

Conversion of Glycerol to Ethylene Glycol over Pt-modified Ni Catalyst

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In glycerol hydrogenolysis, Ni/ γ -Al₂O₃ gave 1,2-propanediol mainly. In contrast, modification of the Ni/ γ -Al₂O₃ catalyst with a small amount of Pt promoted the conversion to ethylene glycol and CH₄ by hydrocracking. This property is related to the formation of a Pt–Ni alloy surface.

Biomass is the only carbon-based material among various renewable resources. Therefore, biomass will be converted to liquid fuels and chemicals for the partial substitution of petroleum in future biorefineries. Glycerol is regarded as an important building block because of the large production of glycerol from vegetable oils in biodiesel fuel processes.^{1,2} A lot of approaches for the conversion of glycerol to value-added chemicals have been attempted. One approach is the hydrogenolysis of glycerol. It has been reported that various catalysts are effective for the hydrogenolysis to 1,2-propanediol^{3,4} and 1,3-propanediol.^{5,6} 1,3-Propanediol is more suitable as a raw material in resin production than 1,2-propanediol; however, the obtained yield of 1,3-propanediol is much lower than 1,2-propanediol. Ethylene glycol is another target of glycerol hydrogenolysis since much more ethylene glycol is used as raw material in conventional resin production than 1,3-propanediol. In fact, it has been reported that ethylene glycol is formed in low yield as a by-product in the glycerol hydrogenolysis to 1,2-propanediol.⁷ Therefore, more selective catalysts are needed. In addition, biomass-derived ethylene glycol produced from cellulose and sorbitol has attracted attention.⁸ In this letter, we report that Ni/ γ -Al₂O₃ with a small amount of Pt catalyzes the hydrogenolysis of glycerol with high selectivity to ethylene glycol.

The Ni catalysts were prepared by impregnating γ -Al₂O₃ (KHO-24, $S_{\text{BET}} = 133 \text{ m}^2 \text{ g}^{-1}$, Sumitomo Chemical Co., Ltd.) with an aqueous solution of Ni(NO₃)₂·6H₂O. The Ni catalysts modified with Pt were prepared by coimpregnation using a mixed aqueous solution of H₂[PtCl₆]·6H₂O and Ni(NO₃)₂·6H₂O. The loading amount of Ni and Pt in wt% is denoted in parentheses such as Pt(0.5) + Ni(5). Raney Ni (Raney®2800 Nickel, Sigma-Aldrich Co., Ltd. 89% Ni) was also tested. Analysis of products and calculation of conversion and selectivity were the same as described in our previous report.^{3,6} The maximum yield of ethylene glycol (EG) is 66% because one glycerol molecule produces one EG and one C1 molecule. The details of the methods for the catalyst preparation and characterization are described in the Supporting Information.⁹

The results of glycerol hydrogenolysis are summarized in Table 1. Monometallic Ni catalysts have activity to some extent (Entries 1–3), and the selectivities are similar to the reported values for Ni/Al₂O₃ (41% Ni).⁴ The C–O hydrogenolysis to 1,2-

propanediol (1,2-PrD) was the main reaction, and the target hydrocracking reaction to EG was minor. For Ni(5) and Ni(10), the selectivity ratio of EG/CH₄ was close to the stoichiometry (EG/CH₄ = 2). In the case of Raney Ni, the conversion was lower than Ni(5) although the Ni content in Raney Ni was 18 times as high as that in Ni(5). In addition, the selectivity to CH₄ was higher than half of the selectivity to EG, indicating that the consecutive reactions of the primary products to CH₄ proceeded as side reactions. Based on these results, the modification of Ni(5) was investigated. The additive effect of noble metals (Ru, Pd, Rh, Ir, and Pt) at a fixed molar ratio (0.03) was investigated (Entries 4–8). The effect of Ru and Pd addition is not significant, in contrast, the addition of Ir, Rh, and Pt enhanced the selectivity to EG and decreased the selectivity to 1,2-PrD. In particular, the addition of Pt is most effective. The Pt catalyst without Ni showed almost no activity (Entry 12). Catalysts with different amount of additive Pt were compared (Entries 8–11). It is concluded that the optimum amount of Pt was 0.5% in view of both conversion of glycerol and selectivity to EG. Here, the selectivity to EG is higher than that to 1,2-PrD, which means that the hydrocracking reaction to EG becomes the main reaction. In addition, the selectivity ratio of EG to CH₄ was almost 2 on the Pt(0.5) + Ni(5) catalyst, showing that over-hydrocracking to CH₄ hardly proceeded. In order to get higher yield of EG, larger amount of the catalyst and longer reaction time were applied (Entries 13–15). The conversion gradually increased with the reaction time, selectivity to EG decreased, and selectivity to CH₄ increased. The selectivity to 1,2-PrD was hardly changed. The maximum yield of EG on Pt(0.5) + Ni(5) reached 31% at 48 h. In order to explain the product distribution and the decrease in selectivity to EG at higher conversion, the reaction of 1,2-PrD, EG, and methanol over Pt(0.5) + Ni(5) was also tested (Entries 16–18). The reactivity of 1,2-PrD and EG was lower than that of glycerol. The reaction of 1,2-PrD produced ethanol and CH₄, and no EG was formed. Therefore, both 1,2-PrD and EG were directly produced from glycerol. The main product of reaction of EG was CH₄, suggesting that the consecutive reaction of EG to CH₄ proceeded at longer reaction time in the reaction of glycerol. It should be noted that the reactivity of methanol was as high as of glycerol (Entries 8 and 18). This tendency can explain higher selectivity to CH₄ than that to methanol in the reaction tests using various substrates.

In the XRD patterns of Ni(5) and Pt(0.5) + Ni(5), only the peaks assigned to γ -Al₂O₃ were observed after the passivation, suggesting that the Ni species is highly dispersed on both catalysts (Figure S1).⁹ In contrast, the catalysts after use gave the peaks assigned to Ni metal and boehmite (AlOOH). The BET surface area of Pt(0.5) + Ni(5) after passivation and catalytic use was 133 and 28 m² g⁻¹, respectively. The decrease

Table 1. Results of the activity tests of nickel-based catalysts^a

Entry	Catalyst	Catalyst weight /g	Reactant	Time /h	Conv. /%	Selectivity/% ^b					
						EG	EtOH	CH ₄	CH ₃ OH	1,2-PrD	Others
1	Ni(5)	0.2	Glycerol	24	12	17	1	8	0	74	0
2	Ni(10)	0.2	Glycerol	24	11	20	1	10	0	69	0
3	Raney Ni	0.2	Glycerol	24	10	38	1	28	0	33	0
4	Ru + Ni(5) ^c	0.2	Glycerol	24	12	12	3	8	1	76	0
5	Pd + Ni(5) ^c	0.2	Glycerol	24	10	13	3	8	1	74	1
6	Rh + Ni(5) ^c	0.2	Glycerol	24	11	32	2	26	1	38	1
7	Ir + Ni(5) ^c	0.2	Glycerol	24	9	35	2	26	1	35	1
8	Pt(0.5) + Ni(5) ^c	0.2	Glycerol	24	16	48	0	25	0	27	0
9	Pt(0.1) + Ni(5)	0.2	Glycerol	24	15	38	1	20	0	41	0
10	Pt(1) + Ni(5)	0.2	Glycerol	24	10	47	0	23	0	29	1
11	Pt(5) + Ni(5)	0.2	Glycerol	24	9	38	0	18	0	41	3
12	Pt(0.5)	0.2	Glycerol	24	<1	0	0	Trace	0	Trace	0
13	Pt(0.5) + Ni(5)	1.0	Glycerol	24	64	42	3	37	2	15	1
14	Pt(0.5) + Ni(5)	1.0	Glycerol	48	79	39	4	40	2	14	1
15	Pt(0.5) + Ni(5)	1.0	Glycerol	72	83	36	5	42	2	14	1
16	Pt(0.5) + Ni(5)	0.2	1,2-Propanediol	24	4	0	59	35	2	—	4
17	Pt(0.5) + Ni(5)	0.2	Ethylene glycol	24	4	—	12	67	21	—	0
18	Pt(0.5) + Ni(5)	0.2	Methanol	24	11	—	—	100	—	—	—

^aReaction conditions: 5 mass % aqueous solution, 20 mL; initial H₂ pressure, 8.0 MPa; reaction temperature, 453 K. ^bEG ethylene glycol, PrD propanediol. ^cNoble metal/Ni molar ratio 0.03.

Table 2. Curve fitting result of Pt L₃-edge EXAFS of Pt(0.5) + Ni(5) after the catalytic use

Catalyst	Shells	CN ^a	R/10 ⁻¹ nm ^b	σ/10 ⁻¹ nm ^c	ΔE ₀ /eV ^d	R _f /% ^e
Pt(0.5) + Ni(5)	{ Pt–Ni Pt–Pt }	{ 5.8 1.4 }	{ 2.52 2.70 }	{ 0.083 0.070 }	{ 2.7 9.6 }	{ 1.0 }

^aCoordination number. ^bBond distance. ^cDebye–Waller factor.

^dDifference in the origin of photoelectron energy between the reference and the sample. ^eResidual factor. Fourier filtering range: 0.147–0.288 nm.

of the surface area can be due to the structural change of γ -Al₂O₃ to boehmite under hydrothermal conditions as reported previously.¹⁰ The Ni metal particle size on Pt(0.5) + Ni(5) and Ni(5) after catalytic use was estimated to be 32 and 23 nm from the linewidth of the (111) peak ($2\theta = 44^\circ$). The Pt L₃-edge EXAFS of Pt(0.5) + Ni(5) after the catalytic use was measured (Figure S2),⁹ and Table 2 shows the curve fitting result. The Pt–Ni and Pt–Pt bonds were detected. The length of the Pt–Ni bonds (0.252 nm) and Pt–Pt bonds (0.270 nm) was between that of the Ni–Ni bond in Ni metal (0.249 nm) and that of the Pt–Pt bond in Pt metal (0.277 nm). This behavior can be due to the alloy formation of Pt–Ni. The higher coordination number of the Pt–Ni bond than that of the Pt–Pt bond is reflected by the small molar ratio of Pt/Ni (0.03) on the Pt(0.5) + Ni(5). The surface Pt atom on the Ni-rich Pt–Ni alloy surface¹¹ can enhance the selectivity to EG. According to a previous report, glycerol to EG proceeds via retro-aldol reaction of glyceraldehyde.¹² One possible explanation of the Pt effect is promotion of the retro-aldol reaction. Another explanation is promotion of the dissociation of C–C bond. In order to elucidate the additive effect of Pt, further investigation is necessary.

References and Notes

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