Selective Conversion of Cellulose into Sorbitol over Pt/Carbon Nanotube Catalysts

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1. Introduction

The production of fuels and chemicals from renewable biomass resources has attracted much attention in recent years. Cellulose is the most abundant source of biomass, comes mainly from grass and wood waste. Thus far, the conversion of cellulose into fuels and industrially important chemicals has been regarded as one of the most promising approaches to sustainable energy production. In recently, Fukuoka and Dhepe reported the conversion of cellulose directly to sugar alcohols in water under H_2 over a Pt/Al_2O_3 catalyst [1]. The reaction process included the hydrolysis of cellulose to glucose and the reduction of glucose to sorbitol and mannitol. Sorbitol was used as a sweetener in diet foods and a potential raw material for the synthesis of variety of value-added chemicals such as isosorbide, 1,4- sorbitan, glycols, glycerol, lactic acid and L-sorbose. Mannitol is also a sweetener and a precursor to useful compounds. Cellobiose is a glucose dimer connected by a glycosidic bond and represents the simplest model molecule for cellulose. CNT are ideal catalyst supports because of its excellent performance such as high surface area, excellent electronic conductivity, and good resistance to acidic/basic chemicals at high temperature. It is noteworthy that CNT-based catalysts often show higher activity and/or selectivity than other catalysts with nanoparticles supported on conventional supports, like alumina, silica, or even activated carbon (AC).

In the report, the cellobiose was replaced cellulose to research the catalytic performance of catalyst. The catalytic performance of CNTs after acid treatment was researched firstly. Then, Pt was loaded on CNTs through different methods to improve catalytic performance. In the last, the effect of support was researched.

2. Experimental

The CNT were pretreated in concentrated HNO_3 (65 wt%) at 395K under refluxing conditions. Pt nanoclusters loaded on CNTs were prepared by impregnating the CNTs with $Pt(NH_3)_2(NO_3)_2$ solution, followed by drying, calcination in Ar at 623K, and reduction by H_2 at 673K for 2h and passivated by 1% O_2 diluted by N_2. The catalyst was defined as 5%Pt-CNTs. The 5%Pt-AC and 5%Pt-SiO_2 was prepared by the same method. 5%Pt-CNTs-EG was prepared by mixing the CNTs, $Pt(NH_3)_2(NO_3)_2$ solution and ethylene glycol. After being treated ultrasonically for 0.5 h, the mixture was refluxed at 393 K for 12 h. The solid product was then recovered by filtration followed by drying. The Pt content of all catalysts was 5.0 wt%

3. Results and conclusions

Table 1 showed that the hydrolysis of cellobiose could be achieved under higher temperature even in the absence of catalyst. However, the yield of mannitol and sorbitol was below 1%, which means the catalyst should be introduced to improve the yield of mannitol and sorbitol. After introducing the CNTs the selectivity of glucose decreased from 28.4 to 0.1 and the selectivity of sorbitol increased from 1.1 to 11.8 indicated that most of glucose was transferred into sorbitol. However, the yield of sorbitol still lower and failed to application.

Table 1 Catalytic performance of CNTs and Pt supporting on different supports.

Catalysts	Cellobiose coversion (%)	Selectivity (wt %)			
		Glucose	Mannitol	Sorbitol	Others
blank	95.8	28.4	1.0	1.1	69.5
CNTs	91.9	0.1	2.2	11.8	85.9
5%Pt/AC	84.5	4.7	26.1	4.6	64.6
5%Pt/SiO_2	100	6.8	8.3	11.5	73.4
5%Pt/CNTs	100	3.4	9.4	86.5	0.7
5%Pt/CNTs-EG	100	0.8	13.7	9.8	75.7

Reaction conditions: catalysts weight =0.05 g; Cellobiose weight =0.1711g, reaction time= 3 h; Temprature=463K; pressure=5 MPa; H_2 as reaction gas.

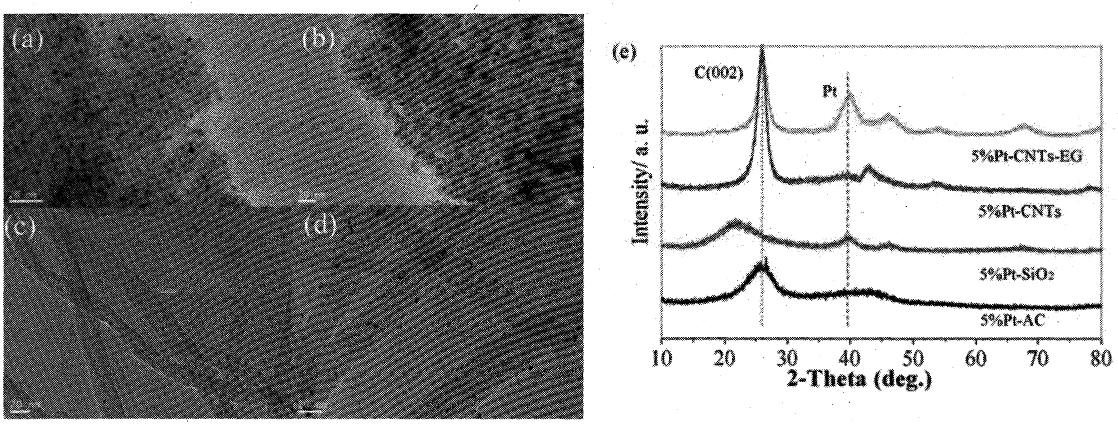

Fig. 1 TEM images of (a) 5%Pt-AC, (b) 5%Pt-SiO_2, (c) 5%Pt-CNTs, (d) 5%Pt-CNTs-EG and (e) XRD patterns of catalysts.

The Pt loaded CNTs catalyst was prepared through impregnation method or EG reduction method for improving the yield of sorbitol. As shown in table 1, the sorbitol selectivity of 5%Pt-CNTs catalyst was higher than 5%Pt-CNTs-EG catalyst with the same convention to cellobiose. The relationship of catalytic performance with the structure of catalyst was research by TEM (Fig. 1) and XRD (Fig. 1e) analysis. As shown in Fig. 1, the average diameter of Pt nanoparticles was about 1.2nm for 5%Pt-CNTs and 3.7nm for 5%Pt-CNTs-EG. The higher dispersion also was approved by the XRD. The effect of support to catalytic performance was also researched. For the catalysts prepared by the same impregnation method, the order of selectivity to sorbitol was: 5%Pt-CNTs > 5%Pt-SiO_2 >5%Pt-AC. TEM and XRD patterns showed that well dispersion of Pt was also obtained on 5%Pt-AC or 5%Pt-SiO_2. The different selectivity comes from the support materials.

In summary, both the support materials and the preparation method influence the catalytic performance. The 100% convention and 86.5% selectivity to sorbitol was obtained when used 5%Pt-CNTs as catalyst.

[1] A. Fukuoka and P. L. Dhepe, Angew. Chem. Int. Ed., 2006, 45, 5161.