

# Conversion of Cellulose into Sorbitol over Carbon Nanotube-Supported Ruthenium Catalyst

Weiping Deng · Xuesong Tan · Wenhao Fang ·  
Qinghong Zhang · Ye Wang

Received: 22 July 2009 / Accepted: 18 August 2009 / Published online: 2 September 2009  
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**Abstract** Cellulose samples with different crystallinities (33–85%) were prepared by treating a commercial cellulose (crystalline, 85%) with phosphoric acid under different conditions. Supported Fe, Co, Ni, Pd, Pt, Rh, Ru, Ir, Ag, and Au catalysts were examined for the conversion of cellulose with a crystallinity of 33% in water medium in the presence of hydrogen, and Ru was found to be the most effective catalyst for the formation of sorbitol. We demonstrated that carbon nanotubes (CNTs) were the most efficient support of Ru for cellulose conversion, and the mean size of Ru nanoparticles over CNT was  $\sim 8.8$  nm.  $\text{NH}_3$ -TPD and  $\text{H}_2$ -TPD characterizations suggest that plenty of acid sites and unique hydrogen species over the Ru/CNT are important for sorbitol formation through hydrolysis and hydrogenation of cellulose. A 40% yield of hexitols (including 36% of sorbitol) could be achieved over the Ru/CNT catalyst for the conversion of the commercial cellulose (crystalline, 85%), and this yield was the highest one reported to date for the direct conversion of cellulose into sugar alcohols.

**Keywords** Cellulose · Sorbitol · Ruthenium · Carbon nanotubes · Hydrogenation · Acidity

## 1 Introduction

Biomass is a kind of important resource within the energy and carbon recycle in nature. The efficient utilization of

biomass [1–4] has great potential for reducing greenhouse gas emissions, because the amount of  $\text{CO}_2$  released from the process of biomass conversions may be balanced by that captured in the growth of plants. Because cellulose is the major component of plant biomass, investigations on the conversion of cellulose selectively to fuels and useful chemicals under mild conditions will benefit to the change from the current fossil society burdened with serious environment problems to a more sustainable one [5–8]. However, as cellulose possess robust crystalline structure [9], it is not easy to convert cellulose selectively under mild condition.

As one of the conversion approach, syngas or bio-oils production by gasification or pyrolysis at high temperatures has been proposed, but these methods suffered from high-energy input and low selectivity [5–8]. From viewpoint of reducing energy consumption, the formation of platform molecules through low-temperature process is favored, and the platform molecules should be transformed into valuable chemicals or liquid fuels readily [10]. Sorbitol is one of the promising platform molecules [10], through which hydrogen, liquid alkanes and oxygenates can be obtained [11–13]. Moreover, sorbitol can also be used as sweetener in food additives directly or for vitamin C production.

However, the selective production of platform molecules is a challenge, and only scarce studies have succeeded in converting cellulose into sorbitol or other high-valued chemicals [14–17]. Kou and co-workers [14] reported the conversion of cellulose to hexitols catalyzed by Ru nanocluster dispersed in an ionic liquid medium, but the conversion of cellulose is low ( $\sim 15\%$ ). Fukuoka and Dhepe [15] studied the conversion of cellulose to sugar alcohols in water under  $\text{H}_2$  over a  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst, and obtained 31% yield of sugar alcohols including 25% sorbitol and 6% mannitol at 190 °C. Liu and co-workers [16]

W. Deng · X. Tan · W. Fang · Q. Zhang · Y. Wang (✉)  
State Key Laboratory of Physical Chemistry of Solid Surfaces,  
National Engineering Laboratory for Green Chemical  
Productions of Alcohols, Ethers and Esters, Department of  
Chemistry, College of Chemistry and Chemical Engineering,  
Xiamen University, 361005 Xiamen, China  
e-mail: wangye@xmu.edu.cn

developed a two-step transformation of cellulose to polyols catalyzed by acids reversibly formed by high temperature water and Ru nanoclusters supported on active carbon, and they reported a 39% yield of hexitols (including ~30% of sorbitol) at relatively high temperature (245 °C). Although exciting progress has been made by several groups, intensive studies are still required for exploring high-performance catalysts and for illustrating key factors for cellulose conversion. In this paper, we report the superior catalytic performances of Ru/CNT catalyst for the conversion of cellulose in water media. The factors influencing the conversion of cellulose to sorbitol will also be discussed.

## 2 Experimental

### 2.1 Preparation of Catalysts

CNTs with outer diameters of 20–60 nm and inner diameters of 3–5 nm were prepared by a reported method [18]. The CNT were typically pretreated in concentrated HNO<sub>3</sub> (68 wt%) at 110 °C under refluxing conditions to remove amorphous carbon and the remaining Ni catalyst used for CNT preparation and to create function groups (e.g., carboxylic and hydroxyl groups) for anchoring metal precursors. Ru catalysts loaded on various supports (including CNT) were prepared by impregnating the supports with an aqueous solution of RuCl<sub>3</sub>, followed by drying, calcination in air at 350 °C, and reduction by H<sub>2</sub> at 350 °C for 0.5 h.

### 2.2 Characterization of Catalysts

NH<sub>3</sub> temperature-programmed desorption (NH<sub>3</sub>-TPD) and H<sub>2</sub> temperature-programmed desorption (H<sub>2</sub>-TPD) were performed on a Micromeritics AutoChem 2920 II instrument. Typically, 200 mg of sample loaded in a quartz reactor was first pretreated in He gas flow at 350 °C for 1 h, and then cooled down to adsorption temperature. For NH<sub>3</sub>-TPD experiments, the samples were exposed to a NH<sub>3</sub>-He (10 vol% NH<sub>3</sub>) gas mixture and kept at 120 °C for 1 h for adsorption. After removing the NH<sub>3</sub> in gas phase by purge with He, NH<sub>3</sub>-TPD was performed in a He flow by heating the sample up to 700 °C at a rate of 10 °C min<sup>-1</sup>. The desorbed NH<sub>3</sub> were monitored by ThermoStar GSD 301 T2 mass spectrometer with the signal of  $m/e = 16$ . For H<sub>2</sub>-TPD, the adsorption of H<sub>2</sub> was carried out at 80 °C for 1 h, and the desorbed H<sub>2</sub> was monitored with the signal of  $m/e = 2$ .

H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) for the samples was performed with a flow system equipped with a thermal conductivity detector (TCD). In a typical measurement, the sample was pretreated in a quartz reactor in an air flow at 350 °C for 1 h. After cooling down to room

temperature, the samples were switched to a H<sub>2</sub>-Ar (10 vol% H<sub>2</sub>) gas mixture, and then heated up to 600 °C at a rate of 10 °C min<sup>-1</sup>.

X-ray photoelectron spectra (XPS) were recorded with a Quantum 2000 Scanning ESCA Microprob instrument (Physical Electronics) using Al K $\alpha$  radiation. The binding energy was calibrated using C1s photoelectron peak at 284.6 eV as a reference.

TEM measurements were performed on a FEI Tecnai 30 electron microscope (Phillips Analytical) operated at an acceleration voltage of 300 kV.

### 2.3 Preparation of Cellulose with Different Crystallinities and Catalytic Reactions

Cellulose samples with different crystallinities and degrees of polymerization (DP) were obtained by treating the purchased cellulose (Alfa Aesar) in 85 or 43 wt% H<sub>3</sub>PO<sub>4</sub> [19] at different temperatures followed by recovering with water, filtration, washing and drying. The crystallinity of the regenerated cellulose was determined by powder X-ray diffraction (XRD) method [20] performed on a Panalytical X'pert PRO diffractometer. IR spectra were recorded on a Nicolet 380 instrument. The DP of cellulose was determined by a viscosity method [21].

The conversion of cellulose was performed in a 100 mL teflon-lined stainless-steel autoclave. Microcrystalline cellulose (viscosity average degree of polymerization of 221; relative crystallinity of 85%) purchased from Alfa Aesar or samples pretreated with H<sub>3</sub>PO<sub>4</sub> were used as starting reactant. After cellulose (0.16 g, equivalent to 1 mmol C<sub>6</sub>H<sub>10</sub>O<sub>5</sub> unit) and the catalyst (0.050 g) were added into the autoclave pre-charged with H<sub>2</sub>O (20 mL), H<sub>2</sub> of 5 MPa was introduced. The reaction was started by heating the mixture up to 185 °C, and then the reaction continued for 24 h with stirring. The liquid-phase products were analyzed by HPLC (Shimazu LC-20A) equipped with a RI detector and a Transgenomic<sup>TM</sup> CARBONSep CHO-620 column (10  $\mu$ m, 6.5  $\times$  300 mm) using water as a mobile phase.

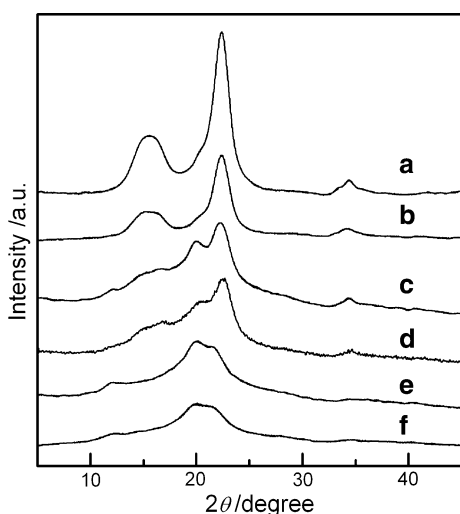
## 3 Results and Discussion

### 3.1 Preparation and Characterization of Cellulose with Different Crystallinities

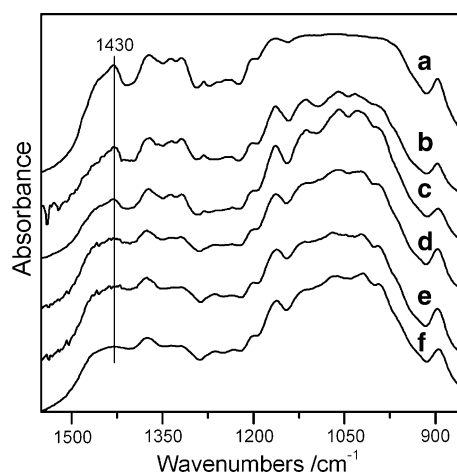
Cellulose is a linear compacted polymer constructed by D-anhydroglucopyranose connected with  $\beta$ -1,4-glucosidic bond with a degree of polymerization within 100–20,000. As the adjacent cellulose molecules are extensively hydrogen bonded each other [22], the crystalline structure of cellulose is extremely stable which is hard to be attacked

**Table 1** Treatment conditions used for preparation of cellulose samples with different crystallinities

Sample no	Treatment conditions	Crystallinity <sup>a</sup> (%)	DP <sup>b</sup>
1	Commercial cellulose (Alfa Aesar)	85	221
2	In 43% H <sub>3</sub> PO <sub>4</sub> at 25 °C for 1 h	79	209
3	In 85% H <sub>3</sub> PO <sub>4</sub> at 100 °C for 9 min	56	125
4	In 85% H <sub>3</sub> PO <sub>4</sub> at 0 °C for 1 h	46	197
5	In 85% H <sub>3</sub> PO <sub>4</sub> at 25 °C for 1 h	39	125
6	In 85% H <sub>3</sub> PO <sub>4</sub> at 50 °C for 40 min	33	106

<sup>a</sup> Measured by XRD [20]<sup>b</sup> Measured by a viscosity method [21]**Fig. 1** XRD patterns of cellulose samples with different crystallinities. *a* 85%; *b* 79%; *c* 56%; *d* 46%; *e* 39%; *f* 33%

by other chemicals. Several research groups have developed a procedure to enhance the reactivity of cellulose through a treatment with H<sub>3</sub>PO<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub>-swollen cellulose has become one of the most common cellulose substrates [19, 23–25]. We prepared cellulose samples with different crystallinities by treating the commercial cellulose (Alfa Aesar, crystallinity of 85%) with H<sub>3</sub>PO<sub>4</sub> under different conditions (Table 1). XRD patterns of these treated samples are shown in Fig. 1. Commercial cellulose exhibited strong diffraction peaks at  $2\theta$  of 15.0°, 16.0° and 22.5° which are characteristic diffractions of [101], [10 $\bar{1}$ ] and [002] planes in cellulose I crystal. After treatment with H<sub>3</sub>PO<sub>4</sub>, the diffraction peaks decreased evidently, while the amorphous peak at  $2\theta$  around 20° increased, indicating that the crystalline degree of the treated cellulose sample was decreased. The crystallinity evaluated by XRD method and the DP estimated by a viscosity method for these treated samples are summarized in Table 1. With changing treatment conditions including the concentration of H<sub>3</sub>PO<sub>4</sub>, the

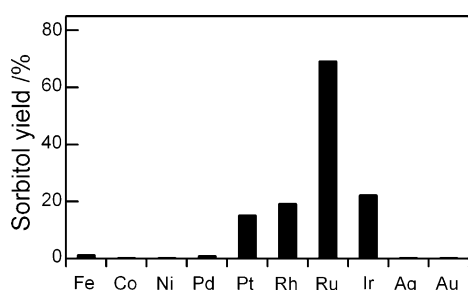
**Fig. 2** IR spectra of cellulose samples with different crystallinities. *a* 85%; *b* 79%; *c* 56%; *d* 46%; *e* 39%; *f* 33%

temperature and the time of treatment, cellulose samples with crystallinities in range of 33–85% were obtained. At the same time, the degrees of polymerization were also reduced from 221 of commercial cellulose (crystallinity of 85%) to 209–106 for the samples with crystallinities of 79–33%.

FT-IR spectra in Fig. 2 demonstrate the changes in the main structures of cellulose samples after the treatment with H<sub>3</sub>PO<sub>4</sub>. The band at 1,430 cm<sup>-1</sup> assigned to CH<sub>2</sub> scissoring motion in cellulose I crystal was strong for the commercial cellulose, but it became weaker and broader for the treated cellulose, indicating the change of the conformation of CH<sub>2</sub>OH at C<sub>6</sub> position in cellulose from regular arrangement to random ones [26]. In addition, the band around 1,320–1,376 and 1,032–1,165 cm<sup>-1</sup>, which were assigned to various CH and CO bond of glucose anhydride ring deformed gradually after treatment with H<sub>3</sub>PO<sub>4</sub>. However, 900 cm<sup>-1</sup> band belong to COC vibration of  $\beta$ -glycosidic linkage was almost unchanged, suggesting that the COC bond of  $\beta$ -glucoside was kept in all the treated samples. In literature, the IR band at 1,430 cm<sup>-1</sup> is typically assigned to the crystalline feature of cellulose [27], and the ratio of the intensity for the band at 1,430 cm<sup>-1</sup> to that at 900 cm<sup>-1</sup> is used as one empirical crystalline index for cellulose [28]. FT-IR results for these samples further confirmed that, with H<sub>3</sub>PO<sub>4</sub> treatment, we obtained cellulose samples with different crystallinities, while most  $\beta$ -glucoside structure in the cellulose molecule was sustained.

### 3.2 Catalytic Conversion of Cellulose

We have mainly investigated the performances of various catalysts for the conversion of the treated cellulose with a crystalline of 33%. Figure 3 shows the sorbitol yield from



**Fig. 3** Sorbitol yield in the conversion of cellulose catalyzed by various transition metals loaded on CNT (metals loading, 1.0 wt%). Reaction conditions: catalyst, 0.050 g; H<sub>2</sub>O, 20 cm<sup>3</sup>; H<sub>2</sub>, 5 MPa; temperature, 185 °C; cellulose (crystallinity, 33%), 0.16 g; time, 24 h

cellulose over several metallic catalysts supported on CNTs including elements in group VIII and IB. Compared to Fe, Co and Ni, supported noble metals such as Pd, Pt, Rh and Ir were more active for the formation of sorbitol, and Ru/CNT gave the highest yield of sorbitol among the examined catalysts. Fukuoka et al. [15] once reported that supported Pt and Ru catalysts were effective for cellulose conversion to sugar alcohols. In our case, over CNT support, Ru catalyst demonstrated higher activity than Pt catalyst.

We have compared the catalytic performances of Ru catalysts loaded on different supports. Table 2 shows the yields of sorbitol, mannitol, erythritol, and glycerol from cellulose over Ru catalysts loaded on supports including SiO<sub>2</sub>, CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, and CNT at 185 °C in water medium. The content of Ru was adjusted to 1.0 wt% in each case. The neutral and basic oxides such as SiO<sub>2</sub>, CeO<sub>2</sub> and MgO were not effective supports from the standpoint of sorbitol yield, while the acidic Al<sub>2</sub>O<sub>3</sub>-supported Ru showed a better catalytic performance. Among these catalysts, Ru/CNT catalyst exhibited the highest sorbitol yield. In other words, CNT was the most effective support for Ru catalyst for the conversion of cellulose into sorbitol. It is of interest to note that Pan et al. [29] have reported that the CNT-supported Ru catalyst is much effective than the Al<sub>2</sub>O<sub>3</sub>- and SiO<sub>2</sub>-supported Ru and Raney Ni catalysts for

**Table 2** Conversion of cellulose over various supported Ru catalysts

Catalyst	Product yield (mol %)			
	Sorbitol	Mannitol	Erythritol	Glycerol
Ru/SiO <sub>2</sub>	7.0	1.0	0	0
Ru/CeO <sub>2</sub>	5.0	2.0	6.0	7.0
Ru/MgO	0	0	13	3.0
Ru/Al <sub>2</sub> O <sub>3</sub>	22	3.0	8.0	6.0
Ru/CNT	69	4.0	5.0	5.0

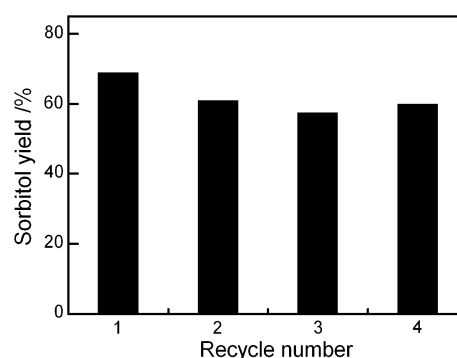
Reaction conditions: cellulose (crystallinity, 33%), 0.16 g; catalyst (Ru loading, 1.0 wt%), 0.050 g; H<sub>2</sub>O, 20 cm<sup>3</sup>; H<sub>2</sub>, 5 MPa; temperature, 185 °C; time, 24 h

**Table 3** Effect of Ru loading on the conversion of cellulose over Ru/CNT catalyst

Ru loading (wt%)	Product yield (mol%)			
	Sorbitol	Mannitol	Erythritol	Glycerol
0.2	13	1	6	2
0.5	64	3	7	2
1.0	69	4	5	5
3.0 <sup>a</sup>	31	25	5	–
5.0 <sup>a</sup>	14	12	5	8

Reaction conditions: cellulose (crystallinity, 33%), 0.16 g; catalyst, 0.050 g; H<sub>2</sub>O, 20 cm<sup>3</sup>; H<sub>2</sub>, 5 MPa; temperature, 185 °C; time, 24 h

<sup>a</sup> Other degradation products such as methane and some unknown compounds were also detected



**Fig. 4** Repeated uses of 1.0 wt% Ru/CNT catalyst for cellulose conversion. Reaction conditions: catalyst, 0.05 g; H<sub>2</sub>O, 20 cm<sup>3</sup>; H<sub>2</sub>, 5 MPa; temperature, 185 °C; cellulose (crystallinity, 33%), 0.16 g; time, 24 h

the conversion of glucose to sorbitol. To clarify the role of CNT support in our case, we have carried out more detailed studies on Ru/CNT catalysts.

The influence of Ru loading on catalytic activity of Ru/CNT was investigated. As shown in Table 3, over the catalyst with a Ru loading of 0.2 wt%, a sorbitol yield of 13% was obtained. With increasing the Ru loading to 0.5 wt%, the sorbitol yield increased significantly. The highest sorbitol yield was attained over the 1.0 wt% Ru/CNT catalyst. However, further increases in Ru loading decreased sorbitol yield. At the same time, many other products, which were mostly formed by degradation or isomerization of sorbitol, were observed.

The reuse of catalyst was also performed for the conversion of cellulose with a crystallinity of 33%. After the reaction, the 1.0 wt% Ru/CNT catalyst was recovered by centrifugation, washed with deionized water and added into the autoclave for the next run. The result for four recycles is shown in Fig. 4. Sorbitol yield decreased slightly after the first run from 69 to 61% and then kept at ~61%.

### 3.3 Characterization of Supported Ru Catalysts

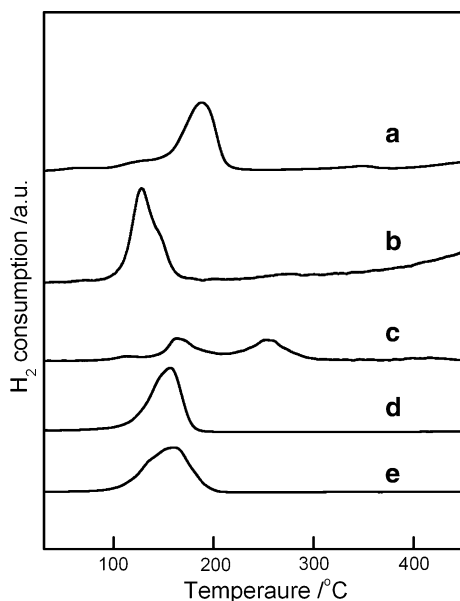
Table 4 summarizes some physicochemical properties of Ru catalysts loaded on different supports. No obvious correlation can be found between the catalytic performance of sorbitol formation and the specific surface area of the catalysts. In order to confirm the oxidation state of Ru species on the catalysts, H<sub>2</sub>-TPR experiments were performed for the samples before H<sub>2</sub> reduction. H<sub>2</sub>-TPR profiles shown in Fig. 5 indicated that, during catalyst preparation stage, Ru species on most of the catalysts could be reduced completely at 350 °C except for Ru/MgO. The quantification of the reduction peaks revealed that the reduction degree was higher than 90% over most of the catalysts except for Ru/MgO (Table 4). Moreover, XPS results in Fig. 6 showed that the binding energy (BE) of Ru 3d<sub>5/2</sub> for these catalysts were in the range of

**Table 4** Some properties of Ru catalysts loaded on different supports

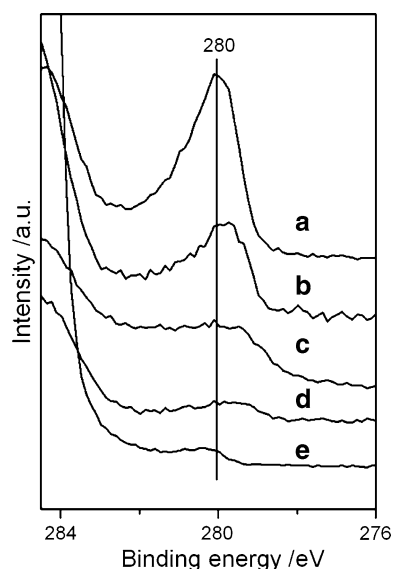
Catalyst	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Ru reduction degree <sup>a</sup> (%)	Amount of H <sub>2</sub> adsorbed <sup>b</sup> (μmol g <sup>-1</sup> )
Ru/SiO <sub>2</sub>	184	95	<5
Ru/CeO <sub>2</sub>	3	95	<5
Ru/MgO	80	71	<5
Ru/Al <sub>2</sub> O <sub>3</sub>	196	95	50
Ru/CNT	142	95	100

<sup>a</sup> Calculated from H<sub>2</sub> consumption below 350 °C in H<sub>2</sub>-TPR experiment (Fig. 4)

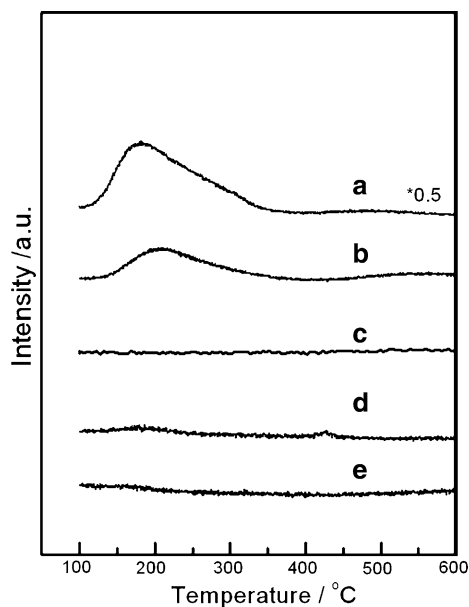
<sup>b</sup> Estimated from H<sub>2</sub>-TPD measurements (Fig. 6)



**Fig. 5** H<sub>2</sub>-TPR profiles of the Ru catalysts loaded on various supports. *a* Ru/ Al<sub>2</sub>O<sub>3</sub>; *b* Ru/CNT; *c* Ru/ MgO; *d* Ru/CeO<sub>2</sub>; *e* Ru/SiO<sub>2</sub>



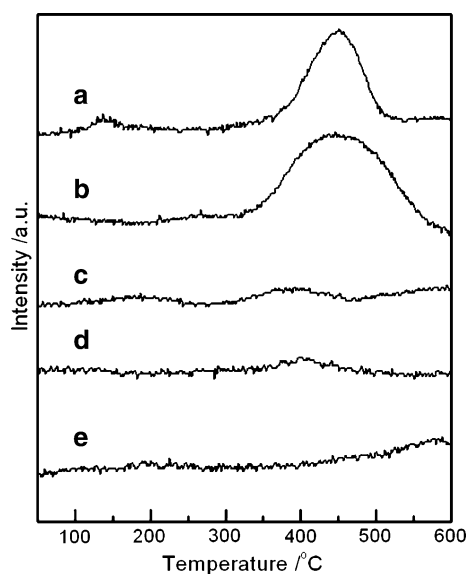
**Fig. 6** XPS spectra of Ru3d<sub>5/2</sub> for the Ru catalysts loaded on various supports. *a* Ru/SiO<sub>2</sub>; *b* Ru/CeO<sub>2</sub>; *c* Ru/MgO; *d* Ru/ Al<sub>2</sub>O<sub>3</sub>; *e* Ru/CNT



**Fig. 7** NH<sub>3</sub>-TPD profiles for the Ru catalysts loaded on various supports. *a* Ru/ Al<sub>2</sub>O<sub>3</sub>; *b* Ru/CNT; *c* Ru/MgO; *d* Ru/CeO<sub>2</sub>; *e* Ru/SiO<sub>2</sub>

279.7–280.3 eV, which could be assigned to metallic Ru species [30].

It is known that solid acids can catalyze the hydrolysis of cellulose to glucose [1–4, 31], a possible intermediate for sorbitol formation [3, 4, 14]. The acidity of the catalysts is expected to influence the conversion of cellulose. NH<sub>3</sub>-TPD profiles in Fig. 7 clarified that obvious NH<sub>3</sub> desorption could only be observed from Ru/Al<sub>2</sub>O<sub>3</sub> and Ru/CNT catalysts, which were more effective for sorbitol formation (Table 2), while almost no acidic sites were observed over



**Fig. 8**  $\text{H}_2$ -TPD profiles for the Ru catalysts loaded on various supports. *a* Ru/ $\text{Al}_2\text{O}_3$ ; *b* Ru/CNT; *c* Ru/MgO; *d* Ru/ $\text{CeO}_2$ ; *e* Ru/ $\text{SiO}_2$

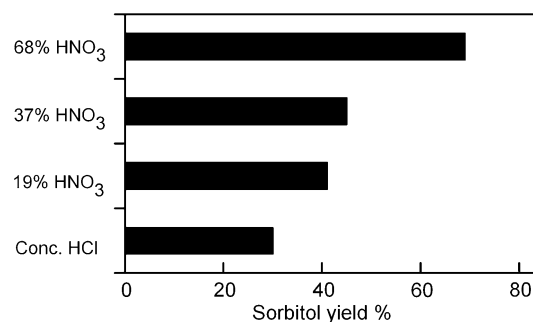
Ru/ $\text{SiO}_2$ , Ru/ $\text{CeO}_2$ , and Ru/MgO catalysts, which showed poorer performances in the conversion of cellulose. This result suggests that the acidity of a catalyst is one important factor for the conversion of cellulose into sorbitol.

However, detailed comparisons of the trends in Fig. 7 and in Table 2 reveal that the order of the acidity is not the same as that of catalytic performance. Dhepe and Fukuoka [4] once compared the catalytic performances of Pt catalysts loaded on different supports for the conversion of cellulose, and they did not find particular relationship between the activity and the acidity of supports. Therefore, there may exist other factors in determining the catalytic performances in addition to the acidity.

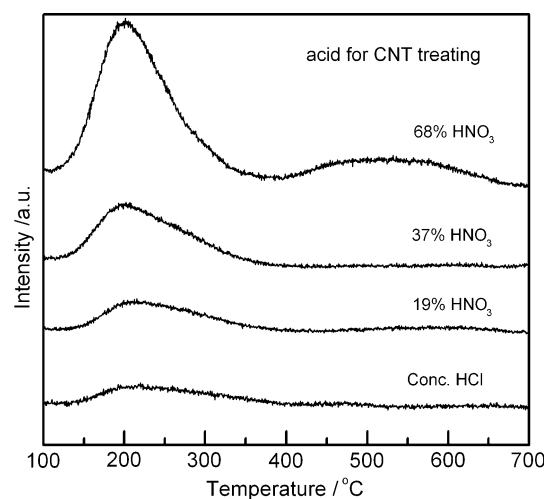
It is known that the unique properties of CNT in  $\text{H}_2$  adsorption, spillover and electron transport make it an extraordinary catalyst support for hydrogenation reactions [32–36].  $\text{H}_2$ -TPD results in Fig. 8 and the quantification of the  $\text{H}_2$  desorption for each samples listed in Table 2 demonstrated that Ru/CNT had a significantly stronger  $\text{H}_2$  adsorption ability compared to other catalysts. This suggests that a larger amount of adsorbed hydrogen species exists over the Ru/CNT surfaces, and this may account for its better catalytic performance for the conversion of cellulose into sorbitol.

### 3.4 Effect of Pretreatment of CNT

The results described above clearly demonstrate that CNT is an efficient support of Ru catalyst for conversion of cellulose into sorbitol. Because the properties of CNT should be related with the conditions used for CNT pretreatment, we have further investigated the performances of



**Fig. 9** Sorbitol yield in the conversion of cellulose over the 1.0 wt% Ru/CNT catalysts prepared using CNT pretreated by  $\text{HNO}_3$  with different concentrations or by concentrated HCl. Reaction conditions: catalyst, 0.05 g;  $\text{H}_2\text{O}$ , 20  $\text{cm}^3$ ;  $\text{H}_2$ , 5 MPa; temperature, 185  $^\circ\text{C}$ ; Cellulose (crystallinity, 33%), 0.16 g; time, 24 h



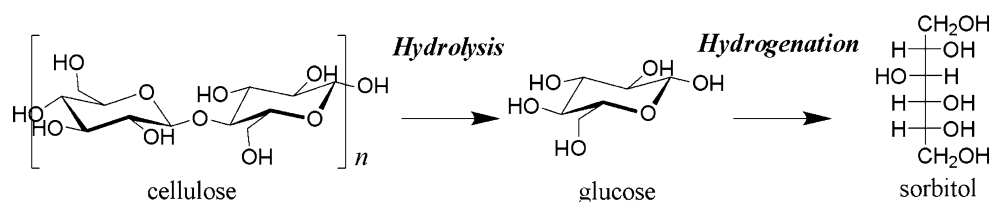
**Fig. 10**  $\text{NH}_3$ -TPD profiles of Ru/CNT catalysts with CNT pretreated by  $\text{HNO}_3$  with different concentrations or by concentrated HCl

catalysts prepared using CNT pretreated under different conditions.

The typical pretreatment of CNT is in a concentrated  $\text{HNO}_3$  (68%) at 110  $^\circ\text{C}$  for 12 h, and with this support, a sorbitol yield of 69% could be achieved. The decrease in the concentration of  $\text{HNO}_3$  used for CNT pretreatment lowered the sorbitol yield correspondingly (Fig. 9). The sorbitol yield was also very low when the CNT pretreated by concentrated HCl was employed as support.

$\text{NH}_3$ -TPD was performed to inspect the difference in acidity generated on CNT surfaces after  $\text{HNO}_3$  treatment (Fig. 10). For the CNT pretreated with 68%  $\text{HNO}_3$ , which was used as a typical support, in addition to the main  $\text{NH}_3$  desorption around 210  $^\circ\text{C}$  ascribed to weak acidic sites, a broad peak at 450–600  $^\circ\text{C}$  was observed, suggesting the generation of medium-strength acidic sites on its surfaces. It is known that the treatment of CNTs by concentrated  $\text{HNO}_3$  can cause the generation of acidic groups such as

**Scheme 1** Possible reaction scheme for the conversion of cellulose into sorbitol



carboxylic groups on their surfaces [37]. The desorption amount of  $\text{NH}_3$  from other pretreated CNTs decreased with a decrease in the concentration of  $\text{HNO}_3$ , indicating a decrease in the amount of acidic sites over these samples. From TEM studies, we checked the size of Ru particles supported on these CNT supports. The mean sizes of Ru particles were quite similar (8.7–8.9 nm) even though the CNT was pretreated with  $\text{HNO}_3$  of different concentrations (19–68%). This observation further confirms that the acidic functional groups generated on CNT surfaces contribute to the conversion of cellulose into sorbitol.

Our present results clearly suggest that the acidity and the unique  $\text{H}_2$  adsorption ability of the catalyst are two important factors for the formation of sorbitol. We propose that the conversion of cellulose to sorbitol may proceed via Scheme 1, including the hydrolysis of the  $\beta$ -1,4-glucosidic bond in the first step and the subsequent hydrogenation of the glucose in the second step. The catalyst requirements can be easily understood because the first step requires acidity while the second step needs active hydrogen species.

### 3.5 Sorbitol Formation from Cellulose with Different Crystallinities

Ru/CNT was investigated as the catalyst for the conversion of cellulose samples with different crystallinities. The results in Table 5 clearly show that the sorbitol yield over the Ru/CNT catalyst strongly depend on the crystallinity of cellulose. The lower crystallinity of cellulose resulted in a

**Table 5** Effect of the crystallinity of cellulose on its conversion over the 1.0 wt% Ru/CNT catalyst

Crystallinity (%)	Product yield (mol%)			
	Sorbitol	Mannitol	Erythritol	Glycerol
85	11	2.0	6.0	Trace
79	15	1.7	4.0	4.0
56	34	3.0	5.0	4.0
46	47	4.0	6.0	5.0
39	58	3.0	6.0	6.0
33	69	4.0	5.0	5.0

Reaction conditions: cellulose, 0.16 g; catalyst, 0.050 g;  $\text{H}_2\text{O}$ ,  $20 \text{ cm}^3$ ;  $\text{H}_2$ , 5 MPa; temperature, 185 °C; time, 24 h

**Table 6** Conversion of cellulose over the 1.0 wt% Ru/CNT catalyst

Catalyst amount (g)	Product yield (mol%)		
	Sorbitol	Mannitol	Erythritol
0	0	0	0
0.05	11	2.0	6.0
0.09	26	6.0	8.0
0.14	36	4.0	6.0
0.17	30	8.0	4.0

Reaction conditions: cellulose (crystallinity, 85%), 0.16 g;  $\text{H}_2\text{O}$ ,  $20 \text{ cm}^3$ ;  $\text{H}_2$ , 5 MPa; temperature, 185 °C; time, 24 h

significantly higher sorbitol yield. The sorbitol yield of 69% was achieved for the conversion of the cellulose with a crystallinity of 33%, while for the commercial microcrystalline cellulose with a crystallinity of 85%, only 11% yield of sorbitol can be obtained under the same reaction conditions.

Table 6 demonstrates that the sorbitol yield increases significantly with increasing the amount of catalyst up to 0.14 g during the conversion of cellulose with a crystallinity of 85%. The yield of sorbitol enhanced to 36%, and the total yields of hexitols (sorbitol and mannitol) reached 40% at 185 °C over the Ru/CNT catalyst. This sorbitol yield was higher than those reported previously over a  $\text{Pt}/\text{Al}_2\text{O}_3$  at 190 °C (25%) [15] and a Ru/AC at 245 °C (30%) [16]. Thus, the Ru/CNT is a highly efficient catalyst for the conversion of cellulose into sorbitol in the presence of  $\text{H}_2$  in water media.

## 4 Conclusions

Ru/CNT is an efficient catalyst for the direct conversion of cellulose into sorbitol in aqueous media. Both the acidic functional groups and the higher concentration of adsorbed hydrogen species on CNT surfaces play key roles in sorbitol formation. A sorbitol yield of 36% can be achieved in the conversion of commercial cellulose (crystallinity, 85%) at 185 °C. The decrease in the crystallinity of cellulose can raise the formation of sorbitol. A sorbitol yield of 69% has been obtained in the conversion of treated cellulose with a crystallinity of 33% over the Ru/CNT catalyst.

**Acknowledgments** This work was supported by the National Natural Science Foundation of China (Nos. 20625310, 20773099 and 20873110), the National Basic Program of China (2010CB732303 and 2005CB221408), and the Program for New Century Excellent Talents in Fujian Province (to Q.Z.). We thank Profs. H. B. Zhang and G. D. Lin for providing CNT.

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