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A Highly Efficient Heterogeneous Catalyst of Cobalt-based Coordination Polymer For Aerobic Epoxidation of Cyclohexene

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Materials and Methods. All reagents and solvents were purchased from commercial sources. The ligand was synthesized according the reference(*CrystEngComm*, 2017, **19**, 2126–2132). FT-IR spectra were measured in the 4000−400 cm^{-1} range on a Mattson Alpha-Centauri spectrometer. Elemental analysis (C, H, N) was performed on a VarioEL III Elemental Analyzer. The catalytic products were measured by GC equipment with a capillary (30 m long × 0.25 mm i.d., WondaCAP 17) and FID detector (GC-2014C, Shimadzu, Japan). UV-Vis spectra was tested by a Cary TU-1900 double beam UV−vis spectrophotometer.

Synthesis of $\{(Co(L)(H_2O))_2(H_2O)\}_n$ (1). HL (13mg) was mixed with H_2O (8 mL), and added with NaOH (0.2 M in water solution) 10 drops. The mixture solution was heated at 45 ^oC for 1 hour. $Co(NO_3)_2{\cdot}6H_2O$ (28mg) was added, and stirred for 30 min. The final mixture was stand at room temperature for one week, and pink plate crystals of **1** in a yield of 45 % (based on L) were obtained.

X-Ray Structural Determination. X-ray diffraction data of **1** (0.2 × 0.1 × 0.1 mm) was collected on Bruker diffractometer using Mo-$K\alpha$ (λ = 0.71073 Å) radiation at room temperature. The structures of complexes were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least squares procedure based on F^2 values. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. CCDC-1834332 (1) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Catalytic Oxidation of Cyclohexene. 1 was added to a solution of cyclohexene (10 mmol), *t*-BuOOH (18.5 mmol, 70% in water), 1,2,4-trichlorobenzene (1.5 mmol; as internal standard), catalyst (0.0135 mmol, based on metal ions) at room temperature.The reaction mixture was stirred at 60 °C. Aliquots of the reaction mixture (about 0.1 mL) were removed after time intervals indicated in the main text. Each sample was diluted with cyclohexane (1 mL) and filtered through a 0.25 mm Acrodisc nylon filter. Then, the sample was identified by GC−MS and quantified by GC. Different ratio of reactants utilized in this experiment had been investigated in a wide range, and the best optimized reaction conditions had been presented in this article. For investigations on metal leaching from the catalyst, the hot reaction mixture was filtered at the reaction temperature after 3 h. To investigate catalyst activities in subsequent multiple runs, the catalysts were separated from the reaction mixture by centrifugation and rinsed five times with cyclohexane before reuse. All yields and conversions were based on cyclohexene. The activation energy of catalytic experiments were carried out at different temperature under the same conditions as above description. And the catalytic results were fitted by NONLIN software by utilizing Arrhenius equation. TON was calculated according to the equation that the number of reactants converted to the final product divide the number of active Cobalt-centers in the heterogeneous catalyst; TOF was calculated according to the equation that the number of reactants converted to the final product divide the product of number of active Cobalt-centers in the heterogeneous catalyst and reaction time.

Table S1 Crystal data and structure refinement for 1.

	1
Empirical formula	$C_{30}H_{32}N_4O_8Co$
Formula weight	16.78
Temperature/K	298.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$

a/Å	7.3720(15)
b/Å	14.623(3)
c/Å	28.356(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3056.8(13)
Z	38
ρ_{calc}g/cm^3	0.346
μ/mm^{-1}	0.154
F(000)	333.0
Crystal size/mm^3	0.1 × 0.08 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.002 to 56.632
Index ranges	$-9 \leq h \leq 9$, $-19 \leq k \leq 18$, $-37 \leq l \leq 28$
Reflections collected	20574
Independent reflections	7530 [R_{int} = 0.0577, R_{sigma} = 0.0544]
Data/restraints/parameters	7530/0/389
Goodness-of-fit on F^2	1.120
Final R indexes [I>=2σ (I)]	R_1 = 0.0483, wR_2 = 0.1078
Final R indexes [all data]	R_1 = 0.0520, wR_2 = 0.1098
Largest diff. peak/hole / e Å^{-3}	0.67/-0.46
Flack parameter	0.011(7)

Table S2 Bond Lengths for 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	N1^1	2.210(3)	C13	O3	1.362(5)
Co1	N2	2.189(3)	C14	C15	1.375(6)
Co1	N4	2.205(3)	C16	C17	1.374(6)
Co1	O1	2.061(3)	C16	N3	1.329(6)
Co1	O4	2.088(3)	C17	C18	1.386(5)
Co1	O7	2.097(2)	C18	C19	1.383(6)
C1	C2	1.371(5)	C18	C21	1.505(5)
C1	N1	1.342(5)	C19	C20	1.374(6)
C2	C3	1.386(5)	C20	N3	1.329(6)
C3	C4	1.378(6)	C21	N4	1.496(4)
C3	C6	1.512(5)	C22	C23	1.534(4)
C4	C5	1.388(5)	C22	C24	1.538(5)
C5	N1	1.338(5)	C22	N4	1.487(4)
C6	N2	1.495(4)	C23	O4	1.274(4)

C7	C8	1.537(5)	C23	O5	1.232(4)
C7	C9	1.531(5)	C24	C25	1.512(5)
C7	N2	1.479(5)	C25	C26	1.379(6)
C8	O1	1.268(4)	C25	C30	1.388(5)
C8	O2	1.241(4)	C26	C27	1.394(5)
C9	C10	1.517(5)	C27	C28	1.401(6)
C10	C11	1.372(6)	C28	C29	1.366(6)
C10	C15	1.392(6)	C28	O6	1.373(4)
C11	C12	1.393(6)	C29	C30	1.385(6)
C12	C13	1.382(6)	N1	Co1^2	2.210(3)
C13	C14	1.369(7)			

Symmetric code: ^{1}2-X,1/2+Y,3/2-Z; ^{2}2-X,-1/2+Y,3/2-Z

Table S3 the comparison of **1** with other Co-based catalyst

Catalyst	Conversion(%)	Main Product	Selectivity(%)	Activation Energy(kJ mol^{-1})
1 at 60 ℃	82.56	P1	71.93	91.98
2a at 60 °C[a]	60.4	P2	73.6	67.3
2 at 60 °C[a]	8.2	P2	66.5	129.6
3 at 70 °C[b]	27.5	P1	66	
3 at 60 °C[c]	83.75	P1	72	91.98

tert-butyl-2-cyclohexenyl-1-peroxide (named as *P1*), followed by the by-product, 2-cyclohexen-1-one (named as *P2*) and cyclohexene oxide (named as *P3*)

(a)H. Ren, R. Yao and X. Zhang, *INORG CHEM*, 2015, **54**, 6312-6318

(b)M. Tonigold, Y. Lu, B. Bredenkoetter, B. Rieger, S. Bahnmueller, J. Hitzbleck, G. Langstein and D. Volkmer, *ANGEW CHEM INT EDIT*, 2009, **48**, 7546-7550.

(c)Fan Yu, Xin Xiong, Kexing Huang, Yinliu Zhou and Bao Li. *CrystEngComm*, 2017, **19**, 2126–2132.

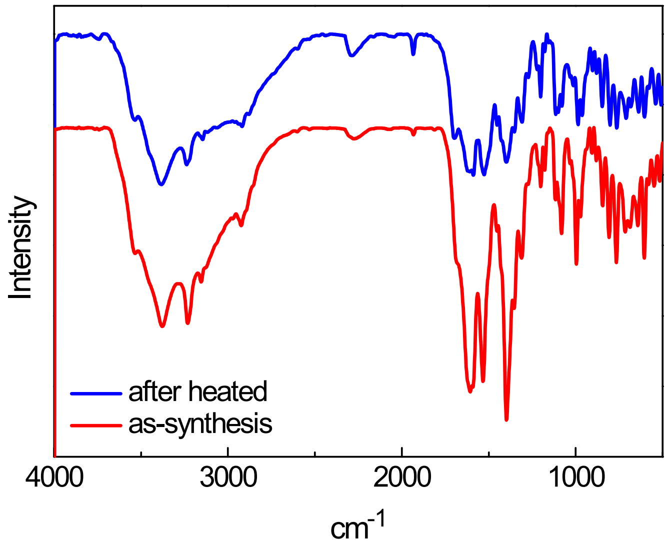

Figure S1 the IR spectra of 1 and activated 1.

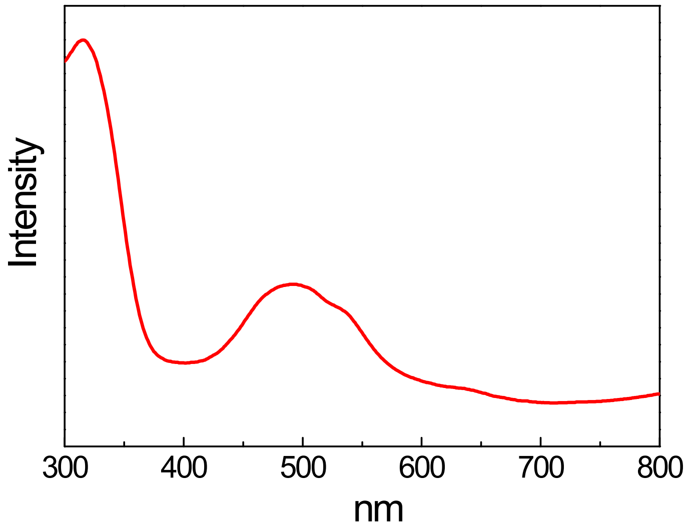

Figure S2. Electronic spectra of phase-pure microcrystal samples of **1**. The pink color of compound **1** is consistent with an octahedral environment of divalent cobalt. One absorption band centered at 226 nm could be assigned to n → π* transitions caused by ligand-centered electronic transitions; the other at 512 nm might be ascribed to [$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$] transitions, in accord with the typical hexa-coordinated octahedral coordination environment of high spin Co(II) species.

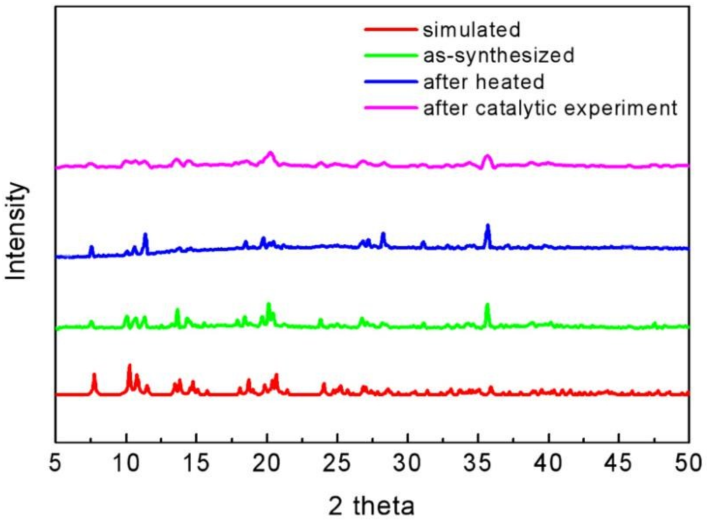

Figure S3. XRD spectra of 1. The sample was heat at 80 ℃.

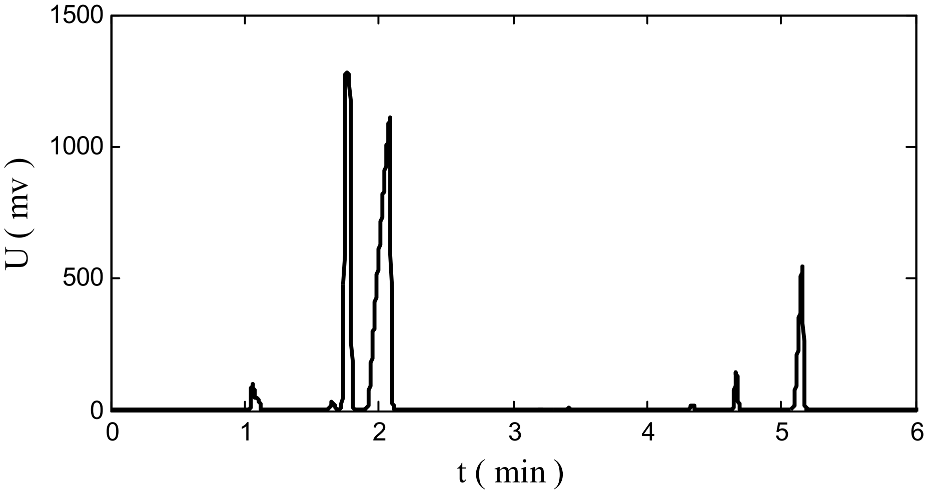

Figure S4. GC spectra for the oxidation of cyclohexene after 15 min.

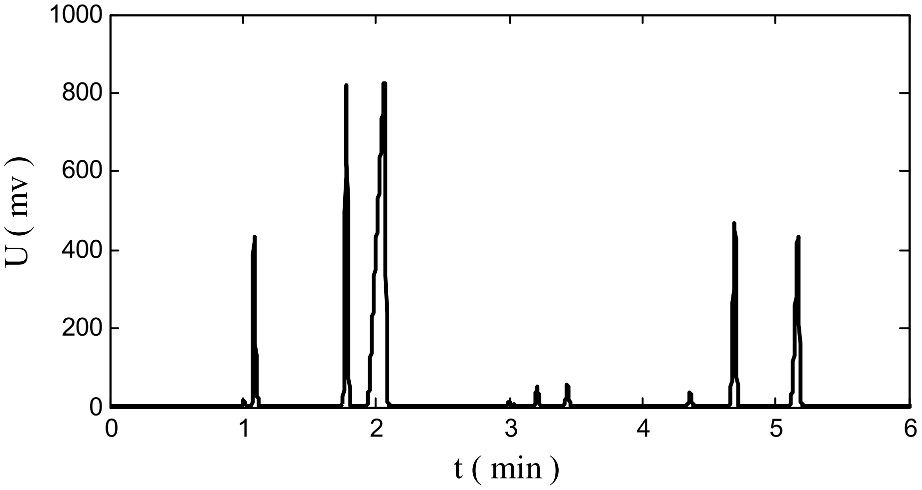

Figure S5. GC spectra for the oxidation of cyclohexene after 8h.

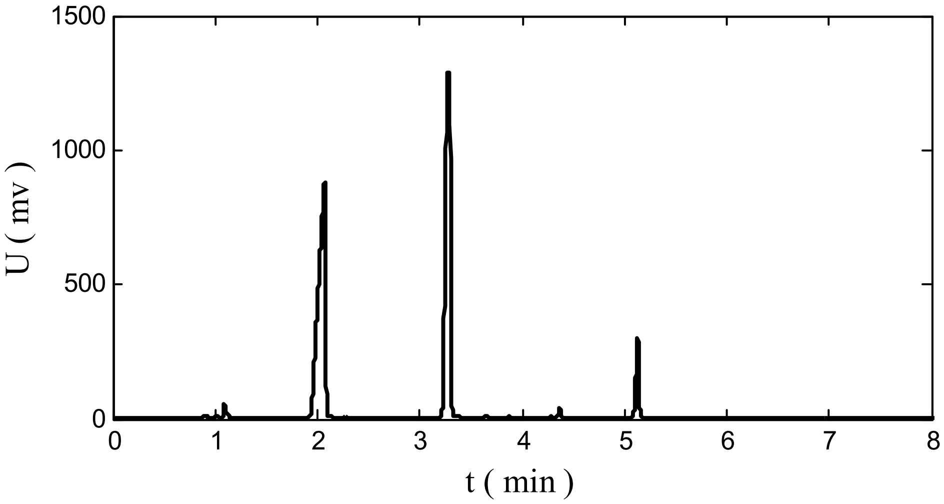

Figure S6. GC spectra for the oxidation of styrene after 15 min.

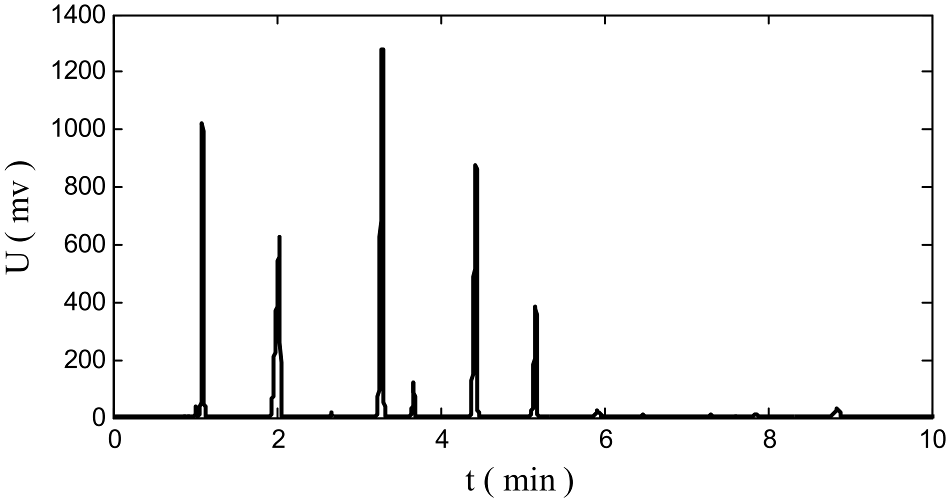

Figure S7. GC spectra for the oxidation of styrene after 8 h.

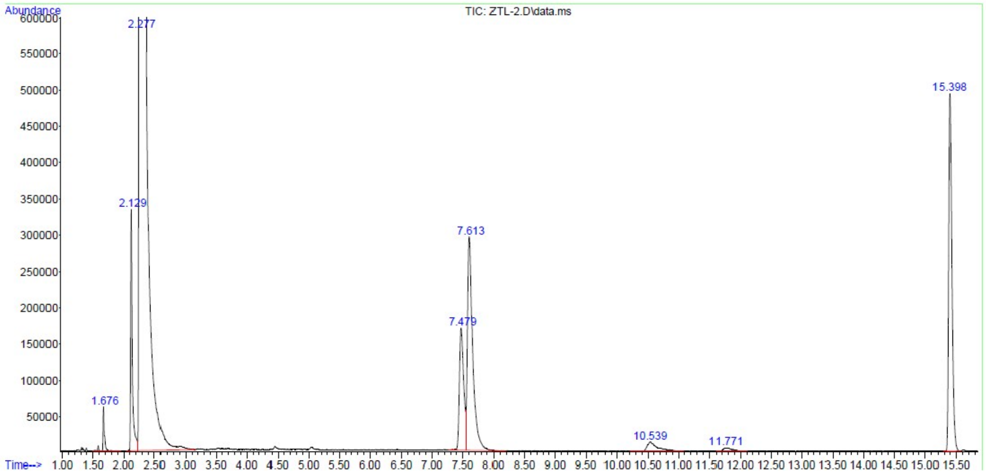

Figure S8. GC-MS spectra for oxidation of cyclohexene after 10 h.

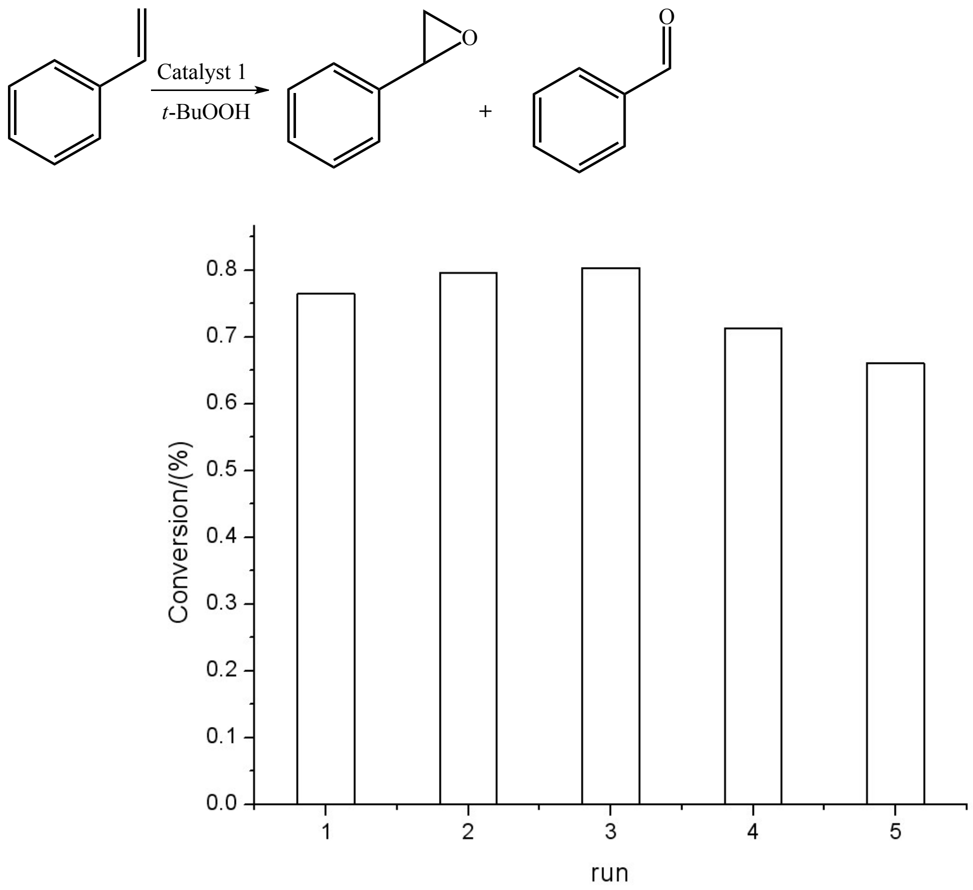

Figure S9. cyclic experiments utilizing the same catalyst at 50 °C. The higher results of cycle 2 and 3 might be caused by the errors in the corresponding experiments. However, the error fall in the rational range.

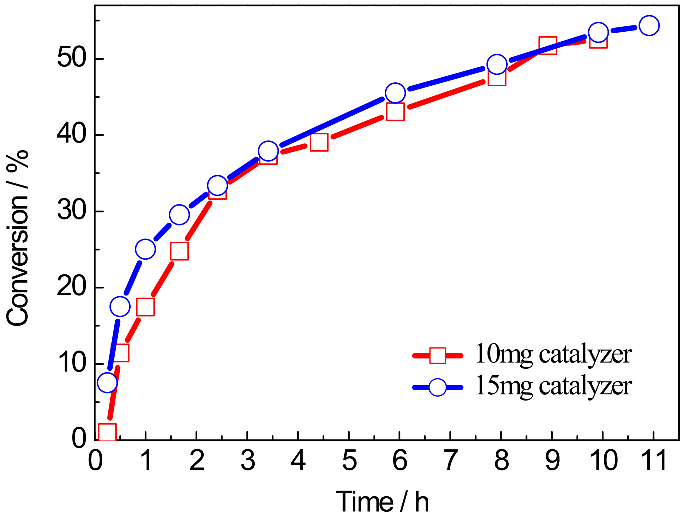

Figure S10. Conversion versus time curves for styrene epoxidation with **1** as catalyst at 65 ℃. Reaction conditions: cyclohexene (12 mmol), *t*-BuOOH (18.5 mmol), 1,2,4-trichlorobenzene (1.5 mmol; as internal standard), **1** (0.075 mmol, based on cobalt).

The reaction was first tested on the oxidation reaction using *t*-BuOOH as oxidant at 65 °C, giving the almost maximum substrate conversion of 55% after 11 h. The main reaction product is styrene oxide, along with a very small amount of benzaldehyde, which could be further validated by combined gas chromatographic and mass spectrometric product analysis. In addition, to efficiently carry out the epoxidation reactions, great efforts were also made to understand the optimal loading of catalyzer. Catalyst loadings of 0.1, 0.15 and 0.2 mmol were used for the oxidation of styrene using *t*-BuOOH. However, no significantly difference in conversion or rate could be observed in the product yield of styrene oxide varied. With the consideration of catalytic efficiency, only 0.1 mmol catalyzer loading might be sufficient for styrene epoxidation. Whatever, all of the catalytic experiments could strongly validate the relatively satisfactory catalytic effect to the unsaturated olefin compounds.

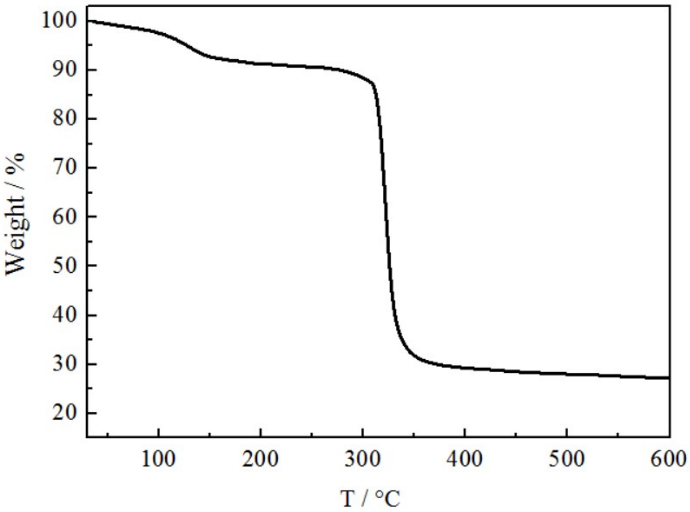

Figure S11. TGA curve of 1.

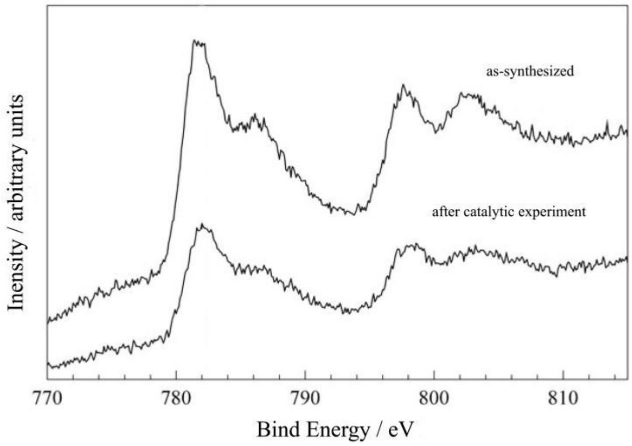

Figure S12. XPS spectra of as-synthesized sample and sample after catalytic experiment.

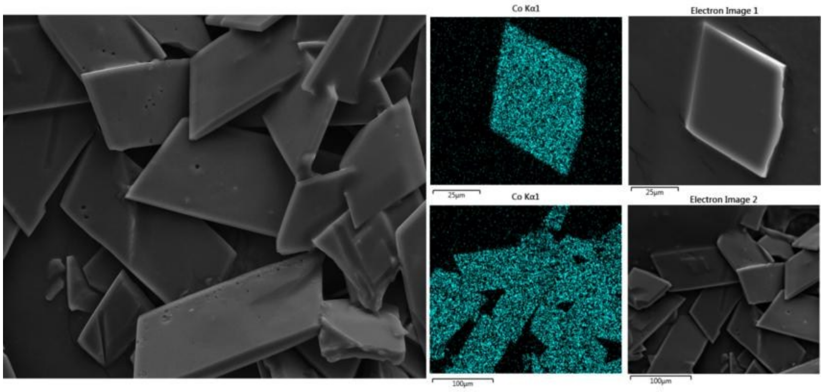

Figure S13. Scanning electron micrographs (SEM) and the element mapping of the as-synthesized samples of **1**.

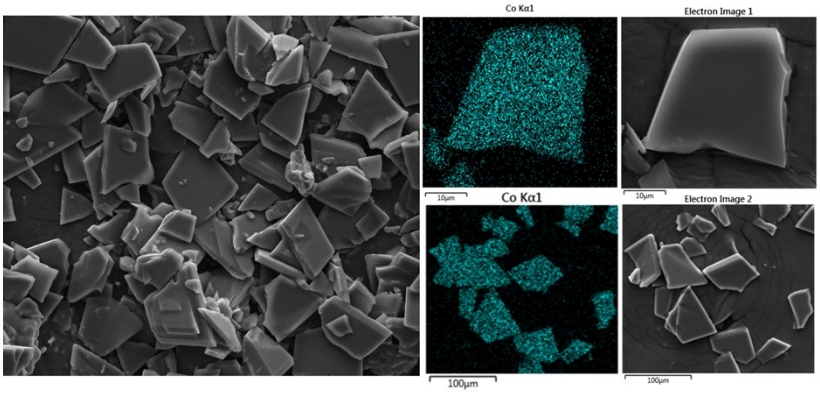

Figure S14. Scanning electron micrographs (SEM) and the element mapping of the as-synthesized samples of **1**.