Electronic Supplementary Information (ESI) for

# Cobalt-Tetraamide-Phthalocyanine immobilized on $Fe_3O_4$/Chitosan Microspheres as an Efficient Catalyst for the Baeyer-Villiger Oxidation

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## Experimental Section

### Materials

The chemical reagents used were 1,2,4-benzeneticarboxylic anhydride, urea, cobalt(II) chloride hexahydrate, ammonium molybdate(VI) tetrahydrate, methanol, acetone, ferrous sulfate heptahydrate, ethanol, iron(III) chloride hexahydrate ($FeCl_3$•$6H_2O$), 2,2,6,6-tetramethylpiperidine-1-oxyl (Tempo), ammonium hydroxide($NH_3 \cdot H_2O$), chitosan, glutaraldehyde, paraffin, acetic acid, ammonium chloride, cyclohexanone, 1,2-dichloroethane, benzaldehyde and N,N-

Dimethylformamide (DMF). All chemical reagents were of analytical grade and were used as received without further purification.

## Characterization method of the catalyst CoTaPc-$Fe_3O_4$/CTO

Fourier transform infrared (FT-IR) spectra of catalysts were obtained from a Magana-IR 500 FT-IR spectrometer (Nicolet, USA). The IR spectra of catalysts were obtained by the KBr tableting method; UV-Vis absorption spectra were recorded on a CARY-100 ultraviolet-visible spectrophotometer (Agilent, USA). Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku Ultimate IV powder diffractometer, using Cu Kα radiation. SEM images was recorded on a Hitachi S-4800 (Chiyoda-ku, Tokyo, Japan) operated under high vacuum with an accelerating voltage of 20 Kv. Column chromatography was generally performed on silica gel (200-300 mesh) and TLC inspections were carried out on silica gel GF254 plates. GC analysis was performed on an GC9790-II with a hydrogen flame ionization detector and an PEG-20M column (0.32 mm×30 m, film: 0.5 um)

Table S1 Screening of solvents[a]

| Entry | Solvent | Temperature | Amount of catalyst | Time | Conversion[b] |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| 1 | EtOAc | 15℃ | 5% | 12h | 84.2% |
| 2 | MeCN | 15℃ | 5% | 12h | 83.5% |
| 3 | DIOX | 15℃ | 5% | 12h | 6.2% |
| 4 | DCE | 15℃ | 5% | 12h | 94.5% |

[a] Reaction condition: cyclohexanone 0.025 mol, $O_2$ 24 ml/min, n(Benzaldehyde) ：n(cyclohexanone)=2：1, solvent amount 25 ml

[b] The conversation and selectivity were determined by GC on the basis of the internal standard method (chlorobenzene).

Table S2 Effect of solvent amount on reaction[a]

| Entry | Amount of solvent | Temperature | Amount of catalyst | Time | Conversion[b] |
|---|---|---|---|---|---|
| 1 | 0 | 15℃ | 5% | 12h | 22.6% |
| 2 | 10 | 15℃ | 5% | 12h | 78.0% |
| 3 | 15 | 15℃ | 5% | 12h | 86.9% |
| 4 | 20 | 15℃ | 5% | 12h | 88.8% |

| | | | | | |
|---|---|---|---|---|---|
| 5 | 25 | 15℃ | 5% | 12h | 94.5% |
| 6 | 30 | 15℃ | 5% | 12h | 90.3% |

[a] Reaction condition: cyclohexanone 0.025 mol, $O_2$ 24 ml/min, solvent DCE, n(Benzaldehyde) ：n(cyclohexanone)=2：1

[b] The conversation and selectivity were determined by GC on the basis of the internal standard method (chlorobenzene).

Table S3. Effect of the benzaldehyde on the reaction[a]

| Entry | Amount of bezaldehyde | Temperature | Amount of catalyst | Time | Conversion[b] |
|---|---|---|---|---|---|
| 1 | 1:1 | 15℃ | 5% | 12h | 69.4% |
| 2 | 1.5:1 | 15℃ | 5% | 12h | 87.0% |
| 3 | 2.5:1 | 15℃ | 5% | 12h | 85.1% |
| 4 | 3:1 | 15℃ | 5% | 12h | 79.5% |

[a] Reaction condition: cyclohexanone 0.025 mol, $O_2$ 24 ml/min, solvent DCE, solvent amount: 25ml

[b] The conversation and selectivity were determined by GC on the basis of the internal standard method (chlorobenzene).

Table S4

| Name | TON | TOF |
|---|---|---|
| CoTaPc-$Fe_3O_4$/CTO | 292 | 24.3 h-1 |

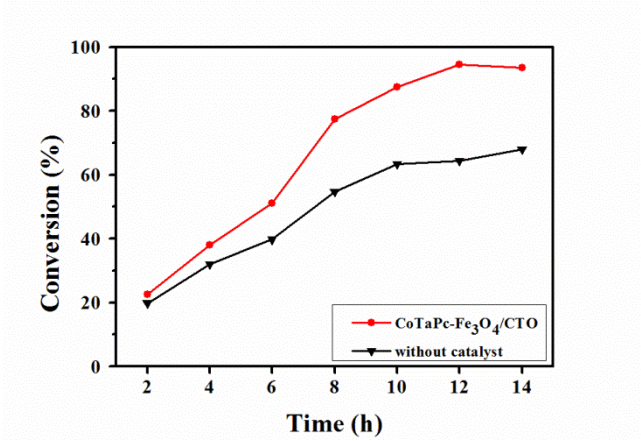


Figure S1. Oxidation of cyclohexanone by $O_2$/benzaldehyde (cyclohexanone 0.025 mol, catalyst 0.12 g, 15℃, 2 equiv. of benzaldehyde)

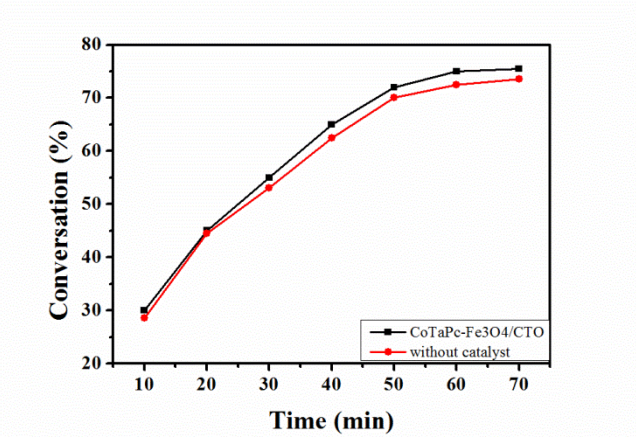


Figure S2. Oxidation of cyclohexanone by m-chloroperbenzoic acid (substrate 2 mmol, catalyst 10 mg, 15℃, 2 equiv. of m-chloroperbenzoic acid)

1. ε-caprolactone. $^{1}$H NMR (500 MHz, $CDCl_3$) δ: 4.22 (m, 2H), 2.62 (m, 2H), 1.84 (m, 2H), 1.75 (m, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ: 25.8, 30.9, 33.7, 35.7, 41.2, 73.1, 178.9.

2. 4-Methyl-ε-caprolactone. $^{1}$H NMR (500 MHz, $CDCl_3$) δ: 4.26 (m, 2H), 2.66 (m, 2H),

1.85 (m, 3H), 1.51 (m, 1H), 1.35(m, 1H), 1.01(d, J=6.6 Hz, 3H). $^{13}$C-NMR (125 MHz, $CDCl_3$) δ: 176.25, 68.12, 37.20, 35.22, 33.18, 30.74, 22.08.

3. 6-Methyl-ε-caprolactone. $^{1}$H NMR (500 MHz, $CDCl_3$) δ: 4.44-4.63 (m, 1H) , 2.59-2.70 (m, 2H), 1.88-1.93 (m, 2H), 1.58-1.71 (m, 4H), 1.36 (d, 3H, J=5.9 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$) δ: 175.57, 68.38, 36.22, 35.01, 28.28, 22.89, 22.58.

4. 4-Ethyl-ε-caprolactone. $^{1}$H NMR (600 MHz, $CDCl_3$) δ: 4.31 (ddd, J = 12.7, 5.9, 1.6 Hz, 1H) , 4.18 (dd, J = 12.8, 10.1 Hz, 1H) , 2.69 (ddd, J = 14.1, 7.6, 1.7 Hz, 1H) , 2.61 (ddd, J = 14.1, 12.4, 2.1 Hz, 1H) , 2.03–1.96 (m, 1H) , 1.93 (dddt, J = 15.1, 7.5, 3.6, 2.0 Hz, 1H) , 1.57–1.43 (m, 2H) , 1.40–1.28 (m, 3H) ,0.92 (t, J = 7.5 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ：176.01, 68.05, 41.73, 34.83, 33.02, 28.98, 28.38, 11.14.

5. δ-Valerolactone. $^{1}$H NMR (500 MHz, $CDCl_3$) δ: 4.35 (t, J = 5.6 Hz, 2H), 2.56 (t, J = 7.0 Hz, 2H), 1.89 (m, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ： 171.42, 69.47, 29.84, 22.31, 19.06.

6. δ-Butyrolactone. $^{1}$H NMR (500 MHz, $CDCl_3$) δ: 4.27 (t, J = 7.4 Hz, 2H) , 2.38–2.44 (m, 2H), 2.13–2.24 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ: 178.1, 68.8, 28.0,

22.3.

7. 4-Oxatricyclo[4.3.1.13.8]undecan-5-one. $^{1}$H NMR (300 MHz, $CDCl_3$) δ: 4.39–4.52 (m, 1H) , 3.01–3.12 (m, 1H), 1.70–2.15 (m, 12H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ: 178.9, 73.1, 41.2, 35.7, 33.7, 30.9, 25.8