

Promoting Effect of Re Addition to Rh/SiO₂ on Glycerol Hydrogenolysis

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Modification of Rh/SiO₂ with ReO_x enhanced the activity of glycerol hydrogenolysis remarkably and suppressed degradation reactions simultaneously. At the same time, the formation of 1,3-propanediol became more favorable on the Rh–ReO_x/SiO₂.

Glycerol is a major by-product in the production of biodiesel by the transesterification of vegetable oils with methanol, and it is also expected to be a building block in future biorefineries. The potential conversion of renewable resources such as glycerol into valuable commodity chemicals can facilitate the replacement of petroleum-based products.^{1,2} From this viewpoint, hydrogenolysis of glycerol to valuable propanediols becomes increasingly important. It is reported here that the modification of Rh/SiO₂ with Re species enhanced the activity and the selectivity in the glycerol hydrogenolysis.

The Rh–MO_x/SiO₂ (M = Re, Mo, and W) catalysts were prepared by impregnation using RhCl₃·3H₂O, NH₄ReO₄, (NH₄)₆Mo₇O₂₄·4H₂O, (NH₄)₁₀W₁₂O₄₁·5H₂O, and SiO₂ (surface area 535 m² g^{−1}) and calcined at 773 K. The amount of Re, Mo, and W is represented in parenthesis as a molar ratio to Rh, and it was optimized from activity tests. Rh loading was 4 wt %. As a reference, commercially available Ru/C (5 wt %),³ Raney Ni,⁴ copper–chromite,⁵ and Amberlyst15³ were used. Activity evaluation of the glycerol hydrogenolysis was carried out in a 190-mL stainless autoclave and 20 mL of 20 wt % aqueous glycerol solution. Procedures for the activity tests and product analysis were carried out, and selectivity of products was calculated in the same way as described in our previous report.³

The modification of Rh/SiO₂ with Re, Mo, and W species enhanced the activity of the glycerol hydrogenolysis remarkably, and the addition of Re is most effective (Table 1, Entries 1 and 3–5). They showed much higher activity than Raney Ni and copper–chromite, which were used at higher reaction temperature (Table 1, Entries 13 and 14). It has been reported that the glycerol hydrogenolysis proceeds by dehydration of glycerol to acetol over Amberlyst and subsequent hydrogenation of acetol to 1,2-propanediol over Ru/C over Ru/C + Amberlyst.³ The Rh–MO_x/SiO₂ showed higher activity than Ru/C and Ru/C + Amberlyst (Table 1, Entries 6 and 7), and this suggests that the hydrogenolysis over Rh–MO_x/SiO₂ can proceed in a direct route. At the same time, modification of Rh/SiO₂ suppressed degradation reactions, which gave ethylene glycol, ethanol, methane, and methanol by dissociation of carbon–carbon bonds in the glycerol molecule. The selectivity of the degradation reaction over Rh/SiO₂ increased at lower H₂ pressure or higher reaction temperature (Table 1, Entries 9 and 11). On the other hand, degradation selectivity on Rh–ReO_x/SiO₂ was maintained to be low even at lower H₂ pressure or higher reaction temper-

ature (Table 1, Entries 8 and 10). Another interesting point is that the modification of Rh/SiO₂ with ReO_x enhanced the selectivity of 1,3-propanediol formation. The selectivity of 1,3-propanediol over conventional catalysts is usually very low. The conversion order was found to be glycerol ≈ 1,3-propanediol > 1,2-propanediol (Table 1, Entries 5, 18, and 20). This result suggests that 1,3-propanediol yield in the glycerol hydrogenolysis can be decreased by the consecutive hydrogenolysis of 1,3-propanediol. On the other hand, the conversion order on Rh–ReO_x/SiO₂ was glycerol > 1,2-propanediol > 1,3-propanediol (Table 1, Entries 2, 17, and 19). The low reactivity of 1,3-propanediol on Rh–ReO_x/SiO₂ can enhance the yield of 1,3-propanediol in the glycerol hydrogenolysis.

In addition, Rh–ReO_x/SiO₂ was also effective in the hydrogenolysis of glycerol without any solvent (Table 1, Entry 15). Compared to the case of the diluted glycerol, the selectivity of 1,3-propanediol was higher. The yield of 1,3-propanediol over Rh–ReO_x/SiO₂ reached 12% (Table 1, Entry 16). It has been reported that Rh(CO)₂(acac) and H₂WO₄ in 1-methyl-2-pyrrolidinone gave 21% yield of 1,3-propanediol at a Rh-based turnover frequency (TOF) of ca. 3 h^{−1} and turnover number (TON) of 79 at 473 K and 32 MPa of synthesis gas (CO:H₂ = 1:2).⁶ In addition, it has recently been reported that Pt/WO₃/ZrO₂ in 1,3-dimethyl-2-imidazolidinone gave 24% yield of 1,3-propanediol at Pt-based TOF of ca. 4 h^{−1} and TON of 73 at 443 K and 8 MPa H₂.⁷ Although the present yield was smaller than these reported results, advantages of Rh–ReO_x/SiO₂ are that the glycerol hydrogenolysis proceeded without the use of organic solvent at a lower reaction temperature; moreover, a much higher TON (1320) and TOF (13.8 h^{−1}) were obtained (Table 1, Entry 16). In addition, in the case of the Rh–ReO_x/SiO₂, water is much more suitable as a solvent than 1-methyl-2-pyrrolidinone and 1,3-dimethyl-2-imidazolidinone. In contrast, Rh/C + H₂WO₄ was ineffective in the aqueous solution (Table 1, Entry 12).⁸

From the results of TEM observation, average metal particle sizes of Rh/SiO₂ and Rh–ReO_x/SiO₂ (Re/Rh = 1/2) were determined to be 3.5 ± 0.4 and 4.3 ± 0.4 nm, respectively. On the other hand, the amounts of CO adsorption (molar ratio: CO/Rh) on Rh/SiO₂ and Rh–ReO_x/SiO₂ were measured to be 0.39 and 0.17, respectively.^{9,10} From comparison of TEM and CO adsorption, Re modification can suppress CO adsorption by the direct interaction between Re and Rh metal particles. Considering the very low activity of ReO_x/SiO₂ the interaction between Rh and ReO_x might be related to the cooperative function as follows: the OH group in the reactants is adsorbed dissociatively on ReO_x species, and hydrogenolysis of the C–O bond catalyzed by neighboring Rh metal surface,¹⁰ although this mechanism is not demonstrated at present. In addition, higher activity of Rh–ReO_x/SiO₂ as compared with the reported catalyst system can

Table 1. Results of the hydrogenolysis of glycerol, 1,3-propanediol, and 1,2-propanediol^a

Entry	Catalysts	Catalyst weight/mg	Temp /K	Time /h	Conc. /%	Conv. /%	Selectivity /% ^d				
							1,3-PrD	1,2-PrD	1-PrOH	2-PrOH	Degradation
Glycerol											
1	Rh–ReO _x /SiO ₂ (1/2)	150	393	5	20	79.0	14.0	41.5	32.9	11.0	0.6
2	Rh–ReO _x /SiO ₂ (1/2)	150	393	2	20	38.4	16.1	46.9	26.7	9.7	0.6
3	Rh–MoO _x /SiO ₂ (1/16)	150	393	5	20	45.8	6.0	32.1	46.3	13.9	1.7
4	Rh–WO _x /SiO ₂ (1/8)	150	393	5	20	33.7	11.3	43.2	32.9	9.8	2.8
5	Rh/SiO ₂	150	393	10	20	7.2	7.9	38.1	35.2	12.6	6.2
6	Ru/C	150	393	10	20	3.5	4.9	26.4	26.7	0.3	41.7
7	Ru/C + Amberlyst	150 + 300	393	10	20	12.9	4.9	55.4	14.1	0.9	24.7
8	Rh–ReO _x /SiO ₂ (1/2)	150	433	2	20	86.2	10.4	42.2	35.2	9.6	2.6
9	Rh/SiO ₂	150	433	10	20	28.2	3.4	23.5	27.6	6.7	38.8
10	Rh–ReO _x /SiO ₂ (1/2) ^b	150	393	5	20	42.1	16.1	41.1	32.3	9.5	1.0
11	Rh/SiO ₂ ^b	150	393	10	20	1.8	6.6	29.7	25.5	4.0	34.2
12	Rh/C + H ₂ WO ₄	150 + 180	453	5	20	5.7	0.0	46.8	0.6	46.8	50.8
13	Raney Ni	1500	453	5	20	5.7	1.5	36.8	0.4	0.4	60.9
14	Copper–chromite	1500	453	5	20	0.8	0.0	53.6	25.4	8.5	12.5
15	Rh–ReO _x /SiO ₂ (1/2)	150	393	5	100 ^c	15.0	28.0	51.2	16.3	3.1	1.4
16	Rh–ReO _x /SiO ₂ (1/2)	50	393	96	100 ^c	61.3	19.7	34.0	38.3	7.2	0.8
1,3-Propanediol											
17	Rh–ReO _x /SiO ₂ (1/2)	150	393	2	20	11.8	0.0	—	97.9	—	2.1
18	Rh/SiO ₂	150	393	10	20	6.6	0.0	—	85.6	—	14.4
1,2-Propanediol											
19	Rh–ReO _x /SiO ₂ (1/2)	150	393	2	20	14.0	—	0.0	81.7	15.1	3.2
20	Rh/SiO ₂	150	393	10	20	2.9		0.0	73.2	25.8	1.0

^aReaction conditions: 8.0 MPa initial H₂ pressure. ^b2.0 MPa initial H₂ pressure. ^cGlycerol 20 g. ^dPrD = propanediol, PrOH = propanol.

be due to the direct interaction of Rh and Re because on the latter metal and metal oxide species can exist separately.^{6–8} The selectivity of the glycerol hydrogenolysis can be dependent on the structure of adsorbed glycerol since the glycerol molecule has two kinds of OH groups. Therefore, spectroscopic observation of adsorbed glycerol as reaction intermediate will contribute to catalyst development with higher selectivity of 1,3-propanediol in the glycerol hydrogenolysis.

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