Selective reduction of 2-furancarboxylic acid into 5-hydroxyvaleric acid derivatives over supported platinum catalyst

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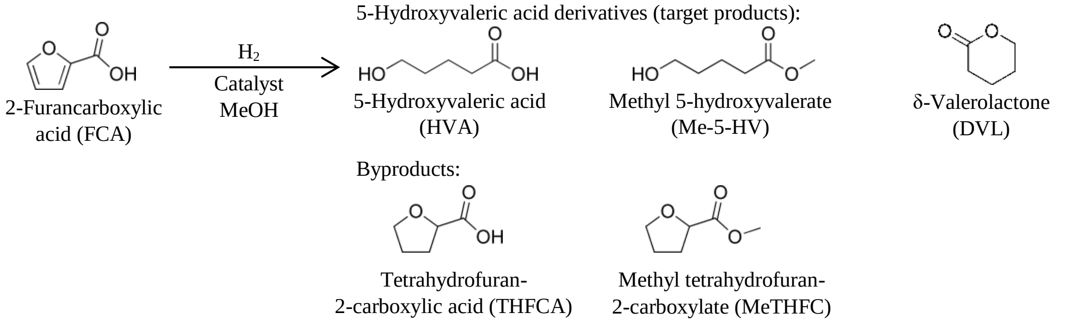
Abstract: The catalyst for selective reduction of 2-furancarboxylic acid (FCA) into 5-hydroxyvaleric acid (HVA) derivatives (HVA, methyl 5-hydroxyvalerate (Me-5-HV) and δ-valerolactone) under hydrogen atmosphere was developed. FCA was selectively converted to Me-5-HV in methanol solvent over Pt/Al_2O_3 catalyst. The highest combined yield of HVA derivatives was 54%. The catalysts with other noble metals were not effective in the production of HVA derivatives. When low molecular weight alcohols (methanol, ethanol, 1-propanol and 1-butanol) were used as a solvent, corresponding 5-hydroxyvalerates were selectively produced. Tetrahydrofuran-2-carboxylic acid was not reactive, suggesting that HVA derivatives were produced via partial hydrogenation of furan ring of FCA.

Keywords: Platinum, Woody biomass, Reduction.

1. Introduction

Producing furanic compounds from woody biomass and converting them into valuable compounds are important processes in biomass refinery. There are several reactions in reduction of biomass-derived furanic compounds such as hydrogenation of furan ring, ring cleavage, and hydrogenation of side chains, and thus it is difficult to convert furanic compounds selectively to one product.

2-Furancarboxylic acid (FCA) is produced by catalytic oxidation of furfural[1] which is derived from hemicellulose contained in woody biomass. The demand of FCA is not large: as a raw material of several medicines; the conversion method is limited[2]. Among C5 oxygenates, 5-hydroxyvaleric acid (HVA) is a very important chemical as a raw material of polyester. In this study, a catalyst for reduction of FCA into HVA derivatives (Scheme 1) was developed.



Scheme 1. Catalytic reduction of FCA into HVA derivatives.

2. Experimental

Pt/Al_2O_3, Pt/SiO_2, Pt/ZrO_2, Pt/TiO_2, Pt/CeO_2 and Pt/MgO catalysts (metal loading amount = 4 wt%) were prepared by impregnation method using aqueous solution of H_2PtCl_6. After evaporating the solvent, the prepared catalyst was dried at 383 K overnight, then calcined at 773 K for 3 h. Ir/Al_2O_3, Ru/Al_2O_3, Rh/Al_2O_3 and Pd/Al_2O_3 catalysts were prepared by the same method, using H_2IrCl_4*aq*, $Ru(NO)(NO_3)_x(OH)_y$ ($x + y = 3$) nitric acid solution, $Rh(NO_3)_3$*aq* and $Pd(NO_2)_2$*aq* as the precursor, respectively. 5 wt% Pt/C (Platinum on activated carbon) catalyst was purchased from Wako Pure Chemical Industries, Ltd.

Catalytic conversion of FCA into HVA derivatives was performed in a 190 mL stainless steel autoclave with an inserted glass vessel. The typical reaction conditions were as follows: 100 mg catalyst (4 wt% metal), 29 g methanol, 10 mmol FCA, 4 MPa H_2, 373 K, 4 h. The reactor contents in the both of liquid and gas phase were collected and analyzed by gas chromatography.

3. Results and discussion

The results of reduction of FCA over various noble metal catalysts supported on alumina are shown in Table 1. Only platinum catalyst gave high selectivity to target products (mostly obtained as methyl 5-hydroxyvalerate (Me-5-HV). Hydrogenation of furan ring to tetrahydrofuran-2-carboxylic acid (THFCA) mainly proceeded over ruthenium, rhodium and palladium catalysts. Iridium catalyst was not active in these reaction conditions.

The solvent effect was investigated (Table 2). When low molecular weight alcohol, especially methanol, was used, corresponding 5-hydroxyvalerate (5-HV) was obtained in high selectivity. Thus, methanol was adopted as the standard solvent.

Table 1. Reduction of 2-furancarboxylic acid (FCA) over various noble metal catalysts.

Entry	Catalyst	Conv. [%]	Selectivity [%]						C.B. [%]
			Me-5-HV	DVL	HVA	THFCA	MeTHFC	Others	
1	Pt/Al_2O_3	94	56	1	n.d.	2	26	4	90
2	Ir/Al_2O_3	2	5	n.d.	n.d.	29	n.d.	44	99
3	Ru/Al_2O_3	97	6	<1	n.d.	45	33	7	88
4	Rh/Al_2O_3	>99	3	<1	n.d.	69	29	<1	103
5	Pd/Al_2O_3	>99	n.d.	n.d.	n.d.	65	35	<1	101

Reaction conditions: 4 wt% M/Al_2O_3 (100 mg), MeOH (29 g), FCA (10 mmol), 4 MPa H_2, 373 K, 4 h.
Conv.: conversion, C.B.: carbon balance, n.d.: not detected, Me-5-HV: methyl 5-hydroxyvalerate,
HVA: 5-hydroxyvaleric acid, DVL: δ-valerolactone, THFCA: tetrahydrofuran-2-carboxylic acid,
MeTHFC: methyl tetrahydrofuran-2-carboxylate.

Table 2. Solvent effect in reduction of FCA over Pt/Al_2O_3 catalyst.

Entry	Solvent	Conv. [%]	Selectivity [%]							C.B. [%]
			5-HV	DVL	HVA	OVA	THFCA	MeTHFC	Others	
1	1,4-Dioxane	74	n.d.	37	3	n.d.	43	n.d.	<1	87
2	H_2O	96	n.d.	16	5	8	30	n.d.	2	63
3	AcOH	86	n.d.	60	<1	n.d.	30	n.d.	5	96
4	MeOH	94	56	1	n.d.	n.d.	2	26	4	90
5	EtOH	>99	59	<1	<1	n.d.	8	18	2	87
6	1-PrOH	>99	57	2	n.d.	n.d.	17	10	2	88
7	1-BuOH	>99	53	2	<1	n.d.	21	8	<1	85
8	2-PrOH	95	35	16	2	n.d.	29	<1	<1	84
9	^{t}BuOH	>99	<1	37	8	n.d.	32	n.d.	2	77

Reaction conditions: 4 wt% Pt/Al_2O_3 (100 mg), solvent (29 g), FCA (10 mmol), 4 MPa H_2, 373 K, 4 h.
5-HV: 5-hydroxyvalerates, OVA: 5-oxovaleric acid.

Additionally, the effect of support in Pt/support catalysts was investigated and optimization of reaction conditions was conducted. As a result, 54% of combined yield of target products (Me-5-HV and δ-valerolactone (DVL)) was achieved with following conditions: 4 wt% Pt/Al_2O_3 (100 mg), methanol (29 g), FCA (10 mmol), 4 MPa H_2, 373 K, 4 h.

In order to determine the reaction route, the reduction of hydrogenated substrate, THFCA, was conducted with Pt/Al_2O_3 catalyst. THFCA was hardly converted in the standard reaction conditions. From this result, it was suggested that conversion of FCA into HVA derivatives proceeds via partial hydrogenation of furan ring of FCA.

4. Conclusions

Pt/Al_2O_3 catalyst was effective for selective reduction of FCA into HVA derivatives with hydrogen. By using low molecular weight alcohol (methanol, ethanol, 1-propanol and 1-butanol) as a solvent, the corresponding 5-HV was obtained in good yield (53-59%). HVA derivatives were probably produced via partial hydrogenation of furan ring of FCA.

References

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