

Transesterification of Ethyl-10-undecenoate Using a Cu-Deposited V_2O_5 Catalyst as a Model Reaction for Efficient Conversion of Plant Oils to Monomers and Fine Chemicals

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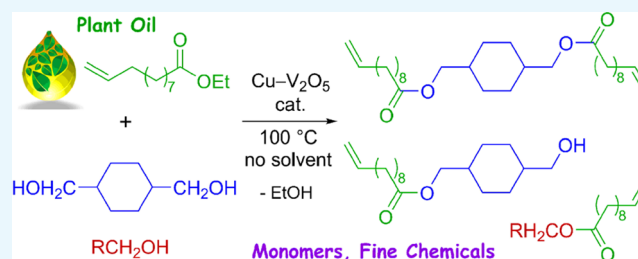


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ABSTRACT: Transesterification of ethyl-10-undecenoate (derived from castor oil) with 1,4-cyclohexanedimethanol over a recyclable Cu-deposited V_2O_5 catalyst afforded 1, ω -diene, the corresponding cyclohexane-1,4-diylbis(methylene) bis(undec-10-enoate), a promising monomer for the synthesis of biobased polyesters, in an efficient manner. Deposition of Cu plays an important role in proceeding the reaction with high selectivity, and both the activity and the selectivity are preserved for five recycled runs by the addition of the substrates. The present catalyst was effective for transesterification with other alcohols, especially primary alcohols, demonstrating a possibility of using this catalyst



for efficient conversion of plant oil to various fine chemicals.

INTRODUCTION

Subjects on efficient conversion of plant oil attract considerable attention to establish the circular economy as well as to reduce concerns of global warming as alternative feedstocks of fossil fuels.^{1–5} Plant oils, generally obtained as fatty acids (FAs) and their esters (FAEs) by chemical modifications, have been considered as a useful renewable feedstock for the synthesis of biofuels,^{6–10} biobased aliphatic polyesters,^{1,3–5,12–15} and fine chemicals (such as surfactants, cosmetic ingredients, and plasticizers).^{1,3–5,16,17} There have been many reports concerning the transesterification of FAs and FAEs for the synthesis of biofuels^{6,18–28} and their catalysis study for efficient conversion of fine chemicals,^{17,29–37} and many catalysis studies applied for organic synthesis^{38–40} have also been known.

As described above, the development of plant oil-derived biobased aliphatic polyesters, which display tunable mechanical properties and biodegradability by precise polymerization techniques, attracts considerable attention. There have been two major pathways for the synthesis, (i) condensation polymerization and (ii) acyclic diene metathesis (ADMET) polymerization and subsequent hydrogenation, and the latter pathway requires transesterification of unsaturated long-chain aliphatic carboxylic acid esters with diols for the synthesis of monomers, 1, ω -diene, through the diester linkage (Scheme 1). These monomers, especially derived from methyl (or ethyl) 10-undecenoate, were prepared in the presence of excess 1,1'-carbonyl diimidazole,³² *p*-toluene sulfonic acid or Sc(CF_3SO_3)₃,³³ NaOMe,³⁴ or NEt₃ and 4,4-dimethylaminopyridine;³⁵ these monomers can also be prepared by treatment of

the acid chloride with diols in the presence of NEt₃.^{36,37} Development of a simple catalytic transesterification method should be thus required for the efficient conversion of the unsaturated fatty acid esters not only to monomers for the ADMET polymerization but also to fine chemicals.

We, therefore, herein report that a Cu-deposited V_2O_5 catalyst could be a promising candidate for the purpose, especially for selective transesterification of ethyl-10-undecenoate (derived from castor oil) with various alcohols, as exemplified with 1,4-cyclohexanedimethanol (Scheme 2). The catalyst could be recycled several times by simply adding substrates without decreasing both the activity and selectivity, and various alcohols could also be used by adopting this catalysis.

RESULTS AND DISCUSSION

Transesterification of Ethyl-10-undecenoate (1) with 1,4-Cyclohexanedimethanol (2) by a Metal-Oxide Catalyst. Table 1 summarizes the results of transesterifications of ethyl-10-undecenoate (1) with 1,4-cyclohexanedimethanol (2) in the presence of various metal oxides (preparation of the oxides, see the Experimental Section). These reactions were

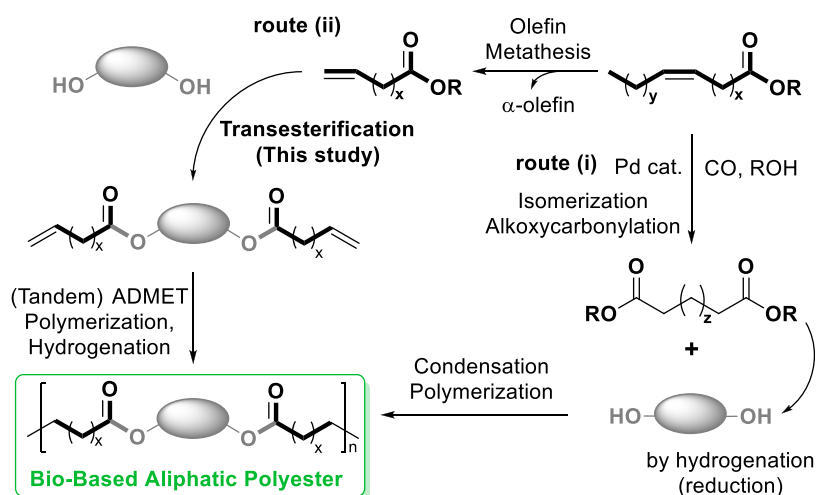
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Scheme 1. Synthesis of Polyesters from Plant Oils (Unsaturated Long-Chain Aliphatic Esters) via (i) Isomerization Alkoxycarbonylation and Polycondensation or (ii) Acyclic Diene Metathesis (ADMET) Polymerization and Subsequent Hydrogenation¹¹



Scheme 2. Catalytic Transesterification of Ethyl-10-undecenoate with 1,4-Cyclohexanedimethanol in the Presence of a Cu-Deposited V_2O_5 Catalyst

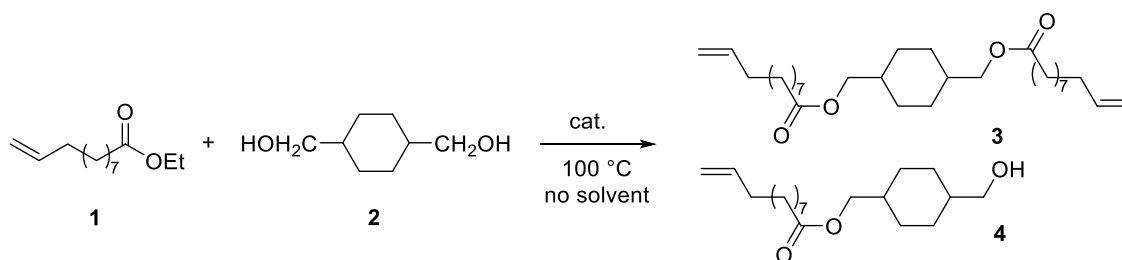


Table 1. Transesterification of Ethyl-10-undecenoate (1) with 1,4-Cyclohexanedimethanol (2): Effect of Metal-Oxide Catalysts^a

run	catalyst	conversion ^b (%)		yield ^{b,c} (%)		
		1	2	3	4	3 + 4
1	La ₂ O ₃	6	3	0.1	0.3	0.4
2	ZnO	10	16	0.6	13	13.6
3	CuO	6	3	0.1	1.3	1.4
4	SiO ₂	23	22	0.1	2.5	2.6
5	NiO	2	3	trace	1.1	1.1
6	CeO ₂	15	5	0.2	3.3	3.5
7	Al ₂ O ₃	10	5	trace	1.2	1.2
8	Co ₃ O ₄	25	18	0.1	3.9	4
9	ZrO ₂	8	3	trace	1.7	1.7
10	Fe ₂ O ₃	25	14	0.1	3.7	3.8
11	TiO ₂	26	32	0.3	4.0	4.3
12	MnO ₂	16	22	trace	1.2	1.2
13	Ta ₂ O ₅	18	12	0.3	4.4	4.7
14	Nb ₂ O ₅	16	35	0.3	3.1	3.4
15	SnO ₂	22	15	0.2	3.3	3.5
16	V ₂ O ₅	40	94	56	8.2	64.2
17	WO ₃	20	22	0.1	3.0	3.1

^aReaction conditions: 50 mg of catalyst, ethyl-10-undecenoate (1, 4.0 mmol, 849 mg), 1,4-cyclohexanedimethanol (2, 1.0 mmol, 144 mg), 100 °C, 23 h. ^bQuantitative analysis by GC using internal standards. ^cYields on the basis of 1,4-cyclohexanedimethanol (2).

conducted at 100 °C without a solvent under rather excess 1 for conversion of 2 (1:2 = 4.0:1.0, molar ratio), and the conversions of substrates (1,2) and the reaction products, corresponding monoester (4, Scheme 2) and the diester (3), were analyzed quantitatively by GC in the presence of an internal standard (*n*-dodecane). The experimental details including typical GC chromatograms and their identifications (synthesis of standards and the nuclear magnetic resonance (NMR) spectra etc.) are shown in the Supporting Information.

It turned out that V₂O₅ (nanosized vanadium pentoxide) prepared by thermal decomposition of vanadyl oxalate in air,^{41,42} converted 2 to afford the diester 3 in a moderate yield (run 16), whereas the other metal oxides showed low yields (0.4–4.7%); the selectivity in the reaction by ZnO was rather high (85%, based on 2, run 2) compared to that by V₂O₅ (68%). As introduced in Table 2 (runs 16, 18), the reaction with V₂O₅ proceeded with a high conversion of 2 even after 3 h (81%) to afford a mixture of the diester (3) and the monoester (4), and further reaction increased the yield of 3 without decreasing the selectivity. It has been known that certain Lewis acids [such as ZrCl₄(THF)₂, ZrCl₄(THF)₂, etc.]³⁸ are effective for transesterification of carboxylic acids,³⁸ and V₂O₅ has a Lewis acid site as well as a Brønsted acid site.^{41,42} It thus seems likely that V₂O₅ may play a role as a Lewis acid catalyst.

A series of metal-doped or metal-deposited V₂O₅ catalysts were thus prepared (details in the preparation procedure are described in the Experimental Section) to improve both the activity and selectivity. Table 2 summarizes the results in the

Table 2. Transesterification of Ethyl-10-undecenoate (1) with 1,4-Cyclohexanedimethanol (2) by Metal-Doped/Deposited V₂O₅ Catalysts: Effect of Metal Deposition on V₂O₅^a

run	catalyst	time	conversion ^b (%)		yield ^{b,c} (%)			select. A ^d	select. B ^e
			1	2	3	4	3 + 4	(%)	(%)
18	V ₂ O ₅	3	27	81	28	26	55	68	76
16	V ₂ O ₅	23	40	94	56	8	64	68	75
19	Ti–V ₂ O ₅	3	14	50	5	29	34	68	68
20	Ti–V ₂ O ₅	23	36	99	44	9	53	53	67
21	Zr–V ₂ O ₅	3	20	72	10	34	44	61	67
22	Zr–V ₂ O ₅	23	40	99	56	7	63	64	74
23	Nb–V ₂ O ₅	3	18	62	10	33	43	69	73
24	Nb–V ₂ O ₅	23	40	99	57	14	71	72	80
25	Ni–V ₂ O ₅	3	8	30	1	13	14	47	46
26	Ni–V ₂ O ₅	23	28	86	19	30	48	56	60
27	Mo–V ₂ O ₅	3	14	50	5	28	33	65	67
28	Mo–V ₂ O ₅	23	41	98	65	13	78	79	87
29	W–V ₂ O ₅	3	21	70	15	41	56	80	82
30	W–V ₂ O ₅	23	43	99	64	1	65	66	75
31	Mn–V ₂ O ₅	3	11	39	4	27	31	79	80
32	Mn–V ₂ O ₅	23	38	100	49	1	49	50	65
33	Fe ³⁺ –V ₂ O ₅	3	6	17	2	14	16	91	80
34	Fe ³⁺ –V ₂ O ₅	23	36	100	38	1	39	39	54
35	Fe ²⁺ –V ₂ O ₅	23	41	100	62	10	72	72	82
36	Co–V ₂ O ₅	3	8	31	2	21	23	75	77
37	Co–V ₂ O ₅	23	29	92	20	25	45	49	57
39	Cu–V ₂ O ₅	3	20	64	18	35	53	82	89
40	Cu–V ₂ O ₅	23	46	99	85	7	91	92	96
41	Sn–V ₂ O ₅	3	20	65	11	37	48	73	73
42	Sn–V ₂ O ₅	23	36	99	41	10	51	51	63
43	Zn–V ₂ O ₅	3	15	53	3	20	23	44	42
44	Zn–V ₂ O ₅	23	27	91	14	23	37	41	48
45	Ce–V ₂ O ₅	3	10	35	3	27	31	87	85

^aReaction conditions: 50 mg of catalyst (V₂O₅ doped with 3.5 mol % metals except for Cu–V₂O₅, where 3.5 mol % Cu is deposited on V₂O₅), ethyl-10-undecenoate (1, 4.0 mmol, 849 mg), 1,4-cyclohexanedimethanol (2, 1.0 mmol, 144 mg), 100 °C. ^bQuantitative analysis by GC using internal standards. ^cYields on the basis of 1,4-cyclohexanedimethanol (2). ^dBased on alcohol (2). ^eBased on ester (1).

Table 3. Time-Course Dependence in Transesterification of Ethyl-10-undecenoate (1) with 1,4-Cyclohexanedimethanol (2) by a Cu-Deposited V₂O₅ Catalyst^a

run	catalyst	time	conv. 2 ^b	yield ^{b,c} (%)			select. A ^d	select. B ^e
			(%)	3	4	3 + 4	(3 + 4) ^d	(3 + 4) ^e
46	V ₂ O ₅	3	65	7	32	39	60	68
47	V ₂ O ₅	6	87	14	27	41	48	54
48	V ₂ O ₅	16	97	33	16	49	50	58
49	Cu–V ₂ O ₅	3	42	10	27	37	90	91
50	Cu–V ₂ O ₅	6	90	47	38	85	95	96
51	Cu–V ₂ O ₅	16	96	73	17	91	95	97

^aReaction conditions: 25 mg of catalyst (deposited with 3.5 mol % Cu on V₂O₅), ethyl-10-undecenoate (1, 4.0 mmol, 849 mg), 1,4-cyclohexanedimethanol (2, 1.0 mmol, 144 mg), 100 °C. ^bQuantitative analysis by GC using internal standards. ^cYields on the basis of 1,4-cyclohexanedimethanol (2). ^dBased on alcohol (2). ^eBased on ester (1).

presence of various metal-doped or metal-deposited catalysts (3.5 mol % on V₂O₅). It turned out that improvements in the yields (3 and 4) were observed when the reactions were conducted in the presence of Nb–V₂O₅, Mo–V₂O₅, and Cu–V₂O₅ catalysts after 23 h (runs 24, 28, 40), whereas the catalysts doped on Mn and Fe³⁺ initially showed improvement in the selectivity after 3 h (runs 31 and 33), but the yields (total 3 and 4) became low after 23 h (49 and 39%, respectively). No (significant) improvements in both the activity and the selectivity were observed by adding Ti, Zr, Ni, Co, Sn, Zn, and Ce. It should be noted that the reaction by

Cu-deposited V₂O₅ catalyst afforded the diester (3) in a high yield (85%) with high selectivity (92% on the basis of 2, 96% on the basis of 1). It seems that the reaction proceeds with a rather low selectivity (after 3 h, run 39) at the initial stage, but further reaction afforded esters with high selectivity (run 40).

Table 3 summarizes the time course in the transesterification of 1 with 2 in the presence of the Cu–V₂O₅ catalyst (less catalyst loading from Table 2), and the results in the presence of the V₂O₅ catalyst are also placed for comparison. Figure 1 also shows the plots of the yields and the selectivities over the time course. It turned out that Cu–V₂O₅ showed improvement

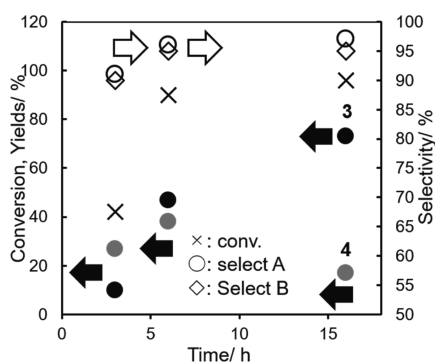


Figure 1. Time course for transesterification of ethyl-10-undecenoate (1) with 1,4-cyclohexanedimethanol (2) by a Cu-deposited V_2O_5 catalyst. Data are shown in Table 3.

in the selectivity compared to V_2O_5 (runs 46–48 vs runs 49–51), whereas the conversion of 2 after 3 h was low (run 46 vs run 49). Further reaction over V_2O_5 afforded the products (3 + 4) with a slight decrease in the selectivity (run 48). In contrast, as described above, the reaction by the Cu– V_2O_5 catalyst initially proceeded with a rather low selectivity (90% on the basis of 2, run 49), which is, however, apparently higher than that by V_2O_5 (60%, run 46), and further reactions proceeded with high selectivity affording esters in a high yield (91%, run 51) after 16 h; the conversion of 2 reached 90% after 6 h (run

50). It is thus clear that the deposition of Cu on V_2O_5 was effective, especially in terms of selectivity.

On the basis of the results in Tables 2 and 3, Cu– V_2O_5 catalysts with different Cu contents were prepared to explore the effect of Cu on both the activity and the selectivity. The results conducted for 3, 6, and 16 h are summarized in Table 4. To check the initial selectivity as well as to explore the catalyst performance, the reactions were conducted with low catalyst loading (10 mg) compared to those conducted in Tables 2 and 3 (25 or 50 mg). TON (turnover numbers) on the basis of the molar amount of metals (Cu and V) was used to evaluate the performance in this catalysis, although all of these metals do not play a role as catalysts.

It turned out that conversion of the diol (2) in the reaction after 3 h decreased upon addition of Cu (even with 0.5 mol % deposition) with an increase of the selectivity of esters (3,4) on the basis of 2; the selectivity decreased with further deposition (>6.5 mol %, runs 57, 58). The reactions proceeded without significant deactivations in all cases (runs 52–72), affording the esters (3,4) in better selectivity (86–93% based on 2). In terms of yields and selectivity, the Cu– V_2O_5 catalyst with 3.5 mol % Cu deposition thus showed better catalyst performances (runs 55, 62, and 69). As also shown below (Table 5), the catalyst with low Cu deposition (0.5 mol %) showed a lower selectivity compared to that with 3.5 mol %.

Table 4. Transesterification of Ethyl-10-undecenoate (1) with 1,4-Cyclohexanedimethanol (2) by a Cu-Deposited V_2O_5 Catalyst: Effect of Cu Deposition on V_2O_5 and Reaction Temperatures^a

run	catalyst		temp. (°C)	time (h)	conv.2 ^b (%)	yield ^{b,c} (%)			select. A ^d		select. B ^e		TON ^f
	(mol %)-Cu					3	4	3 + 4	3 + 4		3 + 4		
52	0		100	3	42	1	13	14	32		33		1.4
53	0.5		100	3	25	6	16	22	86		92		2.5
54	2.5		100	3	20	5	13	18	91		90		2.1
55	3.5		100	3	20	5	13	18	89		92		2.1
56	4.5		100	3	25	6	16	21	86		86		2.5
57	6.5		100	3	17	2	11	13	75		75		1.4
58	10		100	3	22	3	12	15	68		65		1.6
59	0		100	6	72	3	19	23	32		36		2.3
60	0.5		100	6	60	19	32	51	85		88		6.4
61	2.5		100	6	51	15	29	44	86		87		5.3
62	3.5		100	6	49	16	29	45	92		95		5.5
63	4.5		100	6	50	16	28	44	87		87		5.4
64	6.5		100	6	48	11	29	41	85		84		4.6
65	10		100	6	57	22	27	49	85		91		6.4
66	0		100	16	90	9	21	30	33		39		4.5
67	0.5		100	16	99	72	13	85	86		91		14
68	2.5		100	16	97	69	15	84	87		93		14
69	3.5		100	16	97	73	17	90	93		94		15
70	4.5		100	16	98	73	14	87	89		92		14
71	6.5		100	16	99	68	17	85	86		93		14
72	10		100	16	99	67	18	86	86		93		14
73	3.5		60	16	trace								0
74	3.5		80	16	29	8	19	27	93		98		3.2
75	3.5		100	16	97	72	17	89	92		96		15
69	3.5		100	16	97	73	17	90	93		94		15
76	3.5		120	16	>99	81	8	89	89		92		15

^aReaction conditions: 10 mg of catalyst (deposited with 0–10 mol % Cu on V_2O_5), ethyl-10-undecenoate (1, 4.0 mmol), 1,4-cyclohexanedimethanol (2, 1.0 mmol). ^bQuantitative analysis by GC using internal standards. ^cYields on the basis of 1,4-cyclohexanedimethanol (2). ^dBased on alcohol (2). ^eBased on ester (1). ^fTON (turnovers) = (molar amount of 1 reacted for transesterification)/(molar amount of Cu and V).

Table 5. Transesterification of Ethyl-10-undecenoate (1) with 1,4-Cyclohexanedimethanol (2) by a Cu-Deposited V₂O₅ Catalyst: Catalyst Recycling Experiments (1)^a

run	catalyst	substrates		time	conv.2 ^b	yield ^{b,c} (%) ^{d,e}			select. ^d	TON ^e
		1:2 (mmol)		(h)	(%)	3	4	3 + 4	3 + 4	
77	V ₂ O ₅	4.0:1.0		6	87	14	27	41	48	2
78	V ₂ O ₅	4.0 + 4.0:1.0 + 1.0		6 + 6 ^f	70	13	30	43	61	4.1
79	V ₂ O ₅	4.0 + 4.0:1.0 + 1.0		6 + 16 ^f	89	29	43	72	80	7.3
80	V ₂ O ₅ ^g	4.0 + 2.0:1.0 + 1.0		6 + 16 ^g	59	2	19	21	36	4.2
81	Cu-V ₂ O ₅	4.0:1.0		6	90	47	38	85	94	4.8
82	Cu-V ₂ O ₅	4.0 + 4.0:1.0 + 1.0		6 + 6 ^f	92	50	40	90	97	10
83	Cu-V ₂ O ₅	4.0 + 4.0:1.0 + 1.0		6 + 16 ^f	98	84	12	96	98	13
84	Cu-V ₂ O ₅	4.0 + 8.0:1.0 + 2.0		6 + 16 ^h	96	74	18	91	95	18
60	Cu-V ₂ O ₅ ⁱ	4.0:1.0		6	63	19	32	51	85	6.4
85	Cu-V ₂ O ₅ ⁱ	4.0 + 2.0:1.0 + 1.0		6 + 16 ^f	91	57	24	81	89	25
62	Cu-V ₂ O ₅ ^j	4.0:1.0		6	49	16	29	45	92	5.5
86	Cu-V ₂ O ₅ ^j	4.0 + 2.0:1.0 + 1.0		6 + 16 ^f	89	54	30	84	94	25

^aReaction conditions: 25 mg of catalyst (deposited with 3.5 mol % Cu on V₂O₅), ethyl-10-undecenoate (1, 4.0 mmol), 1,4-cyclohexanedimethanol (2, 1.0 mmol), 100 °C. ^bQuantitative analysis by GC using internal standards. ^cYields on the basis of 1,4-cyclohexanedimethanol (2). ^dBased on alcohol (2). ^eTON (turnovers) = (molar amount of 1 reacted for transesterification)/(molar amount of Cu and V). ^fAfter the reaction for 6 h, 1 (4.0 mmol) and 2 (1.0 mmol) were added, and the results were evaluated after an additional 16 h. ^gCatalyst (V₂O₅) (10 mg), 1 (2.0 mmol), and 2 (1.0 mmol) were added after 6 h, and the results were evaluated after an additional 16 h. ^hAfter the reaction for 6 h, 1 (8.0 mmol) and 2 (2.0 mmol) were added, and the results were evaluated after an additional 16 h. ⁱCatalyst (10 mg; deposited with 0.5 mol % Cu on V₂O₅). ^jCatalyst (10 mg; deposited with 3.5 mol % Cu on V₂O₅).

Table 6. Transesterification of Ethyl-10-undecenoate (1) with 1,4-Cyclohexanedimethanol (2) by a Cu-Deposited V₂O₅ Catalyst: Catalyst Recycling Experiments (2)^a

run	recycle runs	yields, selectivity, and TON (total)					yields, selectivity, and TON (independent run)							
		conv.2 ^b	yield ^{b,c} (%)			select. ^d	TON ^e	conv.2 ^b	yield ^{b,c} (%)			select. ^d	TON ^e	
		(%)	3	4	3 + 4	3 + 4		(%)	3	4	3 + 4	3 + 4		
87	fresh	97	73	17	90	93	15	97	73	17	90	93	15	
88	1 ^f	96	69	20	89	93	29	93	65	22	87	94	14	
89	2 ^f	94	57	30	87	93	39	88	31	48	79	90	10	
90	3 ^f	92	52	34	86	93	50	85	29	48	78	92	10	
91	4 ^f	92	53	33	86	93	65	81	50	25	75	92	11	
92	5 ^f	91	51	33	84	92	74	77	39	31	69	90	10	

^aReaction conditions: 10 mg of catalyst (deposited with 0–10 mol % Cu on V₂O₅), ethyl-10-undecenoate (1, 4.0 mmol), 1,4-cyclohexanedimethanol (2, 1.0 mmol), 100 °C, 16 h. ^bQuantitative analysis by GC using internal standards. ^cYields on the basis of 1,4-cyclohexanedimethanol (2). ^dBased on alcohol (2). ^eTON (turnovers) = (molar amount of 1 reacted for transesterification)/(molar amount of Cu and V). ^fAfter the reaction, 1 (2.0 mmol) and 2 (1.0 mmol) were added into the reaction solution for the recycled runs.

As summarized in Table 4, the transesterification did not proceed (or the activity was negligible) at 60 °C (run 73), and the activity increased at high temperatures (80–120 °C, runs 69, 74–76). Since the selectivity decreased at 120 °C, the reactions conducted at 100 °C seem preferred in this catalysis. The results are reproducible under these conditions (runs 69, 75).

Recycled Experiments in Transesterification of Ethyl-10-undecenoate (1) with 1,4-Cyclohexanedimethanol (2) by a Cu-Deposited V₂O₅ Catalyst. To explore the catalyst performance (long-lived, recyclable), ethyl-10-undecenoate (1) and 1,4-cyclohexanedimethanol (2) were further added to the reaction mixture in the presence of a Cu-deposited V₂O₅ catalyst after 6 h, and the solution was stirred for an additional 6 or 16 h. The results are summarized in Table 5, and the results using V₂O₅ are also presented for comparison.

Note that the reactions by the Cu-V₂O₅ catalyst exhibited high 2 conversion after the additional 6 h even upon further addition of substrates (1,2) without a decrease in the selectivity (runs 81, 82), and further stirring for the additional

16 h afforded the esters (3,4) with high selectivity (98%, run 83). Moreover, the selectivity seems to improve in the additional (recycled, re-fed) runs (runs 82, 83), probably because, as suggested from the results in Tables 2–4, the reaction showed a rather low selectivity at the initial stage. Interestingly, the reaction with increased addition of 2 (2.0 mmol in run 84 in place of 1.0 mmol in runs 82, 83) also reached high conversion to afford the esters with high selectivity.^a These results thus suggest that the present catalyst (Cu-V₂O₅) can be used in the recycled runs, although it seems difficult to recover the catalyst quantitatively by simple filtration in this reaction scale (slurry conditions with tiny catalyst powder with a small amount).

A similar trend was observed when these reactions were conducted under conditions with low catalyst loading (runs 62, 86). Interestingly, similar reactions using V₂O₅ (runs 77–79) and Cu(0.5 mol %)-deposited V₂O₅ (runs 65, 85) catalysts also showed improvements in the selectivity, whereas observed selectivities were apparently lower than those by the Cu(3.5 mol %)-deposited V₂O₅ catalyst.^a As also observed in Table 4,

the Cu–V₂O₅ catalyst with 3.5 mol % Cu deposition thus showed better catalyst performance.

On the basis of the results in Table 5, the catalyst reusability was checked in this transesterification by the repeat addition of substrates (1, 2.0 mmol; 2, 1.0 mmol) into the reaction mixture after every 16 h (at 100 °C) without the addition of the catalyst. The results after five repeated runs are summarized in Table 6. The conversions, selectivities, and the turnover numbers in the total and independent runs are shown for evaluating catalyst performances in each recycled run. Figure 2 also shows plots of TON, conversions, and selectivity in each runs.

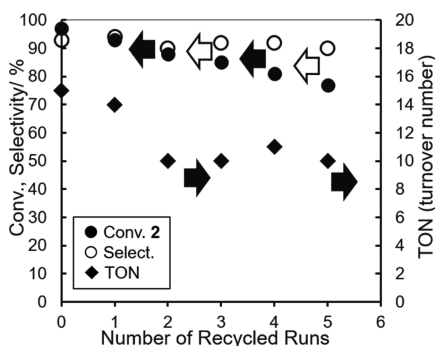


Figure 2. Plots of conversion of 1,4-cyclohexanedimethanol (2), selectivity of esters (3,4), and TONs vs number of catalyst recycled runs in transesterification of ethyl-10-undecenoate (1) with 2 by Cu-deposited V₂O₅ catalysts. Data are shown in Table 6.

It turned out that the reactions proceeded without a significant decrease in selectivity (90–94% in runs 88–91), whereas the conversion of 2 seemed slightly decreasing over recycled runs. TON value did not change after two recycled runs (up to five recycled runs, runs 89–91). Reasons for decreases in the activity (TON after 1st recycled run) and the conversion of 2 could be considered as due to the remaining 2 in each runs (which increase the initial molar amount of 2), the changes in the molar ratios (1 and 2), and decrease in the catalyst (and substrate) concentration. Interestingly, no significant decreases in the selectivity could suggest that Cu could be remained on V₂O₅ to perform the high selectivity.^a Considering these points, we could conclude that the catalyst performance remained up to five reaction runs, and a TON of 74 has thus been achieved in these catalysis runs.^a

Transesterification of 1 with 2-phenyl ethanol was conducted under the same conditions [molar ratio of

1:PhCH₂CH₂OH = 2.0:6.0 (mmol)], and the substrates were further added to the reaction mixture to explore the catalyst performance and reusability; the re-feeding of substrates was conducted twice (Scheme 3). The selectivity on the basis of the alcohol initially increased upon feeding but did not change in the second feed [selectivity = 84% (1st run), 94% (2nd run), and 93% (3rd run), calculated on the basis of molar amount of the ester vs conversion of alcohol] without a decrease in the activity (TON), suggesting that the catalyst performance was preserved in this catalysis. The results thus suggest a wide substrate scope, as described below.

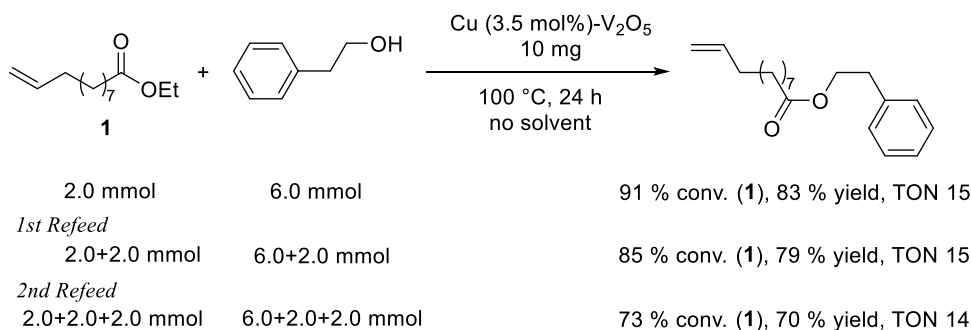
Substrate Scope in the Transesterification of Ethyl-10-undecenoate (1) with Alcohols by a Cu-Deposited V₂O₅ Catalyst. On the basis of the results described above, transesterifications of 1 with various alcohols were thus conducted under the same conditions (100 °C, 24 h), and the results are summarized in Scheme 4.

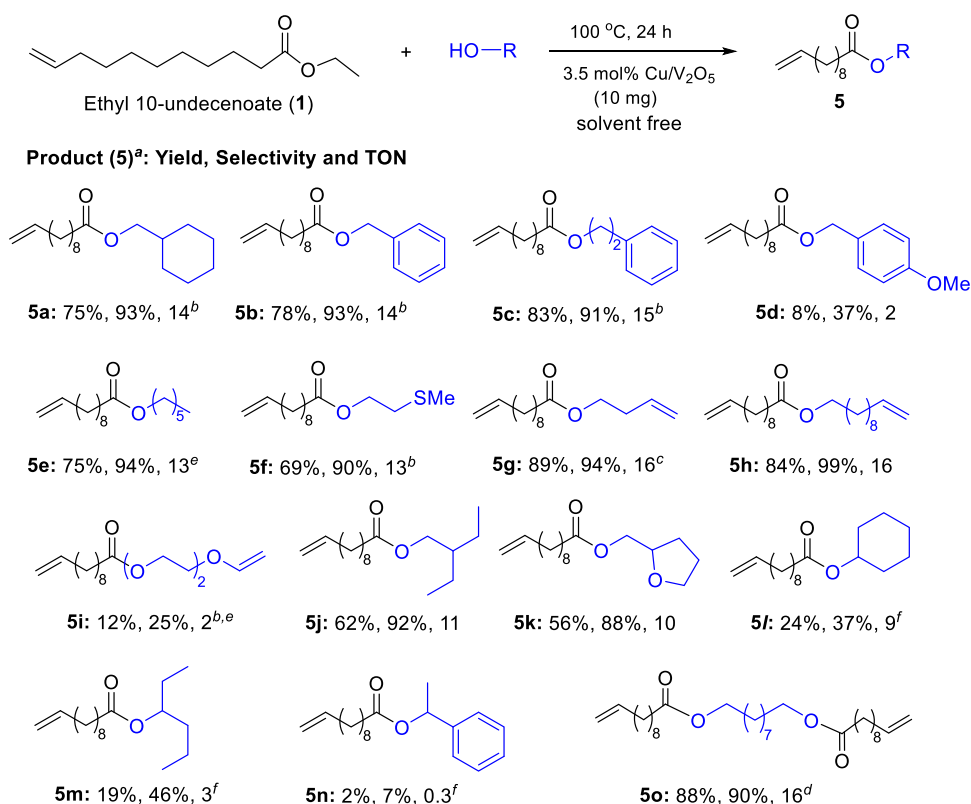
The primary alcohols, cyclohexyl methanol, benzyl alcohol, and 2-phenyl ethanol afforded the corresponding esters (5a–c) in high selectivity, and similar trends were observed in the reaction with *n*-hexanol, 2-methylthioethanol, 3-buten-1-ol, 10-undecen-1-ol to afford the corresponding esters (5e–h), whereas the reaction with 4-methoxybenzyl alcohol showed low activity and selectivity. Although the reaction with 2-ethylbutanol, (oxolan-2-yl)methanol also afforded esters with high selectivities (5j,k), both the conversion and the selectivity were low in the reaction with 2-(2-ethenoxyethoxy)ethanol (for the synthesis of 5i), cyclohexanol (for 5l), hexan-3-ol (for 5m), and with 1-phenyl ethanol (for 5n) under these conditions (further optimization of the conditions might be required). As expected in the reaction of 1 with 2, the reaction with 1,9-nonanediol afforded the diester (5o) in high yields. These results thus demonstrate that the present catalyst showed a wide substrate scope, especially for the reaction with primary alcohols (with less steric bulk).

CONCLUDING REMARKS

We have shown that transesterification of ethyl-10-undecenoate (1) with 1,4-cyclohexanedimethanol (2) in the presence of a Cu-deposited V₂O₅ catalyst proceeded with high selectivity to afford esters, and notable decreases in the activity and selectivity were not observed in the five catalyst recycled runs by addition of substrates into the reaction mixture. Deposition of Cu on V₂O₅ plays a role in exhibiting the high selectivity, and 3.5 mol % seems suitable in this catalysis. The activity was affected by the reaction temperature (100 °C is the most suitable), and the diester, cyclohexane-1,4-diylbis-

Scheme 3. Catalytic Transesterification of Ethyl-10-undecenoate with 2-Phenyl Ethanol in the Presence of a Cu-Deposited V₂O₅ Catalyst



Scheme 4. Substrate Scope in the Transesterification of Ethyl-10-undecenoate (1) with Other Alcohols in the Presence of a Cu (3.5 mol %)-Deposited V₂O₅ catalyst^{a,b,c,d,e,f}


^aReaction conditions: 10 mg of catalyst (3.5 mol % Cu-deposited V₂O₅), ethyl-10-undecenoate (**1**, 2.0 mmol), alcohol (4.0 mmol), 100 °C, 24 h. Yields and selectivity on the basis of ethyl-10-undecenoate (**1**). ^bAlcohol 6.0 mmol. ^cAlcohol 8.0 mmol. ^d**1** (4.0 mmol) and alcohol (1.0 mmol): yield and selectivity on the basis of 1,9-nonanediol. ^eReaction 16 h. ^fTemperature at 150 °C.

(methylene) bis(undec-10-enoate) (**3**), was obtained from the monoester, (4-(hydroxymethyl)cyclohexyl)methyl undec-10-enoate (**4**), over longer reaction hours. The present catalyst was effective for the reaction of **1** with various alcohols, especially primary alcohols, suggesting a scope of efficient conversion of plant oils to fine chemicals and monomers for the synthesis of polyesters in this catalysis. We highly believe that the present catalyst can also be used for various fatty acid esters (FAEs), and we thus believe that the results could introduce a promising possibility of development of the catalysis process, including the design of more efficient catalysts.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out in oven-dried glassware. Commercially available chemicals were used without further purification. Chemicals of reagent grades such as ethyl-10-undecenoate >97.0% (GC) and 1,4-cyclohexanedimethanol >99.0% (GC) were purchased from Tokyo Chemical Industry, Co., Ltd., and dodecane (>99.0%), oxalic acid >98% (Titration), ammonium vanadate (V) (special grade reagent), copper(II) nitrate trihydrate >99.0% (Titration) were purchased from Fujifilm Wako Pure Chemical Industries, Ltd., and were used as received. Analytical thin-layer chromatography (TLC) was performed on a Merck TLC silica gel 60 F₂₅₄ plate, and visualization was accomplished with phosphomolybdic acid stain.

All NMR spectra were acquired on a Bruker AV500 spectrometer (500.13 MHz for ¹H, 125.77 MHz for ¹³C)

under an ambient temperature using CDCl₃ as the solvent. All chemical shifts were reported in parts per million (ppm) with reference to SiMe₄ at 0.00 ppm. The GC analysis was performed on a Shimadzu gas chromatograph (GC-2014) equipped with a flame ionization detector (FID) and DB-1MS column (30 m × 0.250 mm × 0.25 μm) with N₂ as the carrier gas under the following thermal conditions. Injector temperature and flame ionization detector temperature was set to 300 and 280 °C, respectively, the column temperature began with a 5 min hold at 110 °C, followed by a linear ramp of 20 °C min⁻¹ to 280 °C and held for 25 min at that temperature. Atmospheric pressure chemical ionization (APCI) mass spectrometry was carried out on a Bruker Micro TOF II-SDT1.

Preparation of V₂O₅.⁴¹ NH₄VO₃ (4.97 g, 42.4 mmol) and oxalic acid (11.5 g, 128 mmol) were dissolved in 20 mL of water, and the aqueous solution was stirred for 10 min to obtain the blue vanadium (IV) oxalate solution. Then, the vanadium oxalate solution was heated at 120 °C to evaporate the water. The resulting blue solid was calcined at 300 °C for 4 h twice to obtain the V₂O₅.

Preparation of Other 3.5 mol % Different Metal-Doped V₂O₅ Catalysts (3.5 mol % M–V₂O₅).⁴¹ V₂O₅ catalysts doped with different metals (Ni, Ti, Fe²⁺, Fe³⁺, Co, Zn, Mn, Zr, Nb, Mo, Sn, Ce, W) were prepared using the impregnation method. In general, V₂O₅ catalyst doped with 3.5 mol % (with respect to V₂O₅) metal [NiCO₃, Ti[OCH-(CH₃)₂]₄, Fe(C₂O₄)₂·2H₂O, Fe(NH₃)₃(C₂O₄)₃·3H₂O, Co(CO₂)₂·2H₂O, Zn(NO₃)₂·6H₂O, Mn(CO₃)₂, Zr(H₂N₂O₈),

$\text{Nb}(\text{HC}_2\text{O}_4)_5 \cdot x\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, $\text{Sn}(\text{C}_2\text{O}_4)_2$, $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$] was prepared by dissolving a prescribed amount of metal precursor in the blue vanadium(IV) oxalate solution. The vanadium(IV) oxalate solution was prepared by dissolving oxalic acid (128 mmol, 11.5 g) and ammonium vanadate (42.4 mmol, 4.97 g) in 20 mL of water, followed by 10 min stirring at room temperature. The mixture was stirred at 120 °C until the complete removal of water. The obtained solid was calcined at 300 °C for 4 h twice to obtain the metal-doped V_2O_5 catalysts.

Preparation of the Cu-Deposited V_2O_5 Catalyst (0.5, 2.5, 3.5, 4.5, 6.5, and 10 mol % Cu– V_2O_5). To prepare the 3.5 mol % Cu– V_2O_5 catalyst, 0.12 mmol of copper precursor [$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (28.8 mg)] was dissolved in 20 mL of water, and then 3.29 mmol V_2O_5 (300 mg) was added to this solution. The mixture was stirred at 120 °C until the complete evaporation of water. The obtained solid was calcined at 300 °C for 4 h, twice to obtain the Cu (3.5 mol %)- V_2O_5 catalyst. The other Cu– V_2O_5 catalysts (0.5, 2.5, 4.5, 6.5, and 10 mol % of Cu with respect to V_2O_5) were prepared by the same procedure.

General Procedure for the Transesterification of Ethyl-10-undecanoate. An oven-dried reaction tube equipped with a magnetic stirring bar was charged with a prescribed amount of catalyst (10 mg), ethyl-10-undecanoate (**1**, 4.00 mmol, 849 mg), and 1,4-cyclohexanedimethanol (**2**, 1.00 mmol, 144 mg). The reaction mixture was then heated under solvent-free conditions at 100 °C for a prescribed time in an Eyla Personal Synthesizer (ChemiStation). After completion of the reaction, the mixture was cooled down to room temperature, diluted with 5 mL of CHCl_3 , and the catalyst was separated out by centrifugation. The centrifugate was analyzed with a gas chromatogram using dodecane as an internal standard to determine the conversion and the yield.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c06157>.

Calculations for reaction products by GC, synthesis of standards, reaction products and their identifications, the selected NMR spectra, and selected GC charts (PDF)

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Notes

The authors declare no competing financial interest. As demonstrated in Tables 2–4 and the recycled runs in Tables 5 and 6, no significant differences in selectivity were observed if these reactions were conducted with different catalyst loadings (10 or 25 mg). Moreover, significant decreases in both the activity and the selectivity were not observed even after five recycled runs. These results suggest that the extent of Cu leach should be low under these conditions, although we have not yet conducted the catalyst leaching test (by filtration) due to difficulty in handling tiny amounts of catalyst (10 or 25 mg) versus ca. 1 g of substrates (or total ca. 3.8 g of substrates in the recycled runs, Table 6) suspended in the solution.

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