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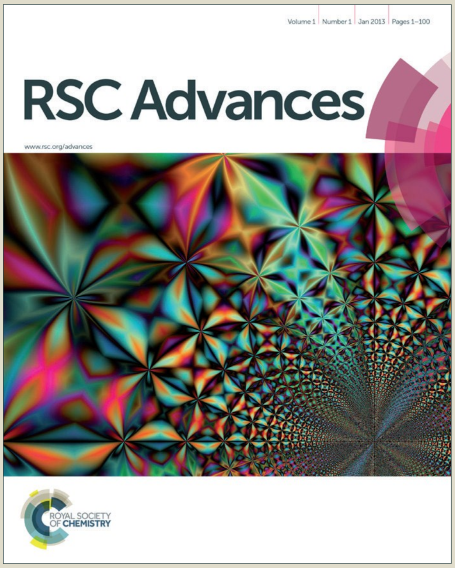

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Catalytic conversion of cellulose for efficient ethylene glycol production and insights into the reaction pathways

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Abstract

As promising and environmentally friendly catalysts, tungsten-containing heteropoly acids with the conbination of supported noble metals were used for one-pot hydrothermal conversion of cellulose into polyols in the presence of pressurized hydrogen. The microcrystalline cellulose was completely converted over a mixed catalyst consisting of a low concentration of phosphotungstic acid (PTA) (0.03 wt%) and Ru/activated carbon (Ru/AC) via an one-pot hydrothermal reaction, with an ethylene glycol (EG) yield up to 53.1% under optimal conditions. The catalytic activity of the mixed catalyst gradually decreased with increasing reaction runs, which could be mainly ascribed to the aggregation of Ru/AC particles, and to the coverage of active sites of Ru due to the deposition of organic materials. Cellobiose was used as a model feedstock for a comparative study on the reaction pathways of the conversion of cellulose, and the results revealed that catalytic conversion of cellobiose consisted of at least three important parallel reactions under the presnet hydrothemal conditions, which also were most likely involed during the catalytic converison of cellulose for EG production. Effective control of those reactions would be helpful to further maximize the EG yield during the catalytic conversion of celllulose.

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Keywords: cellulose, mixed catalyst, ethylene glycol, reaction pathway, deactivation mechanism

1. Introduction

Cellulose is a polysaccharide simply consisting of a large amount of β-1,4 linked glucose structural units, which is the most abundant renewable carbon source on the earth, thus has been considered as a fascinating alternative to fossil resources for the sustainable production of various chemicals.[1-4] Currently, efficient catalytic conversion of cellulose to ethylene glycol (EG) has attracted significant attention, because EG is a very important bulk chemical that is mainly produced using petroleum so far.[5] To enable this new route for industrial application, the development of high-performance catalysts for efficient conversion of cellulose to EG is of significant importance.

Among the reported catalysts, so far, the catalyst consisting of a transition metal and tungsten species has been identified as the most active for conversion of cellulose to EG, and the multifunction of this catalyst has been clarified during the catalytic process.[6–9] Under hydrothermal conditions, cellulose is first hydrolyzed to water-soluble oligosaccharides and glucose at elevated temperatures. The catalysis of tungsten species enable C-C bond cleavage in the water-soluble oligosaccharides and glucose, yielding the important intermediate product of glycolaldehyde (GA), while the transition metal subsequently catalyzes the hydrogenation of GA, eventually resulting in the formation of EG[7–11]. Since GA is the key intermediate product for the synthesis of EG during this reaction, selective conversion of cellulose to GA at the early stage over a highly active tungsten species is, thus, of vital importance. Experimental observations have confirmed that the final EG yield is significantly affected by the tungsten species.[7–11] Therefore, the use of a highly active tungsten species in the catalyst is very important to achieve a high EG yield.

Phosphotungstic acid (PTA) is a commercial available water-soluble heteropoly acid, which has been known as a low-cost and environmentally friendly catalyst in various reactions.[12,13] Considering the acidic properties of the aqueous solution of

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phosphotungstic acid, the presence of considerable H^+ would effectively facilitate the hydrolysis of cellulose under hydrothermal conditions,[14] which ensures that cellulose is completely hydrolyzed to water-soluble oligosaccharides and glucose. Furthermore, as a water-soluble tungsten species, phosphotungstic acid can act as a homogeneous catalyst, which would further enhance the C-C bond cleavage reaction to form GA in comparison with most of the heterogeneous catalysts, finally resulting in a high yield of EG.

In the present study, a mixed catalyst combining PTA and activated carbon supported Ru (PTA-Ru/AC) was developed for the catalytic conversion of cellulose into EG. This mixed catalyst was highly active and a high EG yield was successfully achieved even though the concentration of PTA was extremely low in the reaction solution. The durability and deactivation mechanism of the PTA-Ru/AC mixed catalyst were discussed. Finally, in order to gain insights into the reaction pathways of catalytic conversion of cellulose for EG production, cellobiose was selected as a model feedstock for a comparative study of this catalytic process.

2. Experimental

2.1 Materials

Ru/AC, Pt/AC, Pd/AC (5 wt% loading), microcrystalline cellulose (average particle size: ~50 μm) and cellobiose were purchased from Aladdin Industry Inc. PTA and silicotungstic acid (STA) were obtained from Tianjin Kemiou Chemical Reagent Co. Ltd.

2.2 Catalytic tests

Hydrothermal conversion of cellulose (or cellobiose) to EG was carried out in a 100 ml high-pressure stainless-steel autoclave (Series 5100 HP Compact Reactors, Parr Instrument Company). Briefly, Ru/AC (or Pt/AC, Pd/AC) (0-0.1 g), PTA (or STA) (0-900 ppm), water (50 g) and microcrystalline cellulose (or cellobiose) (0.5 g) were transferred into the reactor. Then, the reactor was first purged with H_2 to remove the air in the system at atmospheric pressure, and the reactor was subsequently

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pressurized with hydrogen at a pressure of 6 MPa at room temperature. After sealing the reactor, the mixture was heated up to temperatures of 230–250 °C and maintained for 30–90 min, under at a constant stirring rate of 1000 rpm. After the reaction, the reactor was rapidly cooled down to room temperature with ice water. The liquid products were collected after permeating through a membrane filter with an average pore size of 0.45 μm, and the components in the liquid phase were analyzed using an ultra performance liquid chromatography instrument (Agilent 1290, Agilent Technologies) coupled with a quadrupole time-of-flight mass spectrometer (Agilent 6540, Agilent Technologies). Solid residue obtained after filtration was washed with deionized water, followed by drying at 105 °C in a vacuum oven overnight. The yield of EG was approximately calculated based on the weight of EG and original cellulose sealed into reactor. Cellulose conversion was calculated by the weight difference of cellulose before and after the reaction with an uncertainty of ±3%.

2.3 Characterization methods

The concentration of Ru ions in the liquid phase after reaction was determinated using a flame atomic absorption spectrometry (AAS) (novAA 350, Analytik Jena). X-ray photoelectron spectra (XPS) was recorded using an X-ray photoelectron spectrometer (ESCALAB 250XI, Thermo Scientific) with nonmonochromatized Al Kα radiation as the excitation source. Thermogravimetric analysis was carried out using an analyzer (STA449 F3, NETZSCH) operated at temperatures that ranging from 25 to 700 °C under a nitrogen atmosphere. The morphologies of fresh and recycled solid catalysts were determined using a scanning electron microscope (SEM) (Merlin, Zeiss) and transmission electron microscope (TEM) (JEM-2100F, JEOL).

3. Results and discussion

3.1 Screening of mixed catalysts for cellulose conversion

A variety of mixed catalysts consisting of different tungsten species and supported noble metals were screened for the cellulose conversion process, and their catalytic performances are summarized in Table 1. Although all the mixed catalysts showed quite high cellulose conversions (95~100%), however, the final product distribution differed significantly under the same reaction conditions. Among these mixed catalysts, the PTA-Ru/AC mixed catalyst was the most selective for the production of EG and sorbitol, and the yields of EG and sorbitol were up to 53.1 and 12.4%, respectively. However, for the production of 1,2-propylene glycol (1,2-PG), the PTA-Pd/AC and PTA-Pt/AC mixed catalysts were much more active than the PTA-Ru/AC mixed catalyst. On the other hand, comparing the catalytic performance of PTA-Ru/AC and STA-Ru/AC mixed catalysts with the same noble metal component, PTA-Ru/AC showed a much higher EG yield (53.1%) than that of STA-Ru/AC (16.3%). This result indicated that tungsten species also exerted a very important effect on the catalytic performance, since tungsten species was the active phase for the C-C cleavage reaction during the catalytic process[7–11]. Therefore, based on the EG productivity, the PTA-Ru/AC was selected as the most active mixed catalyst for catalytic conversion of cellulose for EG production. It should be noted that attempts using a higher cellulose amount of 1.5wt% to increase the EG productivity generally resulted in a much lower EG yield < 30% even the reaction time was increased from 50 to 150 min, which could be mainly ascribed to the serious cocking effect under a high cellulose concentration during the reaction.[15] Therefore, a relatively low cellulose concentration was necessary in order to convert into EG very selectively.

3.2 Catalytic performance of the PTA-Ru/AC mixed catalyst for cellulose conversion

Fig. 1 shows the catalytic performance of the PTA-Ru/AC catalyst for cellulose conversion under difference conditions. The effects of the amount of PTA and Ru/AC in the mixed catalyst on the catalytic activity for cellulose conversion were studied, and the distribution of the main polyol products is illustrated in Fig. 1a and b. When the PTA amount in the reactor was fixed at 500 ppm, the conversion of cellulose increased with increasing the Ru/AC amount in the mixed catalyst, and the cellulose was completed converted when the Ru/AC amount in the mixed catalyst was larger than 0.025 g. However, both EG and 1,2-PG yields followed almost the same trend

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that showed a maximum value as the amount of Ru/AC further increased. This was mainly because a high Ru/AC amount in the mixed catalyst favored the hydrogenation of glucose into sorbitol.[16] However, much excess Ru/AC amount in the mixed catalyst caused a decrease in the sorbitol yield, due to the enhanced isomerization of glucose to fructose.[17] Fig. 1b shows the effect of PTA amount on the catalytic performance of cellulose conversion, with a fixed Ru/AC amount of 0.025 g in the mixed catalyst. As the PTA amount increased, the conversion of cellulose increased to 100%, because the hydrolysis of cellulose was enhanced under acidic conditions.[18] The EG yield initially increased rapidly at low PTA concentrations, and it was much higher than the yields of 1,2-PG and sorbitol, which could be attributed to selective C-C bond cleavage via a retro-aldol reaction by the catalysis of PTA.[19] It should be noted that the enhancement of the EG yield was very notable although the PTA concentration was extremely low, this was mainly because the PTA acted as a homogeneous catalyst. The EG yield gradually decreased with a further increase of PTA concentration, which could be ascribed to that a high acidity facilitated the conversion of glucose to by-products.[20] Obviously, the tuning of composition of the PTA-Ru/AC is of significance to control the product distribution of the catalytic conversion of cellulose, and the use of a low PTA concentration allow both high catalytic activity and selectivity for the production of EG from cellulose.

Fig. 1c shows the effect of temperature on the catalytic performance of conversion of cellulose with optimal amounts of PTA and Ru/AC in the mixed catalyst. With the temperature increased from 230 to 250 °C, the yields of 1,2-PG and sorbitol showed slightly changes, while the EG yield increased from 40 to 51% due to the increased conversion of cellulose at high temperatures. Fig. 1d shows the time course of catalytic performance of the mixed catalyst for EG production. The EG yield was as high as 37% although the reaction had been conducted for only 20 min, which again confirmed a quite high reaction rate even a small amount of PTA in the mixed catalyst. The EG yield initially increased with increasing the reaction time and then reached a maximum EG yield of 53.5% at 50 min. This high EG yield is comparable with that of reported catalysts[19] although the amount of tungsten species

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was much lower in the present system.

3.3 The stability and reusability of the PTA-Ru/AC mixed catalyst

The stability and reusability of the mixed catalyst is an important concern for practical EG production. Since PTA is soluble in water and acts as homogenous catalysis, the stability of the mixed catalyst would be mainly dominated by the Ru/AC component for the final hydrogenation reaction. Therefore, the catalytic performance of the catalyst was evaluated using recycled Ru/AC with fresh PTA for several reaction runs. Fig. 2 shows the catalytic performance of the mixed catalyst for EG production at different reaction runs. The EG yield decreased with increasing the recycled times of Ru/AC, *e.g.*, the EG yield decreased obviously from 53.5 to 33% after 3 reaction runs, which indicated that deactivation had occurred for Ru/AC in the mixed catalyst under present hydrothermal conditions.

To gain insights into the deactivation mechanism of Ru/AC in the mixed catalyst, the recycled Ru/AC was studied using various techniques. The AAS measurements showed that there was no Ru ion in the liquid phase after each catalytic runs (Table 2), which indicated that no leaching occurred for the Ru metal during the entire catalytic process. Fig. 3 shows the Ru 3p XPS spectra of the fresh and recycled catalysts with different catalytic runs. The binding energies centered at 462.7 and 484.3 eV, which could be ascribed to the metallic state of Ru,[21] were almost the same. This result revealed that the metallic Ru in the catalyst was maintained during the whole hydrothermal treatment. Fig. 4 shows the SEM images of the fresh and recycled Ru/AC with different catalytic runs. Compared with the fresh Ru/AC catalyst (Fig. 4a), there was no obvious difference in their particle size (~10 μm) when the Ru/AC catalyst was used once (Fig. 4b). This result was well consistent with their similar catalytic performance. When the catalyst was used for 2 and 3 times (Fig. 4c and d), the catalyst obviously aggregated to make particles as large as millimeters, which corresponded to the much lower catalytic activities again, showing good correlation between the catalytic performance and Ru/AC particle size. The above observation indicated that the Ru/AC particles suffered from serious aggregation after several catalytic runs. This could be probably due to the hydrophobic surface of the activated carbon support,[22] which made the homogeneous dispersion of Ru/AC in water difficult. The aggregation of Ru/AC particles might efficiently increase the diffusion resistance of the reactant to the active sites of Ru nanoparticles, resulting in degradation of catalytic performance of Ru/AC. Fig. 5 shows the TEM images of the fresh and used Ru/AC after the catalytic conversion of cellulose. Ru nanoparticles with an average size of several nanometers were homogeneously distributed on the AC support for the fresh Ru/AC, while the Ru/AC used after 3 times was largely covered by unknown materials. To further confirm that, both the fresh Ru/AC and recycled Ru/AC with 3 catalytic runs were analyzed using TG (Fig. 6). It clearly showed that the weight loss of recycled Ru/AC catalyst was much larger than the fresh one at high temperatures, which confirmed the deposition of organic materials on the recycled catalyst. As a result, the effective active sites of Ru nanoparticles significantly decreased and the channels in the support for mass transport were partly blocked, which also should be substantially contributed to the deactivation of catalytic activities. Previously, Tai *et al*. reported[19] catalytic conversion of cellulose into EG using Ru/AC and H_2WO_4 mixed catalyst, the acid in that system was much higher and the catalyst showed better stability, which could be most likely ascribed to the fact that a higher acidity probably be helpful to suppress the deposition of polymer on the catalyst.

Although the mixed catalyst consisting of an extremely low concentration of phosphotungstic acid and AC supported Ru showed excellent catalytic activity for efficient production of EG, the durability of the catalytic performance was efficient hindered by the deactivation of Ru/AC during the catalytic reaction. The analyses of the deactivation mechanism described above lead us to believe that the catalyst support must be improved for Ru loading in the present system, because the hydrophobic properties of AC make the Ru/AC easily aggregated in aqueous solution at high temperatures, and the small pore size of AC make the diffusion difficult and thus is easily blocked since the involvement of relatively large molecules in this catalytic reaction (*e.g.*, glucose). This conclusion inspires us to further improve the

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catalytic performance by designing new catalytic support materials with excellent hydrophilic properties and looser structures.

3.4 Comparative study on catalytic conversion of cellulose and cellobiose for EG production

According to the previous studies,[6–11] catalytic conversion of cellulose into EG involves multi-step reactions including (Ⅰ) hydrolysis of cellulose to form glucose and soluble monosaccharide under acidic conditions, (Ⅱ) C-C cleavage of glucose to form glycolaldehyde via retro-aldol reaction over W species, and (Ⅲ) the hydrogenation of glycolaldehyde to EG with the aid of metal catalysts, as the reaction pathways illustrated in the Scheme 1. Since cellulose is a polysaccharide with considerable large amount of β-1,4 linked glucose structural units, further study of the details of the reaction mechanism becomes inconvenient. To simplify the problem, cellobiose, which is glucose dimer connected by the same β-1,4-glycosidic bond as in glucose and represents the simplest model compound for cellulose, is usually used as an ideal model compound to study the transformation behaviors of cellulose in different systems.[23–25] Therefore, in order to gain insights into the reaction pathways for catalytic conversion of cellulose, catalytic conversion of cellobiose into EG was examined as a model reaction for a comparative study in the present work.

Fig. 7 shows the mass spectra of the liquid products of catalytic conversion of cellobiose using the PTA-Ru/AC catalyst. As expected, glucose and sorbitol were clearly identified in the products when cellobiose was used as the feedstock, and their formation could be mainly ascribed to the hydrolysis of cellobiose and subsequent hydrogenation of glucose. However, new components, such as 3-β-glucopyranosyl-D-glucitol, glucosyl-erythrose and glycosyl-ethylene glycol, also were detected. The formation of 3-β-glucopyranosyl-D-glucitol could be attributed to the hydrogenation of cellobiose over the Ru/AC catalyst, while the generation of glucosyl-erythrose and glycosyl-ethylene glycol could be thought as the evidence of retro-aldol condensation of cellobiose. Based on the above results, we could conclude that the catalytic conversion of cellobiose over Ru/AC-TPA consisted of at least three

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parallel reactions that occurred simultaneously during the catalytic process: hydrolysis, hydrogenation and retro-aldol condensation of cellobiose, as shown in Scheme 2. Similar results also were reported in a previous study.[23] Table 3 compares the distribution of main products in the liquid phase for the catalytic reaction using cellulose and cellobiose as the feedstock. The yield of EG together with that of the other components were comparable for both cellulose and cellobiose as the feedstock, which indicated that cellulose and cellobiose might undergo similar reaction pathways, since cellobiose represents the basic structural unit for cellulose and can be obtained via the hydrolysis of cellulose. Therefore, when cellulose was used as the feedstock for EG production, in addition to the retro-aldol condensation of glucose that is hydrolyzed completely from cellulose during the catalytic process, effective tuning of other reactions, such as retro-aldol condensation of cellobiose, also would be of significant in order to maximize the EG yield.

Conclusions

A highly active mixed catalyst with Ru/AC and an extremely low concentration of phosphotungstic acid was studied for catalytic conversion of cellulose to EG. The catalyst showed excellent catalytic performance, with a cellulose conversion and EG yield of 100 and 53.1%, respectively, under optimal conditions. The durability of the catalyst was investigated and confirmed the deactivation of the catalyst during the hydrothermal reaction. The decreased catalytic performance could be mainly attributed to the degradation of Ru/AC, due to the aggregation of Ru/AC particles and the loss of active site of Ru due to the deposition of organic materials. This finding revealed that a catalyst support with hydrophilic property and a looser structure would result in better catalytic performance. Cellobiose was used as model feedstock for a comparative study in order to gain insights into the reaction pathways of catalytic conversion of cellulose for EG production. The results showed that catalytic conversion of cellobiose consisted of at least three parallel reactions including direct retro-aldol condensation of cellobiose to produce EG, which also might involved in

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the catalytic conversion of cellulose. Effective tuning of the above reactions would be helpful to further maximize the EG yield via catalytic conversion of cellulose.

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Figures and tables:

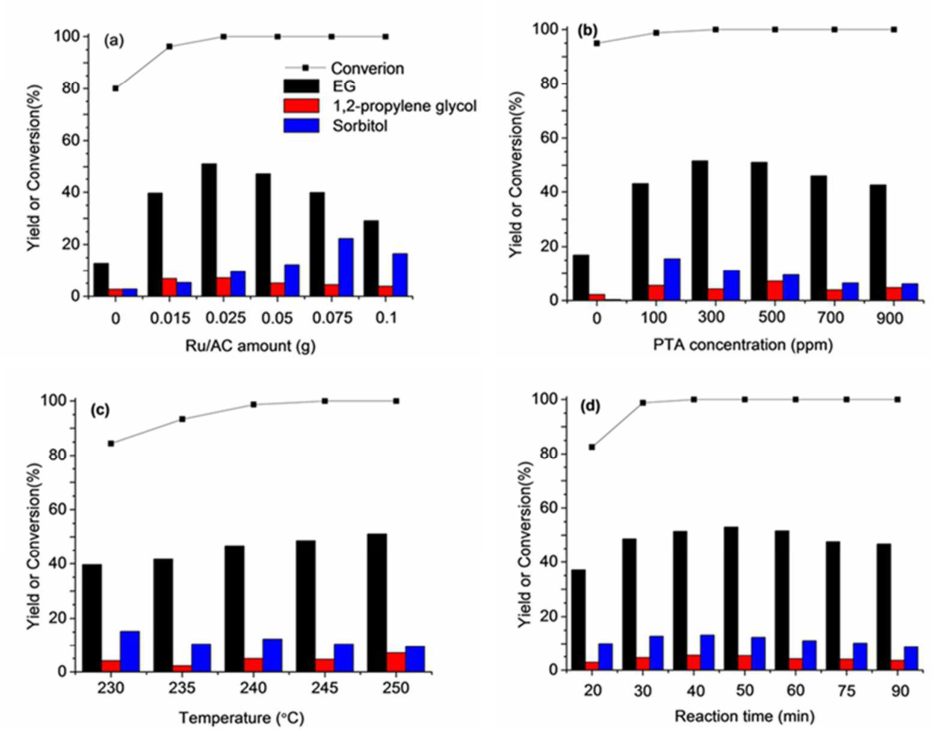

Fig. 1 Catalytic performance of the PTA-Ru/AC mixed catalyst for conversion of cellulose under different reaction conditions.

Reaction conditions: (a) 0.5 g microcrystalline cellulose, 50 g deionized water, 500 ppm PTA, 6 MPa H_2 (room temperature), 250 °C and 60 min; (b) 0.5 g microcrystalline cellulose, 50 g deionized water, 0.025 g Ru/AC, 6 MPa H_2 (room temperature), 250 °C and 60 min; (c) 0.5 g microcrystalline cellulose, 50 g deionized water, 0.025 g Ru/AC, 300 ppm PTA, 6 MPa H_2 (room temperature) and 60 min; (d) 0.5 g microcrystalline cellulose, 50 g deionized water, 0.025 g Ru/AC, 300 ppm PTA, 6 MPa H_2 (room temperature) and 250 °C.

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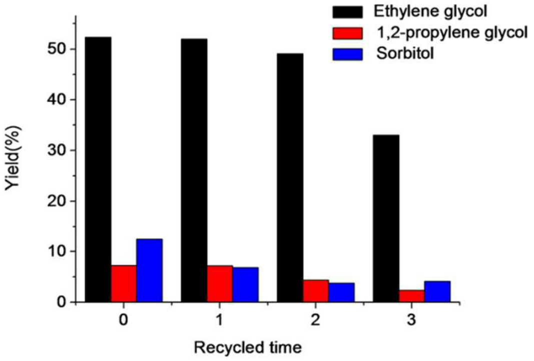

Fig. 2 Catalytic performance of the PTA-Ru/AC mixed catalyst with recycled Ru/AC.

Reaction conditions: 0.5 g microcrystalline cellulose, 50 g deionized water, 0.025 g Ru/AC, 300 ppm phosphotungstic acid, 250 °C and 50 min.

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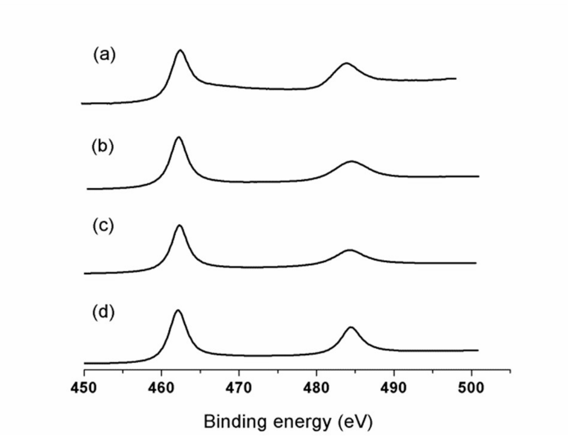

Fig. 3 XPS spectra of Ru 3p of the fresh and recycled Ru/AC. (a) fresh; (b) used once; (c) used twice; (d) used thrice .

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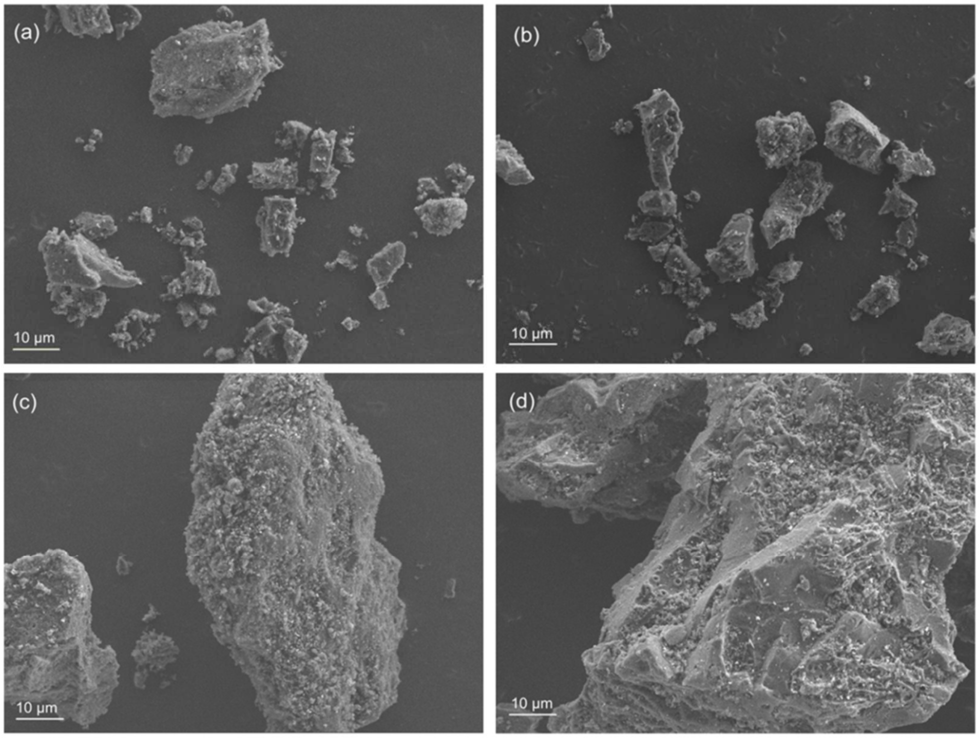

Fig. 4 SEM images of the fresh and recycled Ru/AC in the mixed catalyst. (a) fresh; (b) used once; (c) used twice; (d) used thrice.

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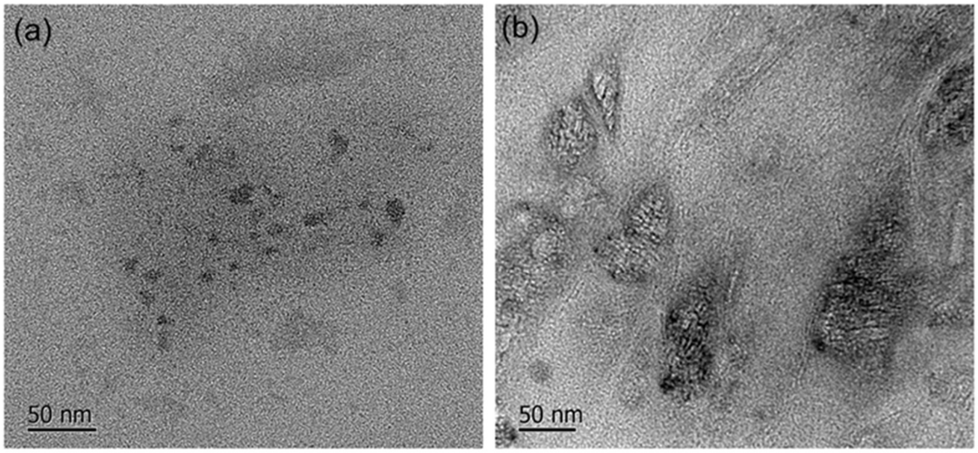

Fig. 5 TEM images of the fresh (a) and used Ru/AC (b) in the mixed catalyst for the conversion of cellulose into EG.

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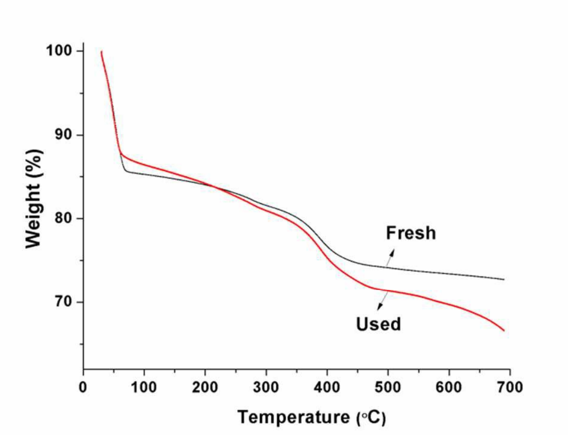

Fig. 6 TG curves of the fresh and used Ru/AC for the conversion of cellulose into EG under a N_2 atmosphere.

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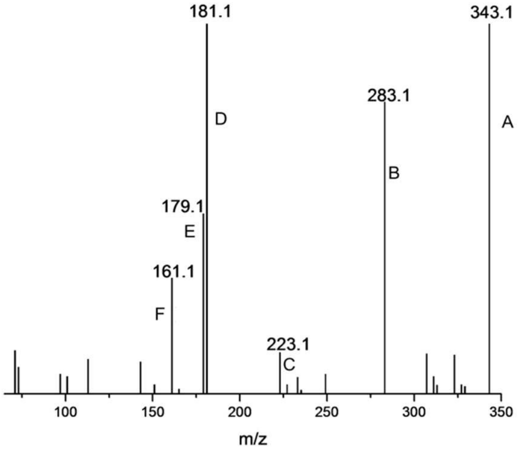

Fig. 7 Mass spectra of the products for catalytic conversion of cellobiose over the PTA-Ru/AC catalyst.

Reaction conditions: 0.5 g cellobiose, 50 g water, 300 ppm PTA, 0.025 g Ru/AC, 6 MPa H_2 (room teperature), 230 °C and 20 min. A: 3-β-glucopyranosyl-D-glucitol ($C_{12}H_{24}O_{11}$), B: glycosyl-erythritol ($C_{10}H_{20}O_9$), C: glycosyl-ethylene glycol ($C_8H_{16}O_7$), D: sorbitol ($C_6H_{14}O_6$), E: glucose ($C_6H_{12}O_6$), F: anhydroglucose ($C_6H_{10}O_5$).

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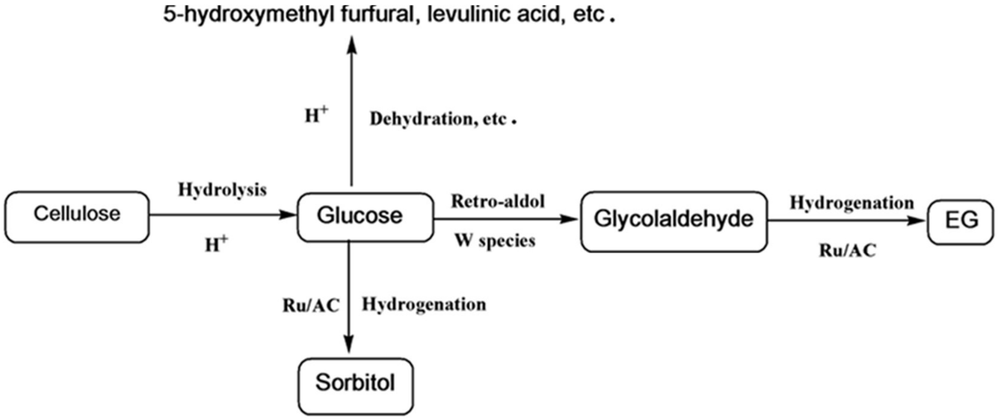

Scheme 1 Reaction pathways of one-pot conversion of cellulose for EG production.

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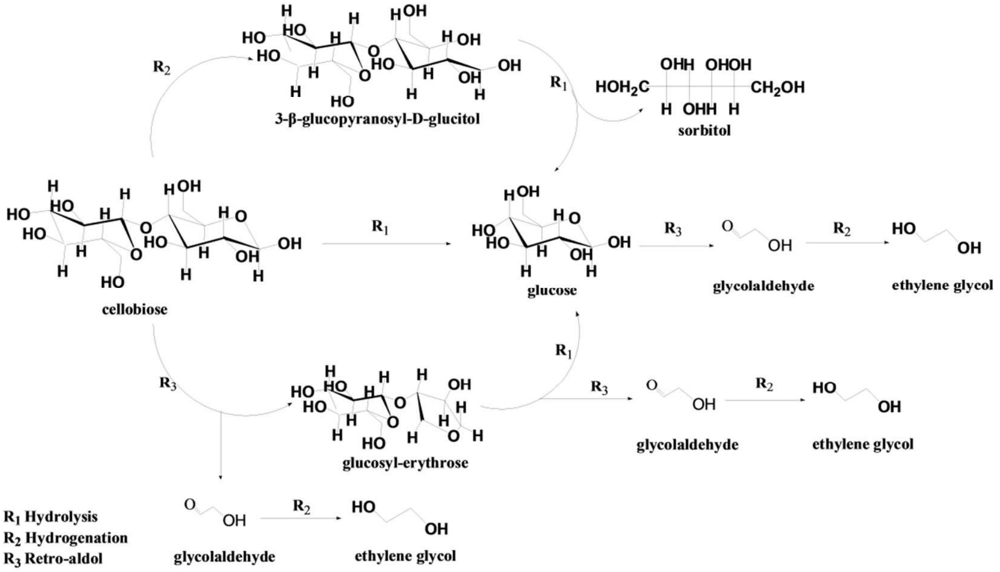

Scheme 2 Reaction pathways for cellobiose conversion catalyzed by PTA-Ru/AC for EG production.

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Table 1 Catalytic performance of different mixed catalysts for cellulose conversion

Entry	Catalyst	Conversion (%)	Yield (%)						
			Ery	EG	1,2-PG	Sor	1,2-BOD	1,3-PG	Man
1	PTA-Ru/AC	100	2.7	53.1	5.5	12.4	6.2	2.2	T
2	PTA-Pd/AC	95.0	T	27.1	15.1	3.0	1.9	T	0.4
3	PTA-Pt/AC	100	T	23.2	12.8	3.3	6.0	T	0.2
4	STA-Ru/AC	95.5	2.8	16.3	6.8	8.5	4.0	2.5	1.8
5[a]	PTA-Ru/AC	N	1.7	27.4	4.9	5.7	7.0	T	1.1
6[b]	PTA-Ru/AC	N	1.6	28.2	3.1	2.6	3.6	T	0.5

Reaction conditions: 0.5 g cellulose, 50 g water, 300 ppm PTA (or STA), 0.025g M/AC (M is the metal), 6 MPa H_2 (room temperature),1000 rpm stirring rate, 250 ºC and 50 min. a) 1.5 g cellulose; b) 1.5 g cellulose, 150 min reaction time. EG, 1,2-PG, 1,2-BDO, 1,3-PG, Ery, Man and Sor are abbreviations for ethylene glycol, 1,2-propylene glycol, 1,2-butanediol, 1,3-propylene glycol, erythritol, mannitol and sorbitol, respectively. T and N represent trace amount and not calculated, respectively.

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Table 2 Ru concentrations in the liquid phase after each reaction detected by AAS.

Recycled time	Ru concentration (ppm)	Leached Ru (wt%)
0	0	0
1	0	0
2	0	0
3	0	0

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Table 3 Comparison of the catalytic performance of cellulose and cellobiose under the same reaction conditions.

Feedstock	Yield (%)						
	Sorbitol	Erythritol	Glycerol	1,2-PG	EG	1,3-PG	GA
cellulose	3.32	1.17	2.08	6.02	31.6	trace	trace
cellobiose	3.40	2.06	2.10	11.4	24.0	trace	trace

Reaction conditions: 0.5 g cellulose (or cellobiose), 50 g water, 300 ppm PTA, 0.025 g Ru/AC, 6 MPa H_2 (room temperature), 1000 rpm stirring rate, 230 °C and 20 min. 1,2-PG, EG, 1,3-PG and GA are the abbreviations of 1,2-propylene glycol, ethylene glycol, 1,3-propylene glycol, glycolaldehyde, respectively.

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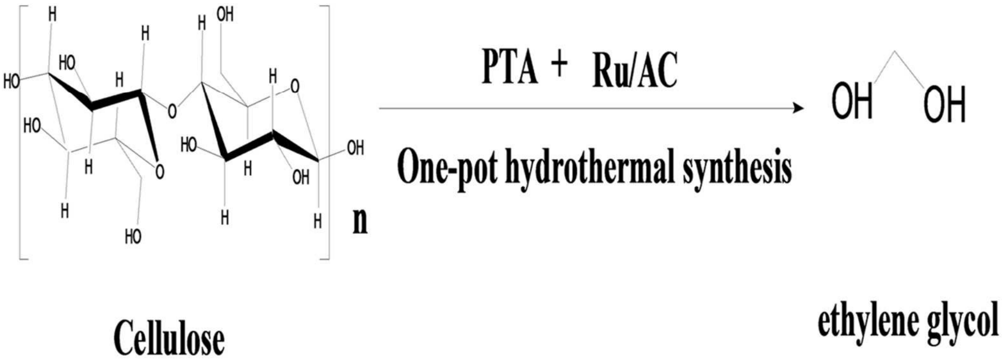

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