Electronic supplementary information for:

Efficient production of adipic acid from 2-methoxycyclohexanone by aerobic oxidation with phosphotungstic acid catalyst

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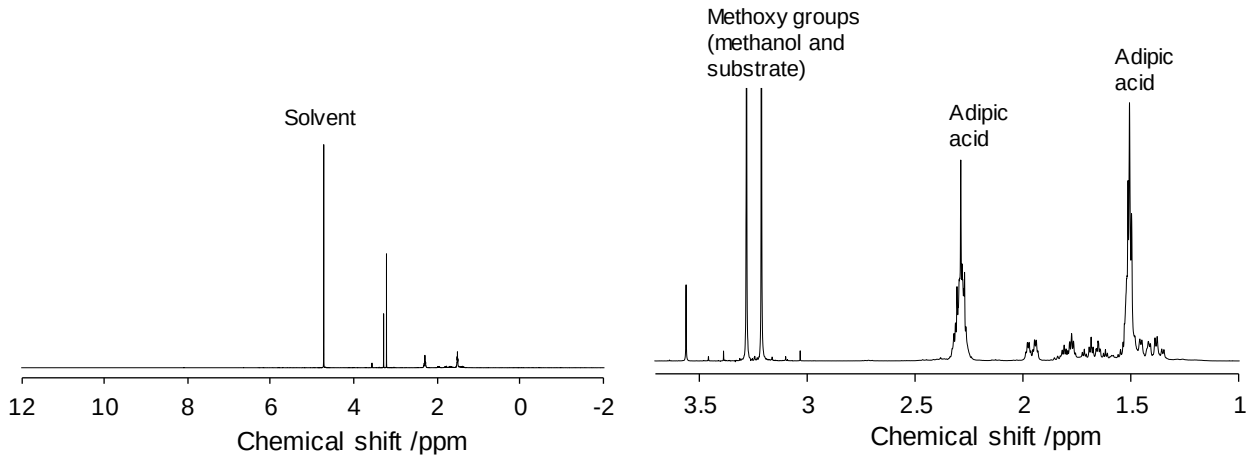

Fig. S1. ^{1}H NMR of reaction solution

Conditions: 2-methoxycyclohexanone (2-MCO) 2.1 mmol, $H_3PW_{12}O_{40}$ 55 μmol, D_2O 5 g, O_2 0.1 MPa (at r. t.), 353 K, 72 h. Reaction was carried out in glass tube with O_2 balloon. Left: full scale, right: enlarged spectra.

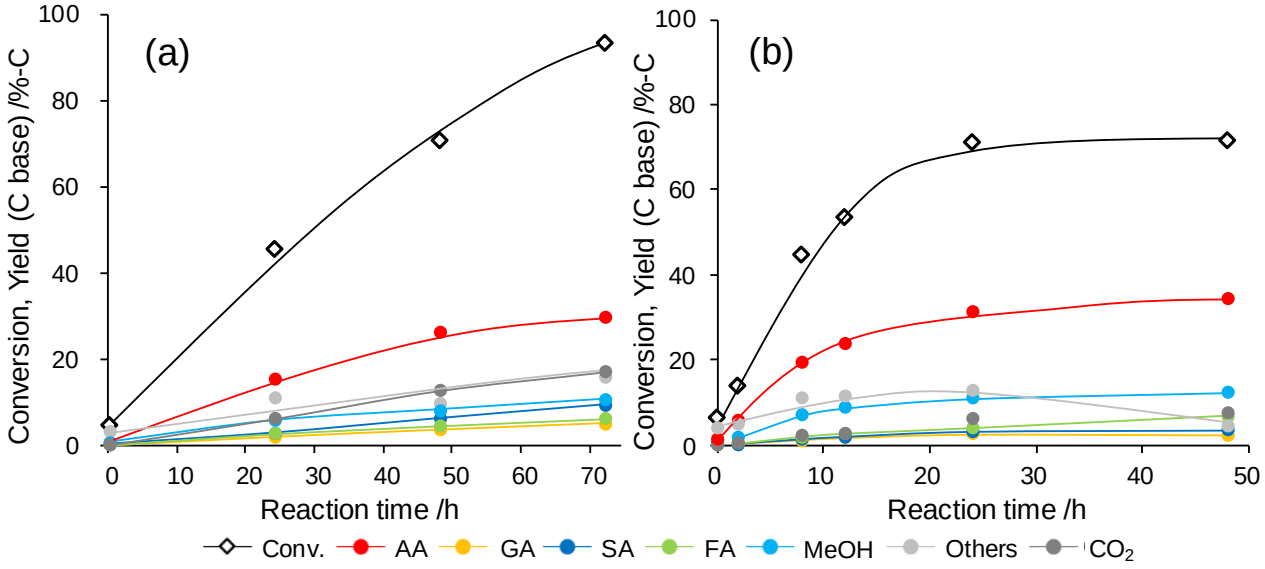

Fig. S2. Time course of the 2-MCO oxidation with typical vanadium catalyst. (a) V_2O_5. (b) $H_5PV_2Mo_{10}O_{40}$.

Reaction condition: 2-methoxycyclohexanone (2-MCO) 4.3 mmol, catalyst 55 μmol, water 10 g, O_2 0.8 MPa (at r. t.), 353 K, 0-72 h. AA: Adipic acid, GA: Glutaric acid, SA: Succinic acid, FA: Formic acid.

Table S1. 2-MCO oxidation with various catalysts.

Entry	Catalyst (Amount /μmol)	Conv. /%	Yield /%-C							AA sel. /%-C	Carbon balance /%
			AA	GA	SA	FA	MeOH	Others	CO_2		
1	Blank	7	1.9	0.2	<0.1	0.1	1.2	3.7	0.1	26	96
2	$H_5PV_2Mo_{10}O_{40}$ (55)	71	31	2.6	3.2	3.9	11	13	6.2	44	97
3	V_2O_5 (55)	31	11	1.4	1.9	1.8	3.9	7.0	3.6	37	105
4	V_2O_5 (55) + $H_3PMo_{12}O_{40}$ (110)	77	46	0.8	0.5	1.2	11	14	3.1	60	100
5	V_2O_5 (55) + $H_3PW_{12}O_{40}$ (110)	79	36	1.9	1.6	2.7	11	21	5.8	45	98
6	V_2O_5 (55) + $H_4SiW_{12}O_{40}$ (110)	84	23	3.7	9.6	8.1	12	8.7	19	28	90
7	$H_3PW_{12}O_{40}$ (110)	60	45	1.1	0.2	0.4	9.7	3.8	0.2	74	97
8	$H_3PW_{12}O_{40}$ (110) [a]	59	42	1.3	0.2	0.4	7.0	7.7	1.0	70	101
9	$H_4SiW_{12}O_{40}$ (110)	38	21	1.0	0.3	0.7	7.9	5.9	0.8	56	108
10	$H_3PMo_{12}O_{40}$ (110)	66	50	0.2	<0.1	1.2	9.5	5.2	0.3	75	102
11	$H_4SiMo_{12}O_{40}$ (110)	60	45	0.2	<0.1	1.1	8.2	4.4	0.2	76	105

Reaction conditions : 2-methoxycyclohexanone 4.3 mmol, catalyst 0-1320 μmol, water 10 g, O_2 0.8 MPa (at r. t.), 353 K, 24 h.

[a] The sheath of autoclave was covered with teflon tube. AA: Adipic acid, GA: Glutaric acid, SA: Succinic acid, FA: Formic acid, MeOH: Methanol.

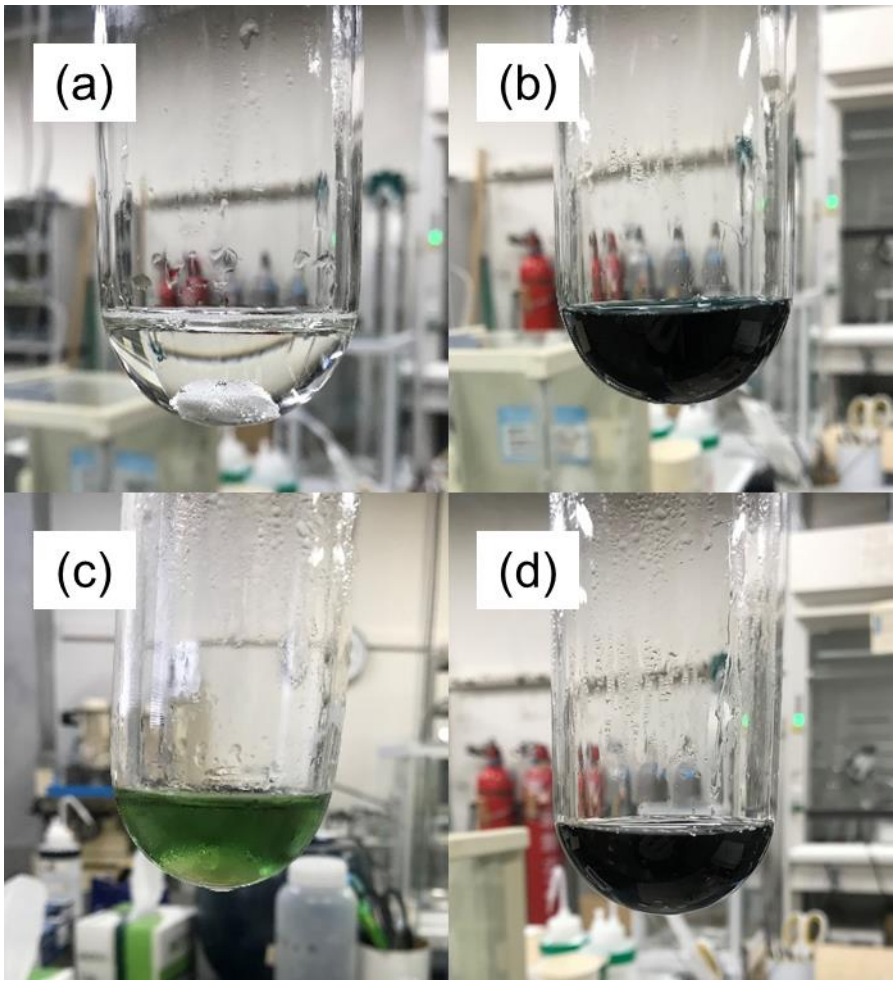

Fig. S3. The color of reaction solution with (a) $H_3PW_{12}O_{40}$, (b) $H_3PMo_{12}O_{40}$, (c) $H_4SiMo_{12}O_{40}$ and (d) $H_3PW_{12}O_{40}$ (at O_2 0 MPa) as catalysts.

Reaction condition: 2-methoxycyclohexanone (2-MCO) 4.3 mmol, catalyst 110 μmol, water 10 g, O_2 or N_2 0.8 MPa (at r. t.), 353 K, 24 h.

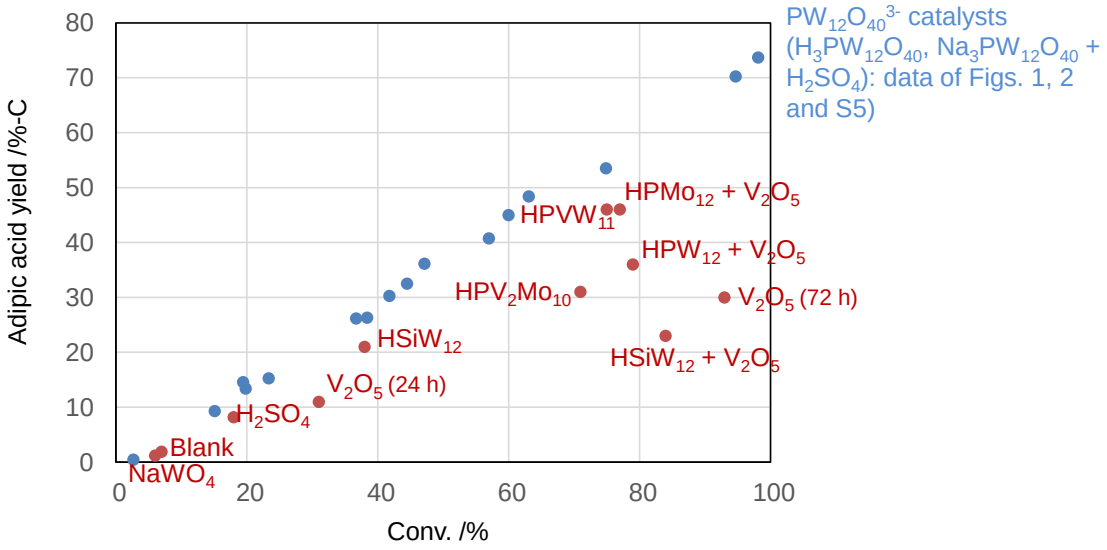

Fig. S4. Comparison of adipic acid yields between catalysts. The data are taken from Figs. 1, 2 and S5, below, for $PW_{12}O_{40}^{3-}$ catalysts (blue color) and Table 1 for other catalysts (red color). The reaction temperature (353 K), 2-MCO concentration (4.3 mmol in 10 g water) and O_2 pressure (0.8 MPa at r.t.) were the same for all data.

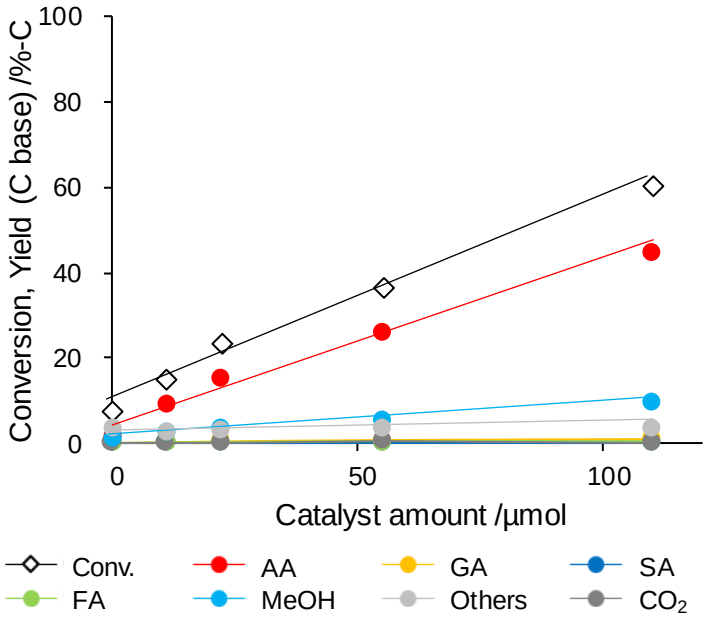

Fig. S5. Effect of amount of $H_3PW_{12}O_{40}$ in 2-MCO oxidation.

Reaction condition: 2-methoxycyclohexanone (2-MCO) 4.3 mmol, $H_3PW_{12}O_{40}$ 0-110 μmol, water 10 g, O_2 0.8 MPa (at r. t.), 353 K, 24 h. AA: Adipic acid, GA: Glutaric acid, SA: Succinic acid, FA: Formic acid.

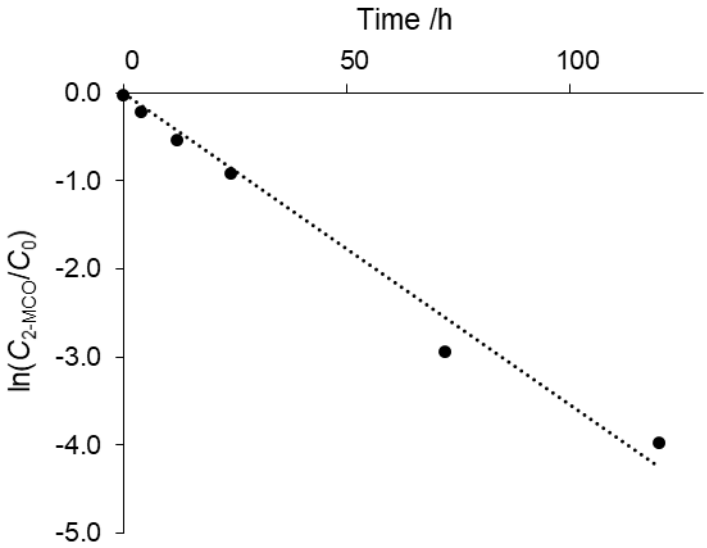

Fig. S6. ln($C_{2\text{-MCO}}/C_0$) vs Time.

Reaction condition: 2-methoxycyclohexanone (2-MCO) 4.3 mmol, $H_3PW_{12}O_{40}$ 110 μmol, water 10 g, O_2 0.8 MPa (at r. t.), 353 K, 0-120 h.