Supplementary Information

One-Step Production of Renewable Adipic Acid Esters from Mucic Acid over an Ir-ReO_x/C Catalyst with Low Ir Loading

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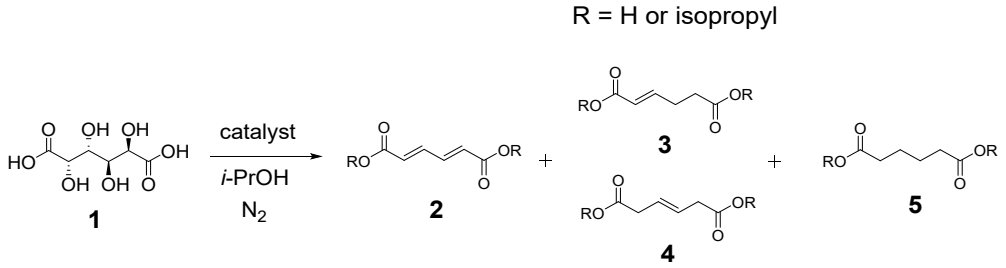
Table S1. Catalyst cost in literature of DODH-hydrogenation of mucic acid.

Entry	Catalyst(s)	T (°C)	Time (h)	Yield (%)	PGM Content (mol%)	Hydrogenation cost/mol product[a,b]	Total catalyst cost/mol product[a,c]	Ref.
1	Step 1. $HReO_4$ Step 2. Pd/C	1. 170 2. RT	1. 15 2. 4	62	7.0 Re, 2.0 Pd	$302	$323	[1]
2	CH_3ReO_3, TsOH, Pt/C	200	48	75	5.0 Re, 3.0 Pt	$265	$277	[2]
3	Step 1. CH_3ReO_3, TsOH Step 2. Pt/C	1. 120 2. 160	1. 12 2. 12	99	5.0 Re, 3.0 Pt	$201	$210	[2]
4	Re/C, Pd/C	120	72	58	9.9 Re, 1.8 Pd	$290	$322	[3]
5	$KReO_4$, Pd/C	140	72	21	8.7 Re, 1.6 Pd	$712	$789	[3]
6	Pd-ReO_x/C, Amberlyst-15	110	24	95	5.4 Re, 0.94 Pd	$92	$103	[4]
7	$KReO_4$, H_3PO_4, Pd/C, activated C	150	48	86	1.0 Re, 0.75 Pd	$82	$84	[5]
8	Pt-ReO_x/C	170	24	85	3.6 Re, 1.4 Pt	$109	$117	[6]
9	Ir-ReO_x/C	200	48	63	3.5 Re, 0.042 Ir	$17	$28	This Work

[a] Price of Re metal from U.S. Geological Survey, Mineral Commodity Summaries 2021.[7] All other PGM prices obtained from Umicore.[8]
[b] Cost based on content of M (Pd, Pt or Ir) used for hydrogenation.
[c] Cost based on total PGM (Re + hydrogenation M) content.

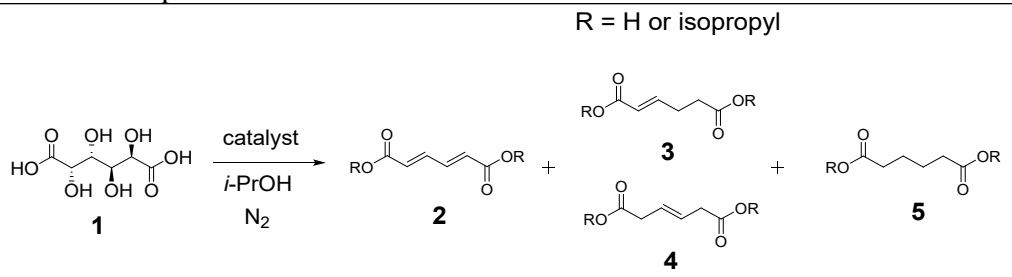
Table S2. DODH-CTH Tandem Reaction of **1** over Ir-ReO_x/C-480.[a]



Entry	T (°C)	Time (h)	Conv.[b] (%)	Products / % yield[b]					
				2	**3**	**4**	**5**	Oxepane	Others
1	180	1	60	47	1	2	0	0	10
2		6	83	24	20	20	2	0	17
3		12	96	8	39	19	4	1	25
4		24	99	1	45	12	16	3	22
5		12+12	99	1	37	7	28	3	23
6	200	12	96	2	32	7	25	4	26
7		24	98	0	27	6	33	4	28
8		48	100	0	2	1	63	7	27
9	220	1	82	17	23	18	3	2	19
10		6	96	0	27	7	29	4	29
11		12	98	0	14	5	42	5	32
12		24	100	0	0	0	59	10	31

[a] Reaction conditions: batch reaction, Ir-ReO_x/C-480 (150mg), **1** (210 mg), *i*-PrOH (40 mL), and N_2 (15 bar).
[b] Conversion and yield are calculated by ^{1}H NMR.

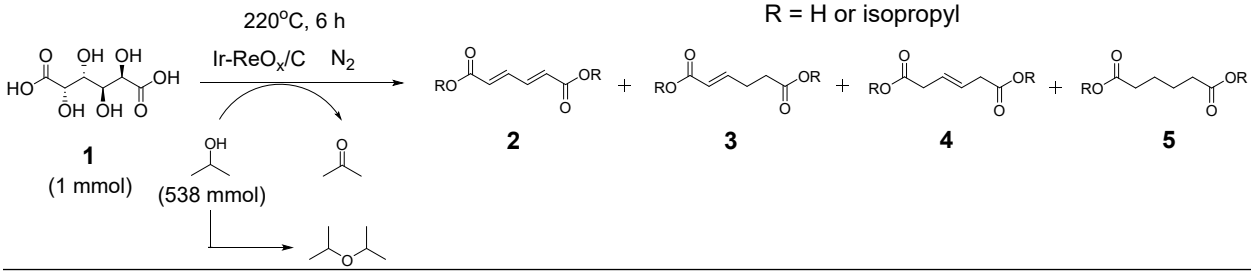
Table S3. DODH-CTH Tandem Reaction of **1** over Ir-ReO_x/C catalysts prepared in different thermal treatment temperatures.[a]



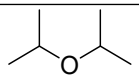
Entry	Catalyst	Conv.[b] (%)	Products / % yield[b]					
			2	**3**	**4**	**5**	Oxepane	Others
1	Ir-ReO_x/C-480	96	0	27	7	29	4	29
2	Ir-ReO_x/C-530	91	0	16	5	34	3	33
3	Ir-ReO_x/C-580	80	0	10	3	31	4	32

[a] Reaction conditions: batch reaction, catalyst (150mg), **1** (210 mg), *i*-PrOH (40 mL), and N_2 (15 bar), 220°C, 6 h.
[b] Conversion and yield are calculated by ^{1}H NMR.

Table S4. Carbon balance of DODH-CTH by Ir-ReO_x/C.[a]

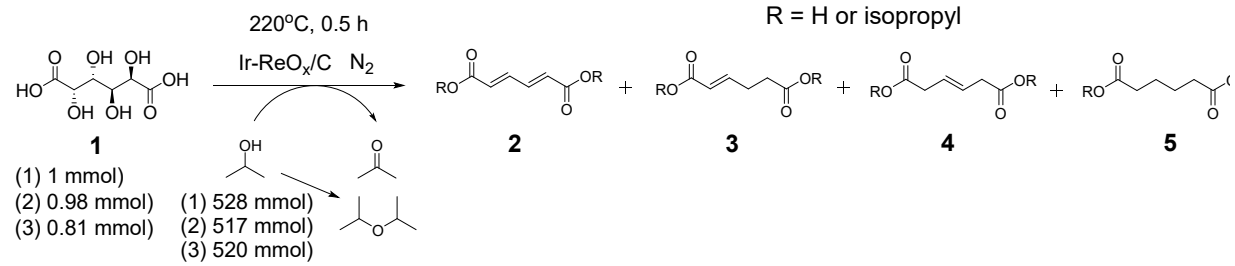


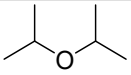
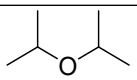
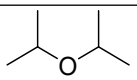
C6 yield (mmol)[b]						
1	**2**	**3**	**4**	**5**	Oxepane	C6 carbon Balance (%)[c]
0.04	0	0.27	0.07	0.29	0.04	71

C3 yield (mmol)[b]				
Liquid phase				C3 carbon Balance (%)[d]
	485	1.4	3.8	91

[a] Reaction conditions: batch reaction, 220 °C, 6 h, Ir-ReO_x/C (150mg, 4.5 wt% Re, 0.045 wt% Ir) **1** (210 mg, 1 mmol), *i*-PrOH (40 mL), and N_2 (15 bar).
[b] Yield is calculated by ^{1}H NMR.
[c] (yield of **1**+**2**+**3**+**4**+**5**+**oxepane**)*100
[d] (yield of all identified C3 products in liquid)/538*100

Table S5. Carbon balance of DODH-CTH by Ir-ReO_x/C-530.[a]



1st Use	C6 yield (mmol)[b]						
	1	**2**	**3**	**4**	**5**	Oxepane	C6 carbon Balance (%)[c]
	0.41	0.14	0.25	0.12	0.01	0.04	97%
	C3 yield (mmol)[b]						
	Liquid phase						C3 carbon Balance (%)[d]
		509	0.70	2.9	0.03	0.72	97%
2nd Cycle	C6 yield (mmol)[b]						
	1	**2**	**3**	**4**	**5**	Oxepane	C6 carbon Balance (%)[c]
	0.21	0.62	0.03	0.04	0.02	0.05	98%
	C3 yield (mmol)[b]						
	Liquid phase						C3 carbon Balance (%)[d]
		461	2.27	22.7	2.65	0.23	95%
3rd Cycle	C6 yield (mmol)[b]						
	1	**2**	**3**	**4**	**5**	Oxepane	C6 carbon Balance (%)[c]
	0.14	0.47	0.01	0.03	0.01	0.11	95%
	C3 yield (mmol)[b]						
	Liquid phase						C3 carbon Balance (%)[d]
		486	1.82	9.93	0.71	0.33	96%

[a] Reaction conditions: batch reaction, 220 °C, 0.5 h, Ir-ReO_x/C (150mg, 4.5 wt% Re, 0.045 wt% Ir) **1** (210 mg, 1 mmol), *i*-PrOH (40 mL), and N_2 (15 bar). Subsequent reuse experiments were scaled down to maintain the 1st cycle catalyst/substrate ratio.
[b] Yield is calculated by ^{1}H NMR.
[c] (yield of **1**+**2**+**3**+**4**+**5**+oxepane)*100
[d] (yield of all identified C3 products in liquid)/initial mmol *i*-PrOH *100

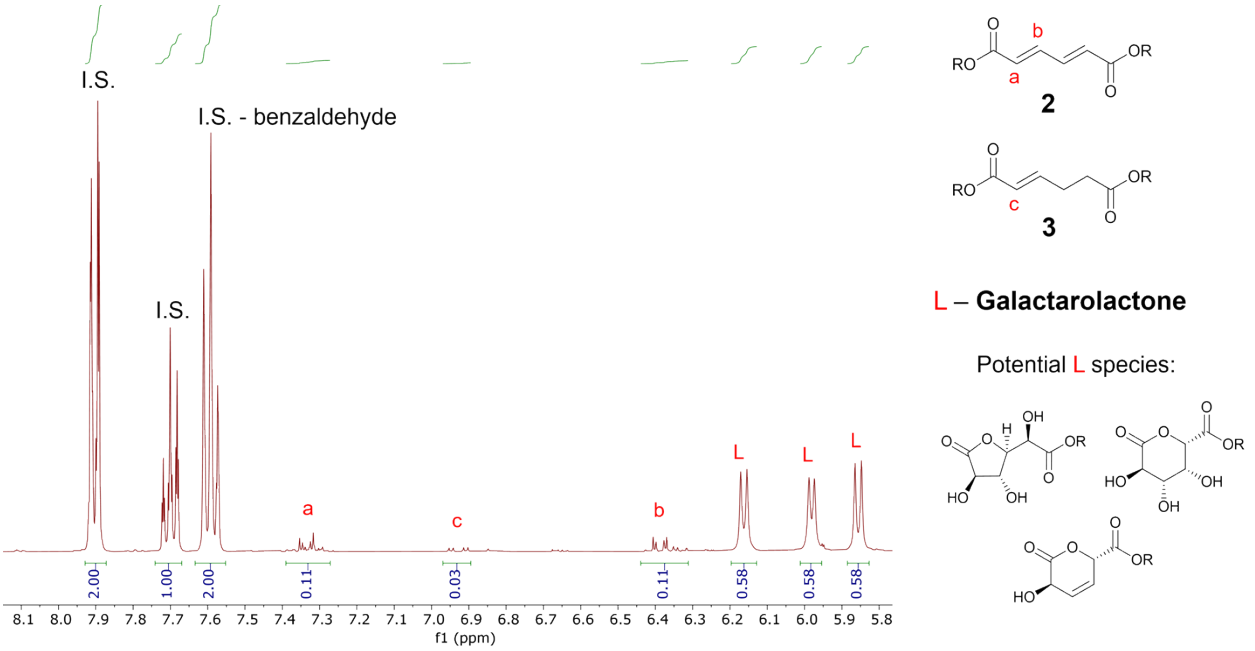


Figure S1. ^{1}H NMR spectra from reaction over MoO_x/C. After the reaction, the reaction solution was concentrated under reduced pressure and dissolved in d_6-DMSO. The sample was analyzed by ^{1}H NMR with benzaldehyde as an internal standard. Reaction conditions: batch reaction, MoO_x/C (150 mg, 4.5 wt% Mo), **1** (210 mg, 1 mmol), N_2 (15 bar), isopropanol (40 mL), 180°C, and 6 h.

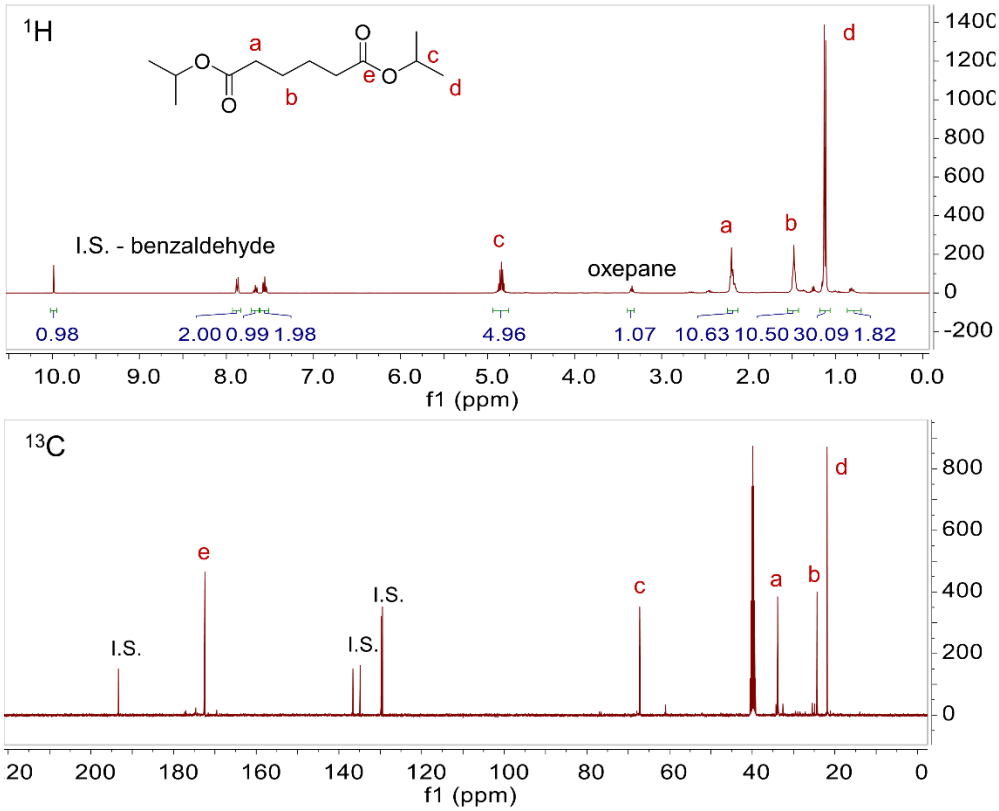


Figure S2. ^{1}H and ^{13}C NMR spectra of the products from DODH-CTH over Ir-ReO_x/C. After reaction, the spent catalyst was filtered, washed with isopropanol(30 mL), and dried in 120°C oven overnight. The reaction solution was concentrated under reduced pressure. The concentrated products were dissolved in d_6-DMSO and analyzed by NMR with benzaldehyde as an internal standard. Reaction conditions: batch reaction, Ir-ReO_x/C-480 (150 mg, 4.33 wt% Re and 0.045 wt% Ir), **1** (210 mg, 1 mmol), N_2 (15 bar), isopropanol (40 mL), 220°C, and 24 h.

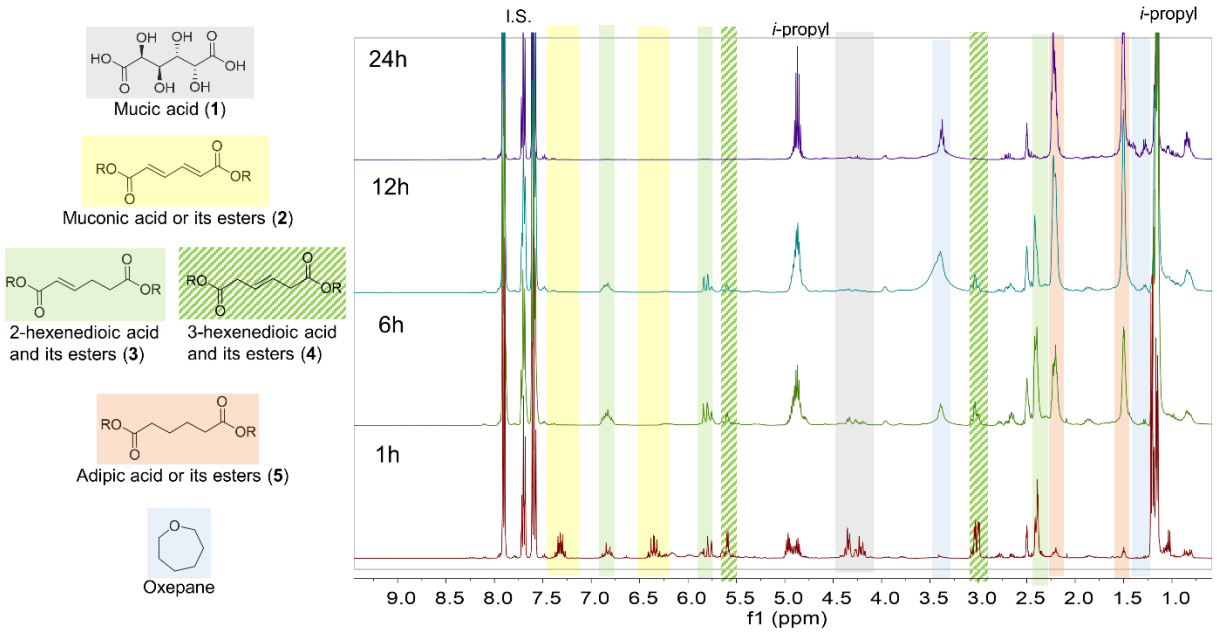


Figure S3. ^{1}H NMR over the course of the DODH-CTH tandem reaction. Reaction conditions: batch reaction, Ir-ReO_x/C-480 (150 mg, 4.33 wt% Re and 0.045 wt% Ir), **1** (210 mg, 1 mmol), N_2 (15 bar), isopropanol (40 mL), and 220°C.

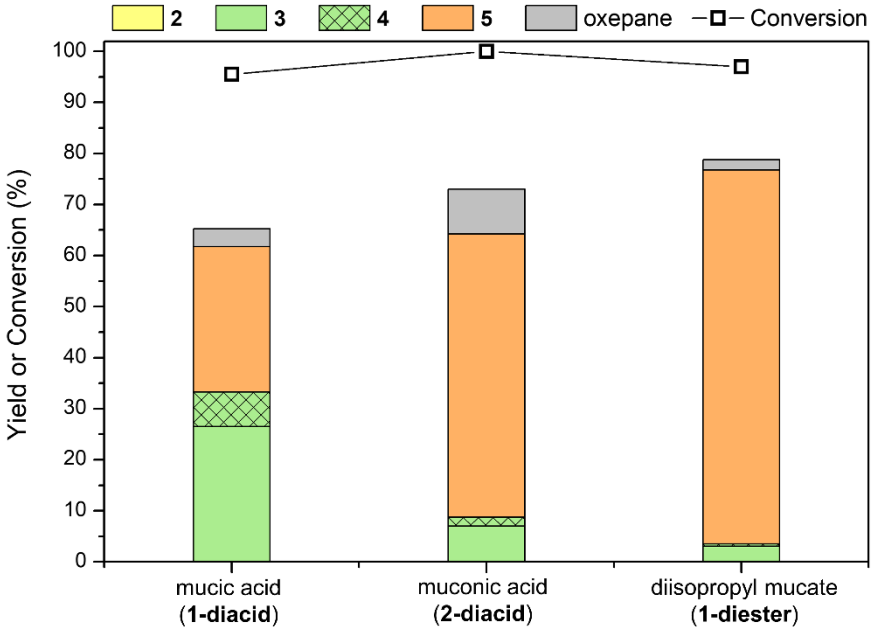


Figure S4. DODH-CTH tandem reaction with different substrates. Reaction conditions: batch reaction, Ir-ReO_x/C-480 (150 mg, 4.33 wt% Re and 0.045 wt% Ir), substrate (1 mmol), N_2 (15 bar), isopropanol (40 mL), and 220°C, and 6 h. Synthesis method of 1-diester was described elsewhere.[6]

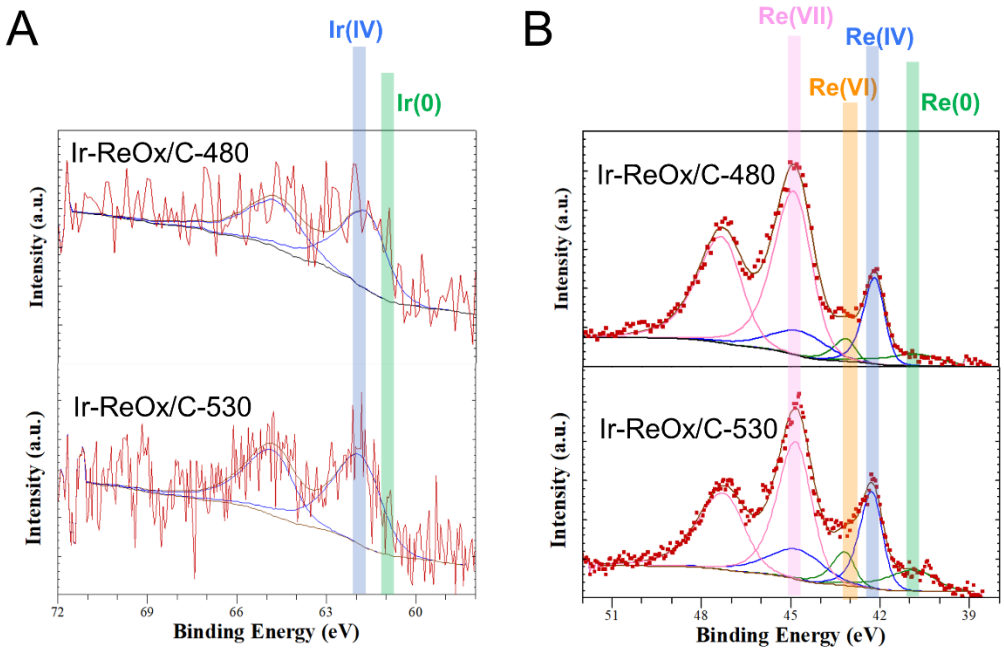


Figure S5. XPS spectra of the Ir-ReO_x/C prepared at 480°C (Ir-ReO_x/C-480) and at 530°C (Ir-ReO_x/C-530) **(A)** Re 4f and **(B)** Ir 4f.

Table S6. Oxidation states of Pt and Re of fresh Ir-ReO_x/C-480, Ir-ReO_x-530, in-situ samples after 24 h reaction, spent Ir-ReO_x/C-530, and regenerated Ir-ReO_x/C-530.

Catalyst	Ir 4f		Re 4f				
	Ir (0), %	Ir (IV), %	Re (0), %	Re (II), %	Re (IV), %	Re (VI), %	Re (VII), %
Fresh – 480°C	0	100	8	-	21	-	71
Fresh – 530°C	0	100	13	-	27	-	60
24 h (in-situ)	100	0	38	-	12	36	14
Spent	0	100	16	-	28	3	53
Regenerated	0	100	-	-	8	-	92

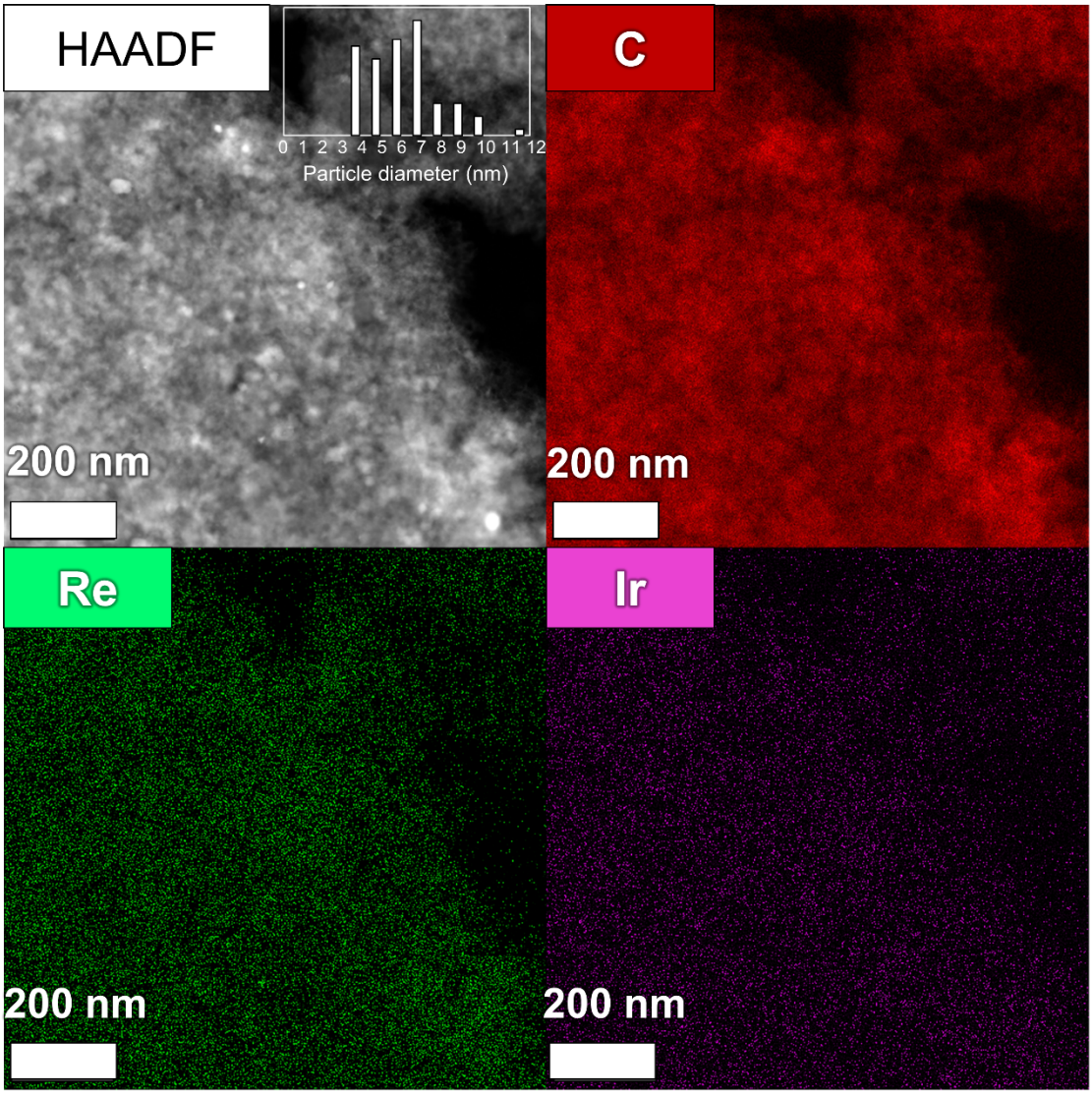


Figure S6. STEM high-angle annular dark-field (HAADF) analysis with particle size distribution and EDX mapping of C, Re, and Ir.

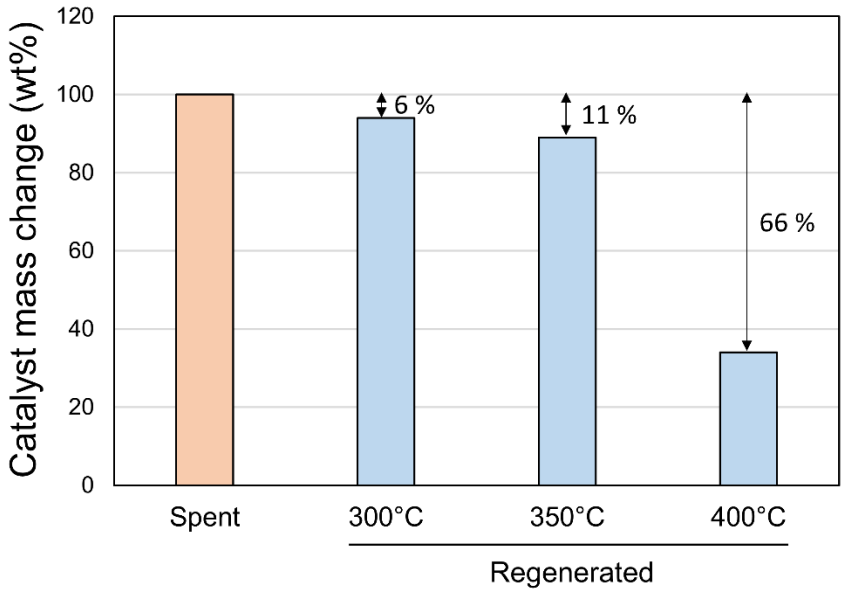


Figure S7. The change in catalyst mass after regeneration at different temperatures. Regeneration conditions: 100 mg spent Ir-ReO_x/C-530 catalyst, thermal temperature (300-400°C), 4h, air flow.

Reference

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(3) Hočevar, B.; Prašnikar, A.; Huš, M.; Grilc, M.; Likozar, B. H_2-Free Re-Based Catalytic Dehydroxylation of Aldaric Acid to Muconic and Adipic Acid Esters. *Angew. Chem. Int. Ed.* **2021**, *60* (3), 1244-1253.

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(6) Jang, J.H.; Ro, I.; Christopher, P.; Abu-Omar, M. M. A Heterogeneous Pt-ReO_x/C Catalyst for Making Renewable Adipates in One Step from Sugar Acids. *ACS Catal.* **2021**, *11* (1), 95-109.

(7) Rhenium. *Mineral Commodity Summaries 2021*; U.S. Geological Survey; Reston, VA, 2021; 134-135.

(8) *Umicore Precious Metals Management Prices*. https://pmm.umicore.com/en/prices/ (accessed 2022-03-10).