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碳纳米管负载钌催化纤维素与纤维二糖加
氢制山梨醇及酸催化纤维素甲醇醇解反应
的研究

Studies on Conversion of Cellulose and Cellobiose to Sorbitol
over Carbon Nanotube-Supported Ruthenium Catalysts and
Conversion of Cellulose in Methanol over Acid Catalysts

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**Studies on Conversion of Cellulose and Cellobiose to
Sorbitol over Carbon Nanotube-Supported Ruthenium
Catalysts and Conversion of Cellulose in Methanol over
Acid Catalysts**

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摘要

本论文以生物质转化制化学品为研究目的,研究了纤维素及其模型分子纤维二糖在碳纳米管负载钌催化剂 (Ru/CNT) 上催化加氢制山梨醇的反应和纤维素在酸催化条件下醇解生成甲基葡萄糖苷的反应。

在不同的条件下使用磷酸对商品纤维素 (结晶度 85%) 进行预处理,制备了一系列不同结晶度 (33%~85%) 的纤维素样品。考察了碳纳米管负载的各种金属催化剂和不同载体负载的钌催化剂在水相中,氢气气氛下催化转化纤维素 (结晶度 33%) 的催化性能。研究发现Ru/CNT对生成山梨醇显示高活性。该催化剂可转化商品纤维素获得 36%的山梨醇收率 (六元醇的总收率达 40%), 为目前文献报道的直接转化纤维素制山梨醇的最高收率。NH₃-TPD和H₂-TPD表明Ru/CNT催化剂表面充足的酸性位和独特的氢吸附物种是影响纤维素水解加氢生成山梨醇的重要因素。

以纤维二糖为模型分子研究了 Ru/CNT 催化水溶液中纤维素催化加氢的详细过程。纤维二糖转化经历以下步骤: (1) 纤维二糖中的一个葡萄糖环加氢生成 3-β-D-吡喃-D-糖醇中间体 (2) 3-β-D-吡喃-D-糖醇中间体水解断裂 β 糖苷键生成葡萄糖和山梨醇, 其中葡萄糖迅速加氢生成山梨醇; (3) 山梨醇连续转化, 异构得到甘露醇或降解为甘油等产物。(4) 与上述步骤不同, 少量纤维二糖经水解生成葡萄糖继而转化为山梨醇及其它产物。具有不同 Ru 粒径(2.4-12 nm)的 Ru/CNT 催化剂上纤维二糖催化加氢性能差异明显。具有小粒径 Ru (2.4、5.1 nm) 的 Ru/CNT 催化剂易于催化第 (1)、(3) 步加氢反应, 而对第 (2) 步糖苷键断裂活性较低; 具有大粒径 Ru (8.7、12 nm) 的 Ru/CNT 催化剂, 不利于第 (3) 步山梨醇加氢降解, 对第 (2) 步糖苷键断裂生成糖醇中间体的转化显示较高活性。小粒径 Ru 的 Ru/CNT 催化剂上较少的酸量可能是导致其不利于水解反应的原因。

研究了在酸催化条件下纤维素甲醇醇解转化为甲基葡萄糖苷的反应。研究发现, 硫酸、杂多酸 (H₄SiW₁₂O₄₀和H₃PW₁₂O₄₀) 和木质素磺化所得固体酸催化剂 (S-Lignin-17%) 对纤维素甲醇醇解有较高的反应活性。甲基葡萄糖苷收率可达 50~60%。较水体系中纤维素的水解反应, 在相同条件下纤维素在甲醇醇解反应中的转化率高, 生成的甲基葡萄糖苷收率较水体系中生成葡萄糖的收率高 40%。

关键词：纤维素；纤维二糖；Ru/CNT；催化加氢；甲基葡萄糖苷

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Abstract

Aimed at production of valuable chemicals from biomass, this dissertation studied the sorbitol production from the hydrogenation of cellulose and cellobiose, a model molecular of cellulose, over Ru/CNT catalysts and the methyl glucoside formation through the methanolysis of cellulose in methanol over acid catalysts.

Cellulose samples with different crystallinities (33-85%) were prepared by treating a commercial cellulose (crystalline, 85%) with phosphoric acid under different conditions. Supported different metal catalysts and Ru catalysts supported on different supports were examined for the conversion of cellulose with a crystallinity of 33% in water medium in the presence of hydrogen. The carbon nanotube supported- Ru catalyst (Ru/CNT) was found to be the most effective for the formation of sorbitol. 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. NH_3 -TPD and H_2 -TPD characterizations suggested that plenty of acid sites and unique hydrogen species over the Ru/CNT were important for sorbitol formation through hydrolysis and hydrogenation of cellulose.

As a model reaction for cellulose transformation, hydrogenation of cellobiose in water medium over Ru/CNT catalysts was studied. The conversion of cellobiose went through the following steps: (1) cellobiose was converted into 3- β -D-glucopyranosyl-D-glucitol via the hydrogenolysis; (2) this intermediate was transformed into sorbitol and glucose through the cleavage of β -1,4-glycosidic bond, after which glucose was converted to sorbitol rapidly; (3) sorbitol could undergo consecutive reactions through epimerization and degradation to form mannitol and degradation products such as glycerol. (4) Different from the steps mentioned above, a small amount of cellobiose was hydrolyzed firstly, and then converted to sorbitol and other products. Ru/CNT catalysts with Ru nanoparticles ranged from 2.4-12 nm showed distinct performances in the hydrogenation of cellobiose. The catalysts with smaller Ru nanoparticles (2.4, 5.1 nm) favored the hydrogenation steps (step 1 and

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