Modified Cu/Cr Catalysts for Glycerol Conversion into 1,2-Propandiol in Aqueous Phase Hydrogenolysis

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Introduction

Conversion of glycerol into high valued chemicals has been a focus of many recent research due to exponential growth in biodiesel production in the world [1,2]. Cu/Cr catalysts have been applied for glycerol conversion into 1,2-propanediol (PG) [3]. A common issue with Cu/Cr catalysts for glycerol conversion is low activity. We report here a preliminary study of using modified Cu/Cr catalysts for glycerol conversion.

Materials and Methods

Commercial Cu/Cr catalysts from Sud-Chemie were used as base material. Different promoters were dip-coated on the commercial Cu/Cr catalysts. Catalysts were calcined and characterized by Temperature Programmed Reduction (TPR). Catalyst activity was tested for glycerol conversion by using Parr autoclave. Liquid samples were taken every hour and analyzed by HPLC. 20 grams of catalysts and 300ml 25 wt% glycerol as feed were used for all tests.

Results and Discussion

Commercial Cu-chromite catalyst (Cu/Cr) and two modified catalysts were tested. TPR results are presented in Figure 1. Clearly, addition of promoters resulted in an increase in reduction temperature of Cu from a peak temperature of ca. 150 ºC to 164 ºC. Reduction temperatures for promoters are significantly lower than normal reduction temperatures, indicating a possible high dispersion of promoters on the Cu/Cr catalyst.

Results of activity tests for glycerol conversion are presented in Table 1. Addition of modifiers significantly increased the activity of Cu/Cr catalyst, but selectivity towards PG varies. Pure Cu/Cr catalyst achieved highest selectivity for PG, whereas Cu/Cr-M2 has a little lower selectivity but much higher activity.

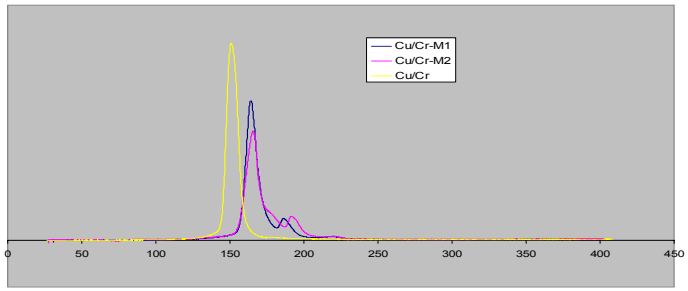

Figure 1. TPR results of Cu/Cr and modified Cu/Cr Catalysts

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Table 1. Activity for Glycerol Conversion

Catalyst	Glycerol Conversion [a] (%)	PG selectivity [b] (%)	CO_2 (mol %)	CH_4 (mol%)
Cu/Cr	16.0	82.0	0.65	0
Cu/Cr-M1	37.3	63.3	0.20	0.03
Cu/Cr-M2	43.1	73.8	0.49	0

Note: a. conversion was calculated at 240 min reaction time.
b. selectivity is defined as weight of PG produced over total glycerol consumed. Also calculated at 240 min reaction time.

Significance

Effective, stable and robust catalysts are in urgent need in industry for biomass conversion in aqueous phase reaction. Conversion of glycerol as by-product from the biodiesel industry is a good example for this application.

References

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2. Lang, X, et al, Bioreour. Technol, 80, 53 (2001)
3. Dasari, M.A., et al, Appl Catal A., 281, 225 (2005)