Glycerol Hydrogenolysis over Ruthenium Catalyst Supported on Multiwall Carbon Nanotubes

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Introduction

The production of glycols such as propanediols (PDO) and ethylene glycol (EG) by glycerol hydrogenolysis has attracted much attention in recent years. Ru catalysts have performed higher activity in the glycerol hydrogenolysis, but they often promote excessive C-C cleavage, resulting in lower selectivities to PDO and EG. Herein, we report our recent work on the glycerol hydrogenolysis over Ru catalyst supported on multiwall carbon nanotubes (Ru/MCNTs). We have found that the Ru/MCNTs showed superior performance in the glycerol hydrogenolysis under mild conditions.

Materials and Methods

The Ru/MCNTs catalysts were prepared by impregnating the HNO_3-pretreated MCNTs with an aqueous solution of $RuCl_3$, followed by drying, calcination in air and then reduction by H_2. They are denoted as Ru/MCNTs-IM. The glycerol hydrogenolysis was performed in a 100 mL-stainless steel autoclave equipped with a mechanic stirrer and a temperature controller. Typically, 20 mL of 20 wt% glycerol aqueous solution was added with 250 mg catalyst powder. After reaction, the gas-phase products were analyzed by using an on-line gas chromatograph equipped with a thermal conductivity detector. The liquid phase products, after being separated from the catalyst powder by filtration, were analyzed by using a gas chromatograph equipped with a flame ionization detector. A known amount of 1,4-butanetiol was used as an internal standard for the analysis. The catalysts were characterized by XRD, SEM, TEM, H_2-TPD, TPR and XPS.

Results and Discussion

Table 1 compares the performance of Ru catalysts supported on several carriers such as CH_4-derived-MCNTs, active carbon (AC), graphite, TiO_2 and Al_2O_3 for the hydogenolysis of 20% glycerol aqueous solution. Clearly, among the catalysts tested, the Ru/MCNTs exhibited the highest selectivities to 1,2-PDO (60.2%) and EG (20.4%). The catalysts with AC, TiO_2 and Al_2O_3 as supports gave higher conversion of glycerol, but they favored to produce CH_4. The Ru catalyst supported on graphite also showed higher selectivities to 1,2-PDO and EG, but its activity was much lower than that over Ru/MCNTs.

The glycerol hydrogenolysis on the Ru/MCNTs as a function of Ru loading is depicted in Figure 1. It can be seen that the glycerol conversion increased steeply with the increase in the Ru loadings, but the selectivities to 1,2-PDO and EG increase slightly when the loading weight lower than 5 wt%. After that they dropped gradually. The XRD patterns in Figure 2 revealed that the intensity of Ru diffraction peak increased with the increasing of loading, but the peak width did not changed significantly against the loading weight, which indicating that there were a good dispersion of Ru nanoparticles on the surfaces of MCNTs and the mean Ru particle size was about 10 nm in these samples.

To clarify the Ru particle size effect on the catalytic performance, we prepared the MCNTs-supported Ru catalysts by the reduction in liquid phase using EG (the sample was denoted as Ru/MCNTs-EG). The mean Ru particle size in 5 wt% Ru/MCNTs-EG sample was less than 5 nm. Such Ru/MCNTs-EG catalyst showed higher glycerol conversion of 64.1% but lower selectivity of 40.3% to 1,2-PDO (see Table 1). Preliminary evidences suggested that the metallic Ru particles with proper mean sizes might be required for the efficient conversion of glycerol to glycols. Further experiments are currently under way of progress.

Table 1. The effect of different supports on glycerol hydrogenolysis [a]

Catalysts (Ru loading=5 wt%)	Conversion / %	Selectivity / %					
		1,2-PDO	EG	C_2H_5OH	1-PO	CH_4	CO_2
Ru/MCNTs-IM	42.3	60.2	20.4	1.9	2.3	6.6	5.1
Ru/MCNTs-EG	64.1	40.3	23.8	3.3	7.9	14.4	0.7
Ru/AC-IM	46.6	20.3	19.3	6.0	2.0	36.9	3.0
Ru/TiO_2-IM	83.5	10.0	1.2	5.8	1.4	38.4	2.8
Ru/Al_2O_3-IM	82.0	18.4	7.9	4.9	2.5	35.6	2.9
Ru/Graphite-IM	16.0	53.0	18.3	4.7	9.0	5.0	1.3

[a] Reaction conditions: 20 wt% glycerol aqueous solution=20 mL, pressure=4.0 MPa, temp.=473K, time=12 h, stirring speed=500 rpm, PO=propanol.

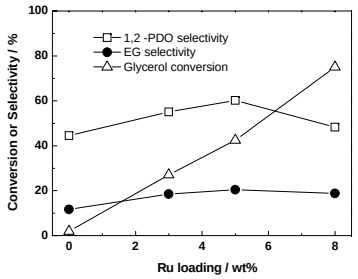

Figure 1. The effect of Ru loading on the glycerol hydrogenolysis.

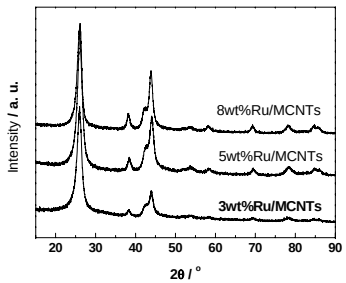

Figure 2. The XRD patterns of different loading Ru/MCNTs-IM.

Significance

The performance of Ru catalysts in the glycerol hydrogenolysis was essentially governed by the carriers, Ru particle size, Ru loading and reaction conditions. The Ru/MCNTs can be functioned as a novel class of efficient catalysts for the glycerol hydrogenolysis.

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