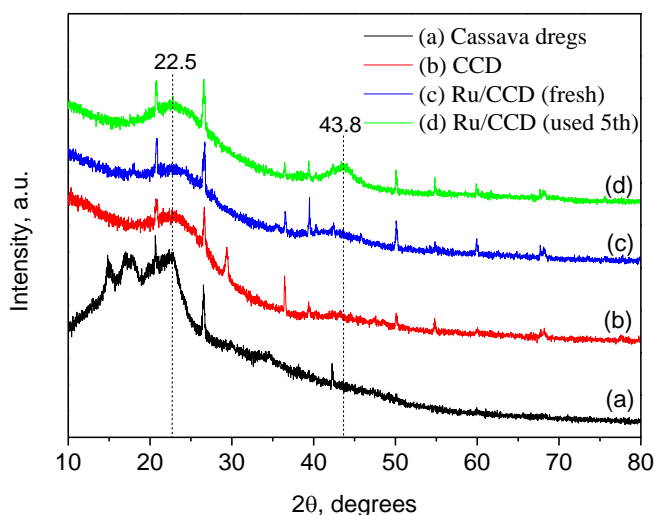
of the cassava dregs did not change considerably. In addition, the cassava dregs, CCD, and Ru/CCD had similar pore volumes. This indicated that neither the carbonization treatment nor the loading of the Ru nanoparticles impacted the porous structure of the cassava dregs. However, after the carbonization treatment, the oxygen and hydrogen contents of the cassava dregs decreased significantly. Relatively speaking, the carbon content of cassava dregs increased. On the other hand, after the Ru nanoparticles were deposited, the carbon content of CCD decreased slightly. The reason may have been the introduction of the Ru nanoparticles. The content of the Ru nanoparticles was 4.38% as detected using ICP-AES. This was lower than the theoretical value. The results suggested that the Ru nanoparticles were lost slightly in the preparation of the catalysts.

**Table 1.** Textural and Physicochemical Properties of Catalysts

Sample	$S_{BET}$ ( $m^2 g^{-1}$ )	$V_P$ ( $cm^3 g^{-1}$ )	Content (%)					
			C	H	O <sup>1</sup>	N	S	Ru <sup>2</sup>
Cassava dregs	9.251	0.001	39.60	6.50	53.49	0.37	0.04	0
CCD	10.502	0.001	69.50	3.22	26.48	0.78	0.02	0
Ru/ CCD	9.688	0.001	65.82	3.27	25.67	0.84	0.02	4.38

<sup>1</sup>O=100-C-H-N-S-Ru

<sup>2</sup>Determined by ICP-AES



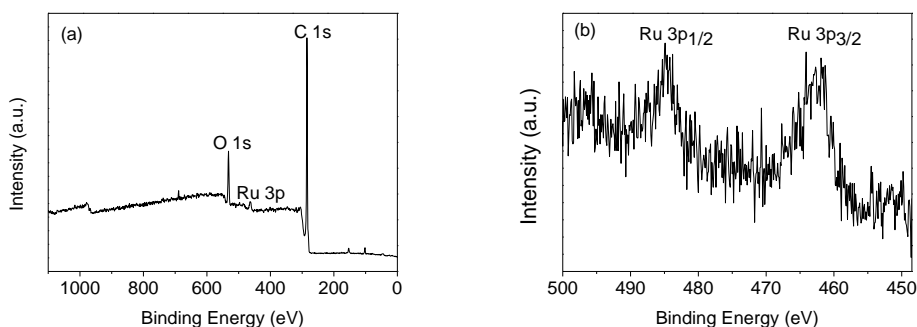
**Fig. 2.** XRD patterns of (a) cassava dregs, (b) CCD, (c) Ru/CCD (fresh), (d) Ru/CCD (used 5<sup>th</sup>)

#### XRD test

The XRD patterns of (a) cassava dregs, (b) CCD, (c) Ru/CCD (fresh), and (d) Ru/CCD (used 5<sup>th</sup>) are shown in Fig. 2. A characteristic diffraction peak was clearly observed at  $2\theta$  of  $22.5^\circ$  in Fig. 2. However, there was an obvious decrease in the intensity of the diffraction peak at  $2\theta$  of  $22.5^\circ$  in sample (b) as compared with (a). This result indicates that the crystalline content of cellulose was destroyed by the carbonization treatment. There were no apparent differences between the XRD patterns of samples (b) and (c), indicating a higher dispersion of Ru on the support surface. Nevertheless, after the catalyst was used five times, a small peak appeared at  $2\theta$  of  $43.8^\circ$  in the XRD pattern, and these generally arise due to the slight aggregation of Ru, indicating the growth of Ru particle size.

### XPS analysis

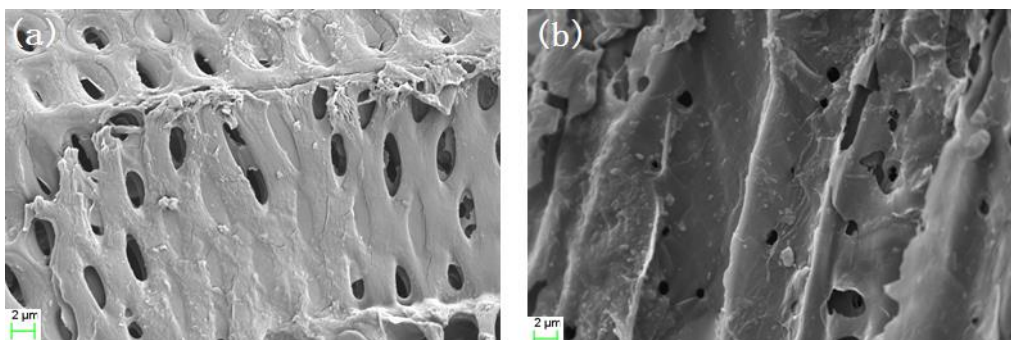
Figure 3 illustrates the XPS spectra of the Ru/CCD catalyst. As shown in Fig. 3 (a), the peaks with binding energy at 284.6, 484.2, and 532.6 eV were distributed to C 1s, Ru 3p, and O 1s, which implied that the catalyst contained the elements of C, Ru, and O in the survey scan of Ru/CCD. Moreover, in order to get more insight about the state of Ru nanoparticles on the catalyst surface, a high-resolution scan of the XPS spectra of Ru 3p was performed. As can be seen in Fig. 3 (b), two strong peaks at 462.7 and 484.6 eV were apparent, which were attributed to Ru 3p<sub>3/2</sub> and Ru 3p<sub>1/2</sub>, respectively. Also, Aasif *et al.* reported binding energies of 462.1 eV (Ru 3p<sub>3/2</sub>) and 484.2 eV (Ru 3p<sub>1/2</sub>) for Ru supported on an amine functionalized nanoporous polymer catalyst (Dabbawala *et al.* 2016). It indicated that the Ru existed with zero oxidation state on the catalyst surface.



**Fig. 3** XPS spectra of (a) Ru/CCD and (b) Ru 3p in Ru/CCD

### SEM analysis

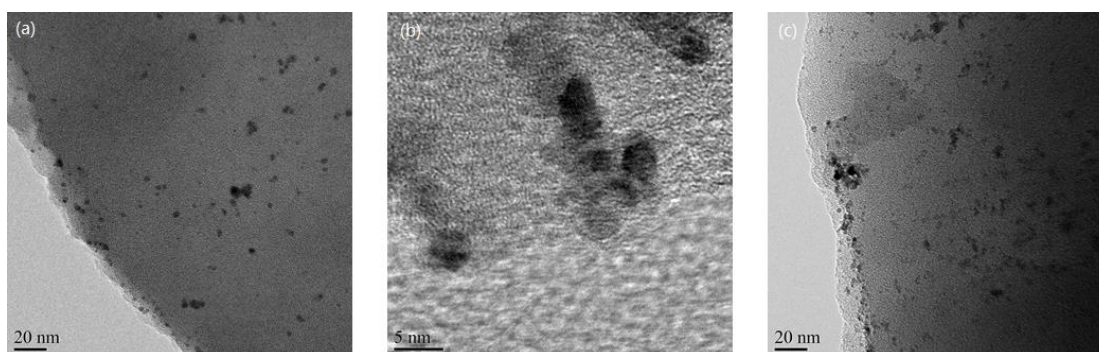
SEM images of (a) Cassava dregs and (b) CCD are given in Fig. 4. The cassava dregs and CCD both have a porous structure, and the surface morphology of CCD is similar to that of the cassava dregs. This indicated that the surface morphology of the cassava dregs was not changed by the carbonization treatment.



**Fig. 4.** SEM images of (a) Cassava dregs and (b) CCD

### TEM analysis

The catalysts were characterized by TEM and HR-TEM to investigate the Ru particle distribution and crystalline nature. As shown in Fig. 5 (a), the Ru particle was supported on CCD support and widely dispersed all over the CCD surface. Furthermore, the HR-TEM image of the Ru/CCD catalyst revealed that the size of the Ru nanoparticles was approximately 4 nm. Nevertheless, slight aggregation of Ru nanoparticles was observed in Fig. 5 (c), which may have led to the slight deactivation of catalyst.



**Fig. 5.** (a) TEM and (b) HR-TEM images of Ru/CCD (fresh) and (c) TEM image of Ru/CCD (used 5<sup>th</sup>)

## Catalytic Performance for the Conversion of D-Glucose

### *Influence of carbonization temperature on catalyst performance*

The prepared catalysts were employed in the catalytic conversion of D-glucose into D-sorbitol at 120 °C and 3 MPa H<sub>2</sub> for 1.5 h with a catalyst dosage of 1.0 wt.%. The effect of the carbonization temperature of cassava dregs on the catalyst performance was shown in Table 2 (entries 1 through 5). The carbonization temperature played an important role in the conversion of D-glucose into D-sorbitol. The D-glucose conversion increased from 41.5% to 99.7%, and the D-sorbitol yield increased from 36.8% to 98.6% accordingly, as the carbonization temperature increased from 300 °C to 450 °C. However, with the increase of the carbonization temperature to 500 °C, obvious decreases in glucose conversion and D-sorbitol yields were observed. The main reason was that the carbon content of the carbonized cassava dregs was increased at higher carbonization temperatures. This led to a decrease in binding sites for Ru. As shown in Table 3, the carbon content of CCD was increased and the oxygen and hydrogen content of CCD were decreased when the carbonization temperature increased. Therefore, the optimum carbonization temperature was set to 450 °C.

**Table 2.** Element Composition of CCD under Different Carbonization Temperature

Entry	Carbonization Temperature (°C)	Content (%)				
		C	H	O <sup>1</sup>	N	S
1	300	56.80	4.25	38.27	0.67	0.01
2	350	63.75	4.16	31.33	0.75	0.01
3	400	66.90	3.77	28.53	0.78	0.02
4	450	69.50	3.22	26.48	0.78	0.02
5	500	76.04	2.96	20.11	0.88	0.01

<sup>1</sup>O=100-C-H-N-S

### *Influence of reaction time on D-glucose hydrogenation*

Table 3 (entries 4 and 6 through 10) shows the effect of reaction times ranging from 0.5 to 3 h on D-glucose conversion and D-sorbitol yield. At the early period of D-glucose hydrogenation, D-glucose was rapidly converted into D-sorbitol, and the D-sorbitol yield was increased with the prolongation of reaction time. In 1.5 h, the D-glucose was completely converted, and the D-sorbitol yield reached its highest level of 98.6%. When the reaction was further prolonged, the chemical equilibrium of the D-glucose hydrogenation was reached. Therefore, the D-glucose conversion and the D-sorbitol yield were not changed significantly. The optimum reaction time was set to 1.5 h in this experiment.

*Influence of reaction temperature on D-glucose hydrogenation*

Subsequently, the influence of reaction temperature on D-glucose hydrogenation was studied. As shown in Table 3 (entries 4 and 11 through 14), the D-glucose conversion and D-sorbitol yield were low at lower reaction temperatures but escalated significantly with an increase of reaction temperature. When the reaction temperature rose above 120 °C, the D-sorbitol yield showed a maximum with 98.6%. Although higher reaction temperatures led to a slight increase of D-glucose conversion, the yield of D-sorbitol decreased to 88.0%, and the yield of D-mannitol increased to 6.3%. The results indicated that the produced D-sorbitol is decomposed to some by-product such as mannitol at a higher reaction temperature. This demonstrated that an appropriate reaction temperature was crucial for the conversion of D-glucose into D-sorbitol. Therefore, the optimum reaction temperature was selected as 120 °C for further study.

**Table 3.** Effects of Various Parameters on D-Glucose Hydrogenation

Entry	Carbonization Temperature (°C)	Reaction Time (h)	Reaction Temperature (°C)	D-Glucose Conversion (%)	D-Sorbitol Yield (%)	D-Mannitol Yield (%)
1	300	1.5	120	41.5	36.8	0.6
2	350	1.5	120	85.6	82.9	1.3
3	400	1.5	120	87.8	84.6	1.0
4	450	1.5	120	99.7	98.6	1.0
5	500	1.5	120	84.3	80.1	1.0
6	450	0.5	120	57.5	55.0	0.7
7	450	1.0	120	86.7	83.4	1.0
8	450	2.0	120	100.0	98.5	1.4
9	450	2.5	120	100.0	98.0	1.1
10	450	3.0	120	100.0	98.1	1.1
11	450	1.5	80	25.4	24.1	0.3
12	450	1.5	100	59.5	58.1	0.5
13	450	1.5	140	100.0	96.0	2.2
14	450	1.5	160	100.0	88.0	6.3

Reaction conditions: 25 mL 10 wt.% D-glucose solution, catalyst dosage of 1.0 wt.%, 3 MPa H<sub>2</sub>, 600 rpm

**Conversion of the D-Glucose into D-Sorbitol over Various Catalysts**

The catalytic evaluation of the hydrogenation of D-glucose at 120 °C and 3 MPa H<sub>2</sub> for 1.5 h using different catalysts is shown in Table 4. When no catalyst (Table 4, entry 1) or only CCD (Table 4, entry 2) was used, no sugar alcohols were detected, although the conversions of D-glucose were 9.8% and 20.6%, respectively. However, when Ru supported on CCD was used on D-glucose hydrogenation (Table 3, entry 3), a high D-glucose conversion of 99.7% was obtained, and D-sorbitol yield was able to reach 98.6%. Small amounts of D-mannitol were also observed. Meanwhile, the Ru/AC catalyst also afforded high catalytic performance, and the D-glucose conversion of 100% and D-sorbitol yield of 96.5% were obtained (Table 4, entry 4). These results implied that in the presence of a metal Ru site, the hydrogenation of glucose into D-sorbitol occurred rapidly at a relatively moderate temperature of 120 °C. This result indicated that Ru nanoparticles played an important role in the hydrogenation of D-glucose into sorbitol. Moreover, the influence of different metals was also investigated. When Pt supported on CCD was employed as a catalyst (Table 4, entry 5), the D-glucose was completely converted, and the D-sorbitol yield of 93.3% was observed. These results indicated that Ru showed higher catalytic performance than Pt on the hydrogenation of D-glucose into D-sorbitol.

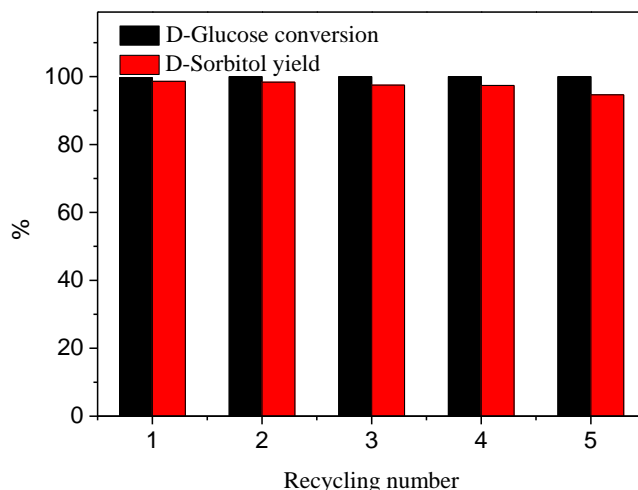
**Table 4.** Conversion of the D-Glucose into D-Sorbitol over Various Catalysts

Entry	Catalyst	D-Glucose Conversion (%)	D-Sorbitol Yield (%)	D-Mannitol Yield (%)
1	No catalyst	9.8	0	0
2	CCD	20.6	0	0
3	Ru/CCD	99.7	98.6	1.0
4	Ru/AC	100.0	96.5	1.0
5	Pt/CCD	100.0	93.3	2.2

Reaction conditions: 25 mL 10 wt.% D-glucose solution, catalyst dosage of 1.0 wt.%, 3 MPa H<sub>2</sub>, 600 rpm, 120 °C, 1.5 h

### Catalyst Recycling

The recyclability of the Ru/CCD catalyst on the D-glucose hydrogenation was evaluated under the optimized reaction conditions. After the reaction was finished, the Ru/CCD catalyst was recycled by filtering the final solution, and then dried in a vacuum oven without other complex processing. As shown in Fig. 6, the catalytic performance did not decrease after being reused four times, and the D-glucose conversion and D-sorbitol yields showed no differences. After being reused five times, the D-glucose conversion did not decrease significantly, but the D-sorbitol yield decreased slightly, from 98.6% to 94.7%. A possible reason was that some reaction products could have bonded and accumulated on the surface of the catalyst, which resulted in a decline in catalyst performance (Zhang *et al.* 2013). In addition, slight aggregation of the Ru nanoparticles was observed from the TEM images (Fig. 5(c)), which may have led to the slight deactivation of the catalyst. These results clearly indicated the Ru nanoparticles could be well loaded in the CCD support, and the Ru/CCD was effective for the hydrogenation of D-glucose into D-sorbitol and was stable during the reaction process. On the other hand, no leaching of the Ru species was detected in the reaction solution by ICP-AES, indicating that this catalyst was stable against the chelating effect of the reactant and the product (Wang *et al.* 2015).



**Fig. 6.** Recyclability of Ru/CCD catalyst on D-glucose hydrogenation; 25 mL 10 wt.% D-glucose solution, catalyst dosage of 1.0 wt.%, 3 MPa H<sub>2</sub>, 600 rpm, 120 °C, 1.5 h



## CONCLUSIONS

1. A carbonized cassava dregs-supported ruthenium nanoparticle catalyst was prepared by a simple impregnation-chemical reduction method, which was efficient for the conversion of D-glucose into D-sorbitol.
2. The D-glucose conversion and D-sorbitol yield were influenced by the carbonization temperature of cassava dregs. The D-glucose conversion of 99.7% and D-sorbitol yield of 98.6% were attained at 120 °C for 1.5 h with 3 MPa H<sub>2</sub> and a catalyst dosage of 1.0 wt.%.
3. The Ru nanoparticles played an important role in the hydrogenation of D-glucose into D-sorbitol, and the Ru particle was widely dispersed all over the CCD support surface.
4. The recyclability and stability of the Ru/CCD catalyst was excellent, and the Ru/CCD catalyst was reused for up to five successive runs with a slight decrease in D-sorbitol yield.

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