Bifunctional Materials for the Catalytic Conversion of Cellulose into Soluble Renewable Biorefinery Feedstocks

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Introduction

The increasing world's energy needs combined with diminishing petroleum resources as well as growing environmental concerns, such as global warming, have triggered great interest in our society to search for new renewable sources of energy and chemicals. Among the environmentally friendly sources of energy such as photovoltaic, hydroelectric, geothermal, and wind power, biomass is the only natural, renewable carbon resource that is sufficiently large to be used as a potential substitute for fossil fuels [1]. The catalytic conversion of lignocellulosic biomass into intermediates that can be used to produce fuels and high-value chemicals, as well as substitutes for petroleum-based feedstocks, in an integrated biorefinery is a novel technology that can help meet the growing energy demand while dramatically reducing greenhouse gas emissions. This work presents the development of bifunctional nanostructured materials for the catalytic conversion of cellulose into sugar alcohols that can be used as a sustainable source of renewable biorefinery feedstock. Hydrolysis of cellulose to glucose followed by the corresponding reduction produces mainly sorbitol and mannitol.

Materials and Methods

Supported Ru catalysts were prepared by evaporative deposition of ruthenium (III) nitrosyl nitrate on various ordered mesoporous silica (SBA-15, Santa Barbara Amorphous) with different functionalities. SBA-15 was synthesized using Pluronic P123 triblock copolymer (P123) as the structure directing agent and tetramethyl orthosilicate (TMOS) as the silica source [2]. A sulfonic acid or an amine were incorporated into SBA-15 through a "one-pot" synthesis using 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane or 3-aminopropyl-trimethoxysilane to prepare the functionalized mesoporous catalyst SBA-15S or SBA-15A, respectively [3]. A 5%Ru/C sample was used as a reference material. The catalysts were characterized using Nitrogen Adsorption (BET), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Thermogravimetric Analysis (TGA). The activity and selectivity of the bifunctional catalysts were studied by monitoring the cellulose conversion and production of sugar and sugar alcohols in a magnetically stirred, temperature controlled autoclave reactor at 483 K, under 35 bar H_2 for 1 h. Product formation was monitored using HPLC analysis.

Results and Discussion

The powder XRD patterns of all the samples confirmed the formation of two-dimensional well-ordered hexagonal arrays of one-dimensional channels with p6mm hexagonal symmetry typical of SBA-15 mesoporous silica [2]. No peaks corresponding to Ru were detected in the patterns, suggesting that the Ru particle size is lower than the detection limit of XRD. SEM images of the samples confirm that our procedure produces fiber-like mesoporous silica SBA-15. The nitrogen adsorption/desorption results indicate that the SBA-15 catalysts yield type IV isotherms with H1-type hysteresis that are typical of mesoporous materials with 1D cylindrical channels.

Table 1 shows the conversions and selectivities for the SBA-15 catalysts and for Ru/C. Using SBA-15A as a catalyst increases the conversion by over 30% when compared with the same reaction conditions but without a catalyst. The conversion in the absence of a catalyst appears to be caused by the *in situ* formation of H_3O^+ ions that leads to auto hydrolysis of cellulose. Adding the sulfonic functionality to SBA-15 raises the conversion by about 24% when compared to SBA-15A. The enhancement may be the result of the higher acidity of this sample, but also the surface area and the pore volume of SBA-15S are higher than the other catalysts. Depositing Ru on the SBA-15 samples decreases the conversion when compared to the parent material, but more importantly changes the product distribution. There is a marked reduction in the yield of sugars degradation products such as hydroxymethylfurfural (HMF) and organic acids. Concurrently, there is a substantial improvement in the yield of sugar alcohols (mainly sorbitol and mannitol). The conversion for the Ru/SBA-15S catalyst is slightly lower than for Ru/C but the selectivity towards sugar alcohols is 21% higher. In fact, the overall selectivity to sugars and sugar alcohols (90%) is almost 30% higher than over Ru/C. It has recently been shown that such compounds may be readily converted into conventional transportation fuels [5].

Table 1. Cellulose conversions and selectivities over SBA-15 catalysts at 483 K.

Sample	Cellulose Conversion (%)	Sugars (%)	Sugar Alcohols (%)	Degradation Products (%)	Other Products (%)
SBA-15A	32.6	46.8	9.8	36.5	7.0
SBA-15	37.9	53.0	5.5	34.7	6.8
SBA-15S	40.3	51.7	13.5	29.0	5.8
Ru/SBA-15A	27.1	4.2	47.9	0.0	47.9
Ru/SBA-15	24.6	6.6	59.2	3.3	30.9
Ru/SBA-15S	28.7	9.6	80.5	0.0	9.9
5%Ru/C	31.8	4.3	66.6	14.0	15.2

Significance

The bifunctional Ru/SBA-15S catalysts offer a potential pathway for the conversion of abundant inexpensive cellulose into high-value products.

References

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