Electronic Supplementary Information (ESI) for
A Large-Scale Continuous-flow Process for Green Production of Adipic Acid via Catalytic Oxidation of Cyclohexene with H_2O_2 Cyclohexene

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1. The influence of acidic promoter on green oxidation of cyclohexene

Table S1. Effect of different acidic promoters.[a]

Acidic promoters	Product yield (%)	Decomposition of H_2O_2 (%)
Oxalic acid	83.6	6.9
5-Sulfosalicylic acid	88.0	5.5
Phosphoric acid	80.4	6.1
Sulfuric acid	89.5	12.8
Nitric acid	84.3	17.3
Hydrochloric acid	75.0	18.8
— [b]	77.7	20.5

[a] Reaction conditions: H_2WO_4, acidic promoter, cyclohexene, and H_2O_2 in a molar ratio of 1: 1: 50: 220 (all other conditions same as defined in Experimental Section "*Typical procedure of catalytic oxidation in batch reactor*").

[b] No acidic promoter.

Table S2. The influence of acidity on green oxidation of cyclohexene

Reaction	I [a]	II [b]	III[c]	IV[d]	V [e]
TOF of cyclohexene (h^{-1}) [f]	25.7	24.3	16.4	4.1	——
Yield of epoxycyclohexane (%) [f]	0[g]	0[g]	0[g]	6.1	——
Yield of cyclohexanediol (%) [f]	54.0	51.6	33.1	4.0	——
Yield of adipic acid (%)	90.2	87.0	79.2	8.5	25.1
Purity of crude product (%)	98.0	98.3	96.0	77.6	88.7
Decomposition of H_2O_2 (%)	7.2	14.0	6.5	35.8	30.3

[a] Reaction condition: the procedure was described in Experiment Section "*Typical procedure of catalytic*

oxidation in batch reactor".

[b] Reaction condition: H_2WO_4, H_2SO_4, cyclohexene and aqueous H_2O_2 in a molar ratio of 1: 1.04: 50: 220 were added in a batch reactor (without H_3PO_4), and all other conditions were unchanged.

[c] Reaction condition: H_2WO_4, H_3PO_4, cyclohexene and aqueous H_2O_2 in a molar ratio of 1: 0.56: 50: 220 were added in a batch reactor (without H_2SO_4), and all other conditions were unchanged.

[d] Reaction condition: H_2WO_4, H_2SO_4, H_3PO_4, cyclohexene and aqueous H_2O_2 in a molar ratio of 1: 1.04: 0.56: 50: 220 were added into a batch reactor. The pH value of aqueous phase of this reaction system was adjusted to 7 by adding Na_2CO_3, and all other conditions were unchanged.

[e] Reaction condition: H_2WO_4, H_2SO_4, H_3PO_4, 1,2-cyclohexanediol and aqueous H_2O_2 in a molar ratio of 1: 1.04: 0.56: 50: 220 were added into a batch reactor. The pH value of aqueous phase of this reaction system was adjusted to 7 by adding Na_2CO_3, and all other conditions were unchanged.

[f] The reaction mixture was sampled at 2 h later.

[g] Beyond the detection limit.

2. The pathway of green oxidation of cyclohexene to adipic acid with aqueous H_2O_2

According to previous experiments and the reaction pathway proposed by Noyori,[1,46] this reaction should include the organic-water heterogeneous reaction stage (stage A) and the homogeneous reaction stage (stage B).

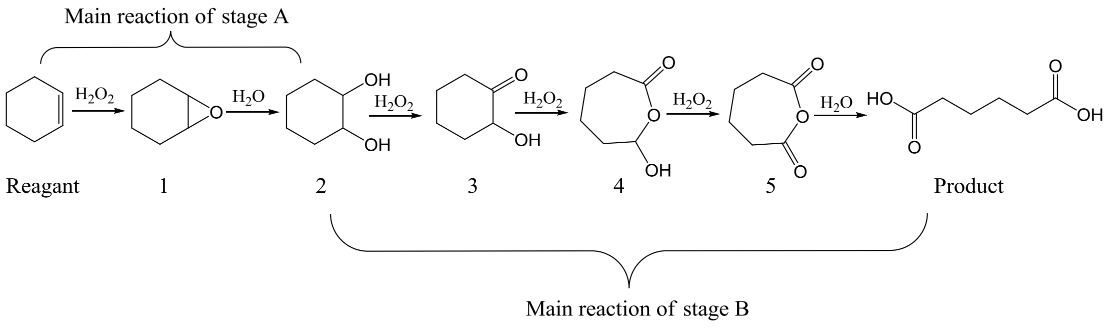

Figure S1. The pathway of green oxidation of cyclohexene to adipic acid with aqueous H_2O_2

3. The activity of H_2WO_4-H_2SO_4-H_3PO_4 and H_2WO_4-H_2SO_4 in low H_2O_2 concentration solutions

(a) H_2WO_4, H_2SO_4, H_3PO_4 and aqueous H_2O_2 in a molar ratio of 1: 1.04: 0.56: 22 were added into a beaker. The solution was heated to 90 ^{o}C for 8h with stirring. Water was added to the solution to avoid dryout. Finally, the concentration of H_2O_2 in solution was lower than 1% and a pale yellow solution was obtained. Diethyl ether was added into part of solution, and the etherate was evaporated in vacuum until an off-white precipitate was produced. The sample produced was dried in fume hood and characterized by FTIR and XRD (as shown in figure S2a and figure S3a), which has been identified to be $H_3PW_{12}O_{40}$.[S1-S4] The rest of solution was concentrated and used as the catalyst of oxidation of 1,2-cyclohexanediol to AA with 5% H_2O_2 (as shown in table S3).

(b) H_2WO_4, H_2SO_4, and aqueous H_2O_2 in a molar ratio of 1: 1.04: 22 were added into a beaker. The solution was heated to 90 °C for 8h with stirring. Water was added to the solution to avoid dryout. Finally, the concentration of H_2O_2 in solution was lower than 1% and a yellow suspension was obtained. Part of the suspension obtained was aged and centrifuged. The yellow precipitate was washed repeatedly with water, dried in vacuum and characterized by FTIR and XRD (as shown in figure S2b and figure S3b). The precipitate has been identified to be H_2WO_4.[S5-S7] The rest of suspension was concentrated and used as the catalyst of oxidation of 1,2-cyclohexanediol to AA with 5% H_2O_2 (as shown in table S3).

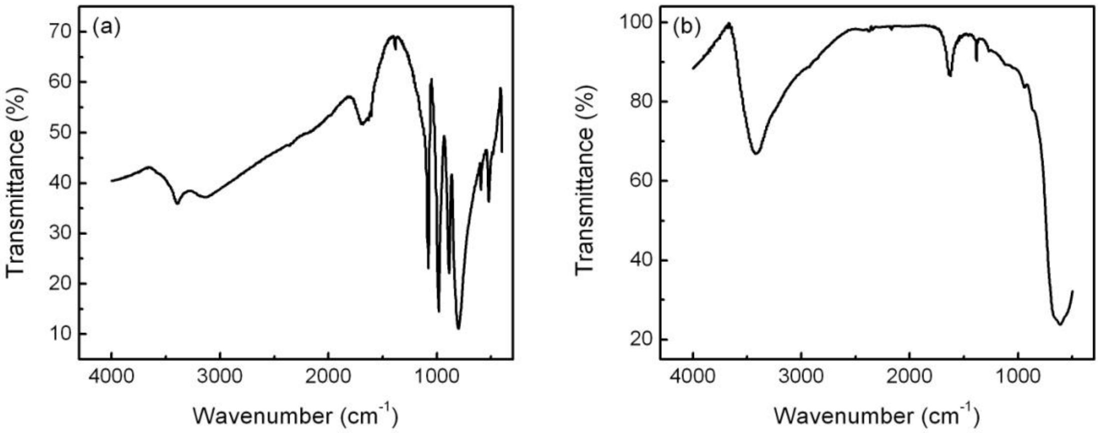

Figure S3. IR spectra of (a) extract from H_2WO_4-H_2SO_4-H_3PO_4 and (b) precipitate from H_2WO_4-H_2SO_4 in low H_2O_2 concentration solution

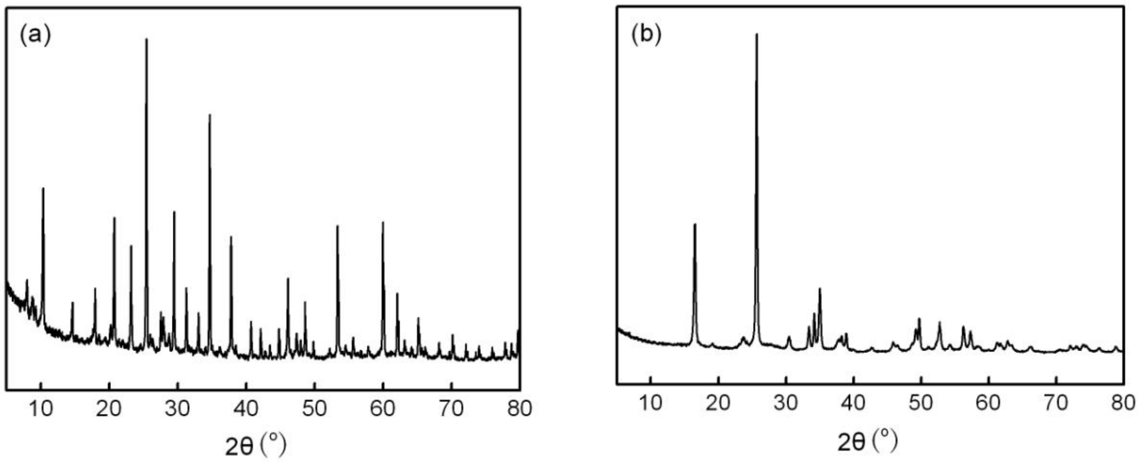

Figure S3. XRD patterns of (a) extract from H_2WO_4-H_2SO_4-H_3PO_4 and (b) precipitate from H_2WO_4-H_2SO_4 in low H_2O_2 concentration solution

Table S3. The catalytic activity of H_2WO_4-H_2SO_4-H_3PO_4 and H_2WO_4-H_2SO_4 in low H_2O_2 concentration solution

Catalyst system	Conversion of diol (%)	Yield of AA (%)
H_2WO_4-H_2SO_4-H_3PO_4	10.7	4.3
H_2WO_4-H_2SO_4	3.1	0

[a] Reaction conditions: The solution with catalyst, diol, and H_2O_2 in a molar ratio of 1: 50: 170 (W: diol: H_2O_2) was heated to 90 ºC for 6 h with stirring.

4. The lab-scale device of continuous-flow reaction

The lab-scale device of continuous-flow reaction is shown in Figure S4. This device is made up of CSTRs (R1~R4), equipped with Teflon agitator (R1 and R2 are equipped with mechanical agitator, and R3, R4 are equipped with magnetic stirrer) and reflux condenser, peristaltic pumps (P1 is used for the feed of cyclohexene and P2 is used for the feed of catalyst and H_2O_2), reagent container (RC1 is loaded with cyclohexene and RC2 is loaded with the mixture of catalyst and H_2O_2) and temperature controllers equipped with thermo element (TC1 and TC2). The reagent containers, CSTRs and pumps were connected with pipe of viton.

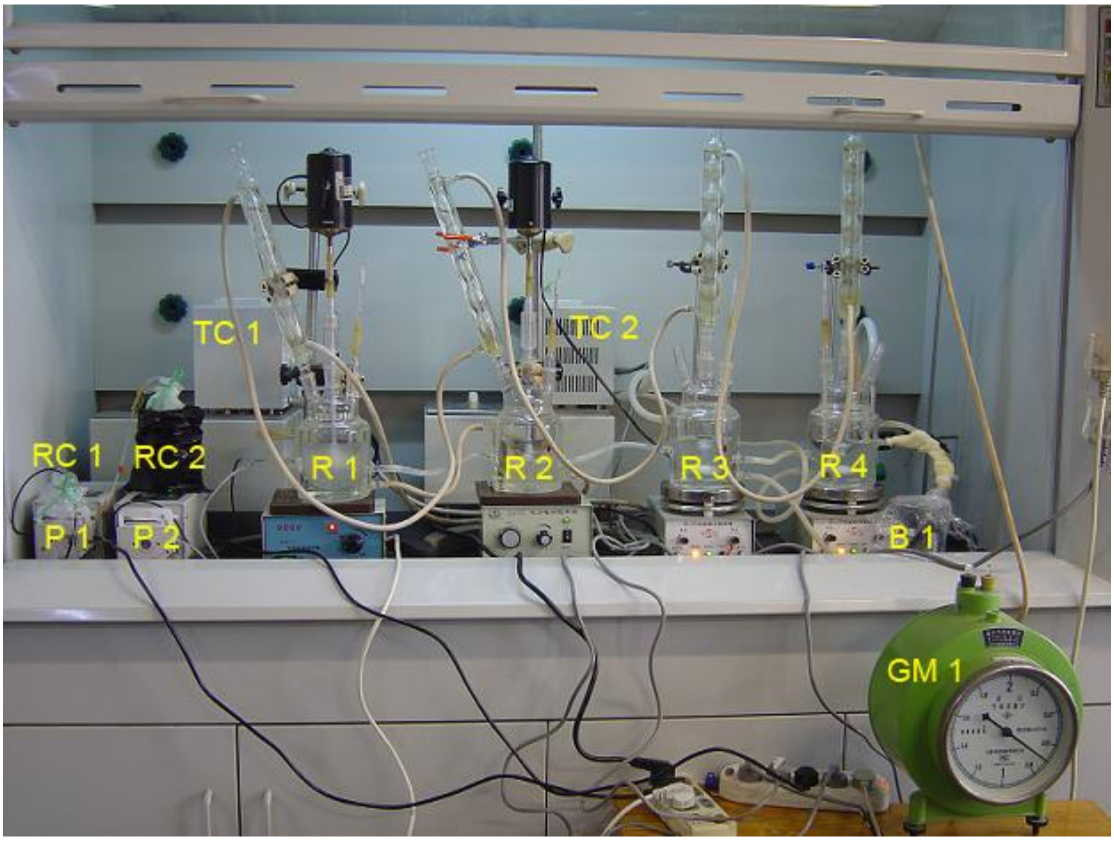

Figure S4. The lab-scale device of continuous-flow reaction. Abbreviations: B, beaker; P, pump; R, reactor; RC, reagent container; TC, temperature controller and thermo element; GM, gas flow meter.

5. The reproducibility of the lab- and scale-up experiments

Table S4. The scale-up in batch reactor[a]

Reactor volume (L)	Yield of 1st (%)	Yield of 2nd (%)	Yield of 3rd (%)	Average yield (%)
0.5	93.7	92.0	91.1	92.3
5	92.1	92.3	94.4	93.0
100	87.5	91.6	89.2	89.5
2000	98.8	95.7	94.3	96.3
5000	94.0	95.9	97.4	95.8

[a] Reaction condition is described in Experiment Section “*A typical procedure of catalytic oxidation in batch reactor*”

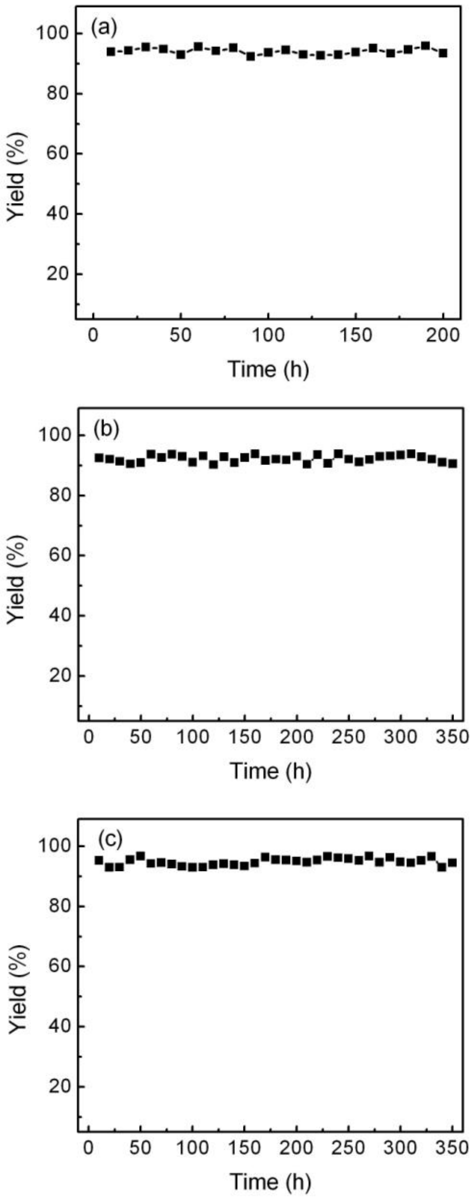

Figure S5. The continuous-flow reaction in (a) 4×0.5L CSTRs, (b) 4×100L CSTRs and (c) 4×5000L CSTRs

References

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