Ruthenium Nanoparticles Supported on Carbon Nanotubes for Selective Hydrogenolysis of Glycerol to Glycols

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Ru nanoparticles supported on carbon nanotubes showed efficient reactivity for hydrogenolysis of aqueous glycerol solution to produce glycols of 1,2-propanediol and ethylene glycol. The glycerol conversion along with the product selectivity depended essentially on the mean size of Ru nanoparticles. The Ru mean size around 5 nm showed the highest yield of glycols. The results indicated that the hydrogenolysis of glycerol catalyzed by the supported Ru nanoparticles might be structure-sensitive.

Glycerol is a potentially important renewable resource and feedstock, available from animal oil and fat, vegetable oil, or sugars by simple processes.[1] Recently, considerable efforts have been made for the transformation of glycerol to valuable commodity chemicals. Among them, the catalytic hydrogenolysis of glycerol has attracted much attention to produce glycols like propanediols (1,2-PDO and 1,3-PDO) and ethylene glycol (EG). For instance, Dasari et al. have explored CuCr catalysts which catalyzed glycerol hydrogenolysis to 1,2-PDO in high selectivity of 85% under the conditions of 473 K and 1.4 MPa.[2] However, the toxicity of Cr species inhibits further development considering green chemistry. Several groups have studied the hydrogenolysis of aqueous glycerol solution over CuZn catalysts, achieving quite promising selectivity to 1,2-PDO.[3] In fact, Ru catalysts have shown high activity in glycerol hydrogenolysis, but they often promote excessive C–C cleavage, resulting in lower selectivities to PDO and EG. Tomishige et al. have developed a Ru-based catalyst combined with ion-exchange resin (Amberlyst), which showed metal–acid bifunctions and high activity for glycerol hydrogenolysis under a high pressure of 8.0 MPa.[4] However, the heat resistance of the ion-exchange resin might be of concern under the hydrogenolysis temperatures. Herein, we report our recent work on glycerol hydrogenolysis over Ru nanopartcles supported on multiwalled carbon nanotubes (Ru/CNTs). We have found that the Ru/CNTs exhibited superior performance in glycerol hydrogenolysis, affording 1,2-PDO and EG as the major products.

The CNTs with outer diameter of 10–60 nm were prepared by the catalytic decomposition of CH_4.[5] The CNTs were pretreated and purified in concentrated HNO_3 at 363 K for 4 h to remove the residual contamination and amorphous carbon and also to create functional groups at the surface. The Ru/CNTs catalysts were prepared by impregnating the HNO_3-pretreated CNTs with an aqueous solution of $RuCl_3$, followed by drying, calcination in air, and then reduction by 5% H_2–N_2 at 300 °C for 4 h. They are denoted as Ru/CNTs-IM. For comparison, we have also prepared the CNTs-supported Ru catalysts by reduction in liquid phase using EG, followed by vacuum drying and then reduction with H_2. The samples are denoted as Ru/CNTs-EG. The mean size of metallic Ru particles formed in the functioning catalysts was estimated by the Sherrer equation and confirmed by TEM observations. The glycerol hydrogenolysis was performed in a 100-mL stainless steel autoclave equipped with a mechanical stirrer and a temperature controller. Typically, 20 mL of 20 wt % aqueous glycerol solution was added with 250-mg catalyst powder. After reaction, the gas-phase products were analyzed using an on-line gas chromatograph (GC) equipped with a thermal conductivity detector. The liquid-phase products, after being separated from the catalyst powder by filtration, were analyzed by using a GC equipped with a flame ionization detector. A known amount of 1,4-butanethiol was used as an internal standard for the GC analysis.

Table 1 compares the performance of Ru catalysts supported on several carriers such as CNTs, active carbon (AC), graphite, TiO_2, and Al_2O_3 for the hydogenolysis of 20% aqueous glycerol solution. Clearly, among the catalysts tested, the Ru/CNTs-IM exhibited the highest selectivity to 1,2-PDO (60.2%) and moderate selectivity to EG (20.4%). The catalysts with AC, TiO_2, and Al_2O_3 as supports gave higher conversion of glycerol, but they favored production of CH_4 rather than 1,2-PDO and EG. The Ru/graphite catalyst also showed higher selectivities to 1,2-PDO and EG, but its activity was much lower than the others. The Ru/CNTs-EG which prepared by reduction in liquid phase using EG showed higher glycerol conversion of 82.9% but lower selectivity of 30.0% to 1,2-PDO. Interestingly, the selectivity to CH_4 was considerably depressed over catalysts like Ru/CNTs and Ru/graphite. The intrinsic property of support may influence the catalyst structures such as the dispersion of Ru particles, and thus the catalysts exhibited different performances.

The glycerol hydrogenolysis on the Ru/CNTs-IM as a function of Ru loading is summarized in Table 2. It can be seen that the glycerol conversion increased gradually with the increase of Ru loadings and reached a maximum on the catalyst with Ru loading weight at 8 wt %. The 1,2-PDO selectivity also increases slightly with the Ru loadings and peaks with Ru loading weight of 5 wt %. As for the EG selectivity, it remained essentially at

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

Catalyst	Conv.	Selec./%					
	/%	1,2-PDO	EG	EtOH	1-PO	CH_4	CO_2
Ru/CNTs-IM	42.3	60.2	20.4	1.9	2.3	6.6	5.1
Ru/CNTs-EG	82.9	30.0	23.0	3.3	8.1	19.8	1.5
Ru/AC-IM	51.6	24.4	23.2	6.9	2.2	31.7	2.6
Ru/TiO_2-IM	81.7	35.2	12.7	8.3	6.7	25.3	1.5
Ru/Al_2O_3-IM	80.8	26.7	11.5	7.1	3.6	36.1	2.9
Ru/graphite-IM	16.0	53.0	18.3	4.7	9.0	5.0	1.3

[a]Reaction conditions: catalyst amount, 250 mg (Ru loading = 5 wt %); 20 wt % aqueous glycerol solution, 20 mL; H_2 pressure, 4.0 MPa; temp, 473 K; time, 12 h; stirring speed, 500 rpm; PO, propanol.

Table 2. Effect of Ru loading weight on the glycerol hydrogenolysis over Ru/CNTs-IM[a]

Ru loading	Conv.	Selec./%						TOF	Yield
/wt %	/%	1,2-PDO	EG	EtOH	1-PO	CH_4	CO_2	$/h^{-1}$	/%[b]
0	1.9	44.5	11.7	10.9	8.7	12.2	6.0	/	1.1
1	11.6	50.7	23.0	5.0	8.1	3.4	3.3	17.3	8.5
3	27.1	55.1	18.5	4.0	4.9	5.9	2.9	12.3	19.9
5	42.3	60.2	20.4	1.9	2.3	6.6	5.1	11.7	34.1
8	75.0	48.3	18.8	4.5	9.6	8.1	2.5	12.0	50.3
10	56.5	60.3	16.8	1.6	5.4	8.2	0.7	7.9	43.6

[a]The reaction conditions are the same as in Table 1. [b]Yield of glycols (1,2-PDO and EG).

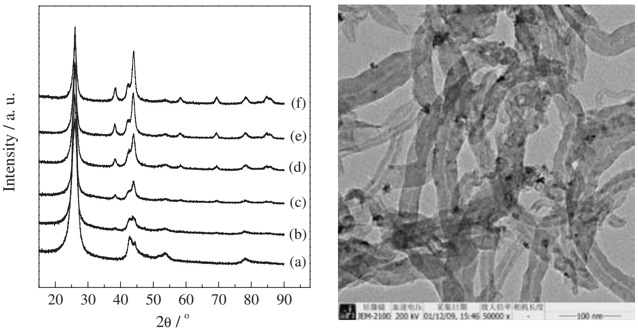

Figure 1. Left: XRD patterns of CNTs and Ru/CNTs-IM with different Ru loadings. (a) CNTs, (b) 1 wt % Ru, (c) 3 wt % Ru, (d) 5 wt % Ru, (e) 8 wt % Ru, (f) 10 wt % Ru.

around 20% over the variation of Ru loadings. The highest turnover frequency (TOF, moles of product by per mole of ruthenium species per hour, mol-product mol-Ru^{-1} h^{-1}, for short, h^{-1}) was obtained in the case of 1 wt % Ru loading weight, but it remained fairly stable over Ru loadings ranging from 3–8 wt %. Among them, Ru/CNTs-IM with Ru loading weight at 8 wt % affords the highest yield of glycols.

The XRD patterns and TEM image of Ru/CNTs-IM are depicted in Figure 1. As expected, the intensity of metallic Ru diffraction lines gradually increased with the increase of Ru loading. The mean size of Ru nanoparticles with Ru loadings ranging from 1–10 wt % was estimated to be around at 3–10 nm (see Supporting Information).[6] Therefore, besides the variation of Ru loadings, a subtle difference in the mean size of Ru nanoparticles may be the crucial issue accounting for the results in Tables 1 and 2.

To clarify the Ru particle size effect on the catalytic performance, we have prepared 5 wt % Ru/CNTs-IM catalyst with different mean sizes of Ru particles by means of employing different calcination and reduction temperatures. Plots of TOF and product selectivities versus the mean size of Ru particles are displayed in Figure 2. It becomes clear that the reaction TOF, selectivity, and yield of glycols considerably depend on the mean size of Ru particles. The reaction TOF declined continuously, while the selectivities to 1,2-PDO and EG essentially increased with the increase in the mean size of Ru particles. The catalysts with larger or smaller mean sizes of Ru particles exhibited lower yield of glycols. Taking the yield of glycols into account, the Ru particles with mean size around 5 nm may be requisite for the glycerol hydrogenalysis to produce glycols.

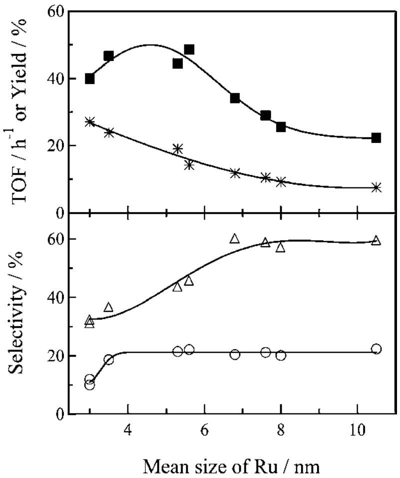

Figure 2. Dependence of glycerol conversion, selectivity, and yield of glycols on the mean size of Ru particles. (■) yield of glycols (1,2-PDO and EG), (✳) TOF, (△) 1,2-PDO selectivity, (○) EG selectivity.

In summary, the Ru nanoparticles supported on CNTs showed higher performance for glycerol hydrogenolysis to produce glycols of 1,2-PDO and EG in comparison with that supported on other carriers. The mean size of Ru particles played a key role in the glycerol conversion and product selectivities. The yield of glycols showed a maximum at the Ru particles with mean size around 5 nm. The CNTs may not take part in the construction of the active sites, and the beneficial action is more probably indirect, including enhancing the adsorption/desorption and promoting the spillover/activation of hydrogen species. Further investigation on this issue is under way of progress.

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6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.