

SORBITOL HYDROGENOLYSIS TO GLYCOLS OVER CARBON NANOFIBERS/GRAPHITE-FELT COMPOSITE SUPPORTED RUTHENIUM CATALYST IN TRICKLE BED REACTOR

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Summary

Carbon nanofibers (CNFs) were in-situ grown on graphite-felt (GF), and then Ru was supported to synthesize Ru/CNFs/GF structured catalyst. It was found that Ru/CNFs/GF structured catalyst was more suitable than powdered Ru/CNFs catalyst for sorbitol hydrogenolysis in trickle bed reactor. For the structured catalyst, increasing the linear velocities would increase the sorbitol conversion, but not significantly change the glycols selectivity, which was due to the intensified mass transfer, while increasing the thickness of CNFs layer would decrease significantly the glycols selectivity, which was because of the increased diffusion distance for hydrogen and glycols in the mesopores of CNFs layer.

Keywords

Rational design of catalysts, Clean coal/heavy oil/frontier resources/biomass processing technologies
CNFs/GF composite and the effect of catalyst bed structure characteristics on sorbitol hydrogenolysis.

Introduction

Sorbitol hydrogenolysis to propylene glycol (PG) and ethylene glycol (EG) affords the opportunity to utilize a renewable resource for the large-scale production of commodity chemicals¹. Thanks to the unique properties of carbon nanofibers (CNFs), powdered Ru/CNFs catalyst has displayed attracting performance in sorbitol hydrogenolysis in autoclave². However, it is difficult to practically apply this Ru/CNFs catalyst, for the nano-ordered CNFs will induce severe problems, namely, difficulty in catalyst separation and product purification if the catalyst is used in industrial autoclave and high pressure gradient along the catalyst bed if the catalyst is used in trickle bed reactor. The method proposed recently to overcome these difficulties is to synthesize CNFs-related composite by in-situ growing CNFs on structured substrates. In the past several years, some relevant studies, mainly focusing on the synthesis and characterization of the CNFs composites, have been performed using different substrates, but there was little information available on the application of these composites, especially on the application in trickle bed reactor³.

In our latest work, we synthesized a CNFs/graphite-felt (GF) composite and further prepared a Ru/CNFs/GF structured catalyst⁴. The structured catalyst not only overcame aforementioned difficulty but also remarkably improved glycols selectivity in autoclave. In this work, we applied the Ru/CNFs/GF structured catalyst in trickle bed reactor, and mainly investigated the textural properties of

Experimental

CNFs/GF composite was synthesized by catalytic chemical vapor deposition of ethane on Ni/GF catalyst (cylinder with diameter of 12.2 mm and height of 10.0 mm) and the gas superficial velocity was same as that in our previous work⁴. Then the as-synthesized composite was purified twice in 4 M HNO₃ aqueous solution. The CNFs amount in composite, defined as the weight ratio of CNFs to Ni/GF catalyst and denoted as R, was ca. 0.20, 0.75 and 1.80 for the CNFs growth time of 4, 5 and 6 h. 3.0 wt% Ru/CNFs/GF structured catalysts, denoted as Ru/CNFs/GF-R (R=0.20, 0.75 and 1.80), were prepared using Ru(NO)(NO₃)₃ (Alfa) as precursor. Before being used, all the catalysts were reduced in H₂/Ar atmosphere. Sorbitol hydrogenolysis was conducted in trickle bed reactor at 240 °C and 6.0 MPa. The gas feedstock was pure hydrogen and the liquid feedstock was a 10 wt% sorbitol aqueous solution containing basic promoter NaOH (0.10 mol/kg). The gas hourly space velocity (GHSV) and the liquid hourly space velocity (LHSV) were kept at 2571 h⁻¹ and 17 h⁻¹, respectively, which gave a 12:1 H₂-sorbitol molar ratio. CNFs/GF composites or CNFs powder being the packing in trickle bed reactor, the pressure drop along the packed bed was measured with the working fluids same as those in sorbitol hydrogenolysis.

Results and discussion

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Table 1. Textural properties of CNFs layer in CNFs/GF composites.

Sample	External surface area (cm ² /g CNFs)	Pore volume (cm ³ /g CNFs)
CNFs/GF-0.20	201	0.36
CNFs/GF-0.75	148	0.28
CNFs/GF-1.80	120	0.20

SEM images show that the diameter of graphite microfibers in GF was ca. 15 μm and the thickness of CNFs layer wrapping the graphite microfibers increased from 1-2 μm to 10-12 μm with R increasing from 0.20 to 1.80. The diameter of CNFs was ca. 120 nm and much larger than that (ca. 60 nm) in our another work⁴, which indicated that the physical dimension of GF substrate had significant influence on the diameter of CNFs. Moreover, the longer CNFs growth time was, the looser the intertexture of CNFs layer was, which should be responsible for the fact, shown in Table 1, that the external surface area and the pore volume of CNFs layers were reduced with the R increasing. CO-chemisorption results demonstrated that Ru dispersion was ca. 20% in all the structured catalysts without regard to the external surface area of CNFs layer in composite.

As was expected, pressure gradient of composite packing was much lower than that of CNFs powder packing (Fig. 1) owing to the relatively high porosity of CNFs/GF composite. This clearly indicated that using CNFs/GF composite as catalyst support could successfully overcome the high pressure gradient encountered by Ru/CNFs powder catalyst when it was used in trickle bed reactor.

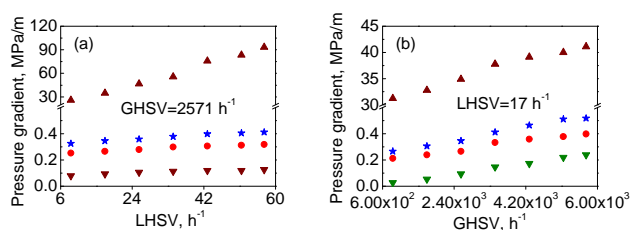


Fig. 1. Pressure gradient versus LHSV (a) and GHSV (b) for the packing of CNFs/GF composites and CNFs powder. (▲) CNFs powder; (▼) CNFs/GF-0.20; (●) CNFs/GF-0.75; (★) CNFs/GF-1.80.

Sorbitol hydrogenolysis experiments indicated that structured catalyst performed better than powdered Ru/CNFs catalyst. Noticeably, it was found that the structure characteristics of structured catalyst bed had interesting effect on sorbitol hydrogenolysis. Increasing catalyst amount improved sorbitol conversion but almost had no effect on glycols selectivity, which can be rationalized by considering the intensification of mass transfer in the bulk liquid phase and the polyol hydrogenolysis mechanism. With R increasing, sorbitol conversion was improved but glycols selectivity was decreased. The improvement of sorbitol conversion was due to the intensification of mass transfer in the bulk liquid phase and the existence of more Ru active sites,

while the reduction of glycols selectivity was due to the increase in the diffusion distance for reactants and products in CNFs layer. An overall analysis of the experiment results indicated that using Ru/CNFs/GF catalyst with less CNFs and increasing the amount of catalyst loaded in trickle bed reactor were helpful to increase the yield of glycols.

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