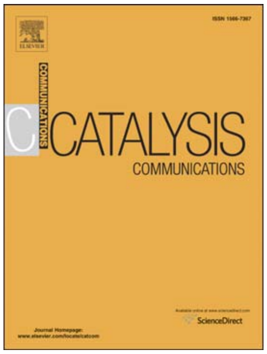

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Aqueous phase hydrogenolysis of glucose to 1,2-propanediol over **copper catalysts supported by sulfated spherical carbon**

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Abstract

Aqueous phase hydrogenolysis of glucose was carried out **over copper catalysts supported by sulfated spherical carbon** for selective production of 1,2-propanediol. **The sulfated carbon** shows higher acidity by sulfation of its resin precursor than unsulfated or commercial ones. **By changing copper loading**, the hydrogenolysis capability and the acidity of catalysts were modified to suitable extents, which can optimize the selectivity to 1,2-propanediol. At a moderate copper loading, 5.0Cu/s-AC catalyst has the highest yield of 1,2-propanediol. This catalyst has lifetime of over 300 h. However, its stability **is required** to be further improved.

Keywords: Glucose; Hydrogenolysis; **1,2-propanediol**; copper catalysts; **sulfated spherical carbon**

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Introduction

Fossil carbon resources (mainly petroleum and coal) provide most of daily needed transportation fuels, materials and chemicals. With diminishing fossil carbon resources and growing concerns about greenhouse gas emissions, great efforts are being made worldwide to look for their alternatives. Biomass, the only renewable organic carbon on earth, can be converted into diverse fuel components and basic chemicals [1]. Glucose, the most abundant monosaccharide in biomass, has the potential to be an alternative to fossil resources for sustainable production of chemicals and fuels. One of the most attractive routes for the glucose utilization is its direct conversion into value-added compounds, such as sorbitol [2], 5-hydroxymethylfurfural [3], and propanediol [4].

Propanediols are important commodity chemicals in the production of polyester resins, pharmaceuticals, tobacco humectants, paints, cosmetics, and antifreeze [5]. Propanediols are conventionally synthesized from petroleum-based feedstocks. Nowadays, more and more attentions focus on the conversion of biomass based feedstock (e.g. glycerol, cellulose or monosaccharides) to propanediols. Early studies indicated that propanediols could also be synthesized from monosaccharides. V.I. Sharkov[6] reported that the hydrogenolysis of monosaccharides (pentoses, hexoses, and their mixtures) can yield a mixture containing 35-40 % glycerol, 30-35 % propanediols, and 30 % unreacted polyhydric alcohols. Many researches reported the catalytic production of ethylene glycol and propanediols from higher polyols such as sorbitol and xylitol. The highest selectivities reported for the hydrogenolysis of sorbitol to ethylene glycol and propanediols are approximately 65 %, which is not high enough to be commercially viable [7-12]. Recently, many researchers use cellulose as feedstock to synthesize the polyhydric alcohols [13]. However, there is no latest report for the direct conversion of glucose to propanediols.

Catalysts **play important roles** in the conversion of sugar or polyols. Among transition metal hydrogenolysis catalysts, Cu-based catalysts have moderate hydrogenolysis activities and possess an intrinsic ability to cleave the C–O bond in preference to the C–C bond, which endow them specific selectivities for value-added chemicals [14]. For example, the hydrogenolysis of glycerol with copper chromium-based catalysts yielded only 1,2-propanediol [15]. Carbon material is one of the best choices as the catalyst support due to its excellent stability under hydrothermal conditions and large surface area for dispersing active components [16]. Activated carbons have carboxyl groups on surface, endowing them some extents of acidity. Surface acidic sites could catalyze the dehydration reaction [17] and promote the conversion of glucose. The acidities of activated carbons are usually weak, which would not cause a severe coking. However, as a support in hydrogenolysis, activated carbons usually show no acid-catalyzing activity [18], possibly because the dehydration activity of weak acids cannot compete with high hydrogenolysis activity of active metals. Sulfated carbons have robust acid sites in hot water, even stronger than resin-type or oxide-type solid acids [19]. By sulfation of the precursor in the preparation of activated carbons, the surface acidity and hydrophilicity/hydrophobicity can be obtained. These properties could enhance the adsorption of glucose on catalysts and facilitate the conversion of glucose.

In this paper, **a sulfated spherical carbon** (s-AC) was prepared **by sulfation of a resin precursor and following carbonization**. Cu/s-AC catalysts were prepared by incipient wetness impregnation, and used to investigate glucose hydrogenolysis. The performances of the Cu/s-AC catalysts were compared with those of an unsulfated carbon and a commercial carbon supported copper catalysts in terms of activity and selectivity. Over the **sulfated spherical carbon** supported copper catalysts, glucose can be directly converted into 1,2-propanediol **with** a maximum yield of 72.4 %.

Experimental

A commercial spherical macropore **polystyrene** resin (JX-101, Jinxiang Chemicals Co., Ltd., China) was used as the precursor in the preparation of activated carbons. **The resin has a specific area of about 200-270 m^2/g and sulfur content below 0.1**

wt%. The **sulfated spherical carbon** was prepared by swelling-sulfation methods. Briefly, 100 g of spherical resins were mixed with dichloroethane in weight ratio of 1:1 in a round-bottomed flask under stirring at 80 ^oC for 30 min. Then, the swelled resins were mixed with 500 ml concentrated sulfuric acid. The mixture was heated to 190 ^oC and kept reacting for 120 min. After reaction, the mixture was cooled to room temperature, filtered and washed using diluted sulfuric acid and deionized water to obtain sulfated resins. The sulfated resins were carbonized under N_2 atmosphere at 850 ^oC for 30 min and then activated with steam to obtain **the final s-AC globule**. For comparison, **an unsulfated spherical carbon** (AC) was prepared using the same procedure without the sulfation step. A commercial granular coconut carbon (purchased from Blue Sky Activated Carbon Co., Ltd., China) was also used as a support (c-AC, 20−40 mesh, S_{BET} = 1077 m^2/g). **It should be noted that a commercial acidic ion-exchange resin could also be used as a precursor to increase the acidity of activated carbon.**

The carbon supported copper catalysts (XCu/s-AC, X = 0.5, 1.0, 2.0, 5.0 and 10 in weight percentage) were prepared by incipient wetness impregnation of s-AC support with an aqueous solution of copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$, Sinopharm Chemical Reagent Co., Ltd., China). The catalyst was first dried in stagnant air at ambient temperature, further dried at 120 °C for 12 h in an oven, and then calcinated at 300 ^oC in N_2 for 5 h. For comparison, 5.0Cu/AC and 5.0Cu/c-AC catalysts were prepared by incipient wetness impregnation of AC and c-AC supports.

N_2 adsorption–desorption isotherms were measured at –196 °C using a Micromeritics ASAP 2420 instrument (Mircromeritics, USA) after degassing at 300 °C to remove physically adsorbed impurities for 8 h in vacuum. BET surface area and BJH pore size distribution were calculated according to the desorption branch of the isotherms.

The morphology of activated carbons was obtained using a JSM-6360LV (JEOL, Japan) scanning electron microscopy (SEM). **Elemental** contents in activated carbons were obtained using an elemental analyzer (ELEMENTAR, Vario EL cube, Germany). **The copper contents in catalysts were determined by inductively coupled plasma/optical emission spectroscopy (ICPES) (Optima2100DV, PerkinElmer)**.

Powder X-ray diffraction (XRD) patterns were obtained on a D/max-RA X-ray diffractometer (Bruker, Germany), with Cu-Kα radiation operated at 30 KV and 100 mA. The XRD patterns were recorded in 2θ values ranging from 10^o to 80^o.

Adsorptive decomposition of N_2O was conducted using the method reported previously [20]. The exposed copper surface area and copper particle size were calculated based on the assuming spherical shape of the copper metal particles and 1.4×10^{19} copper atoms/m^2. For one measurement, the catalyst was reduced at 350 ^{o}C in a 10 vol% H_2/Ar flow for 15 min firstly, then purged with N_2O at 40 ^{o}C for 30 min, then changed the gas flow to Ar (50 mL/min) and held for 30 min to clean the catalyst surface. Finally, the H_2-TPR was recorded with the 10 vol% H_2/Ar flow.

NH_3-TPD was performed in Auto Chem. II 2920 equipment (Mircromeritics, USA). **Prior to the adsorption**, the catalyst (0.30 g) was pretreated in He at 400 °C **for 1 h** to clean the surface from moisture and other adsorbed gases. After cooling to 100 °C, the catalyst was saturated with pure NH_3 for 30 min and then purged with He to remove the physisorbed NH_3 for 30 min. Subsequently, the sample was heated to 700 °C at a ramp of 5 °C/min and the NH_3 desorption was detected by a mass spectrometer (Omnistar, Pfeiffer, Germany).

Hydrogenolysis of glucose was performed in a vertical fixed bed reactor (i.d. 12 mm, length 600 mm)**, which was made of a stainless steel tube.** Typically, 4.0 g catalyst (20–40 mesh) was loaded into the constant temperature section (100 mm) of the reactor between two layers of quartz sand. Prior to each test, **the catalyst was reduced** in flowing H_2 (100 cm^3/min) at 200 °C for 5 h at atmospheric pressure. After the reduction, the system was cooled to 180 °C and pressured to 4.0 MPa. A 10 wt.% glucose aqueous solution was continuously pumped into the reactor with a high pressure pump along with co-feeding H_2 **at a flow rate of 100 cm^3/min**. The liquid and gas products were condensed and collected in a gas–liquid separator immersed in an ice-water trap. In order to avoid frequent pressure fluctuation, the liquid products were collected and released from the reactor every 12 h. An on-line gas chromatograph (GC) (models 6890N, Agilent, USA) was used to analyze the gas products in the tail gas. However, there are nearly no gas products in the tail gas except for a trace amount of furans on some catalysts. For comparison, **AC and c-AC supported copper catalysts** (5.0Cu/AC and 5.0Cu/c-AC) were tested in glucose hydrogenolysis under the same reaction conditions.

The liquid product mixture was analyzed by an HPLC system (HP1100, Agilent, USA) equipped with an RID detector. The separation of product mixture was achieved using a Platisil ODS C18 column at 25 °C. Redistilled water was used as mobile phase at a flow rate of 0.5 mL/min and a typical analysis run lasted 40 min. On the basis of the carbon atom balance in reaction, the selectivity to specific product was expressed as the ratio of the glucose converted into this product to the total glucose converted.

The conversion of glucose $X_{Glucose}$ was determined based on the weight amount of glucose fed into the reactor $m_{Glucose,i}$ and the unreacted one in the exit solution after reaction $m_{Glucose,o}$.

$$X_{Glucose} = \frac{m_{Glucose,i} - m_{Glucose,o}}{m_{Glucose,i}} ´ 100 \qquad (1)$$

The yield of one product Y_P was determined based on the mole carbon amount of one known component in the product mixture $N_{C,P}$ and the total mole carbon amount of glucose used in the reaction $N_{C,Glucose}$.

$$Y_P = \frac{N_{C,P}}{N_{C,Glucose}} \times 100 \qquad (2)$$

Results and discussion

Figure 1 shows the SEM images of activated carbons and catalysts. The commercial coconut c-AC has irregular shapes. The average particle diameter is about 650 μm. Microscopically, c-AC shows the tunnel pores of plant tissue. The self-prepared AC and s-AC **show perfectly spherical shapes** with diameters between 0.8 to 1.0 mm. Microscopically, **both carbons are also no essential difference**. They are piled up by thousands of smaller particles. For 5.0Cu/c-AC catalyst, there is an apparent particle agglomeration in pores of activated carbons. Comparing 0.5Cu/s-AC and 5.0Cu/s-AC, some small pores disappear on 5.0Cu/s-AC catalyst, indicating that higher copper loading could block the smaller pores of activated carbons. The BET areas, pore diameters and surface acidities of AC, c-AC, s-AC and corresponding carbon supported catalysts are listed in Table 1. It can be seen that AC and c-AC have almost identical surface areas (1136 and 1077 m^2/g) and average pore diameters (2.9 nm). With a sulfation of resin precursor, the as-prepared s-AC has a decreased surface area (787 m^2/g) and an increased pore diameter (3.5 nm), respectively. With the impregnation of copper, the resulted catalysts have quite different surface areas and pore structures. A small amount of copper (<2.0 wt%) slightly increases the surface areas while high copper contents decrease the surface areas. At low copper contents, the adsorbed solution probably created new pores and increased the surface area in the procedure of catalyst preparation. However, a large amount of copper could fill the pores of activated carbons and decreased the surface area. Micropores are usually blocked by metal particles. Therefore, the average pore diameters increased with the impregnation of copper. It is consistent with the results of SEM images.

Three kinds of carbon supports have quite different acidities. The c-AC support has the lowest acidity. The AC support has a medium acidity while the s-AC support has the highest acidity. The **ammonia** adsorption amount on s-AC is 3-5 times higher than those on AC or c-AC supports. Elemental analysis results indicated that s-AC has higher sulfur content than unsulfated AC and c-AC. The higher acidity of s-AC is probably related to the higher sulfur content in the sample. **The ammonia adsorption amount decreases with the impregnation of copper and it continuously decreases with increasing copper contents in the s-AC supported catalysts. It indicates that copper decreases the surface acidity, probably due to copper cations occupying the surface acid sites.** Figure 2 shows the NH_3-TPD profiles of supports and catalysts. Ammonia desorption occurs at about 130 ^{o}C for all supports and catalysts. It is indicated that all these supports and catalysts mainly contain weak acid sites.

Table 1 also shows the copper contents, copper surface areas and copper particle sizes in the s-AC supported catalysts. The actual copper contents are close to the designed copper loadings. With increasing the copper loading, the copper surface area firstly decreases and then increases with a minimum at copper loading of 2 wt%. The copper particle size increases linearly with increasing the copper loadings. At lower copper loading, the particle sizes estimated from XRD method are apparently larger than those calculated by N_2O method. It is indicated that some of copper particles are below the detect limit of XRD method. At the same time, it also indicates that the copper particles have a wide distribution at low copper loadings.

All the carbon supported copper catalysts were tested for the selective hydrogenolysis of glucose in aqueous phase. At low temperatures (<160 ^{o}C), the hydrogenolysis activity is low and glucose is mainly hydrogenated to sorbitol over these copper-based catalysts **(see Table 1s in supplementary information)**. The selectivity to 1,2-propanediol increases at elevated temperature. However, the catalysts deactivate quickly at temperatures higher than 190 ^{o}C. Usually, the catalyst bed was totally plugged once deactivating. The acid-catalyzed glucose dehydration could lead to 5-hydroxymethylfurfural, levulinic acid and polymeric side products called humines or humic acids [21]. These compounds are highly thermosensitive. The deactivation at higher temperatures is probably due to coking of some thermosensitive products. Therefore, the reaction temperature was set to 180 ^{o}C in order to reach a higher selectivity to 1,2-propanediol.

Table 2 lists the catalytic activity and yields of major products in glucose hydrogenolysis over catalysts. From the table, the copper loading has an important influence on the activity and selectivity of glucose hydrogenolysis. At lower copper loadings, glucose cannot be completely converted under the reaction conditions. Meanwhile, the reactions were unstable. The catalysts quickly deactivated in a period of 50 h, which usually accompanied a blockage or pressure rising in catalyst bed. The total carbon amount in aqueous is far below the balance (71.4 % of carbon balance over 0.5Cu/s-AC), indicating some products was retained in the reactor. It is probably due to coking or polymeric side products occurring in lower glucose conversions. Increasing the copper loading can apparently increase the glucose conversion and improve the carbon balance (> 93 %).

The product distributions are complex at low copper loadings. For example, 0.5Cu/s-AC catalyst produces a wide range of products, mainly composing of sorbitol, glycerol, **ethylene glycol, 1,2-propanediol, 1,3-propanediol,** 5-hydroxymethylfurfural, 2,5-dimethylfuran, and many unidentified compounds **(see Figure 2s in supplementary information)**. 1,2-propanediol is the dominant compound in these products. But its yield is low over the catalyst. The selectivity is also influenced by the copper loading. The yield of 1,2-propanediol increases with increasing copper loadings. There is a maximum for 1,2-propanediol formation at copper loading of 5 wt%. It declines with further increasing copper loading. The yield of sorbitol and glycerol show a continuous increasing tendency. Moreover, the unsaturated products (furfurals and furans) are largely decreased at higher copper loadings. No cyclic compounds (2,5-dimethylfuran and 2,5-dimethyltetrohydrofuran) were detected in product spectrum of 10Cu/s-AC catalyst.

The hydrogenation of unsaturated bonds (C=O and C=C) can only take place on metallic active sites. **However, the 0.5Cu/s-AC catalyst does not possess the lowest**

surface copper area, i.e. copper sites. Actually, the yield of sorbitol has a good correlation with copper particle size. It indicates that copper particle size has an important influence on the hydrogenation of unsaturated bonds. Probably, ultra small copper particles cannot provide enough spaces for adsorption and hydrogenation of glucose. Therefore, the increase of sorbitol and the decrease of unsaturated products could be attributed to the increased copper particle size on catalysts with high copper loading. Acid sites can catalyze the formation of cyclic compounds in glucose conversion [3, 22, 23]. It is in agreement with the decrease of acidity with increasing copper loading. In literature, hydrogenolysis of sorbitol can produce 1,2-propanediol. However, the variation of 1,2-propanediol does not coincide with the sorbitol. It seem that the hydrogenolysis of sorbitol to 1,2-propanediol is not the only route for 1,2-propanediol formation in glucose hydrogenolysis. Surface acid sites play important roles in the 1,2-propanediol formation. For comparison, the catalytic performances of low acidity catalysts (5.0Cu/AC and 5.0Cu/c-AC) were also shown in Table 2. It is obvious that, at the same copper loading, Cu/AC and Cu/c-AC catalysts have quite lower 1,2-propanediol selectivities than s-AC supported catalysts. It can be confirmed that the acidity has an important influence on the 1,2-propanediol formation. Meanwhile, the hydrogenolysis sites are necessary for the **1,2-propanediol** formation. Under the combined action of acid and hydrogenolysis sites, 1,2-propanediol passes through complex intermediates in the glucose hydrogenolysis compared with the sorbitol hydrogenolysis.

At higher copper loadings, deactivation is largely mitigated by the enhanced hydrogenation capability. For example, 5.0Cu/s-AC can operate over 300 h as shown in Figure 3. Unfortunately, the reactor was completely plugged at about 320 h. After **dismounting** the reactor, **the catalyst remains it perfect spherical shape** and there is no powder in catalyst bed, indicating that the blockage was not caused by the break of catalyst **globules**. In contrast, the catalyst globules are **agglomerated** together probably due to coking. **After the stability testing, the catalyst sample was carefully collected, dried and calcined using the same procedure as the catalyst preparation.**

The spent catalyst sample was analyzed using elemental analysis. The elemental composition of the spent 5.0Cu/s-AC catalyst is listed in Table 2s. Compared with the as-prepared 5.0Cu/s-AC, copper, sulfur and nitrogen contents decreased, carbon content remained nearly unchanged while hydrogen and other element contents apparently increased in the spent sample. Other elements include mainly oxygen and a trace of mineral components. The decreased sulfur and copper indicate that parts of the surface acid and hydrogenation sites were probably leached off. The apparently increased H and O are probably resulted from the deposition of glucose and its derives (deoxyglucose, humine or coke), which have higher H and O contents than activated carbons. The deposits could also relatively decrease sulfur and copper contents in the spent catalyst. All in all, deactivation is a severe problem in present study. A thorough research on the stability of the catalyst should be carried out in the future.

Conclusions

The sulfation of resin precursor can apparently improve the acidity of activated carbons. The surface acidity has important influences on the formation of 1,2-propanediol in glucose hydrogenolysis. The acid sites should work together with hydrogenolysis sites for improving 1,2-propanediol selectivity. In this work, 5.0Cu/s-AC catalyst possesses suitable acid-catalyzing and hydrogenolysis capabilities, which produced the highest yield of 1,2-propanediol among all tested catalysts. Catalyst bed blockage is a severe problem in present study. Improving hydrogenation capability can prolong the lifetime of catalysts. However, the stability **is required to be further improved.**

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Reference

Tables and Figures

Table 1 Physicochemical properties of catalysts.

Table 2 Catalytic performances of catalysts in glucose hydrogenation.

Figure 1 SEM images of c-AC and s-AC.

Figure 2 NH_3-TPD profiles of activated carbons and activated carbon supported copper catalysts.

Figure 3 The stability of 5wt%Cu/s-AC catalyst in glucose hydrogenation. **Reaction conditions: 180 ^{o}C, 4 MPa, glucose concentration of 10 wt%, catalyst (3g), liquid feed rate of 1.2ml/h, H_2 to glucose ratio of 383 (mole ratio).**

Table 1 Physicochemical properties of catalysts.

Catalyst	S_{BET}[a], m^2/g	D_{Pore}, nm	S, wt%	Acid amount (μmol NH_3/g)	**Cu, wt%**	**S_{Cu}[b], m^2/g**	**d_{Cu}, nm**	
							XRD[c]	**N_2O[b]**
AC	1136	2.9	0.21	31.8	**-**		**-**	**-**
c-AC	1077	2.9	0.13	20.1	**-**		**-**	**-**
s-AC	787	3.5	1.11	111.9	**-**		**-**	**-**
0.5Cu/s-AC	843	3.5	1.05	108.2	**0.52**	**0.76**	**16**	**5**
1.0Cu/s-AC	809	3.5	1.02	96.8	**1.03**	**0.60**	**20**	**12**
2.0Cu/s-AC	795	3.6	0.98	87.5	**2.07**	**0.44**	**26**	**32**
5.0Cu/s-AC	763	3.9	0.98	87.8	**5.31**	**0.56**	**54**	**64**
10Cu/s-AC	638	5.8	0.93	71.2	**11.60**	**1.03**	**81**	**76**
5.0Cu/AC	1040	3.1	0.20	22.2	**5.14**		**-**	**-**
5.0Cu/c-AC	923	3.0	0.12	22.5	**4.96**		**-**	**-**

Max error = ±3%.

[a] Surface area determined from N_2 adsorption.

[b] The diameter of Cu particle calculated by N_2O-decomposition method.

[c] The diameter of Cu particle estimated from XRD peak of Cu(111) ($2\theta=43.3^o$) by Scherrer formula.

Table 2 Catalytic performances of catalysts in glucose hydrogenation.

Catalysts	Conversion, %	Yield based on carbon, %							C balance, %
		Sorbitol	Glycerol	**EG**	1,2-PDO	**1,3-PDO**	Propanol	**Others**	
0.5Cu/s-AC	90.6	3.3	2.4	**2.1**	15.6	**0.4**	0.0	**47.6**	71.4
1.0Cu/s-AC	95.2	5.2	2.2	**2.5**	39.9	**0.7**	0.3	**35.0**	85.9
2.0Cu/s-AC	99.7	8.7	3.1	**2.0**	64.8	**1.1**	1.4	**10.8**	93.7
5.0Cu/s-AC	100	10.5	2.9	**2.2**	72.4	**1.3**	1.8	**3.1**	94.1
10Cu/s-AC	100	18.9	5.3	**2.7**	55.0	**0.9**	5.7	**5.9**	94.5
5.0Cu/AC	99.5	14.9	3.7	**3.1**	16.2	**0.2**	3.0	**52.3**	93.5
5.0Cu/c-AC	99.7	17.5	8.1	**4.7**	13.7	**0.1**	2.3	**48.5**	94.8

Reaction conditions: Fixed bed reactor, 4 MPa, 180 ^{o}C, glucose concentration of 10 wt%, catalyst (3g), liquid feed rate of 1.2ml/h, H_2 to glucose ratio of 383 (mole ratio).

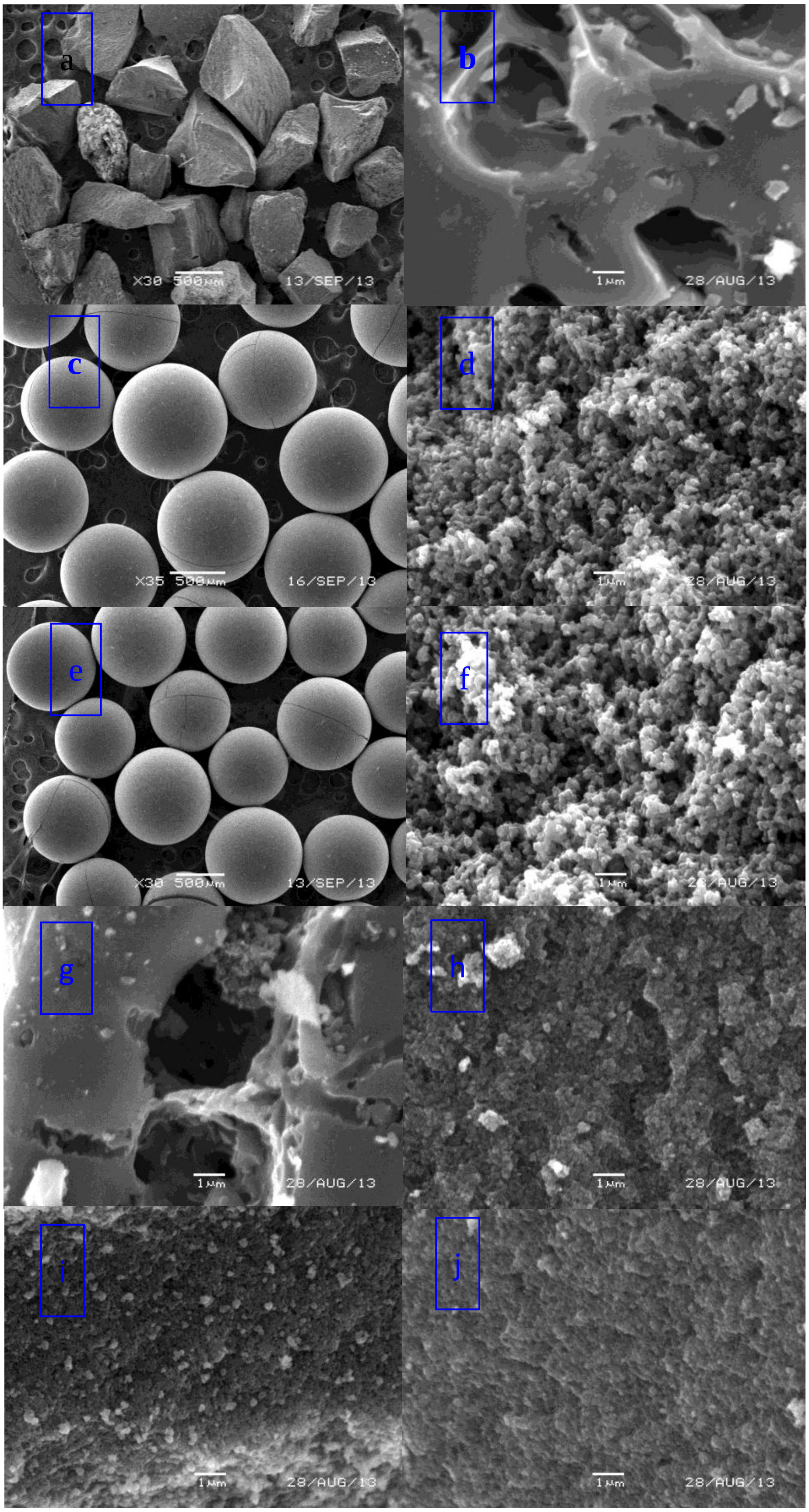

Figure 1 SEM images of c-AC (a, b), AC (c, d), s-AC (e, f), 5.0Cu/c-AC (g), 5.0Cu/AC (h), 0.5Cu/s-AC (i) and 5.0Cu/s-AC (j).

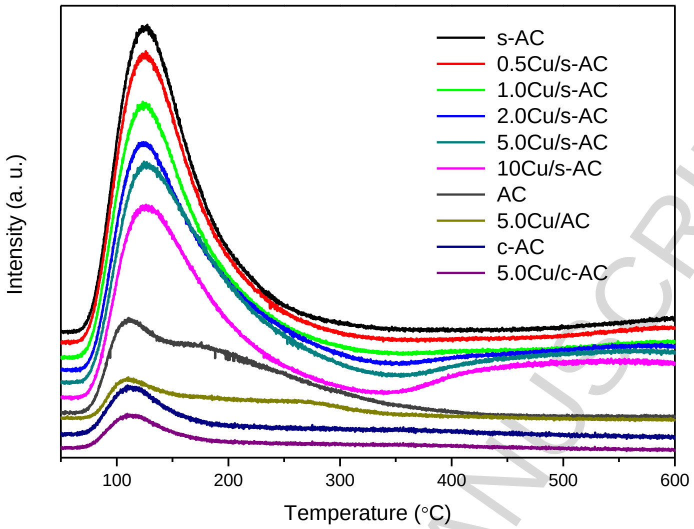

Figure 2 NH_3-TPD profiles of activated carbons and activated carbon supported copper catalysts.

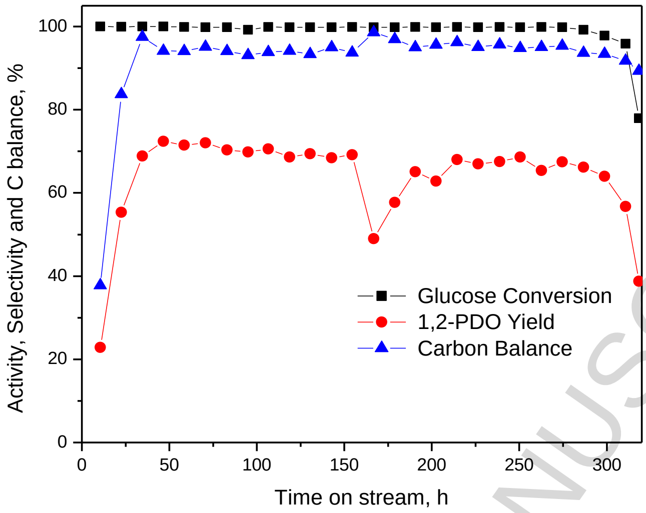

Figure 3 The stability of 5.0Cu/s-AC catalyst in glucose hydrogenation. **Reaction conditions: 180 ^{o}C, 4 MPa, glucose concentration of 10 wt%, catalyst (3g), liquid feed rate of 1.2ml/h, H_2 to glucose ratio of 383 (mole ratio).**

Highlights

1. Sulfation increases the acidity of carbon supported Cu catalysts.
2. Cu content has an important effect on glucose hydrogenation activity.
3. Cu and acid sites have synergetic effects on the selectivity of 1,2-propanediol.
4. 5.0wt% Cu/s-AC catalyst has a maximum yield of 1,2-propanediol over 70%.

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