Re-Pd/SiO_2 catalyst for hydrogenation of dicarboxylic acids to diols

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Abstract: Re-Pd/SiO_2 catalysts with various reduction methods were applied to hydrogenation of dicarboxylic acids to diols. In the reaction, the *ex-situ* liquid-phase (in 1,4-dioxane only) reduced Re-Pd/SiO_2 catalyst showed much higher activity than *in-situ* liquid-phase (in dicarboxylic acid and 1,4-dioxane) and gas-phase reduced ones. High diol yields (71-89%) were achieved in the hydrogenation of various C4-C6 dicarboxylic acids by using the *ex-situ* liquid-phase reduced Re-Pd/SiO_2 catalyst at 413 K.
Keywords: Hydrogenation, Succinic acid, Rhenium.

1. Introduction

Biomass-derived succinic acid (SUC) has attracted much attention as a platform chemical for production of valuable chemicals. 1,4-Butanediol (1,4-BuD) is an important chemical for thermoplastic polymers such as polybutylene succinate and polybutylene terephthalate, and conventionally, 1,4-BuD can be produced from petroleum. Therefore, biomass-derived 1,4-BuD has been required for production of biopolymers, and hydrogenation of SUC is one of the methods to produce biomass-derived 1,4-BuD.

In hydrogenation of SUC, Re_2O_7 catalyst has been known to be effective for the reaction, providing 94% yield of 1,4-BuD (25 MPa H_2, 483 K, no solvent)[1]. In the case of supported catalysts, Re-Pd/TiO_2 (solvent: H_2O)[2], Pd-Re/TiO_2 (solvent: 1,4-dioxane and H_2O)[3], and Re-Ru/mesoporous carbon (solvent: 1,4-dioxane)[4] provided 1,4-BuD yields of 83%, 86%, and 71%, respectively. In hydrogenation of mixtures of SUC, glutaric acid, and adipic acid, the Ru-Sn-Re/C catalyst (15 MPa H_2, 453 K, solvent: H_2O) provided high yields of 1,4-BuD (75%), 1,5-Pentanediol (98%) and 1,6-Hexanediol (96%), respectively[5]. Recently, we reported that the Re-Pd/SiO_2 (Re = 14 wt%, Pd = 1 wt%, Re/Pd = 8) catalyst was effective for hydrogenation of monocarboxylic acids[6,7]. In this study, we applied the Re-Pd/SiO_2 catalysts with various reduction methods to the hydrogenation of C4-C6 dicarboxylic acids, and found that *ex-situ* liquid-phase (in 1,4-dioxane only) reduced Re–Pd/SiO_2 (Re = 14 wt%, Pd = 1 wt%, Re/Pd = 8) catalyst was effective for the reaction, providing high yields of C4-C6 diols (1,4-BuD (89%), 1,5-Pentanediol (71%) and 1,6-Hexanediol (74%)) under relatively mild conditions (8 MPa H_2, 413 K)[8].

2. Experimental

Re-Pd/SiO_2 (Re = 14 wt%, Pd = 1 wt%, Re/Pd = 8), Re/SiO_2 (Re = 14 wt%), and Pd/SiO_2 (Pd = 1 wt%) catalysts were prepared by impregnating SiO_2 (535 m^2/g) with aqueous solutions of $PdCl_2$ and NH_4ReO_4. These catalysts were calcined at 673 K for 3 h. The standard reaction conditions are 1 g of SUC, 19 g of 1,4-dioxane, 0.1 g of catalyst, 8 MPa H_2, 413 K and 4 h. Reduction of the catalysts was conducted by three different methods: *ex-situ* liquid-phase reduction without SUC (*ex*L), *in-situ* liquid-phase reduction with SUC (*in*L), and gas-phase reduction (G). In *ex*L, the calcined catalyst was reduced in an autoclave with a spinner under the conditions: 19 g of 1,4-dioxane, 0.1 g of catalyst, 8 MPa H_2, 413 K and 1 h. After cooling down to room temperature, the substrate was added into the autoclave reactor in N_2. In *in*L, the catalyst was *in-situ* reduced in the presence of the substrate and the solvent under H_2. In G, the catalyst was reduced under H_2 flow (100% H_2, 30 mL min^{-1}) at 473 K for 1 h. Re-Pd(*ex*L, 413) means the Re-Pd/SiO_2 catalyst reduced in *ex*L at 413 K. The catalyst after the activity test is denoted as Re-Pd(*ex*L, 413, Reaction). Products were analyzed by GC-FID and HPLC-RID. Catalysts were characterized by XRD, XPS, and XAFS.

3. Results and discussion

First, hydrogenation of SUC was performed as a model reaction using Re-Pd/SiO_2(Re = 14 wt%, Pd = 1 wt%, Re/Pd = 8), Re/SiO_2(Re = 14 wt%), and Pd/SiO_2(Pd = 1 wt%) catalysts (Table 1). The Re-Pd(*ex*L, 413) catalyst showed a higher averaged conversion rate v (5.4 mmol g_{cat}^{-1} h^{-1}) than the Re-Pd (*in*L, 413) catalyst (0.8 mmol g_{cat}^{-1} h^{-1}) and the Re-Pd(G, 473) catalyst (2.2 mmol g_{cat}^{-1} h^{-1}) with high selectivity to γ-butyrolactone (GBL), which is an intermediate of the formation of 1,4-BuD. A similar tendency was also observed over the Re/SiO_2 catalysts with three reduction methods. On the other hand, Pd(*ex*L, 413) catalyst showed no conversion of SUC. Therefore, Re species works as the main active one, and Pd works as the promoter. Among the three reduction methods, *ex-situ* liquid-phase reduction was the most effective for the reaction. Re-Pd(*ex*L, 413) catalyst provided a high 1,4-BuD yield of 89% at longer reaction time of 96 h, and also provided a high 1,5-Pentanediol yield of 71% at 120 h by hydrogenation of glutaric acid, and a high 1,6-Hexanediol yield of 74% at 96 h by hydrogenation of adipic acid.

Table 1. Results of SUC hydrogenation over Re-Pd/SiO_2, Re/SiO_2, and Pd/SiO_2 catalysts

Entry	Catalyst	Conv. / %	Selectivity / %					v^a / mmol g_{cat}^{-1} h^{-1}
			GBL	1,4-BuD	THF	BA	BuOH	
1	Re-Pd(*in*L, 413)	3.9	94	1.8	0.0	3.8	0.0	0.8
2	Re-Pd(G, 473)	10	94	5.1	0.0	0.8	0.0	2.2
3	Re-Pd(*ex*L, 413)	26	96	3.0	0.0	0.9	0.3	5.4
4	Re(*in*L, 413)	<1	-	-	-	-	-	<0.2
5	Re(G, 473)	<1	-	-	-	-	-	<0.2
6	Re(*ex*L, 413)	7.0	94	3.9	0.0	1.6	0.9	1.5
7	Pd(*ex*L, 413)	<1	-	-	-	-	-	<0.2

SUC, succinic acid; GBL, γ-butyrolactone; 1,4-BuD, 1,4-butanediol; THF, tetrahydrofuran; BA, butyric acid; BuOH, 1-butanol. Reaction conditions: 5 wt% SUC solution 20 g (SUC 1 g, 1,4-dioxane 19 g), catalyst amount 0.1 g, reaction temperature 413 K, H_2 pressure 8.0 MPa, reaction time 4 h. [a]Averaged conversion rate.

The used catalysts were characterized by XRD, XPS, and XAFS. The Pd *K*-edge XANES patterns of the Re-Pd(*in*L, 413, Reaction), Re-Pd(*ex*L, 413), Re-Pd(*ex*L, 413, reaction), and Re-Pd(G, 473, Reaction) catalysts were similar to that of Pd foil, indicating that Pd species were in the metallic state, which was also supported by XPS. Our previous report on stearic acid hydrogenation over Re-Pd(*ex*L, 413) suggested that the interface between (Pd^0+Re^0) and (Re^{3+}+Re^{4+}) forms the catalytically active species[7]. Based on the results of XANES, XPS, and XRD, the ratio of (Re^{3+}+Re^{4+})/(Pd_S^0+Re_S^0) on the Re-Pd(*ex*L, 473, Reaction), Re-Pd(*in*L, 473, Reaction), and Re-Pd(G, 473, Reaction) catalysts was calculated to be 0.94, 7.9, and 0.38, respectively. Considering that Re-Pd(*in*L, 473, Reaction) catalyst showed the best activity, the comparable amount of (Re^{3+}+Re^{4+}) and (Pd_S^0+Re_S^0) is suitable for formation of the active species, the interface between (Re^{3+}+Re^{4+}) and (Pd_S^0+Re_S^0).

4. Conclusions

The *ex-situ* liquid-phase reduced Re-Pd/SiO_2 catalyst (Re-Pd(*ex*L)) was more effective than the *in-situ* liquid-phase and gas-phase reduced ones in hydrogenations of SUC to 1,4-BuD, and high yields of C4-C6 diols were obtained by hydrogenation of the corresponding C4-C6 dicarboxylic acids. Characterization of Re-Pd/SiO_2 catalysts showed that the amounts of (Re^{3+}+Re^{4+}) and (Pd_S^0+Re_S^0) were similar on the Re-Pd(*ex*L), which is suitable for formation of the active site, the interface between (Re^{3+}+Re^{4+}) and (Pd_S^0+Re_S^0).

References

1. H. S. Broadbent, G. C. Campbell, W. J. Bartley and J. H. Johnson, J. Org. Chem. 24 (1959) 1847.
2. B. K. Ly, D. P. Minh, C. Pinel, M. Besson, B. Tapin, F. Epron and C. Especel, Top. Catal. 55 (2012) 466.
3. V. N. M. Rao, US Pat. (1988) 4782167.
4. K. H. Kang, U. G. Hong, Y. Bang, J. H. Choi, J. K. Kim, J. K. Lee, S. J. Han and I. K. Song, Appl. Catal. A 490 (2015) 153.
5. M. Konishi, K. Yokota and E. Ueno, US Pat. (2004) 6706932.
6. Y. Takeda, Y. Nakagawa and K. Tomishige, Catal. Sci. Technol. 2 (2012) 2221.
7. Y. Takeda, M. Tamura, Y. Nakagawa, K. Okumura and K. Tomishige, ACS Catal. 5 (2015) 7034.
8. Y. Takeda, M. Tamura, Y. Nakagawa, K. Okumura and K. Tomishige, Catal. Sci. Technol. 6 (2016) 5668.