Synthesis of butanediols by selective hydrogenolysis of 1,4-anhydroerythritol

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Abstract: We conducted hydrogenolysis of 1,4-anhydroerythritol (1,4-AHERY) to butanediols, especially to those with internal -OH groups, over transition-metal-oxide-modified Rh/SiO_2 and Ir-ReO_x/SiO_2 catalysts. MoO_x-, WO_x-, and ReO_x-modified Rh/SiO_2 catalysts showed over three times higher conversion than Rh/SiO_2. 2,3-Butanediol was obtained with 12% yield over Rh-MoO_x/SiO_2. However, 1,3-butanediol was hardly produced over Rh/SiO_2 and transition-metal-oxide-modified Rh/SiO_2 catalysts (≤3% selectivity). Ir-ReO_x/SiO_2 catalyst showed 25% selectivity to 1,3-butanediol although the activity was similar to Rh/SiO_2.

Keywords: Iridium, Rhodium, Hydrogenolysis, Erythritol.

1. Introduction

Renewable biomass resources are attractive as substitutes for petroleum from the environmental viewpoint, and many industrial chemicals are actually produced from petroleum resources. Erythritol, which can be produced easily by the fermentation of sugars, is regarded as a promising C_4 intermediate from biomass. Butanediols are used in various applications, such as solvents, especially for organic synthesis, and raw material for polyester resin. However, butanediols are produced from petroleum resources, for example, butadiene and acetaldehyde. Recently, our group discovered ReO_x-Pd/CeO_2 catalyst for selective hydrogenolysis of erythritol, to 1,2-butanediol in 77% yield.[1] This catalyst cleaves vicinal -OH bonds preferably, therefore the production of 1,2-butanediol and by-production of 1,4-butanediol are more preferential than that of other butanediols. Hydrogenolysis of erythritol over Ir-ReO_x/SiO_2 catalyst was also reported.[2] This catalyst gave 1,4-butanediol with 24% yield for 24 h reaction. 1-Butanol was also given with 21% yield over the same catalyst. From these characterics, terminal -OH groups of substrates tend to remain in main products by hydrogenolysis over these catalysts. To obtain butanediols in high selectivity from erythritol, the selective hydrogenolysis of C-OH is necessary. 1,4-AHERY, which has no terminal -OH group, can be synthesized by intramolecular dehydration of erythritol with an acid catalyst. Therefore, 1,4-AHERY is also regarded as a C_4 intermediate from biomass. In this study, we explored catalysts for hydrogenolysis of 1,4-AHERY to butanediols, especially to those with internal -OH group(s).[3]

2. Experimental

M/SiO_2 (M=Rh, Ir; M: 4 wt%) was prepared by the impregnation of SiO_2 (Fuji Silysia G-6) with the metal precursors. Rh-M'O_x/SiO_2 (Rh: 4 wt%, M'=Mo, W, Re, Nb, Cr, Mn. M'/Rh=0.13) and Ir-ReO_x/SiO_2 (Ir: 4 wt%, Re/Ir=1) catalysts were prepared by impregnation of dried Rh/SiO_2 or Ir/SiO_2. These materials were calcined in air at 773 K for 3 h after drying at 383 K for 12 h. For Ir-ReO_x/SiO_2, reduction pretreatment was performed in water under 8 MPa H_2 at 473 K for 1 h. Activity tests were performed by using a 190 mL stainless steel autoclave with an inserted glass vessel. Typical reaction conditions were as follows: catalyst 100 mg, 1,4-AHERY 1 g (9.6 mmol), water 4 g, H_2 8 MPa, 393 K, 1 h. The products were analyzed by using both GC (Shimadzu GC-2014) equipped with a flame ionization detector (FID) and HPLC (Shimadzu Prominence) equipped with a refractive index detector.

3. Results and discussion

Results of 1,4-AHERY hydrogenolysis over various catalysts are shown in Table 1. MoO_x-, WO_x-, and ReO_x-modified Rh/SiO_2 catalysts showed much higher conversion (21~29%) than Rh/SiO_2 (6%) and Ir-ReO_x/SiO_2 (8%). NbO_x-, CrO_x-, and MnO_x-modified Rh/SiO_2 catalysts showed almost no activity. In view of selectivity to butanediols, Ir-ReO_x/SiO_2 catalyst showed the highest selectivity to 1,3-butanediol in these catalysts, and Rh-MoO_x/SiO_2 catalyst showed the highest selectivity to 2,3-butanediol. The time-course over these two catalysts was investigated. At 24 h reaction time over Ir-ReO_x/SiO_2 catalyst, the conversion became 63% and the selectivity for 1,3-butanediol was 23%.

Table 1 Hydrogenolysis of 1,4-AHERY.

Catalyst	Conversion [%]	Selectivity [%]								
		1,2-BuD	1,3-BuD	2,3-BuD	1-BuOH	2-BuOH	3-HTHF	1,2,3-BuT	Alkanes	Others
Rh/SiO_2	6	34	2	2	3	2	6	50	2	<1
Rh-MoO_x/SiO_2	21	9	2	12	4	23	9	37	2	2
Rh-WO_x/SiO_2	29	11	3	7	6	17	9	41	5	<1
Rh-ReO_x/SiO_2	29	13	3	6	7	20	7	36	5	<1
Rh-NbO_x/SiO_2	<1	-	-	-	-	-	-	-	-	-
Rh-CrO_x/SiO_2	<1	-	-	-	-	-	-	-	-	-
Rh-MnO_x/SiO_2	<1	-	-	-	-	-	-	-	-	-
Ir-ReO_x/SiO_2	8	4	25	2	3	14	8	43	2	<1
Ir-ReO_x/SiO_2 [a]	63	4	23	2	11	19	4	35	3	1

Reaction conditions: 20 wt% 1,4-AHERY aqueous solution (5 g), $W_{cat.}$=100 mg (Rh/SiO_2: Rh=4 wt%); (Rh-$M'O_x/SiO_2$: Rh=4 wt%, M'/Rh=0.13, M'=Mo, W, Re, Nb, Cr, Mn); (Ir-ReO_x/SiO_2: Ir=4 wt%, Re/Ir=1), H_2 pressure 8 MPa, T=393 K, t=1 h ([a] 24 h). BuD=butanediol. BuOH=butanol. 3-HTHF=3-hydroxytetrahydrofuran. BuT=butanetriol. Alkanes=C4–C1 alkanes. Others=THF+propanols.

The time-course over Rh-MoO_x/SiO_2 is shown in Figure 1. The reaction proceeded to reach nearly 100% conversion at 32 h. The maximum yield of 2,3-butanediol was 12%, which was obtained at 16 h.

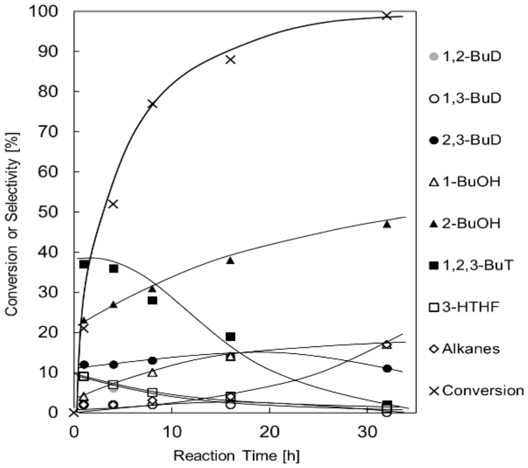

Figure 1 Time-course of hydrogenolysis of 1,4-AHERY over Rh-MoO_x/SiO_2 (Rh=4 wt%, Mo/Rh=0.13). Reaction conditions: 20 wt% 1,4-AHERY aqueous solution (5 g), $W_{cat.}$=100 mg, H_2 pressure 8 MPa, T=393 K, t=1-32 h. BuD=butanediol. BuOH=butanol. 3-HTHF=3-hydroxytetrahydrofuran. BuT=butanetriol. Alkanes=C4–C1 alkanes. Others=THF + propanols.

4. Conclusions

MoO_x-, WO_x-, and ReO_x-modified Rh/SiO_2 catalysts have higher activity of 1,4-AHERY hydrogenolysis than Rh/SiO_2. Rh-MoO_x/SiO_2 has the highest selectivity to 2,3-butanediol (maximum yield 12%). Ir-ReO_x/SiO_2 catalyst gives higher 1,3-butanediol selectivity (>20%) than Rh catalysts (≤3%), although the activity is similar to Rh/SiO_2.

References

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