

Carbon Nanotube-Promoted Cu-Zn Catalysts for Efficient Hydrogenolysis of Glycerol to Glycols

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Introduction

In recent years, considerable efforts have been made for the transformation of glycerol to high value-added chemicals. Among them, the catalytic hydrogenolysis of glycerol has attracted much attention since the process is relatively simple and more importantly, its products such as 1,2-propylene glycol (1,2-PG) and ethylene glycol (EG) are highly demanded in the production of polymers, resins, functional fluids, foods and cosmetics. Currently, the glycerol hydrogenolysis has been essentially carried out using Cu and Ru-based catalysts. On the other hand, the promoted effects in terms of catalytic activity and product selectivity are possibly obtained in the case of using carbon nanotubes as catalyst carrier or promoter. Herein, we report the development a type of multiwall carbon nanotubes (MCNTs)-promoted Cu-Zn catalysts, which display excellent performance for the glycerol hydrogenolysis to produce glycols under mild conditions.

Materials and Methods

The MCNTs with outer diameter 10–60 nm were prepared by a catalytic decomposition of CH_4 [1]. The as-grown MCNTs were pretreated in a concentrated HNO_3 at 90 °C for several hours to remove the residual catalyst and the amorphous carbon and also to create the functional groups at their surfaces. Cu-Zn-MCNTs catalysts were prepared by co-precipitation method. A solution containing $\text{Cu}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$ and another solution of Na_2CO_3 were simultaneously added dropwise into the purified MCNTs at 90 °C with vigorous stirring. The pH of solution was set at around 6.5. After further stirring for 5 h, the mixture was cooled to room temperature and aged for several hours. The precipitates were collected by filtration, followed by washing, drying, calcination in air and then reduction by H_2 . The glycerol hydrogenolysis was performed in a 100 mL-stainless steel autoclave equipped with a mechanic stirrer and a temperature controller. Typically, 24 mL of 20 wt% glycerol aqueous solution was added with 320 mg catalyst powder. After reaction, the gas and liquid products were analyzed by gas chromatographs, respectively. The catalysts were characterized by XRD, H_2 -TPR, SEM, TEM and XPS.

Results and Discussion

Table 1 lists the representative results of $\text{Cu}_{0.75}\text{Zn}_{0.25}$ promoted by MCNTs with varying the pretreatment time. The MCNTs-promoted $\text{Cu}_{0.75}\text{Zn}_{0.25}$ catalysts showed higher glycerol conversion than the non-promoted one under identical conditions. Among them, the

catalyst containing the MCNTs pretreated for 4 and 12 h exhibited considerable increase in the glycerol conversion. In the case of the reaction catalyzed by Cu-Zn-MCNTs, no significant differences in the product selectivities were obtained from each other, but there was a slight decrease in the selectivity to 1,2-PG as compared to that obtained over the non-promoted one.

The MCNTs interacted well with the Cu-Zn moieties as shown in the SEM image (Figure 1). Figure 2 shows the H_2 -TPR profile of $\text{Cu}_{0.75}\text{Zn}_{0.25}$ catalysts with and without MCNTs. The reduction peaks of Cu-Zn-MCNTs were *ca.* 50 °C lower than that of the one without MCNTs, implying that there might contain easier reducible Cu-species in the MCNTs-promoted samples. Also, a higher Cu-dispersion was convinced in the MCNTs-promoted samples.

Table 1. The glycerol hydrogenolysis over $\text{Cu}_{0.75}\text{Zn}_{0.25}$ catalysts with and without MCNTs

Catalyst	Conv. /%	Selectivity / %					C-balance / %
		1,2-PG	EG	CH_4	CO_2	other	
$\text{Cu}_{0.75}\text{Zn}_{0.25}$	44.6	80.4	4.8	0.2	11.9	0.7	97.8
$\text{Cu}_{0.75}\text{Zn}_{0.25}$ -12.5%MCNT_0	59.3	77.7	7.0	0.1	9.0	0.6	94.4
$\text{Cu}_{0.75}\text{Zn}_{0.25}$ -12.5%MCNT_4	73.4	77.1	5.3	0.2	15.9	0.8	99.3
$\text{Cu}_{0.75}\text{Zn}_{0.25}$ -12.5%MCNT_12	72.0	77.8	5.5	0.3	13.9	0.4	97.8
$\text{Cu}_{0.75}\text{Zn}_{0.25}$ -12.5%MCNT_24	57.4	77.9	4.4	0.3	12.9	0.5	96.0

Reaction conditions: 20% glycerol aqueous solution=24 g; catalyst weight=320 mg; reaction time=18 h; pressure=2.5 MPa; temperature=200 °C; stirring speed=800 rpm.

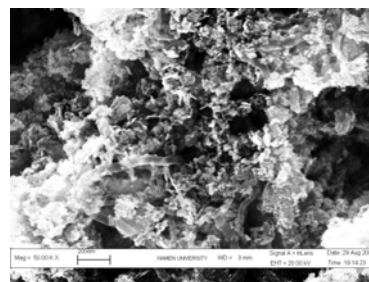


Figure 1. SEM image of $\text{Cu}_{0.75}\text{Zn}_{0.25}$ -12.5%MCNTs_12 catalyst.

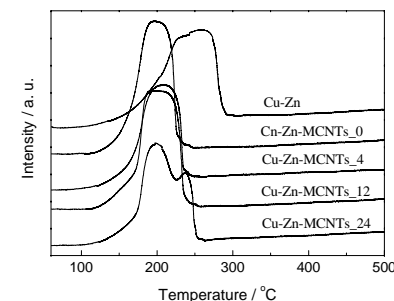


Figure 2. The TPR profile of $\text{Cu}_{0.75}\text{Zn}_{0.25}$ catalysts with and without MCNTs.

Significance

The present work shows that the MCNTs could serve as excellent catalyst-promoters. The MCNTs-promoted Cu-Zn catalysts achieves selective formation of 1,2-PG and EG from the glycerol hydrogenolysis under mild conditions, and demonstrates great potential in commercial use.

Reference

- Chen, P., Zhang, H.B., Lin, G.D., Hong, Q., and Tsai, K.R. *Carbon* 35,1095 (1997).

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