One-Pot Hydrolytic Hydrogenation of Carbohydrates to Hexitols Catalyzed by Ru Loaded P And Si-Containing Hierarchical Porous Biochars with Excellent Catalytic Efficiency

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Abstract

The one-pot hydrolytic hydrogenation of carbohydrates to sugar alcohols is one of the important upgrading conversions of biomass, which still needs to develop the newly acidic carriers to lower the cleavage energy of β -1,4-glycosidic bonds and the concomitant serious side-reactions in the key first-step hydrolysis. This paper discloses that a forestry processing waste bamboo powder can be converted into the P and Si-containing porous biochar (PSBC) *via* inserting silica sol, impregnating concentrated phosphoric acid (H_3PO_4) and heating carbonization. Due to the improved porosity, strong acidity and affinity to β -1,4-glycosidic bonds, the suggested PSBC exhibits an outstanding catalysis performance for the hydrolysis of cellulose, cellobiose, especially sucrose and inulin, affording *ca.* 76.2% glucose yield in cellulose hydrolysis at 150°C. PSBC can efficiently and uniformly load Ru nanometer particles (average size of 1.5 nm) to fabricate 1%Ru/PSBC as an excellent bifunctional catalyst for the one-pot conversion of these carbohydrates to hexitols, affording *ca.* 85.2% hexitols with 51.7 h^{-1} TOF in cellulose conversion under 150°C and 3 MPa H_2 pressure. This work not only provides an effective strategy for the preparation of biomass-derived bifunctional catalysts, but also it opens up new voyages for the development of efficient bio-refining.

1. Introduction

Cellulosic biomass has received focused attention as an abundant and sustainable resource for the production of bio-derived chemicals and fuel (M. Jarvis 2003; G.W. Huber and A. Corma 2010). A particularly promising reaction in water is the one-pot hydrolytic hydrogenation of cellulose and other carbohydrates to sugar alcohols (R. Palkovits et al. 2010; A. Fukuoka and P.L. Dhepe 2006; C. Luo et al. 2010). Among carbohydrates-derived sugar alcohols, sorbitol, as one of the twelve most important bio-based platform chemicals, has been extensively used in food, cosmetic, medical and paper industries (B. Kusserow et al. 2003), also, it is a building block in the synthesis of fine chemicals (B. Kusserow et al. 2003) and a raw material in the production of H_2 and liquid alkane fuels (H. George W 2004; B. Kusserow et al. 2003). Therefore, it is highly appreciated to develop a highly efficient cellulose transformation to sorbitol by two-steps and especially one-step catalytic procedures, but the first step hydrolysis of cellulose catalyzed by acids is a challenging task under mild conditions owing to its robust crystalline structure. So that the early researches are mainly focused on the two-steps way, including cellulose hydrolysis to glucose under the catalysis of enzymes (Y.H. Zhang and L.R. Lynd 2004) or acid catalyst (W.S. Mok et al. 1992), followed by a fast metal-catalyzed hydrogenation of the formed glucose to sorbitol (G. Liang et al. 2012). However, the complex operating procedures and especially the further degradation of unstable glucose into caramel and tars/humins (J. Geboers et al. 2010) cause the two-step method the high operating costs but low conversion efficiency. The one-pot valorization of cellulose to sorbitol catalyzed by bifunctional catalysts bearing acid and metal functions is superior to the above two-steps conversion in cutting the operating costs and improving the upgrading efficiency of cellulose owing to the fast hydrogenation of glucose to the more stable sorbitol. So that the one-pot method has received focused attention and some representative bifunctional catalytic systems summarized in Table

1 could achieve 31-87% sorbitol/hexitol yields with 0.6-53.7 h⁻¹ TOFs in the one-pot conversion of cellulose to sugar alcohols (R. Palkovits et al. 2010; A. Fukuoka and P.L. Dhepe 2006; C. Luo et al. 2010; L.N. Ding et al. 2010; X. Xie et al. 2014; A. Negoii et al. 2014; N. Rey-Raap et al. 2019; Y. Liao et al. 2014; L.S. Ribeiro et al. 2017; Weiping et al. 2009; J. Xi et al. 2013; W. Zhu et al. 2014; Z. Li et al. 2019; J.W. Han and H. Lee 2012; L. Mi et al. 2011; J. Geboers et al. 2010; S. Van de Vyver et al. 2012). The one-pot conversion of microcrystalline cellulose to hexitols usually needs the harsh reaction conditions owing to its robust crystalline structure, providing relatively low hexitol yields of 31-58.2% even at the high temperatures (190-240°C) (A. Fukuoka and P.L. Dhepe 2006; C. Luo et al. 2010; J. Geboers et al. 2010; L.N. Ding et al. 2010; X. Xie et al. 2014). The degradation reactivity of microcrystalline cellulose can be improved by ball-milling or phosphoric acid (H₃PO₄) pre-treatment method owing to the destruction of its super strong hydrogen bonding network (Weiping et al. 2009; J. Xi et al. 2013), as a result, its cascade conversion catalyzed by the bifunctional catalysts (N. Rey-Raap et al. 2019; Y. Liao et al. 2014; L.S. Ribeiro et al. 2017; J. Xi et al. 2013; W. Zhu et al. 2014; J.W. Han and H. Lee 2012; L. Mi et al. 2011; Z. Li et al. 2019; P. Patnukao and P. Pavasant 2008; Weiping et al. 2009; F.Z. Azar 2020; M. Adsuar-García and J.X. Flores-Lasluisa 2018) is more efficiently proceed at relatively low temperature (150-205°C) compared to the untreated one, Ru/AG-CNT₁₂₀₀ (N. Rey-Raap et al. 2019) and Ru/C-ZPA (Y. Liao et al. 2014) provide the highest TOF (53.7 h⁻¹) and sorbitol yield (85.5%), respectively. And the reaction temperature may be reduced to 180-150°C when using strong acidic supports-loaded Ru catalysts (W. Zhu et al. 2014; J.W. Han and H. Lee 2012; Z. Li et al. 2019; S. Van de Vyver et al. 2012). However, in the existing one pot conversion systems, the first step hydrolysis efficiency of cellulose macromolecules is still limited by high reaction energy barrier and low mass transfer rate, which is likely due to the used supports having more or less shortcomings in the acidity, porosity and especially affinity to β-1,4-glycosidic bonds. Still, it is highly desirable to develop the new acidic support to meet with the requirements of cellulose hydrolysis to the excellent solid acid catalysts.

Recently, biomass-derived carbon materials have received focused attention as cheap and potential adsorbents (E. Yang et al. 2018; P. Patnukao and P. Pavasant 2008) and solid acid catalysts (S. Suganuma et al. 2011; Y. Wu et al. 2010; J.A. Sánchez et al. 2011; L. Geng et al. 2011). Among them, the porous biochars carbonized by phosphoric acid under moderate temperature (300-450°C) have rich micro-mesopores and a small amount of strongly acidic sites through the formation of oxygen– phosphorus surface groups (J. Bedia et al. 2009; A.M. Puziy et al. 2010; J. Bedia et al. 2011; F.J. García-Mateos et al. 2018; L. Cao et al. 2018; Z. Fu et al. 2012), and they exhibit good acid-catalytic activities for the etherification (A.M. Puziy et al. 2010) and dehydration (J. Bedia et al. 2011) of alcohols and the conversion of starch-rich food waste into glucose and 5-HMF (L. Cao et al. 2018). And more recently, we found that the P-containing biochar (PBC) fabricated under optimal conditions (F. Mao et al. 2020) has a much stronger affinity to β-1,4-glycosidic bonds and a higher catalytic activity for cellulose hydrolysis compared to our previously reported ionic liquids (ILs)-functionalized biochar sulfonic acids (BCSA-ILs) with mimicking cellulase functions (Zhang et al. 2012), so that PBC is a more potential mimetic catalyst for cellulose hydrolysis. On the other hand, we found that the high porosity of PBC is conducive to fabricate an excellent Ru-based bifunctional catalyst for the hydrolytic hydrogenation of cellulose to sorbitol

(87.1% yield, 4.0 TOF, see Table 1). However, it is necessary to further enhance the strong acidic sites and porosity of PBC and its affinity to β -1,4-glycosidic bonds to improve the mimetic cellulose functions and Ru loading efficiency. In order to achieve these goals, here, we firstly disclose that a forestry processing waste bamboo powder as a main raw material is used to fabricate the P and Si-containing porous biochars (PSBCs) by inserting silica sol, impregnating concentrated phosphoric acid (H_3PO_4) and then heating carbonization. The suggested PSBCs are easily synthesized in low-cost and large-scale by the above three-step procedures (see Scheme 1), but also the PSBC prepared under optimal conditions has significantly improved strong acidity and affinity to β -1,4-glycosidic bonds, as well as its extremely high surface areas mainly contributed by mesopores and macropores, which is very conducive to the first step hydrolysis of cellulose macromolecules *via* lowering the cleavage energy of β -1,4-glycosidic bonds and improving the mass transfer rate. Therefore, PSBC is considered to be a better biomimetic catalyst for cellulose hydrolysis and an acidic carrier for loading Ru NPs than PBC. In the one-step hydrolytic hydrogenation of cellulose to sorbitol in water, the constructed bifunctional catalyst 1%Ru/PSBC, compared to the existing hydrolytic hydrogenating catalysis systems listed in Table 1, possesses the outstanding comprehensive advantages in catalyst availability, reaction conditions, catalysis efficiency and sorbitol yield. We anticipate that this excellent and environmentally benign catalyst will provide a new possibility for the large-scale production of hexitols from the biomass-derived carbohydrates.

Table1 One-pot hydrolytic hydrogenation of cellulose using various bifunctional catalysts.

Catalyst	Substrate	Reaction conditions	Product yield/%	TOF ^a /h ⁻¹	Ref.
H ₂ SO ₄ and 5%Ru/C	Microcrystalline cellulose	160°C, 5 h, 5 MPa H ₂	Hexitol (60.5)	7.6	(R. Palkovits et al. 2010)
2.5%Pt/Al ₂ O ₃	Microcrystalline cellulose	190°C, 24 h, 5 MPa H ₂	Hexitol (31.0)	8.7	(A. Fukuoka and P.L. Dhepe 2006)
4%Ru/C	Microcrystalline cellulose	245°C, 0.5 h, 6 MPa H ₂	Hexitol (39.3)	42.0	(C. Luo et al. 2010)
17%Ni/ZSM-5	Microcrystalline cellulose	230 °C, 6 h, 4 MPa H ₂	Hexitol (58.2)	9.7	(G. Liang et al. 2012)
16%Ni ₂ P/AC(1:2)	Microcrystalline cellulose	225 °C, 1.5 h, 6 MPa H ₂	Sorbitol (48.4)	2.2	(L.N. Ding et al. 2010)
5%Ru/[Bmim] ₃ PW ₁₂ O ₄₀	Microcrystalline cellulose	225°C, 24 h, 6 MPa H ₂	Sorbitol (44.8)	1.2	(X. Xie et al. 2014)
3%Ir/BEA-SnF ₄	Cellulose	180°C, 3 h, 1.6 MPa H ₂	Hexitol (73.0)	22.3	(A. Negoï et al. 2014)
5% Ru-TSu	Cellulose	190°C, 3 h, 5 MPa H ₂	Hexitol (45.2)	22.5	(M. Adsuar-García and J.X. Flores-Lasluisa 2018)
0.4%Ru/AG-CNT ₁₂₀₀	Ball-milled cellulose	205°C, 3 h, 5 MPa H ₂	Sorbitol (64.1)	53.7	(N. Rey-Raap et al. 2019)
ZPA and 5% Ru/C	Ball-milled cellulose	190°C, 2.5 h, 6 MPa H ₂	Hexitol (85.5)	2.2	(Y. Liao et al. 2014)

^a Turnover frequency (TOF) related to the theoretically loaded Ru; ^bTOF related to the actually loaded Ru.

Catalyst	Substrate	Reaction conditions	Product yield/%	TOF ^a /h ⁻¹	Ref.
0.4%Ru-3%Ni/AC or 0.4%Ru-3%Ni/CNT	Ball-milled cellulose	205°C, 1 h, 5 MPa H ₂	Sorbitol (74.0 or 71.0)	19.4	(L.S. Ribeiro et al. 2017)
1%Ru/CNT	H ₃ PO ₄ -treated cellulose	180°C, 24 h, 5 MPa H ₂	Sorbitol (69.0)	0.6	(Weiping et al. 2009)
5%Ru/NbOPO ₄ -pH2	Ball-milled cellulose	170°C, 24 h, 4 MPa H ₂	Sorbitol (59.6)	0.8	(J. Xi et al. 2013)
3%Ru/SiO ₂ -SO ₃ H	Ball-milled cellulose	150°C, 10 h, 4 MPa H ₂	Sorbitol (61.2)	1.5	(W. Zhu et al. 2014)
5%Ru/CCD-SO ₃ H	Ball-milled cellulose	180°C, 10 h, 4 MPa H ₂	Sorbitol (63.8)	1.0	(Z. Li et al. 2019)
10%Ru/AC-SO ₃ H	Ball-milled cellulose	165°C, 36 h, 5 MPa H ₂	Sorbitol (71.1)	10.6	(J.W. Han and H. Lee 2012)
7.5%Ni/ CNFs	Ball-milled cellulose	190°C, 24 h, 6 MPa H ₂	Hexitol (76.0)	0.3	(S. Van de Vyver et al. 2012)
1%Ru/Cs ₃ PW ₁₂ O ₄₀	Ball-milled cellulose	160°C, 24 h, 2 MPa H ₂	Sorbitol(43.0)	1.1	(L. Mi et al. 2011)
1%Ru/SA	Ball-milled cellulose	190°C, 3 h, 5 MPa H ₂	Sorbitol(48.0)	39.9	(F.Z. Azar 2020)
5%Ru/PBC	H ₃ PO ₄ -treated cellulose	150°C, 8 h, 5 MPa H ₂	Sorbitol (87.1)	4.0	(F. Mao et al. 2020)
1%Ru/PSBC	H ₃ PO ₄ -treated cellulose	150°C, 6 h, 3 MPa H ₂	Hexitol (85.2)	51.7/101 ^b	This Work
^a Turnover frequency (TOF) related to the theoretically loaded Ru; ^b TOF related to the actually loaded Ru.					

2. Experimental Section

2.1. Reagents and Materials

Materials and reagents used in this study were forestry processing waste bamboo powder, water glass, concentrated phosphoric acid (H_3PO_4), ruthenium (III) chloride (RuCl_3), ethylene glycol, microcrystalline cellulose, inulin, cellobiose, sucrose, glucose, sorbitol, all of which were of analytical grade. Water used in the laboratory was prepared by a Millipore Milli-Q ultrapure water-purification system.

2.2. Preparation of PSBC catalyst

3 g bamboo powder (BP) was treated with 30 mL deionized water at 100°C for 3 h and then further treated with 300 mL home-made acidic silica sol (0.05 M, pH, 3.5, its preparation could be found in our recent publication(Z. Chen et al. 2019)) at 50°C for 72 h to obtained a silica-inserted BP (SBP) material and the silica content of SBP estimated by high temperature combustion at 950°C for 9 h in air was *ca.*20 wt%. Then, SBP was impregnated with the specified amount of 85 wt% H_3PO_4 (the mass ratio (X) of H_3PO_4 with SBP was 1 to 3) at the stated temperature (Y, 30, 60 and 100°C) for 12 h, followed by that the impregnated sample was heated at rate of $10^\circ\text{C min}^{-1}$ and carbonized at the stated temperature (Z, 300, 350, 400 and 450°C) for 5 h under N_2 atmosphere, Finally, the carbonized sample was repeatedly washed with plenty of hot water and dried at 100°C to obtain the P and Si-containing biochars (marked as PSBC-X-Y-Z). In addition, the optimized PBC-400 without inserting silica previously reported by us (F. Mao et al. 2020), the direct carbonization material (SBC-400) of SBP and the silica activated with three-fold amount of H_3PO_4 (PS-400) at 400°C were used as three control samples. The P contents of these acidic supports measured by ICP method were listed in Table S1 (See Supporting Information (SI)).

2.3. Preparation of 1%Ru/PSBC catalyst

1%Ru/PSBC was prepared using PSBC-3-60-400 (1 g) and RuCl_3 aqueous solution (0.07 M, 0.7 mL, corresponding to 1 wt% Ru theoretical loading) as the two main raw materials and the specific operating procedure could be found in our recently published work (F. Mao et al. 2020). The actual Ru loading amount of 1%Ru/PSBC measured by ICP method was *ca.*0.51 wt%. In addition, by the use of same conditions as 1%Ru/PSBC, 1%Ru/PS and 1%/PBC as two control catalysts were also prepared using PS-400 and PBC-400 as the carriers, respectively.

2.4. Characterization of samples

Surface acid density of samples was measured by chemical titration and the specific operating procedures could be found in our recent publication(F. Mao et al. 2020). Phosphorus content of the samples was determined with an ICP-OES equipment (PerkinElmer 8300). Thermal stability of the samples was examined using the thermogravimetric analysis (TGA) (NETASCH, STA409PC) with temperature from 25 to 960°C under flowing O_2 (heating rate of $20^\circ\text{C min}^{-1}$). Nitrogen adsorption-desorption isotherms of the samples were measured at liquid nitrogen temperature using Tristar 3000

fully automatic surface area and pore analyzer. Transmission FT-IR spectra of the samples were recorded from 400 to 4000 cm^{-1} on a Nicolet Nexus 510P FT-IR spectroscopy using a KBr disk. Powder X-ray diffraction (XRD) analyses of the samples were conducted on a Rigaku 2550 X-ray diffractometer using Cu K α radiation ($\lambda = 0.15406 \text{ nm}$) and a graphite monochromator, operated at a voltage of 40 kV, a current of 250 mA and a slit width of 0.15 mm. XRD patterns were collected in the angular range of 10–80° with a scanning rate 2°/min. X-ray photoelectron spectroscopy (XPS) of the samples was measured on a VG Multi Lab 2000 system with a monochromatic Mg-K α source operated at 20 kV. Transmission electron microscopy (TEM) images of the samples were obtained from a JEOL JEM-2100 transmission electron microscope at an accelerating voltage of 200 kV.

2.5. Adsorption experiment of cellobiose

The affinity of acidic carriers to β -1,4-glycosidic bonds was examined by cellobiose adsorption experiments and the specific operation process of cellobiose adsorption could be found in our previous publications (Zhang et al. 2012).

2.6. Conversion of carbohydrates

The operating processes for cellulose hydrolysis and its hydrolytic hydrogenation were described as follows: 0.3 g carbohydrate (the activation operating of cellulose with H_3PO_4 could be found in our previous work (F. Mao et al. 2020)), 0.05 g PSBC catalyst, and 25 mL deionized water were introduced into a 100 mL high pressure reactor, and the hydrolysis reaction was carried out at 120–150°C for 2–6 h with a stirring rate of 500 rpm. The hydrolytic hydrogenation of carbohydrate catalyzed by 1% Ru/PSBC was carried out under the above conditions and 3 MPa hydrogen atmosphere. After reactions, the catalyst was recovered from the cooled reaction mixture by centrifugation and then repeatedly washed by hot water and dried at 60°C overnight for next use. The obtained filtrate was subjected to the analysis of carbohydrate-derived products using Alltech 1500 HPLC equipped with a BP-100 H^+ carbohydrate column and the specific analysis conditions and quantitative method of the products could be found in our previous work (F. Mao et al. 2020).

3. Results And Discussion

3.1. Catalytic performance of acidic supports for carbohydrate hydrolysis

Table 2 lists the data for the degradation of cellulose and other carbohydrates catalyzed by various acidic supports in water at 150 °C. Entry 1 shows that SBC-400, due to the absence of strong acidity (See Table 4 later), can not degrade cellulose under the present hydrolysis conditions. While another reference carrier PS-400 is active for cellulose hydrolysis owing to its strong acidity, but it only achieves a low 20% glucose yield, along with the production of 2.3% cellobiose (Entry 2), which is likely due to lack of its affinity to β -1,4-glycosidic bonds of cellulose. In sharp contrast, all the P-containing PSBC materials are active for

cellulose hydrolysis (Entries 3-10), providing glucose as the main degradation product (25.6-76.9% yield), along with the production of small amount of cellobiose (0-5.6% yield) and 5-HMF (0.8-2.8% yield). The catalytic activity of PSBC is significantly influenced by the preparation conditions, presenting a continuous increase with hoisting the impregnation dosage of H_3PO_4 (Entries 3-5) or the carbonization temperature (Entries 3, 6-8). In addition, the catalytic activity of PSBC increases first and then decreases with hoisting the impregnation temperature of H_3PO_4 from 30 to 100°C (Entries 4, 9-10). The above reaction results can well reflect a close relationship between the hydrolysis activity of PSBC and its strong acidity and its affinity to β -1,4-glycosidic bonds of cellulose measured later. The best two PSBC carriers can achieve almost 100% cellulose conversion with above 76% glucose yield (Entries 5 and 8), which is higher than the silica-free PBC-400 (Entry 11, 85.3% conversion and 56.7% glucose yield) and most of the sulfonated biochar materials in cellulose hydrolysis (Zhang et al. 2012; S. Suganuma et al. 2011; Y. Wu et al. 2010). And these two PSBC carriers can provide a higher about 10% than PBC-400 in glucose selectivity, suggesting that their hierarchical pores (see Fig. 2 and Table 5 later), can enhance the mass transfer rate of the hydrolyzed intermediates and products, which are favorable of accelerating the hydrolysis of cellulose and lowering the further degradation of the products to caramel, tars and humins (J. Geboers et al. 2010; D.M. Alonso et al. 2013), as supported by the smallest difference (about 20%) between cellulose conversion and the above hydrolyzed products in Entries 5 and 8 as well as the reaction time-dependence of cellobiose conversion and glucose yield shown in Fig. S1, Entries 12 reveals that PSBC-3-60-400 rapidly degrades cellobiose to yield up to 88.8% glucose at 150°C for 2 h. And this acidic support has more outstanding catalytic efficiency for the hydrolysis of sucrose and inulin with relatively active α -1,2-glycosidic bond and β -2,1-glycosidic bond (Y. Dai et al. 2017), affording *ca.* 96% total yield of glucose and fructose even under milder conditions (120°C, 2 h). In addition to the above merits, the significant reduction in the by-products is also noticed upon these two high reactive carbohydrates, which should be due to the rapid hydrolysis and mass transfer rates and milder reaction conditions.

Table 2
Hydrolysis of cellulose and other carbohydrates in water over various acidic carriers^a

Entry	Acidic carrier	Conv. /%	Yield of products /%		
			Cellobiose	Glucose/fructose	5-HMF
1	SBC-400	0	0	0	0
2	PS-400	50.4	2.3	20.0	0
3	PSBC-1-60-400	65.1	5.6	25.6	0.8
4	PSBC-2-60-400	87.2	2.2	49.8	2.1
5	PSBC-3-60-400	99.0	0.1	76.2	2.7
6	PSBC-3-60-300	89.6	1.2	57.1	2.5
7	PSBC-3-60-350	92.5	2.7	63.8	2.3
8	PSBC-3-60-450	99.0	0	76.9	2.8
9	PSBC-3-30-400	78.7	7.3	40.7	1.4
10	PSBC-3-100-400	93.3	0.9	69.8	2.1
11 ^b	PBC-400	85.3	3.7	56.7	1.6
12 ^c	PSBC-3-60-400	99.5	0.5	88.8	1.6
13 ^d	PSBC-3-60-400	100	0	46.6/50.3	0
14 ^e	PSBC-3-60-400	100	0	14.8/80.2	0
^a Reaction condition: cellulose, 0.3 g; catalyst, 0.05 g; H ₂ O, 25 mL; reaction temperature, 150°C; reaction time, 6 h; ^b Data of coming from the literature(F. Mao et al. 2020), catalyst, 0.1 g, reaction time, 8 h; ^c Using cellobiose as a substrate, reaction time, 2 h; ^d Using sucrose as a substrate, reaction temperature, 120°C, reaction time, 2 h; ^e Using inulin as a substrate, reaction temperature, 120°C, reaction time, 2 h.					

In the following experiments, the bifunctional catalytic performance of 1%Ru/PSBC for the one-pot hydrolytic hydrogenation of carbohydrates to sorbitol/mannitol in water under H₂ was investigated using or referencing the optimized variables (0.05 g catalyst, 150°C, 6 h, 3 MPa H₂) of the one-pot conversion of cellulose to sorbitol (see Fig. S2), which was compared to the data obtained from the one-pot conversion of cellulose to sorbitol catalyzed by two reference catalysts 1%Ru/PS and 1%Ru/PBC. As shown in Table 3, 1%Ru/PS has a low activity for the one-step hydrolytic hydrogenation of cellulose owing to the low hydrolytic activity of its carrier, providing *ca.* 38.3% sorbitol and 1% mannitol yields (Entry 1). Entry 2 shows that our previously reported 1%Ru/PBC exhibits a good catalysis activity for this one-pot conversion, providing *ca.* 77% sorbitol yield. But even if using the intensified reaction conditions (doubled 0.1 g catalyst, 5 MPa H₂ and 8 h), this catalytic system still inevitably produces a small amount of

cellobiitol (2.1% yield) as the hydrogenated product of cellobiose. Encouragingly, 1%Ru/PSBC has the highest catalytic activity for the one-step conversion and can achieve 83.2% sorbitol and 2% mannitol as the hydrogenated products under the optimal conditions (Entry 3). The two turnover frequencies (TOFs/h⁻¹) calculated based on the theoretical and practical Ru loadings are up to 51.7 and 101, respectively, which are much higher than the TOF values of two control catalysts. Entry 4 reveals that 1%Ru/PSBC exhibits an slightly enhanced catalysis efficiency for the hydrolytic hydrogenation of cellobiose under the same conditions as Entry 3, giving 85% sorbitol and 2% mannitol yields with 51.4 TOF (101 actual TOF). And even if using more mild conditions of 120°C and 2 h, 1%Ru/PSBC can also well function and exhibit an excellent catalytic efficiency (93.7-93.9% hexitols yields, 166.4-173.5 TOFs or 326-340 actual TOFs) for the one-pot conversion of sucrose and inulin, respectively affording 60.9% sorbitol/33% mannitol and 47% sorbitol/45.7% mannitol as the corresponding hydrogenated products (Entries 4-6). It is noteworthy that the yields of cellulose-hydrogenated products over 1%Ru/PS and 1%Ru/PBC are much higher than those of its hydrolysates over the corresponding acidic carriers, which is likely due to the following facts: The loaded Ru NPs can dissociate H₂ to generate spillover H species and the latter contributes to cellulose hydrolysis (M. Liu et al. 2011). On the other hand, the formed glucose can be rapidly hydrogenated to the more stable sorbitol, thus remarkably blocking-up its polycondensation by-reactions (J. Geboers et al. 2010; D.M. Alonso et al. 2013). In sharp contrast, 1%Ru/PBC and its carrier can achieve almost the same yields of carbohydrates-hydrogenated and -hydrolyzed products, respectively, further confirming that the excellent hydrolytic hydrogenation performance of 1%Ru/PSBC for these carbohydrates should be attributed to the fast hydrolysis and mass transfer rates of its carrier.

Table 3

Synthesis of hexitols from carbohydrates in water over various Ru-loaded carriers^a

Entry	Substrate	Catalyst	TOF ^b /h ⁻¹	Conv. /%	Yield of products /%		
					Cellobiitol	Sorbitol	Mannitol
1	Cellulose	1%Ru/PS	24.5	0	0	38.3	1.0
2 ^c	Cellulose	1%Ru/PBC	18.7	94.3	2.1	77.0	1.0
3	Cellulose	1%Ru/PSBC	51.7/101 ^d	100	0	83.2	2.0
4	Cellobiose	1%Ru/PSBC	51.4/101 ^d	100	0	85.0	2.2
5 ^e	Sucrose	1%Ru/PSBC	166/326 ^d	100	0	60.9	33.0
6 ^e	Inulin	1%Ru/PSBC	174/340 ^d	100	0	47.0	45.7

^a Reaction condition: substrate, 0.3 g; catalyst, 0.05 g; H₂O, 25 mL, 3 MPa H₂, reaction temperature, 150°C; reaction time, 6 h; ^b Turnover frequency (TOF) calculated based on all the hydrogenated products (mole)÷the theoretically loaded Ru (mole) of catalyst÷time (h); ^c Data of coming from the literature (F. Mao et al. 2020), catalyst, 0.1 g, 5 MPa H₂ reaction time, 8 h; ^d TOF values calculated based on the practically loaded Ru; ^e Reaction temperature, 120°C, reaction time, 2 h.

Finally, the recycle runs for one-pot hydrolytic hydrogenation of cellulose and the direct hydrogenation of glucose were used to check the stability of 1%Ru/PSBC under the same conditions as Entry 3 of Table 3. Fig. 1a shows that after three recycle runs, cellulose conversion and sorbitol yield decrease from 100 to 88.7% and from 83.2 to 64.3%, respectively, which corresponds to the generation and increase of cellobiitol, indicating the catalyst gradually deactivates with its recycling times. On the contrary, the catalyst exhibits an excellent recyclability for the hydrogenation of glucose and sorbitol yield always maintains *ca.* 85% during three recycling runs (See Fig. 1b). And the catalyst also exhibits an improved reusability for the hydrolytic hydrogenation of cellobiose (Tables S2). The fact that the strong acid amount of catalyst is remarkably reduced from 0.40 to 0.26 mmol.g⁻¹ after three recycling runs, supporting that the deactivation of catalyst in the recycling runs of cellulose one-pot conversion should be mainly due to the leaching of its strong acid groups. On the other hand, the concomitant by-products (humans) during the one-pot conversion likely deposit on the acidic sites and Ru NPs, thus poisoning the bifunctional activities of catalyst, as supported by the reduction in the BET area and pore volume of the recovered catalyst after three successive runs (See the porosity later-described). Notably, the reusability of 1%Ru/PSBC in the recycle runs for one-pot hydrolytic hydrogenation of cellulose is superior to our previously reported 5% Ru/PBC (F. Mao et al. 2020), which should be mainly ascribed to the reduction in the humans deposited in the catalyst' pores, supported by a fact that the reduction extent (15.8%) of BET areas in

the recovered 1%Ru/PSBC is much lower than that (35%) in the recovered 5%Ru/PBC. This further supports the positive effect of the meso-macropores of 1%Ru/PSBC on improving the mass transfer efficiency and lowering the by-reactions in the one pot conversion of cellulose macromolecules,

3.2. Characterization of catalysts

In order to reasonably explain the above catalytic hydrolysis and hydrogenation data, a serious characterization and analysis methods were used to investigate the acidic supports and bifunctional catalysts and the obtained results are described as follows.

Surface acidity and affinity to β -1,4-glycosidic bonds

Table 4 lists the data for the surface acid density, and cellobiose adsorption value of PSBC materials prepared under different conditions, as well as the compared data for three control samples. Entries 1 and 2 reveal that the phosphorus-free material SBC-400 only has weakly Brønsted acidic (BA) carboxyl (COOH , 0.24 mmol g^{-1}) and hydroxyl (OH , 0.57 mmol g^{-1}) groups, while the biochar-free PS-400 only has the strong BA groups (0.43 mmol g^{-1}), suggesting that the strong and weak BA sites should originate from the oxygen-phosphorus species and biochars, respectively. Entries 3-12 demonstrate that all the H_3PO_4 -activated PSBC materials, including the silica-free PBC-400, have higher weakly BA groups than SBC-400 but also present a strong B acidity attributable to the P-containing acid protons (J. Palomo et al. 2017). It can be further seen from Table 4 that SBC-400 and PS-400 have a poor and even non adsorption cellobiose capacity, while PBC-400 and PSBC materials all exhibit the enhanced adsorption capacities for cellobiose. Notably, several PSBC materials prepared under better conditions possess higher strong BA groups and especially adsorption capacities for cellobiose than PBC-400 (Entries 10-12 vs Entry 3). Moreover, the strong BA groups and cellobiose adsorption amount of PSBC materials are influenced by the preparation conditions, and they can be markedly improved by the use of high H_3PO_4 amount and suitable temperature (60°C) in impregnation and by using highly carbonized temperature (Entries 4-12). The strong BA content (0.40 mmol g^{-1}) and cellobiose adsorption value (213 mg g^{-1}) of a typical PSBC-3-60-400 are higher than those (0.28 mmol g^{-1} , 150 mg g^{-1}) of PBC-400. These findings support that the inserted silica, as supported by the P contents measured with ICP (see Table S1), contribute to the incorporation of P-containing groups into the skeleton of PSBC materials but also significantly enhance the affinity to β -1,4-glycosidic bonds, which should be very beneficial to catalyze the hydrolysis of cellulose and other carbohydrates, as supported by the data in Table 2.

Table 4

Surface acid groups of PSBCs and three control samples and their adsorption values to cellobiose

Entry	Sample	Density of acidic groups (mmol.g ⁻¹)			Cellobiose adsorption value (mg.g ⁻¹)
		Strong acid	-COOH	-OH	
1	SBC-400	0	0.24	0.57	26.3
2	PS-400	0.43	0	0	0
3 ^a	PBC-400	0.28	0.57	0.59	149.7
4	PSBC-2-60-300	0.18	0.59	1.04	133.8
5	PSBC-3-60-300	0.19	0.76	1.14	141.5
6	PSBC-3-60-350	0.33	0.67	1.55	184.3
7	PSBC-1-60-400	0.15	0.46	0.96	117.5
8	PSBC-2-60-400	0.19	0.69	1.15	163.7
9	PSBC-3-30-400	0.09	0.39	0.74	58.7
10	PSBC-3-60-400	0.40	1.13	1.67	213.3
11	PSBC-3-100-400	0.39	0.73	1.48	204.9
12	PSBC-3-60-450	0.42	1.10	1.64	221.1
^a Coming from the literature(F. Mao et al. 2020)					

TGA: The thermal decomposition behavior of SBC-400 and PSBC materials under pure O₂ atmosphere was checked *via* the thermogravimetric analysis (TGA) technique and their TG and corresponding differential TG (DTG) curves are shown in Fig. 2a and 2b, respectively. The DTG curve of SBC-400 exhibits two weightlessness peaks about at 100 and 490°C, which should correspond to an evaporation of the adsorbed water molecules and an oxidation of carbon species. After heating to 900°C, the remaining weight percentage of this material is *ca.* 57.2 wt% based on its TG curve, which can be indicative of silica content in SBC-400. The TG and DTG curves of all PSBC materials display the above two weightlessness events but their weightlessness peaks for the oxidation of carbon species take place a splitting except for PSBC-3-60-450 and their splitting peaks at higher temperature (except for PSBC-3-60-300) has a positive shift of 4-19 °C compared to SBC-400 and such shift degree gradually increases with the carbonized temperature. Notably, the remaining weight percentages of all the PSBC materials are significantly lower than that of SBC-400 (see Fig. 2a and Table S3), presenting a gradual increase with the impregnated H₃PO₄ amount and especially with the carbonized temperature. These findings support that in carbonization of the impregnated SBP, one part of the inserted silica can react with H₃PO₄ to form

soluble Si (H_2PO_4)₄ (SSP), while the other part may be converted into the insoluble $\text{Si}_3(\text{PO}_4)_4$ and $\text{Si}(\text{P}_2\text{O}_7)$ (ISP) species (L. Wen 1994) and the ISP species, as more stable and active components can be generated more at the high H_3PO_4 amount and especially high carbonization temperature, which may improve the strong acid density of PSBC and its affinity to β -1,4-glycosidic bonds as well as the hydrolysis efficiency of carbohydrates, as supported by the data in Table 4 and Table 2.

Porosity

Low temperature nitrogen adsorption was used to measure the porosity of several typical materials and the calculated specific surface areas (S_{BET}), total pore volumes (V_p) and average porous sizes (D) are summarized in Table 5. Fig. 3 is the isotherms and BJH pore distribution curves of two typical materials PSBC-3-60-400 and 1%Ru/PSBC. According to the IUPAC classification, the isotherms of these two samples belong to type IV. At the low relative pressures of 0-0.5, they have a slow-increase of N_2 uptake without hysteresis, which corresponds to the micropore structure (F. Mao et al. 2020). At higher than 0.5 relative pressures, the isotherms present a fast-increase of N_2 uptake with type H4 of broad and conspicuous hysteresis, indicating that these two materials have the character of rich slit-shaped mesopores and macropores (A.M. Puziy and O.I. Poddubnaya 1998; J.C.P. Broekhoff and J.H. De Boer 1968). Different from the single micro-mesopore distribution in the BJH curve of PBC-400 (F. Mao et al. 2020), the BJH curves of these two materials display a typical double-pore distribution character that consists of micro-mesopores smaller than 3 nm and meso-macropores more than 5 nm (see two inset in Fig. 3). The porous parameters listed in Table 5 further reveal that SBC-400, like BC-300 (Z. Chen et al. 2019), is nearly nonporous (J. Zhang et al. 2012), while the PSBC materials, including its loading Ru sample have a very high porosity and their S_{BET} , V_p and D values are commonly higher than those of the corresponding PBC materials previously reported by us (F. Mao et al. 2020). And these three porous parameters are continuously and remarkably enhanced with elevating the carbonized temperature until 400 °C. After that, the S_{BET} and V_p values are obviously reduced at the carbonized temperature of 450°C. The BET areas of PSBC materials are composed of the external ($S_{\text{t-plot}}$) and internal (S_{micro}) surface areas with different ratios and their D values are between 5.33 and 6.28 nm, presenting a gradual and slow increase with the carbonized temperature. Notably, PSBC-3-60-400 has the highest BET area that is mainly contributed by the slit-shaped meso-macropores and the loaded Ru NPs on it remarkably reduce the S_{BET} and V_p values of 1%Ru/PSBC, including a slight decrease of the D value. And the recovered 1%Ru/PSBC after recycling runs has obviously reduced S_{BET} and V_p values compared to the fresh one, along with the increase of micropores. These findings support that H_3PO_4 is an excellent pore-forming agent, and its pore-forming effect is influenced by the carbonization temperature (L. Cao et al. 2018; J. Bedia et al. 2011). And the inserted silica can significantly enhance the pore-forming effect by perhaps reinforcing expansion of cellulosic structure but also contribute to the formation of macropores *via* their leaching in the soluble $\text{Si}(\text{H}_2\text{PO}_4)_4$ form, which should be very favorable of improving the mass transfer rate of carbohydrate macromolecules and responsible for the excellent hydrolytic activity and selectivity of PSBC-3-60-400, as supported by the data in listed in Table 2 and Table 3. The reduction in the porosity

of 1%Ru/PSBC should originate from the occupied pore effect of loaded Ru NPs and the further decrease in its porosity after three catalysis runs may originate from the occupied effect of catalyst's pores by the by-produced polymers in carbohydrate conversion (J. Zhang et al. 2012), which should be one of the reasons that lead to the catalyst deactivation during the cycling runs.

Table 5
Porous parameters of SBC-400, PSBCs and 1%Ru/PSBC.

Sample	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	$S_{\text{t-plot}}$ ($\text{m}^2\cdot\text{g}^{-1}$)	S_{micro} ($\text{m}^2\cdot\text{g}^{-1}$)	Pore Volume ($\text{cm}^3\cdot\text{g}^{-1}$)	Pore Size (nm)
SBC-400	39	–	–	–	–
PBC-400 ^a	1379	1046	233	0.81	2.35
PSBC-3-60-300	969	351	618	0.29	5.33
PSBC-3-60-350	1615	1343	272	1.34	5.51
PSBC-3-60-400	1617	1497	120	1.72	5.77
PSBC-3-60-450	1117	767	350	0.81	6.28
Fresh 1%Ru/PSBC	1549	1428	121	1.52	5.49
Recovered 1%Ru/PSBC	1305	1004	301	1.07	5.54

^a Data of coming from the literature(F. Mao et al. 2020).

FT-IR

Figure 5a illuminates that the FT-IR spectra of SBC-400 and PSBC-3-60-400 exhibit some characteristic absorption bands attributable to biochars and these bands include the stretching vibrations of OH in $3650\text{--}3000\text{ cm}^{-1}$, COOH at 1708 cm^{-1} , Ar-OH at 1610 cm^{-1} and polycyclic aromatics in $1400\text{--}1600\text{ cm}^{-1}$, which can be indicative of the aromatic carbon sheet structure with attached hydrophilic COOH and OH groups(B. Li et al. 2011). In addition, the FT-IR spectrum of SBC-400 exhibits three obvious IR bands at 1080 , 801 and 460 cm^{-1} that are assigned to the asymmetric and symmetric stretching vibrations of Si-O-Si bond and the asymmetric stretching vibration of Si-O-Si bond(Z. Chen et al. 2019), respectively. But these bands attributable to silica become weak and even vague in the FT-IR spectrum of PSBC-3-60-400 likely owing to the leaching of silica and especially their conversion to the insoluble IPS species. In addition, a FT-IR spectrum of the P-containing material displays one band at $1180\text{--}1188\text{ cm}^{-1}$ with a shoulder peak at 1160 cm^{-1} , originating from P=O or C-O stretching vibration in P=OOH or C-O-P groups(A.M. Puziy et al. 2002). And the shoulder band at 1160 cm^{-1} should be due to a P=O stretching vibration in $\text{Si}_3(\text{PO}_4)_4$ and SiP_2O_7 (R. Hubin 1967). But another band near 1082 cm^{-1} for the symmetrical

vibration of P-O-P bond in polyphosphate(S. Bourbigot et al. 1995), is indiscernible since it overlaps with the broad IR band of silica in this region. Also, some IR bands in $760\text{--}490\text{ cm}^{-1}$ are found in PSBC-3-60-400 but are absent in SBC-400 and our previously reported PBC materials(F. Mao et al. 2020), these bands likely originate from the above ISP species, as supported by an FT-IR spectrum of the H_3PO_4 -treated silica at 400°C (PS-400). These findings support the co-existence of P-containing carbonaceous and ISP species (likely including the incorporation of polyphosphate groups) in PSBC-3-60-400 material.

XRD

Figure 3b is the XRD patterns of PS-400, SBC-400, PSBC-3-60-300, PSBC-3-60-400 and 1%Ru/PSBC. A strong broad peak at 23.5° and a very weak broad peak at $35\text{--}50^\circ$ are observed in the XRD patterns of four biochars-containing materials, which are respectively assigned to amorphous carbon composed of aromatic carbon sheets oriented in a random fashion(J. Xi et al. 2013) and a axis of graphite structure(S. Sukanuma et al. 2008; M. Okamura et al. 2006), In addition, a series of sharp peaks in $10\text{--}50^\circ$ are also found in the PSBC materials, and they become strong to some extent when elevating the carbonized temperature from 300 to 400°C . These new diffraction peaks, which are absent in our previously reported PBC materials(F. Mao et al. 2020), should be attributable to the crystallized ISP species in PSBC materials, as supported by the XRD pattern of PS-400. Among these XRD peaks for the ISP species, two peaks at 22.9 and 25.4° are assigned to the crystallized $\text{Si}_3(\text{PO}_4)_4$, while another three peaks at 24.3 , 26.7 and 27.5° belong to the crystallized SiP_2O_7 (S. Zhao 1981). Notably, the characteristic diffraction peaks for meal Ru are not found in the XRD pattern of Ru-loaded catalyst, indicating that the loaded Ru NPs are small size and highly dispersed on PSBC support(J. Xi et al. 2013; B. Feng et al. 2012), as supported by the following TEM images.

XPS

X-ray photo-electron spectroscopy (XPS) was used to investigate the chemical states of the surface atoms of PS-400 and 1%Ru/PSBC and the recorded high resolution XPS spectra for the surface P and Ru atoms are shown in Fig. 4. The survey XPS spectra and surface atomic concentrations of these two samples could be found in Fig S3 and Table S4, respectively. Fig. 4a shows that a broad P 2p peak in $132\text{--}138\text{ eV}$ is found in the XPS spectrum of 1%Ru/PSBC, which can be assigned to the pentavalent tetracoordinated phosphorus of PO_4 species in phosphates and/or polyphosphates(A.M. Puziy et al. 2005). The P2p signal may be further deconvoluted into two main characteristic peaks by Gaussian simulation. One deconvoluted peak at 135.2 eV is consistent with the P 2p peak of PS-400, which should be assigned to phosphorus groups bound to silica (the above ISP species). Another peak at 134 eV , as previously observed in PBC materials(F. Mao et al. 2020), is attributed to phosphorus groups bound carbon through an oxygen atom, such as $\text{C-O-PO}_3\text{H}_2$, $(\text{C-O})_2\text{PO}_2\text{H}$ and $(\text{C-O})_3\text{PO}$ groups(J. Bedia et al. 2011; X. Wu and L.R. Radovic 2006; M.J. Valero-Romero et al. 2017). Fig. 4b reveals that the two broad peaks centered at 484.4 and 462.6 eV appear in the Ru 3P spectrum of 1%Ru/PSBC, and they are assigned to Ru $3p_{1/2}$ and Ru $3p_{3/2}$ in the metallic Ru(W. Zhu et al. 2014; X. Xie et al. 2014), respectively.

The further deconvoluted analysis of these two peaks gives another two weak peaks centered at 486.7 and 464.2 eV, which can be indicative of the Ru³⁺ ions (X. Xie et al. 2014). This indicates that the Ru-loaded sample mainly contains metallic Ru NPs and a small amount of the unreduced Ru³⁺ species. Notably, the surface Ru concentration estimated from Table S4 is 1.9 wt%, which is much higher than the Ru loading amount of 0.51 wt% measured by ICP analysis, indicating that the Ru NPs in the catalyst are mainly located on the surface of PSBC carrier, and they are expected to have high hydrogenation activity.

TEM: Fig. 5 gives the TEM images of SBC-400, PSBC-3-60-400 and 1%Ru/PSBC. In that, SBC-400 presents a large blocky shape and compact layered structure characteristic in its side, and small amount of biochar nanoparticles (NPs, diameter: *ca.* 5-60 nm) are densely irregularly aggregated on its edge (Fig. 5a), likely indicating that the layered SBC-400 material is constructed based on the compact aggregation of these particles *via* strong hydrogen bonding interactions between their surface polar OH and COOH groups. Completely different from SBC-400, the TEM image of PSBC-3-60-400 displays a loosely and irregularly aggregated morphology and its NPs are mainly located between 5 to 100 nm (Fig. 5b). In addition, a few large-sized rectangular crystals are also noticed in its TEM image, which should belong to the crystallized ISP species. The NPs of 1%Ru/PSBC also presents a loosely and irregularly aggregated character and some black dots attributable to metal Ru NPs are scattered on them (Fig. 5c). Fig. 5d illuminates that the dispersed Ru NPs are all between 0.8 and 3.2 nm and their average size (1.5 nm) is smaller than that (4.6 nm) of our previously 5%Ru/PBC (F. Mao et al. 2020), which should be due to the low loading level and high dispersity of Ru NPs on the surface of carrier.

The above characterization results suggest that the enhanced strong acid sites and excellent porosity of PSBC-3-60-400 and its ultra-strong affinity to β -1,4-glycosidic bonds render this acidic support a high catalytic activity for hydrolysis of carbohydrates and the ultrafine Ru NPs loaded can construct the excellent bifunctional active sites with the support for the one-pot hydrolytic hydrogenation of carbohydrates, as supported by the catalytic reaction results in Tables 2 and 3.

4. Conclusion

In conclusion, for the first time we have constructed a simple and excellent catalytic protocol for the synthesis of hexitols from the one-pot hydrolytic hydrogenation of carbohydrates, especially including cellulose, which has the following advantages: i) The use of cheap bamboo powder and water glass as the two main raw materials, the PSBC carrier used in this protocol is readily synthesized in large-scale and low-cost by the simple three-step conversions, possessing the significantly enhanced strong acidity, porosity and affinity to β -1,4-glycosidic bonds, therefore, it, as a novel biomimetic catalyst, has a high acidic-catalytic activity for the hydrolysis of carbohydrates, but also it can be used to construct an excellent bifunctional catalyst with a low 1 wt% loading level of Ru NPs. ii) The bifunctional catalyst can well function under relatively low usage level and mild conditions and provide *ca.* 85% hexitols as the hydrogenated products in the one-pot conversion of cellulose in a green water medium, which has

outstanding competitiveness in lowering cost, saving energy and hydrogen resources, especially improving catalytic efficiency. We are interested in further exploring the newly constructed strategy for improving the acidity and porosity of PSBC as well as the loading efficiency of Ru NPs on it, thus rendering Ru/PSBC a more outstanding hydrolytic hydrogenating efficiency and an improved recyclability for the one-step conversion of cellulose to sorbitol.

Declarations

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Declaration of interests

We declare that we have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figures

Figure 1

Recyclability of 1%Ru/PSBC catalyst for hydrolytic hydrogenation of cellulose (a) and direct hydrogenation of glucose (b). Reaction condition: substrate, 0.3 g; catalyst, 0.05 g; H₂, 3 MPa; H₂O, 25 mL; reaction temperature, 150°C; reaction time, 6 h.

Figure 2

TG (a) and DTG (b) curves of SBC-400, PSBC-3-60-300, PSBC-3-60-350, PSBC-3-60-400 and PSBC-3-60-450 samples

Figure 3

N₂ adsorption-desorption isotherms and BJH pore size distributions for PSBC-3-60-400 (a) and 1%Ru/PSBC (b)

Figure 4

FT-IR spectra (a) and XRD patterns (b) of typical samples

Figure 5

XPS spectra for (a) P 2p of PS-400 and 1%Ru/PSBC, and (b) Ru 3p of 1%Ru/PSBC

Figure 6

TEM images of (a) SBC-400, (b) PSBC-3-60-400 and (c) 1%Ru/PSBC samples

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