

EFFICIENT DIRECT SORBITOL PRODUCTION FROM CELLULOSE WITH Ru SUPPORTED ON HIGHLY MICROPOROUS CARBON/CARBON NANOTUBE HYBRID CATALYSTS

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Introduction

One of the most efficient pathways for a future sustainable society dependent on cellulosic biomass is the direct conversion of cellulose into valuable chemicals [1]. Sorbitol is one of the most promising platform molecules included in the list of the twelve base products of maximum potential derived from biomass, specifically from cellulose [2]. The most common way to obtain sorbitol is the catalytic conversion of cellulose by using supported ruthenium catalysts. Among the different supports that have been studied, carbon materials, such as carbon nanotubes and activated carbons, are the most promising, the former offering the best catalytic performance [3]. However, further research needs to be carried out in an attempt to match or surpass the results obtained with carbon nanotubes by using cheaper carbon supports. Accordingly, the aim of the present work is to use glucose, a monomer of cellulose, as the precursor of the carbon supports.

Materials and Methods

Different carbon materials were prepared by hydrothermal carbonization (HTC): i) a glucose-based material and ii) a glucose/carbon nanotube hybrid. The solid/water ratio (w/v) and the amount of carbon nanotubes (CNT) were fixed at 1:5 and 2 wt.%, respectively. The HTC process was performed at 180 °C for 12 h. The obtained materials were then carbonized at 700 °C under N₂ for 2 h (CG and CG-CNT) or physically activated at 900 °C under CO₂ atmosphere for 2, 4 and 6 h (AG and AG-CNT). Ruthenium catalysts were then prepared by incipient wetness impregnation of Ru (0.4 wt.%) on the prepared carbon supports. The catalysts were denoted as Ru/X, where X is the name of the corresponding support, followed by the value of the surface area. Supports and catalysts were characterized by nitrogen adsorption, microscopy (SEM and TEM), elemental analysis, TGA, TPD, XRD, XPS and ICP. The catalysts were then tested in the one-pot hydrolytic hydrogenation of cellulose into sorbitol. In standard tests, 300 mL of water, 750 mg of ball-milled cellulose and 300 mg of catalyst were placed into a 1000 mL reactor under stirring (150 rpm). After heating under N₂ to 205 °C, the reaction was started by switching from inert gas to H₂ (50 bar) and carried out for 5 h. Samples were periodically withdrawn for analysis by HPLC and total organic carbon (TOC).

Results and Discussion

All the prepared materials display a type I isotherm, which is characteristic of microporous solids. In addition, the microporosity increases due to the increase in the temperature and time of

activation applied. Besides, hybrid samples exhibit a small hysteresis loop which appears as a result of the capillary condensation at medium-high pressures, commonly observed for materials that bear mesopores in their interparticle spaces, like carbon nanotubes. Moreover, the addition of CNT results in materials with a more basic surface. The Ru nanoparticles are in the metallic state and well dispersed over the surface with an average size lower than 5 nm. The prepared Ru catalysts were highly efficient for the one-pot reaction, yielding 100 % cellulose conversion after just 3 h. The acidic surface functionalities favoured the hydrolysis of cellulose into glucose during the first hour of reaction. However, after this first hour, the conversion rate seemed to increase for the materials with the most developed porous structure. Differences in the catalytic selectivity were also observed, highlighting the strong influence of the support properties on the production of sorbitol. The production of sorbitol increases with the surface area (Table 1), probably due to the faster access to the metal, favouring the hydrogenation of glucose into sorbitol. Moreover, the less acidic character of the surface due to the presence of CNT suppresses the isomerization of glucose to fructose, limiting the further conversion to 5-HMF and subsequently to formic acid. Accordingly, the appropriate combination of properties of the Ru/AG-CNT₁₂₀₀ catalyst resulted in the highest sorbitol yield within 3 h (64.1 %).

Table 1. Textural properties and catalytic results

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{DR} ($\text{cm}^3 \text{g}^{-1}$)	Yield of sorbitol (%, 3 h)	Conversion (%, 3 h)
Ru/CG	560	0.21	33	100
Ru/AG ₆₀₀	563	0.22	44	100
Ru/AG ₁₀₀₀	936	0.37	53	100
Ru/AG ₂₂₀₀	1852	0.75	59	100
Ru/CG-CNT	541	0.20	39	100
Ru/AG-CNT ₇₀₀	606	0.23	55	100
Ru/AG-CNT ₁₂₀₀	1151	0.45	64	100

Conclusions

The appropriate combination of activation conditions and the addition of CNT during the polymerization of glucose led to the most efficient catalyst for the production of sorbitol. A yield of 64 % of sorbitol was achieved after just 3 h of reaction, which is the highest value reported for the environmentally friendly one-pot conversion of cellulose to sorbitol over carbon-supported catalysts using a nominal amount of metal as low as 0.4 wt. %.

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