Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary information

Selective hydrogenolysis of 2-furancarboxylic acid to 5-hydroxyvaleric acid derivatives over supported platinum catalyst

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Table S1. Literature survey of reduction of 2-furancarboxylic acid (FCA) and its ester with H_2.

Substrate	Catalyst	Solvent	Substrate/catalyst /solvent g/g/g	$P(H_2)$ /MPa	T /K	t /h	Conv. /%	Main product (Selectivity /%)	Ref.
FCA	Pt/Al_2O_3	Methanol	1.1/0.05/29	4	373	4	>99	Methyl 5-hydroxyvalerate (55)	This work
FCA	$Pt\text{-}MoO_x/TiO_2$	Water	1.1/0.1/19	1.5	413	4	97	Valeric acid (53)	S1
FCA	Pt/TiO_2	Water	1.1/0.1/19	1.5	413	4	19	THFCA (<20)	S1
FCA	$Rh\text{-}MoO_x/TiO_2$	Water	1.1/0.1/19	1.5	413	4	57	THFCA (47)	S1
FCA	$Pd\text{-}MoO_x/TiO_2$	Water	1.1/0.1/19	1.5	413	4	>99	THFCA (81)	S1
FCA	$Ir\text{-}MoO_x/TiO_2$	Water	1.1/0.1/19	1.5	413	4	9	Mixture	S1
FCA	$Ru\text{-}MoO_x/TiO_2$	Water	1.1/0.1/19	1.5	413	4	7	Mixture	S1
FCA	$Au\text{-}MoO_x/TiO_2$	Water	1.1/0.1/19	1.5	413	4	8	Mixture	S1
FCA	Pt oxide	Alcohol	25/0.5/79	<0.2	n.r.	4	n.r.	THFCA (40%**)	S2
FCA	Pt oxide	Acetic acid	n.r.	n.r.	n.r.	n.r.	n.r.	δ-Valerolactone (n.r.)	S3
FCA	$Pd(PPh_3)_4$ + $(^tBuCO)_2O$	THF	0.22/0.02 mmol+6 mmol/4.4	3	353	48	>99	Furfural (87*)	S4
FCA	Pd/Al_2O_3 + cinchonidine	Water	0.5/0.04+0.07 mmol/20	3	rt	1	100	THFCA	S5
FCA	Pd/Al_2O_3 + 1-(1-naphthyl)-ethanol	iPrOH	0.05/0.04+0.034 mmol/7.9	3	Rt	4	37	THFCA	S6
Menthyl ester	PtO_2	iPrOH	0.3 mmol/0.025/12	3	313	6	0	-	S7
Menthyl ester	Pt/C	iPrOH	0.3 mmol/0.025/12	3	298	6	0	-	S7
Menthyl ester	Rh/C	iPrOH	0.3 mmol/0.025/12	3	313	6	100	Menthyl ester of THFCA	S7
Menthyl ester	Ru/C	iPrOH	0.3 mmol/0.025/12	3	313	6	76	Menthyl ester of THFCA	S7
Menthyl ester	Pd/Al_2O_3	iPrOH	0.3 mmol/0.025/12	3	313	6	0	-	S7
Menthyl ester	$Pd(OH)_2/C$	iPrOH	0.3 mmol/0.025/12	3	313	6	98	Menthyl ester of THFCA	S7
MeFC	Ru PNP complex	THF	0.056/0.005 mmol/0.9	3	393	19	n.r.	Furfuryl alcohol (81*)	S8
MeFC	Ir PNP complex + NaOMe	Toluene	0.13/0.02 mmol + 0.1 mmol/1.8	5	403	18	n.r.	Furfuryl alcohol (89*)	S9
FCA	Co triphos complex	THF	0.15 M/0.0075 M	8	373	22	0	-	S10

MeFC	Fe pincer complex	THF	0.13/0.02 mmol/0.9	3	373	18	>99	Furfuryl alcohol (95)	S11
MeFC	Mn Pincer complex + tBuOK	Dioxane	0.13/0.02 mmol + 0.1 mmol/2	3	383	24	n.r.	Furfuryl alcohol (87*)	S12
FCA	Ru-polyEPG-β-CD colloid	Water+ EtOAc	0.22/0.04 mmol/12+5	1	303	1.5	67	THFCA (100)	S13
FCA	Re complex	THF	0.056/0.01 mmol/3.5	4	433	48	n.r.	Furfuryl alcohol (50*)	S14
MeFC	Ru NNS complex + ^{t}BuOK	Toluene	1.9/0.0075 mmol + 0.038 mmol/26	5	353	10	n.r.	Furfuryl alcohol (80*)	S15
FCA	Pd/Re/C + MS4A	EtOAc	0.11/0.11+0.2/4.5	2	403	18	n.r.	Tetrahydrofurfuryl alcohol (69*)	S16
FCA	Pd/C	EtOH	0.2/0.005/4	1	373	6	100	EtTHFC (36), THFCA (64)	S17
FCA	Pd/MIL-101-SO_3H	EtOH	0.2/0.005/4	1	373	6	91	EtTHFC (41), THFCA (59)	S17

FCA: 2-Furancarboxylic acid; MeFC: Methyl 2-furancarboxylate; THFCA: Tetrahydrofuran-2-carboxylic acid; EtTHFC: Ethyl tetrahydrofuran-2-carboxylate; n.r.: not reported; *: yield; **: isolated yield.

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Table S2 Reduction of 2-furancarboxylic acid (FCA) over various catalysts in methanol solvent (detailed data of Table 1)

Entry	Catalyst	Conv.	Sel. /%				
		/%	Me-5-HV	5-HVA	DVL	MeTHFC	THFCA
1	Pt/Al_2O_3	91	51	<0.1	6	12	10
2[a]	Pt/Al_2O_3	>99	55	<0.1	7	20	2
3	Pt/ZrO_2	58	46	<0.1	4	13	6
4	Pt/CeO_2	91	37	<0.1	7	10	24
5	Pt/TiO_2	25	38	<0.1	5	8	8
6	Pt/SiO_2	34	34	<0.1	6	5	23
7[b]	Pt/C	16	24	<0.1	6	5	25
8	Pt/Al_2O_3-sintered[c]	17	32	<0.1	2	9	11
9[b]	Rh/C	>99	6	<0.1	<1	26	60
10[b]	Ru/C	>99	6	<0.1	<1	23	61
11[b]	Pd/C	93	<0.1	<0.1	<0.1	8	89
12	Pt-MoO_x/TiO_2[d]	16	33	<0.1	2	10	11

(continued)

Entry	Catalyst	Sel. /%								C.B.
		MeV	VA	1,5-PeD	Me-2-HV	MeFC	Methane	CO	CO_2	/%
1	Pt/Al_2O_3	<0.1	<1	<1	<1	<1	<1	<1	<1	82
2[a]	Pt/Al_2O_3	<1	<0.1	<0.1	1	<1	<1	<1	<1	86
3	Pt/ZrO_2	<0.1	<1	<0.1	2	<1	<1	<1	<1	84
4	Pt/CeO_2	<0.1	<1	<0.1	<1	<0.1	<1	<1	<1	80
5	Pt/TiO_2	<1	<1	<0.1	2	1	<1	<1	<1	90
6	Pt/SiO_2	<0.1	<1	<0.1	<1	<1	<1	<1	<1	90
7[b]	Pt/C	2	<0.1	<0.1	<0.1	<0.1	<1	<1	<1	94
8	Pt/Al_2O_3-sintered[c]	<0.1	<1	<1	<1	2	<1	<1	<1	93
9[b]	Rh/C	<1	<0.1	<0.1	<0.1	<0.1	<1	<1	<1	93
10[b]	Ru/C	<1	<1	<0.1	<1	<0.1	<1	<1	<1	92
11[b]	Pd/C	<1	<0.1	<0.1	<0.1	<0.1	<1	<1	<1	97
12	Pt-MoO_x/TiO_2[d]	<1	2	<0.1	<0.1	<0.1	<1	<1	<1	93

Reaction conditions: M/Al_2O_3(4 wt% M), W_{cat}=0.050 g, W_{FCA}=1.12 g, W_{MeOH}=29 g, $P(H_2)$=4 MPa at r.t., T=373 K, t=1 h. a: t= 4 h, b: W_{cat}= 0.040 g commercial M/C (5 wt% M) catalyst, c: catalyst calcined at 873 K to decrease Pt dispersion, d: Pt 4 wt%, Mo 0.5 wt% catalyst reported in ref. [S1,18].

Conv.: conversion; Sel.: selectivity; C.B.: carbon balance; FCA: 2-furancarboxylic acid; Me-5-HV: methyl 5-hydroxyvalerate; 5-HVA: 5-hydroxyvaleric acid; DVL: δ-valerolactone; MeTHFC: methyl tetrahydrofuran-2-carboxylate; THFCA: tetrahydrofuran-2-carboxylic acid; MeV: methyl valerate; VA: valeric acid; 1,5-PeD: 1,5-pentanediol; Me-2-HV: methyl 2-hydroxyvalerate; 2-HVA: 2-hydroxyvaleric acid; MeFC: methyl 2-furancarboxylate.

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Table S3 Solvent effect on hydrogenolysis of FCA over Pt/Al_2O_3 (4 wt% Pt) catalyst (detailed data of Table 2)

Entry	Solvent	Conv.	Sel. /%					
		/%	R-5-HV	5-HVA	DVL	AVA	RTHFC	THFCA
1	Methanol	91	51	<0.1	6	-	12	10
2	Ethanol	90	44	<1	13	-	3	19
3	1-Propanol	96	27	3	24	-	1	23
4	2-Propanol	97	4	5	42	-	<1	27
5	*tert*-Butanol	81	<0.1	7	37	-	<0.1	28
6	1,4-Dioxane	88	-	5	34	-	-	35
7	THF	64	-	4	34	-	-	34
8	Acetic acid	55	-	<0.1	66	1	-	27
9	Water	99	-	4	33	-	-	30

(continued)

Entry	Solvent	Sel. /%								C.B.
		RV	VA	1,5-PeD	R-2-HV	RFC	Methane	CO	CO_2	/%
1	Methanol	<0.1	<1	<1	<1	<0.1	<1	<1	<1	82
2	Ethanol	<0.1	<1	<0.1	<1	<0.1	<1	<1	<1	81
3	1-Propanol	<1	<1	<1	<1	<0.1	<1	<1	<1	80
4	2-Propanol	<0.1	<1	<0.1	<0.1	<0.1	<1	<1	<1	79
5	*tert*-Butanol	<0.1	<1	<0.1	<0.1	<0.1	<1	<1	<1	77
6	1,4-Dioxane	-	<1	<1	-	-	<1	<1	<1	78
7	THF	-	<0.1	<0.1	-	-	<1	<1	<1	83
8	Acetic acid	-	<1	<1	-	-	<1	<1	<1	97
9	Water	-	<1	6	-	-	<1	<1	<1	73

Reaction conditions: Pt/Al_2O_3(4 wt% Pt), W_{cat}=0.050 g, W_{FCA}=1.12 g, $W_{solvent}$=29 g, $P(H_2)$=4 MPa at r.t., T=373 K, t=1 h. Conv.: conversion; Sel.: selectivity; C.B.: carbon balance; FCA: 2-furancarboxylic acid; R-5-HV: alkyl 5-hydroxyvalerate; 5-HVA: 5-hydroxyvaleric acid; DVL: δ-valerolactone; AVA: 5-acetoxyvaleric acid; RTHFC: alkyl tetrahydrofuran-2-carboxylate; THFCA: tetrahydrofuran-2-carboxylic acid; RV: Alkyl valerate; VA: valeric acid; 1,5-PeD: 1,5-pentanediol; R-2-HV: alkyl 2-hydroxyvalerate; 2-HVA: 2-hydroxyvaleric acid; RFC: alkyl 2-furancarboxylate.

Table S4 Effect of reaction temperature on hydrogenolysis of FCA in methanol solvent over Pt/Al_2O_3 catalyst (detailed data of Fig. 2)

Entry	*T* /K	Conv. /%	Sel. /%				
			Me-5-HV	5-HVA	DVL	MeTHFC	THFCA
1	343	30	28	<0.1	10	4	17
2	353	46	41	<0.1	9	6	16
3	363	62	47	<0.1	7	8	13
4	373	91	51	<0.1	6	12	10
5	383	94	52	<0.1	6	15	7
6	393	97	53	<0.1	6	16	6
7	403	65	41	<0.1	4	17	5
8	413	49	40	<0.1	2	18	3

(continued)

Entry	*T* /K	Sel. /%								C.B. /%
		MeV	VA	1,5-PeD	Me-2-HV	MeFC	Methane	CO	CO_2	
1	343	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<1	<1	88
2	353	<0.1	<0.1	<0.1	<1	<1	<0.1	<1	<1	87
3	363	<0.1	<0.1	<0.1	<1	<1	<1	<1	<1	85
4	373	<0.1	<1	<1	<1	<1	<0.1	<1	<1	82
5	383	<0.1	<1	<0.1	<1	<1	<1	<1	<1	82
6	393	<0.1	<1	<0.1	1	<1	<1	<1	<1	82
7	403	<0.1	1	<0.1	2	2	1	<1	<1	82
8	413	1	3	<0.1	3	3	<1	<1	<1	87

Reaction conditions: Pt/Al_2O_3(4 wt% Pt), W_{cat}=0.050 g, W_{FCA}=1.12 g, W_{MeOH}=29 g, $P(H_2)$=4 MPa at r.t., *t*=1 h.

Conv.: conversion; Sel.: selectivity; C.B.: carbon balance; FCA: 2-furancarboxylic acid; Me-5-HV: methyl 5-hydroxyvalerate; 5-HVA: 5-hydroxyvaleric acid; DVL: δ-valerolactone; MeTHFC: methyl tetrahydrofuran-2-carboxylate; THFCA: tetrahydrofuran-2-carboxylic acid; MeV: methyl valerate; VA: valeric acid; 1,5-PeD: 1,5-pentanediol; Me-2-HV: methyl 2-hydroxyvalerate; 2-HVA: 2-hydroxyvaleric acid; MeFC: methyl 2-furancarboxylate.

Table S5 Time-course of selective hydrogenolysis of FCA in methanol solvent over Pt/Al_2O_3 (4 wt% Pt) catalyst at 373 K (detailed data of Fig. 2 (I))

Entry	*t* /h	Conv. /%	Sel. /%				
			Me-5-HV	5-HVA	DVL	MeTHFC	THFCA
1	0	20	23	<0.1	9	3	30
2	0.2	40	40	<0.1	9	6	17
3	0.5	64	46	<0.1	7	9	13
4	1	91	51	<0.1	6	12	10
5	2	95	55	<0.1	5	17	5
6	4	>99	55	<0.1	7	20	2

(continued)

Entry	*t* /h	Sel. /%								C.B. /%
		MeV	VA	1,5-PeD	Me-2-HV	MeFC	Methane	CO	CO_2	
1	0	<0.1	<0.1	<0.1	<0.1	<0.1	<1	<1	<1	93
2	0.2	<0.1	<0.1	<0.1	<1	<1	<1	<1	<1	89
3	0.5	<0.1	<0.1	<0.1	<1	<1	<1	<1	<1	85
4	1	<0.1	<1	<1	<1	<0.1	<1	<1	<1	82
5	2	<0.1	<1	<0.1	1	<0.1	<1	<1	<1	84
6	4	<1	<0.1	<0.1	1	<1	<1	<1	<1	86

Reaction conditions: Pt/Al_2O_3(4 wt% Pt), W_{cat}=0.050 g, W_{FCA}=1.12 g, W_{MeOH}=29 g, $P(H_2)$=4 MPa at r.t., T= 373 K.

Conv.: conversion; Sel.: selectivity; C.B.: carbon balance; FCA: 2-furancarboxylic acid; Me-5-HV: methyl 5-hydroxyvalerate; 5-HVA: 5-hydroxyvaleric acid; DVL: δ-valerolactone; MeTHFC: methyl tetrahydrofuran-2-carboxylate; THFCA: tetrahydrofuran-2-carboxylic acid; MeV: methyl valerate; VA: valeric acid; 1,5-PeD: 1,5-pentanediol; Me-2-HV: methyl 2-hydroxyvalerate; 2-HVA: 2-hydroxyvaleric acid; MeFC: methyl 2-furancarboxylate.

Table S6 Time-course of hydrogenolysis of FCA in methanol solvent over Pt/Al_2O_3 (4 wt% Pt) catalyst at 413 K (detailed data of Fig. 2 (II))

Entry	*t* /h	Conv. /%	Sel. /%				
			Me-5-HV	5-HVA	DVL	MeTHFC	THFCA
1	0	27	43	<0.1	3	8	11
2	1	49	40	<0.1	2	18	3
3	2	54	36	<0.1	2	19	1
4	4	53	34	<0.1	2	19	<1

(continued)

Entry	*t* /h	Sel. /%								C.B. /%
		MeV	VA	1,5-PeD	Me-2-HV	MeFC	Methane	CO	CO_2	
1	0	<0.1	<1	<0.1	<1	1	<1	<1	<1	91
2	1	1	3	<0.1	3	3	<1	<1	<1	87
3	2	<1	2	<0.1	5	3	<1	<1	<1	83
4	4	3	1	<0.1	7	6	<1	<1	<1	85

Reaction conditions: Pt/Al_2O_3(4 wt% Pt), W_{cat}=0.050 g, W_{FCA}=1.12 g, W_{MeOH}=29 g, $P(H_2)$=4 MPa at r.t., T= 413 K.

Conv.: conversion; Sel.: selectivity; C.B.: carbon balance; FCA: 2-furancarboxylic acid; Me-5-HV: methyl 5-hydroxyvalerate; 5-HVA: 5-hydroxyvaleric acid; DVL: δ-valerolactone; MeTHFC: methyl tetrahydrofuran-2-carboxylate; THFCA: tetrahydrofuran-2-carboxylic acid; MeV: methyl valerate; VA: valeric acid; 1,5-PeD: 1,5-pentanediol; Me-2-HV: methyl 2-hydroxyvalerate; 2-HVA: 2-hydroxyvaleric acid; MeFC: methyl 2-furancarboxylate.

Table S7 Effect of hydrogen pressure on hydrogenolysis of FCA in methanol solvent over Pt/Al_2O_3 (4 wt% Pt) catalyst (detailed data of Fig. 3)

Entry	$P(H_2)$ at r.t. /MPa	Conv. /%	Sel. /%				
			Me-5-HV	5-HVA	DVL	MeTHFC	THFCA
1	1	33	35	<0.1	6	12	9
2	2	52	45	<0.1	5	13	8
3	3	80	52	<0.1	6	11	9
4	4	91	51	<0.1	6	12	10
5	6	80	49	<0.1	5	13	9
6	8	64	43	<0.1	5	15	10

(continued)

Entry	$P(H_2)$ at r.t. /MPa	Sel. /%								C.B. /%
		MeV	VA	1,5-PeD	Me-2-HV	MeFC	Methane	CO	CO_2	
1	1	<0.1	<1	<0.1	1	1	<1	<1	<1	89
2	2	<0.1	<1	<0.1	<1	<1	<1	<1	<1	86
3	3	<0.1	<1	<0.1	<1	<0.1	<1	<1	<1	83
4	4	<0.1	<1	<1	<1	<0.1	<1	<1	<1	82
5	6	<0.1	<0.1	<0.1	<1	<1	<1	<1	<1	82
6	8	<0.1	<0.1	<0.1	<1	<1	<1	<1	<1	84

Reaction conditions: Pt/Al_2O_3(4 wt% Pt), W_{cat}=0.050 g, W_{FCA}=1.12 g, W_{MeOH}=29 g, T=373 K, t=1 h.

Conv.: conversion; Sel.: selectivity; C.B.: carbon balance; FCA: 2-furancarboxylic acid; Me-5-HV: methyl 5-hydroxyvalerate; 5-HVA: 5-hydroxyvaleric acid; DVL: δ-valerolactone; MeTHFC: methyl tetrahydrofuran-2-carboxylate; THFCA: tetrahydrofuran-2-carboxylic acid; MeV: methyl valerate; VA: valeric acid; 1,5-PeD: 1,5-pentanediol; Me-2-HV: methyl 2-hydroxyvalerate; 2-HVA: 2-hydroxyvaleric acid; MeFC: methyl 2-furancarboxylate.

Table S8 Dependence of initial reaction rate of FCA hydrogenolysis on H_2 pressure (detailed data of Fig. 4)

Entry	$P(H_2)$ /MPa	t /h	Conv. /%	Yield /%				
				Me-5-HV	5-HVA	DVL	MeTHFC	THFCA
1	1	0	1	<1	<0.1	<1	<0.1	<1
2		0.5	8	2	<1	<1	<1	1
3		1	14	5	<1	<1	<1	2
4		1.5	18	7	<0.1	<1	1	2
5	2	0	3	<1	<0.1	<1	<0.1	<1
6		0.5	12	4	<1	<1	<1	2
7		1	21	8	<0.1	1	1	3
8		1.5	31	15	<0.1	1	2	3
9	4	0	1	<1	<0.1	<1	<0.1	<1
10		0.5	16	6	<1	1	<1	3
11		1	24	10	<1	1	1	3
12		1.5	37	18	<1	1	3	4
13	6	0	2	<1	<0.1	<1	<0.1	<1
14		0.5	12	5	<1	<1	<1	2
15		1	21	9	<1	<1	1	3
16		1.5	28	13	<1	1	2	3
17	8	0	1	<1	<0.1	<1	<0.1	<1
18		0.5	10	4	<1	<1	<1	2
19		1	20	8	<1	<1	1	3
20		1.5	23	10	<1	<1	2	2

(continued to next page)

Table S8 (continued)

Entry	$P(H_2)$ /MPa	t /h	Yield /%								C.B. /%
			MeV	VA	1,5-PeD	Me-2-HV	MeFC	Methane	CO	CO_2	
1	1	0	<0.1	<0.1	<0.1	<0.1	<0.1	<1	<1	<1	100
2		0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<1	<1	<1	97
3		1	<0.1	<0.1	<0.1	<0.1	<0.1	<1	<1	<1	95
4		1.5	<0.1	<1	<0.1	<1	<1	<1	<1	<1	94
5	2	0	<0.1	<0.1	<0.1	<0.1	<0.1	<1	<0.1	<1	99
6		0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<1	<0.1	<1	96
7		1	<0.1	<0.1	<0.1	<0.1	<0.1	<1	<0.1	<1	92
8		1.5	<0.1	<0.1	<0.1	<0.1	<0.1	<1	<0.1	<1	91
9	4	0	<0.1	<0.1	<0.1	<0.1	<0.1	<1	<1	<1	100
10		0.5	<0.1	<0.1	<0.1	<0.1	<1	<1	<1	<1	94
11		1	<0.1	<0.1	<0.1	<0.1	<1	<1	<1	<1	91
12		1.5	<0.1	<0.1	<0.1	<1	<1	<1	<1	<1	90
13	6	0	<0.1	<0.1	<0.1	<0.1	<0.1	<1	<0.1	<1	100
14		0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<1	<1	<1	97
15		1	<0.1	<0.1	<0.1	<1	<1	<1	<1	<1	94
16		1.5	<0.1	<0.1	<0.1	<1	<1	<1	<1	<1	92
17	8	0	<0.1	<0.1	<0.1	<0.1	<0.1	<1	<0.1	<0.1	101
18		0.5	<0.1	<0.1	<0.1	<0.1	<1	<1	<0.1	<0.1	97
19		1	<0.1	<0.1	<0.1	<1	<1	<1	<0.1	<1	94
20		1.5	<0.1	<0.1	<0.1	<1	<1	<0.1	<1	<1	92

Reaction conditions: Pt/Al_2O_3(4 wt% Pt), W_{cat}=0.010 g, W_{FCA}=1.12 g, W_{MeOH}=29 g, T=373 K.

Conv.: conversion; Sel.: selectivity; C.B.: carbon balance; FCA: 2-furancarboxylic acid; Me-5-HV: methyl 5-hydroxyvalerate; 5-HVA: 5-hydroxyvaleric acid; DVL: δ-valerolactone; MeTHFC: methyl tetrahydrofuran-2-carboxylate; THFCA: tetrahydrofuran-2-carboxylic acid; MeV: methyl valerate; VA: valeric acid; 1,5-PeD: 1,5-pentanediol; Me-2-HV: methyl 2-hydroxyvalerate; 2-HVA: 2-hydroxyvaleric acid; MeFC: methyl 2-furancarboxylate.

Table S9 Effect of FCA concentration (methanol solvent amount) on hydrogenolysis of FCA over Pt/Al_2O_3 catalyst (detailed data of Table 3)

Entry	W_{MeOH} /g	Conv. /%	Sel. /%				
			Me-5-HV	5-HVA	DVL	MeTHFC	THFCA
1	29	91	51	<0.1	6	12	10
2[a]	29	>99	55	<0.1	7	20	2
3	19	95	54	<0.1	4	18	5
4	9	>99	55	<0.1	3	18	5
5	4	>99	53	<1	4	16	7

(continued)

Entry	W_{MeOH} /g	Sel. /%								C.B. /%
		MeV	VA	1,5-PeD	Me-2-HV	MeFC	Methane	CO	CO_2	
1	29	<0.1	<1	<1	<1	<0.1	<1	<1	<1	82
2[a]	29	<1	<0.1	<0.1	1	<1	<1	<1	<1	86
3	19	<1	<1	<0.1	1	<1	<1	<1	<1	83
4	9	<1	<1	<0.1	1	<1	<1	<1	<1	84
5	4	<1	<1	<0.1	2	<1	<1	<1	<1	82

Reaction conditions: Pt/Al_2O_3(4 wt% Pt), $W_{catalyst}$=0.050 g, W_{FCA}=1.12 g, $P(H_2)$=4 MPa at r.t., T=373 K, t=1 h, a:t=4 h.
Conv.: conversion; Sel.: selectivity; C.B.: carbon balance; FCA: 2-furancarboxylic acid; Me-5-HV: methyl 5-hydroxyvalerate; 5-HVA: 5-hydroxyvaleric acid; DVL: δ-valerolactone; MeTHFC: methyl tetrahydrofuran-2-carboxylate; THFCA: tetrahydrofuran-2-carboxylic acid; MeV: methyl valerate; VA: valeric acid; 1,5-PeD: 1,5-pentanediol; Me-2-HV: methyl 2-hydroxyvalerate; 2-HVA: 2-hydroxyvaleric acid; MeFC: methyl 2-furancarboxylate.

Table S10 Reusability test of Pt/Al_2O_3 without any treatment for hydrogenolysis of FCA

Entry	Used time	Conv. /%	Sel. /%				
			Me-5-HV	5-HVA	DVL	MeTHFC	THFCA
1	1st (fresh)	95	55	<0.1	5	17	5
2	2nd	79	35	<0.1	13	12	13
3	3rd	67	36	<0.1	13	9	15
4	4th	29	29	<0.1	14	9	14

(continued)

Entry	Used time	Sel. /%								C.B. /%
		MeV	VA	1,5-PeD	Me-2-HV	MeFC	Methane	CO	CO_2	
1	1st (fresh)	<0.1	<1	<0.1	1	<0.1	<1	<1	<1	84
2	2nd	<0.1	<1	<0.1	1	<1	<1	<1	<1	81
3	3rd	<0.1	<1	<0.1	<1	<1	<1	<1	<1	83
4	4th	<0.1	<1	<0.1	1	<1	<1	<1	<1	88

Reaction conditions: Pt/Al_2O_3(4 wt% Pt), W_{cat}=0.050 g, W_{FCA}=1.12 g, W_{MeOH}=29 g, $P(H_2)$=4 MPa at r.t., T=373 K, t=2 h. Conv.: conversion; Sel.: selectivity; C.B.: carbon balance; FCA: 2-furancarboxylic acid; Me-5-HV: methyl 5-hydroxyvalerate; 5-HVA: 5-hydroxyvaleric acid; DVL: δ-valerolactone; MeTHFC: methyl tetrahydrofuran-2-carboxylate; THFCA: tetrahydrofuran-2-carboxylic acid; MeV: methyl valerate; VA: valeric acid; 1,5-PeD: 1,5-pentanediol; Me-2-HV: methyl 2-hydroxyvalerate; 2-HVA: 2-hydroxyvaleric acid; MeFC: methyl 2-furancarboxylate.

Table S11 Reusability test of Pt/Al_2O_3 with regeneration by calcination at 573 K for hydrogenolysis of FCA (detailed data of Fig. 6)

Entry	Used time	Conv. /%	Sel. /%				
			Me-5-HV	5-HVA	DVL	MeTHFC	THFCA
1	1st (fresh)	95	55	<0.1	5	17	5
2	2nd	77	41	<0.1	8	11	14
3	3rd	76	38	<0.1	9	8	14
4	4th	78	36	<0.1	11	7	16

(continued)

Entry	Used time	Sel. /%								C.B. /%
		MeV	VA	1,5-PeD	Me-2-HV	MeFC	Methane	CO	CO_2	
1	1st (fresh)	<0.1	<1	<0.1	1	<0.1	<1	<1	<1	84
2	2nd	<0.1	<1	<0.1	1	<0.1	<1	<1	<1	80
3	3rd	<0.1	<1	<0.1	1	<0.1	<1	<1	<1	78
4	4th	<0.1	<1	<0.1	1	<0.1	<1	<1	<1	77

Reaction conditions: Pt/Al_2O_3(4 wt% Pt), W_{cat}=0.050 g, W_{FCA}=1.12 g, W_{MeOH}=29 g, $P(H_2)$=4 MPa at r.t., T=373 K, t=2 h. Conv.: conversion; Sel.: selectivity; C.B.: carbon balance; FCA: 2-furancarboxylic acid; Me-5-HV: methyl 5-hydroxyvalerate; 5-HVA: 5-hydroxyvaleric acid; DVL: δ-valerolactone; MeTHFC: methyl tetrahydrofuran-2-carboxylate; THFCA: tetrahydrofuran-2-carboxylic acid; MeV: methyl valerate; VA: valeric acid; 1,5-PeD: 1,5-pentanediol; Me-2-HV: methyl 2-hydroxyvalerate; 2-HVA: 2-hydroxyvaleric acid; MeFC: methyl 2-furancarboxylate.

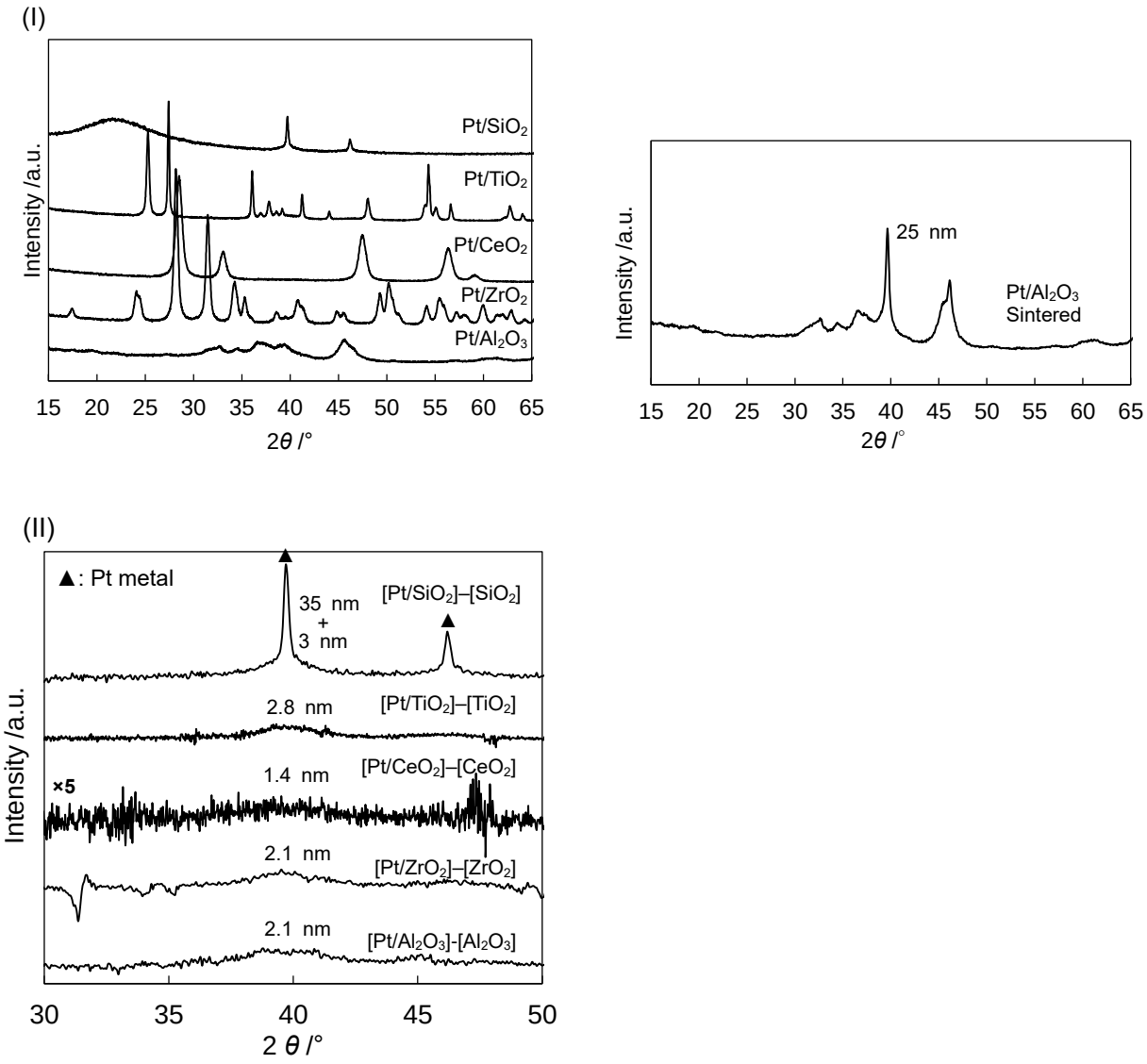

Fig. S1 XRD patterns of reduced Pt/support catalysts (reduced with 4 MPa H_2 (at r.t.) in methanol at 373 K). (I) Raw patterns, (II) difference patterns ([Pt/support]-[support]). For Pt/SiO_2, the signal for Pt metal can be deconvoluted into two signals with different linewidths.

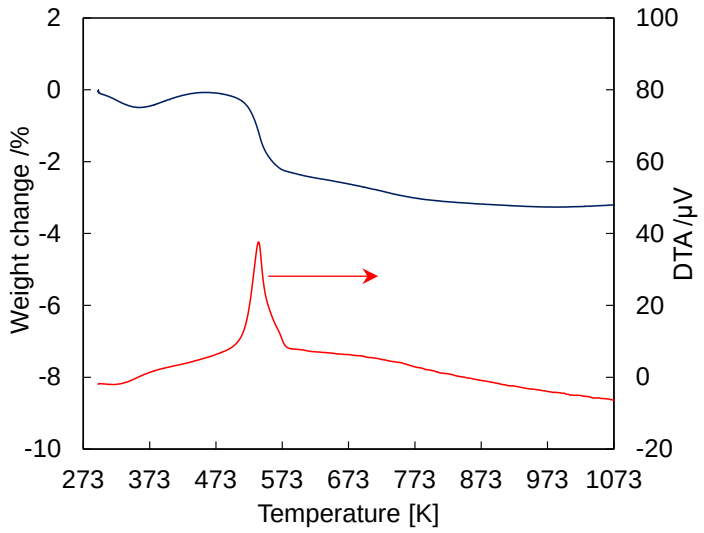

Fig. S2 TG-DTA profile of Pt/Al_2O_3 catalyst after reaction at 413 K.

Measurement conditions: 10 mg Pt/Al_2O_3 (4 wt%, after reaction) and washing with methanol, under air, 308 K→1073 K, 10 K/min.

Reaction conditions: Pt/Al_2O_3 (4 wt% Pt), W_{cat}=0.050 g, W_{FCA}=1.12 g, W_{MeOH}=29 g, $P(H_2)$=4 MPa at r.t., T= 413 K, t= 4 h.

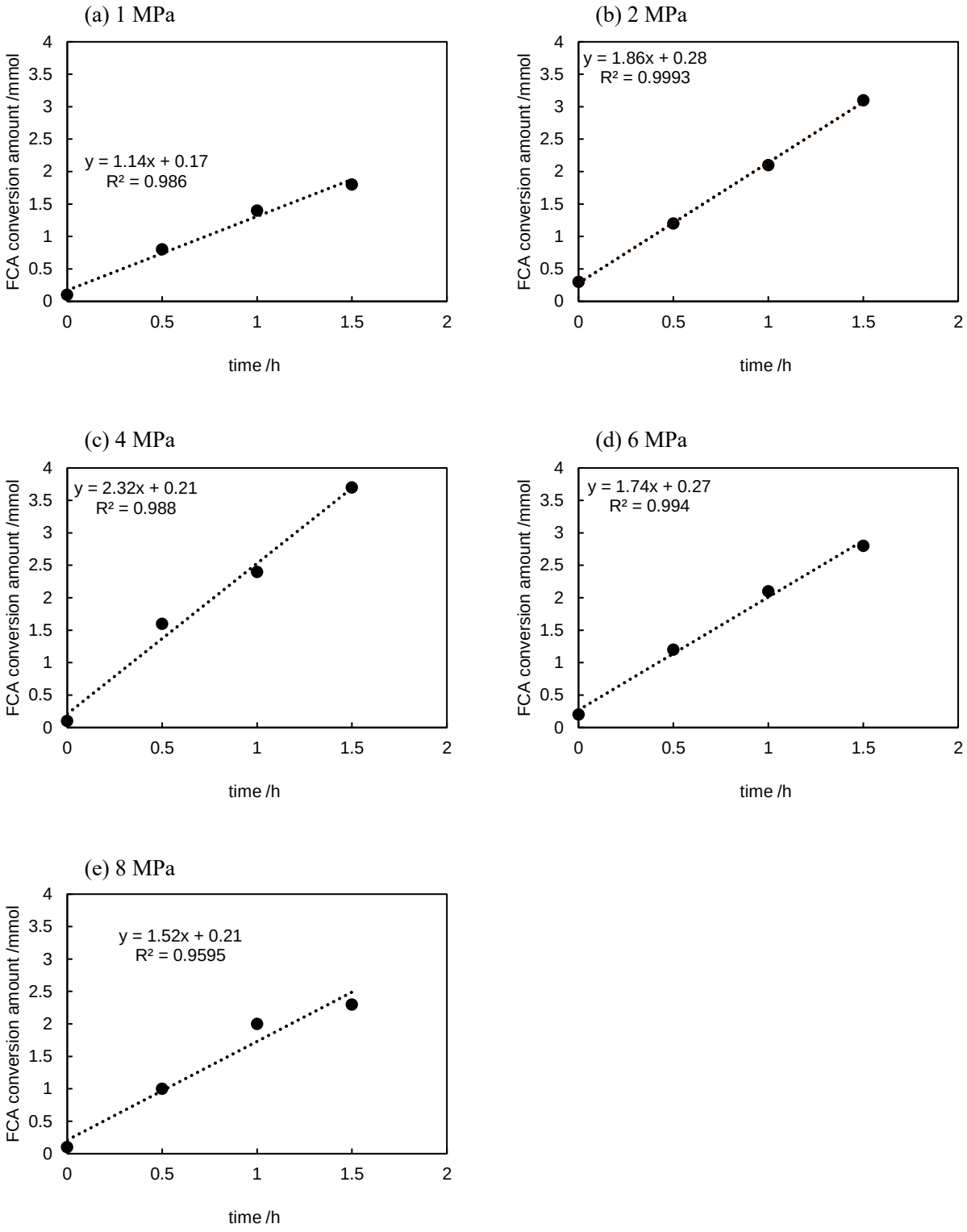

Fig. S3 Determination of FCA conversion rate from the data in Table S8.

(a) $P(H_2)$ at r.t. =1 MPa, (b) $P(H_2)$ at r.t. =2 MPa, (c) $P(H_2)$ at r.t. =4 MPa, (d) $P(H_2)$ at r.t. =6 MPa, (e) $P(H_2)$ at r.t. =8 MPa,

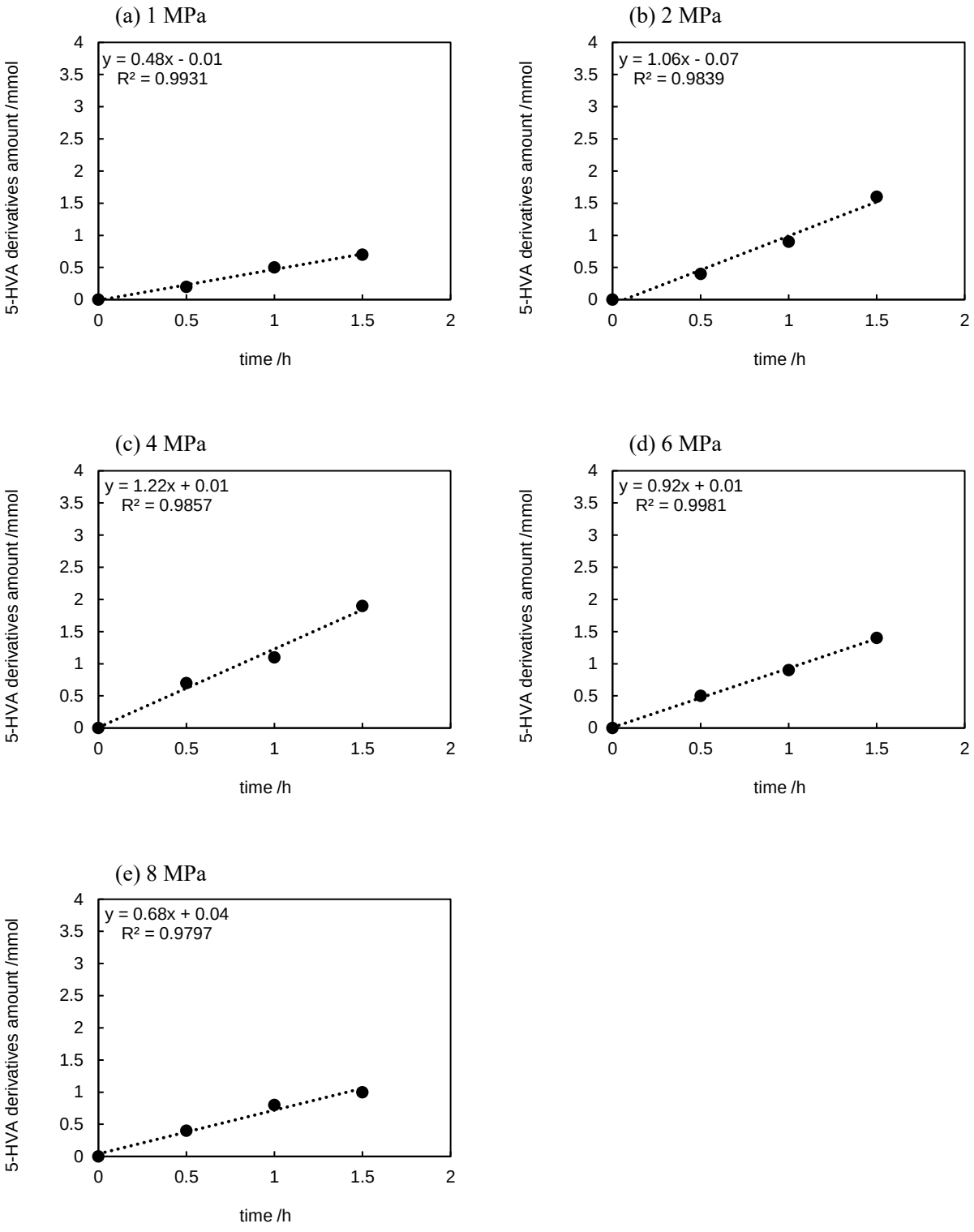

Fig. S4 Determination of 5-HVA derivatives formation rate from the data in Table S8.

(a) $P(H_2)$ at r.t. =1 MPa, (b) $P(H_2)$ at r.t. =2 MPa, (c) $P(H_2)$ at r.t. =4 MPa, (d) $P(H_2)$ at r.t. =6 MPa, (e) $P(H_2)$ at r.t. =8 MPa,