

## Supporting Information

# Effective solvent-free oxidation of cyclohexene to allylic products with oxygen by mesoporous etched halloysite nanotubes supported $\text{Co}^{2+}$

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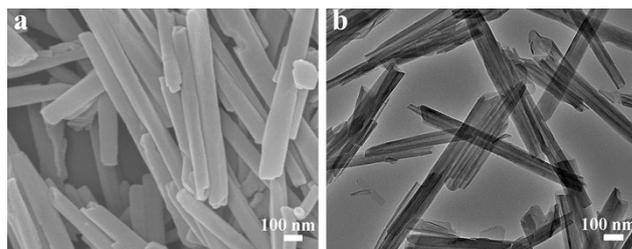


Fig. S1 SEM (a) and TEM (b) images of the halloysite nanotubes (HA).

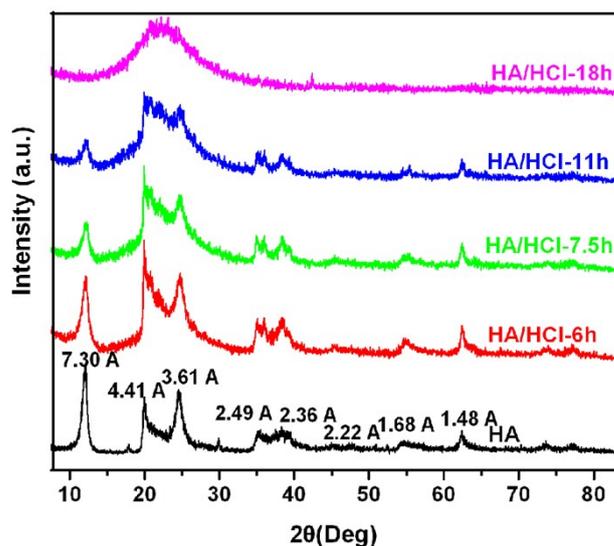


Fig. S2. XRD results of HA and HA/HCl-T. The intensity of the intense basal reflection of halloysite (7.30 Å) representing the single 1:1 layer aluminosilicate thickness, as well as other typical reflections of halloysite (4.41 Å, 3.61 Å, 2.49 Å, 2.36 Å, 2.22 Å, 1.68 Å, 1.48 Å) decrease with etching time, and ultimately disappear with a broad band peak present which is attributed to amorphous SiO<sub>2</sub>.

Table S1 EDX results of HA after being etched with HCl for different time.

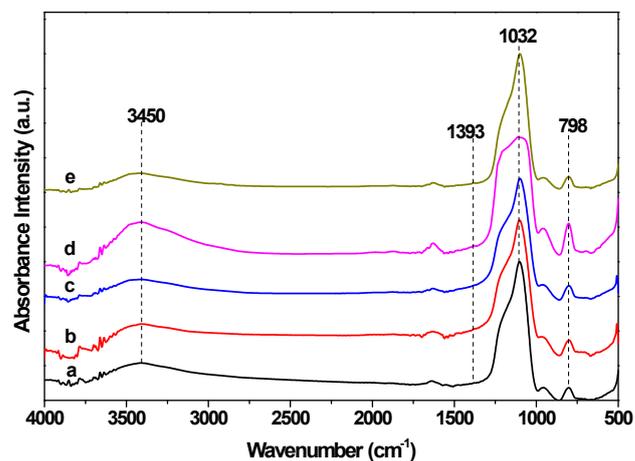
Etching time (h)	Al (at %)	Si (at %)	Al/Si (at %)
0	40.89	59.11	69
6	20.82	79.18	26
7.5	15.26	84.74	18
11	5.52	94.48	6
18	0.01	99.99	0.01

Table S2 The nitrogen adsorption results of HA and HA after etching with HCl for different time.

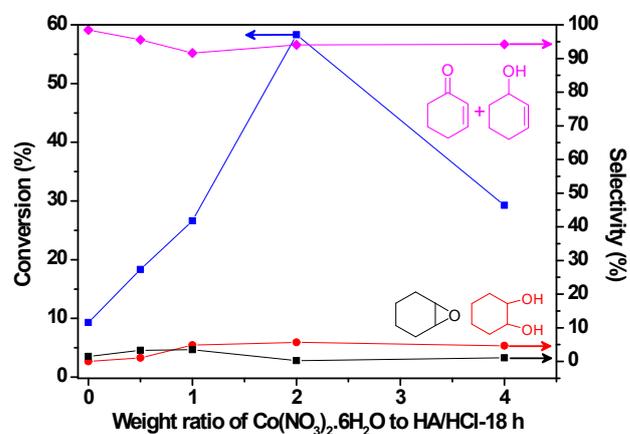
Sample	Pore diameter (nm)	Pore volume (cm <sup>3</sup> /g)	BET surface area (m <sup>2</sup> /g)
HA	11.5	0.16	31.7
HA/HCl-6 h	6.8	0.56	176.5
HA/HCl-7.5 h	8.9	0.58	191.8
HA/HCl-11 h	9.3	0.74	225.7
HA/HCl-18 h	12.0	0.87	228.4

**Table S3** The Al/Si ratio (at) and Co (wt%) of the HA/HCl-18 h/Co<sup>2+</sup>-R determined by EDX.

Sample	Al/Si (at)	Co (wt%)
HA/HCl-18 h/Co <sup>2+</sup> -0.5:1	0.012	0.20
HA/HCl-18 h/Co <sup>2+</sup> -1:1	0.015	0.48
HA/HCl-18 h/Co <sup>2+</sup> -2:1	0.006	0.56
HA/HCl-18 h/Co <sup>2+</sup> -4:1	0.012	0.67



**Fig. S3** FT-IR of mesoporous etched halloysite nanotube supported Co<sup>2+</sup> (eHA@Co<sup>2+</sup>): (a) HA/HCl-18 h/Co<sup>2+</sup>-0:1, (b) HA/HCl-18 h/Co<sup>2+</sup>-0.5:1, (c) HA/HCl-18 h/Co<sup>2+</sup>-1:1, (d) HA/HCl-18 h/Co<sup>2+</sup>-2:1 and (e) HA/HCl-18 h/Co<sup>2+</sup>-4:1.



**Fig. S4** The effect of weight ratio of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O to HA/HCl-18 h in the fabrication on the cyclohexene conversion and selectivity catalyzed by HA/HCl-18 h/Co<sup>2+</sup>-R.

**Table S4** The effect of calcinations on the cyclohexene conversion and selectivity catalyzed by HA/HCl (NaOH)-18 h/Co<sup>2+</sup>-2:1.

Catalyst	Conversion (%)	Selectivity (%)			
					
HA/HCl-18 h/Co <sup>2+</sup> -2:1	58.30	0.27	5.70	54.60	39.43
HA/HCl-18 h/Co <sup>2+</sup> -2:1/550°C-6 h	12.26	0.31	12.00	62.08	25.62
HA/NaOH-18 h/Co <sup>2+</sup> -2:1	29.06	2.05	17.95	54.22	25.77
HA/NaOH-18 h/Co <sup>2+</sup> -2:1/550°C-6 h	50.85	7.53	9.55	43.23	39.69

Reaction conditions: 40 mg catalyst, 0.8 mL cyclohexene, O<sub>2</sub> (10 min), 75°C, 18 h.

**Table S5** The effect of oxidant on cyclohexene oxidation catalyzed by HA/HCl-18 h/Co<sup>2+</sup>-2:1.

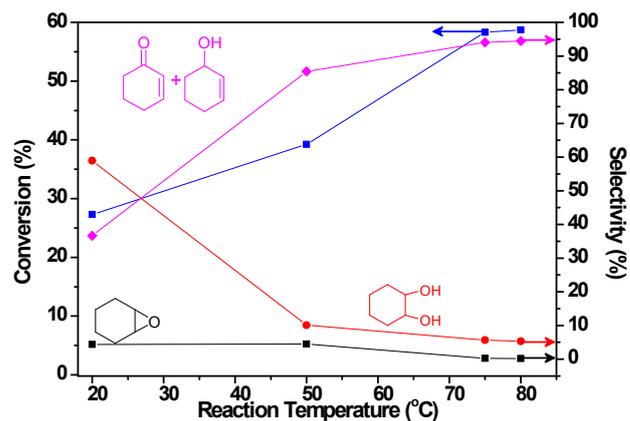
Oxidant	Conversion (%)	Selectivity (%)			
					
O <sub>2</sub>	58.30	0.27	5.70	54.60	39.43
Without bubbling O <sub>2</sub>	10.41	3.26	3.51	51.80	41.43
H <sub>2</sub> O <sub>2</sub> <sup>a</sup>	25.70	0	98.70	1.30	0
H <sub>2</sub> O <sub>2</sub> (catalyst-free) <sup>a</sup>	9.40	0	98.70	0.10	1.20

Reaction conditions: 40 mg catalyst, 0.8 mL cyclohexene, O<sub>2</sub> (10 min), 75°C, 18 h. <sup>a</sup>1.6 mL 30% H<sub>2</sub>O<sub>2</sub> replaces O<sub>2</sub> as oxidant.

**Table S6** The effect of solvent on cyclohexene oxidation catalyzed by HA/HCl-18 h/Co<sup>2+</sup>-2:1.

Solvent	Conversion (%)	Selectivity (%)			
					
Solvent-free	58.30	0.27	5.70	54.60	39.43
Acetonitrile (CH <sub>3</sub> CN)	9.60	5.60	10.50	58.70	25.20
Acetic anhydride	46.80	0.50	41.80	57.20	0.50
n-Heptane	23.90	8.30	25.50	40.10	26.10
CH <sub>2</sub> Cl <sub>2</sub>	0.40	22.30	0	29.30	0.40
THF	0.60	0	4.80	56.30	38.90
DMF	14.30	20.00	3.20	56.80	19.90

Reaction conditions: 40 mg catalyst, 0.8 mL cyclohexene, 4.8 mL solvent, O<sub>2</sub> (10 min), 75°C, 18 h.



**Fig. S5** The effect of reaction temperature on the cyclohexene conversion and selectivity catalyzed by HA/HCl-18 h/Co<sup>2+</sup>-2:1.

**Table S7** The effect of reaction temperature on the cyclohexene conversion and selectivity catalyzed by HA/HCl-18 h/Co<sup>2+</sup>-2:1.

Reaction temperature (°C)	Conversion (%)	Selectivity (%)			
					
20	27.31	4.40	58.94	21.68	14.98
50	39.24	4.50	10.08	49.52	35.90
75	58.30	0.27	5.70	54.60	39.43
80	58.71	0.19	5.34	55.32	39.15

Reaction conditions: 40 mg catalyst, 0.8 mL cyclohexene, O<sub>2</sub> (10 min), 18 h.

**Table S8** The effect of reaction time on the cyclohexene conversion and selectivity catalyzed by HA/HCl-18 h/Co<sup>2+</sup>-2:1.

Reaction time (h)	Conversion (%)	Selectivity (%)			
					
6	18.84	5.15	5.26	57.37	32.21
12	22.06	0.19	5.62	66.39	27.79
18	58.30	0.27	5.70	54.60	39.43
24	59.82	0.35	4.27	63.12	32.26

**Table S9** Recycling study with HA/HCl-18 h/Co<sup>2+</sup>-2:1 as catalyst.

Cycles	Conversion (%)	Selectivity (%)			
					
1	58.30	0.27	5.70	54.60	39.43
2	45.59	0.24	7.08	58.63	34.06
3	37.69	0.28	6.99	57.85	34.88
4	34.34	2.44	62.34	16.13	19.08

Reaction conditions: 40 mg HA/HCl-18 h/Co<sup>2+</sup>-2:1, 0.8 mL cyclohexene, O<sub>2</sub> (10 min), 75°C, 18 h.