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Hydrogenolysis of sorbitol to glycols over carbon nanofibers-supported ruthenium catalyst: The role of base promoter

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ABSTRACT

Sorbitol hydrogenolysis over carbon nanofibers-supported Ru (Ru/CNFs) was carried out with different bases (NaOH, KOH, Mg(OH)$_2$, Ba(OH)$_2$, and CaO) to investigate the role of base promoter. The results indicated that all the bases used significantly enhanced the sorbitol conversion while the glycol selectivities varied with the base type and amount. CaO was the best base in terms of glycol selectivity for two reasons. CaO provided OH$^-$ for the base-promoted cleavage of C–C bonds, while it also supplied Ca^{2+} for complexation with the intermediate aldehydes, thus affecting the reaction pathways. We identified an optimum ratio among sorbitol concentration, Ru/CNFs catalyst, and CaO to achieve favorable glycol selectivities in sorbitol hydrogenolysis. Reaction pathways for sorbitol hydrogenolysis into glycols in aqueous solution in the presence of CaO have been proposed based on the mechanistic study.

1. Introduction

Conversion of renewable biomass to commodity chemicals has received extensive attention as the depletion of fossil fuel reservoirs has continued over the past two decades. Sugars and sugar alcohols, which can be derived from renewable lignocellulosic biomass instead of fossil resources, are considered as potential feedstocks for the future biorefinery to produce useful chemical products through hydrogenolysis [1,2]. Along this line, sorbitol hydrogenolysis is a promising "green process" that can produce important chemicals such as ethylene glycol (EG), propylene glycol (PG), and glycerol (GL), which are widely used in the manufacture of polyesters, surfactants, pharmaceuticals, and functional fluids [3].

Sorbitol hydrogenolysis was first conducted in a study where sugars were submitted to the action of hydrogen [4].

Clark [5] then reported this process for the purpose of biomass conversion to lower carbon glycols. Since then, sorbitol hydrogenolysis to glycols has received much attention in industry circles and a raft of patents on the topic have been issued [6–11]. Most of these patents describe sorbitol hydrogenolysis occurring in the presence of a metal catalyst and base, at a temperature between 180 and 275 °C, and with an elevated H$_2$ partial pressure of 3.4–48.3 MPa. Some academic studies on this process have been reported, mainly focusing on the mechanism of bond cleavage in polyol hydrogenolysis and the development of new catalyst systems. For example, Chen et al. [3] studied sorbitol hydrogenolysis over Ni–MgO catalyst and found that the activity depended strongly on the basicity of catalyst. Banu et al. [12,13] conducted the sorbitol hydrogenolysis over NaY zeolite-based catalysts and discussed the effect of Ca(OH)$_2$ on the conversion and selectivity. Sohounloue et al.

[14] investigated the hydrogenolysis of sorbitol over Ru/SiO₂ in a basic medium and discussed the dependence of bond cleavage on temperature with respect to the retro-aldol condensation mechanism. Montassier et al. [15] conducted a study on the modification of Ru catalyst with sulfur and proposed that the bulk reaction causing C–C bond cleavage in sorbitol hydrogenolysis was a retro-Michael reaction under the action of absorbed nucleophilic species OH⁻. Using 1,3-diols as model compounds, Wang et al. [16] proposed a bond cleavage mechanism (Scheme 1) for polyol hydrogenolysis; retro-aldol condensation was proposed as the dominant mechanism for C–C bond cleavage by thermodynamic and kinetic considerations. The initial dehydrogenation step is thought to occur on the transition metal catalyst.

Previous research in our laboratory [17–20] has shown that Ru catalyst over carbon nanofibers (CNFs) exhibited high catalytic activity in sorbitol hydrogenolysis to EG and PG owing to the mesoporosity and surface chemistry of the CNFs. The Ru catalysts supported on powdered and structured CNFs showed high performance in a batch reactor (slurry) and in a flow-through continuous reactor, respectively. Moreover, it is generally acknowledged that the use of base can significantly affect the activity and selectivity of this reaction; our preliminary results demonstrated that addition of CaO enhanced the conversion of sorbitol [17]. The use of base in sorbitol hydrogenolysis was first thought to prevent leaching of the metal from the catalyst [7, 8], but further work has suggested a more significant role. Banu et al. [13] found that addition of Ca(OH)₂ as a promoter to both Ni and Pt catalysts increased the sorbitol conversion significantly without any significant effect on selectivity. However, studies on the effect of base on glycerol hydrogenolysis found different results that suggested the base aided initial dehydrogenation of glycerol to glyceraldehyde and promoted the dehydration of glyceraldehyde to 2-hydroxyacrolein; hence, the selectivities to different products varied significantly [21–23]. Sun et al. [24] investigated the selective hydrogenolysis of xylitol to EG and PG over different catalysts in the presence of Ca(OH)₂. They revealed that xylitol hydrogenolysis involved the dehydrogenation of xylitol to xylose on the metal surface and subsequent base-catalyzed retro-aldol condensation of xylose to glycolaldehyde and glyceraldehyde. This was followed by direct glycolaldehyde hydrogenation to EG and sequential glyceraldehyde dehydration and hydrogenation to PG. Rass et al. [25] studied the influence of base in the selective oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid over Pd/C catalyst, and demonstrated that the cation of the base had no effect while the carbonate base facilitated hydration of the aldehyde.

Little effort has been made to explain the mechnism of this enhancement by base in sorbitol hydrogenolysis, although almost all previous research has used base additives for this reaction. Given that few details are known about how these base additives affect the reaction pathways, the objective of this study was to explore the role of base in sorbitol hydrogenolysis and to optimize the reaction conditions for higher glycol selectivities. Based on our previous work, the effects of the base type and amount on sorbitol hydrogenolysis were systematically investigated over Ru/CNFs in a batch reactor. The role of base is discussed in combination with the reaction mechanism.

2. Experimental

2.1. Catalyst preparation

CNF catalyst support was synthesized and purified as described by Zhao et al. [17]. 3.0 wt% Ru/CNFs catalyst was prepared by incipient wetness impregnation using RuCl₃·3H₂O (Heraeus) as precursor [17]. NaOH, KOH, Mg(OH)₂, Ba(OH)₂, CaO, and sorbitol were purchased from Alfa Aesar China and used as received.

2.2. Hydrogenolysis reaction of sorbitol

Sorbitol hydrogenolysis was carried out in a 500-mL stainless steel autoclave (Parr 4575A, USA) with magnetic stirring. In a typical run, 330 mL (20 wt% unless specified otherwise) sorbitol aqueous solution, a measured amount of base, and activated Ru/CNFs catalyst were added to the autoclave. After sealing, the autoclave was purged with N₂ for 30 min and then H₂ for 30 min at a stirring rate of 200 r/min at room temperature. After purging, the autoclave was filled with H₂ to 2.0 MPa and then heated to 220 °C by an electrical heater with stirring at 800 r/min. H₂ was continuously fed into the reactor to maintain the pressure at 8 MPa. After reaction for 4 h, the autoclave was cooled with tap water flowing through the cooling coil. The product mixture was then collected, filtered, and analyzed.

The products in liquid phase were analyzed qualitatively and quantitatively by high-performance liquid chromatography (HPLC; HP1100, Agilent, USA) equipped with a refractive index detector. A Platisil ODS C18 AQ column was used at 25 °C to separate the five main products of sorbitol, EG, PG, GL, and an unknown product. Redistilled water (0.6 mL/min) was used as mobile phase. Trace products like ethanol, methanol, and methane were detected in the gas phase in the reactor, but selectivity to gaseous products was less than 1%. The liquid products except the unknown substance were quantified using an external standard method. The selectivity to a specific product was expressed as the ratio of sorbitol converted into product to the total sorbitol converted.
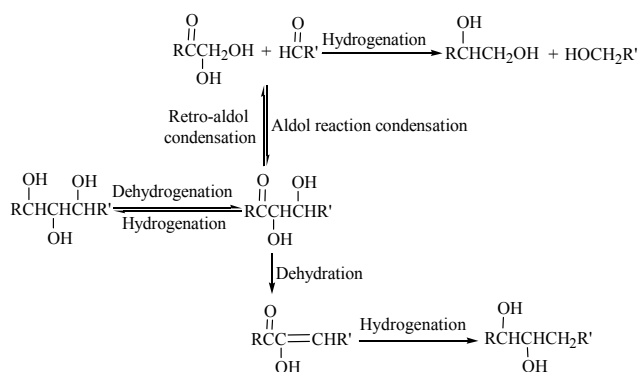
Scheme 1. Mechanism of polyol hydrogenolysis to lower polyols [16].