

EXPERIMENTAL SECTION

Chemicals

Copper(II) nitrate trihydrate was purchased from KANTO chemistry. Chromium(III) nitrate nonahydrate, benzene-1,3,5-tricarboxylic acid, ethanol (95%) and hydrogen peroxide (30%), chromium(III) oxide and *p*-xylene were purchased from Sigma-Aldrich. N,N-dimethylformamide (DMF) and methanol (95%) were purchased from MACRON. Phenol and copper(II) oxide, copper(I) oxide, 2,6-di-tert-butyl-4-methylphenol and guajacol were purchased from Acros. Catechol, hydroquinone, *p*-benzoquinone and anisole were purchased from Alfa Aesar. Deionized water was purified with a Milli-Q system (Millipore, Bedford, MA, USA).

Synthesis of metal organic framework-199 (MOF-199) particles

The procedure of synthesizing MOF-199 particles was modified from a previous paper.¹ In brief, deionized water, ethanol and DMF were mixed with the ratio of 3:3:4 as the solvent. Then, copper(II) nitrate trihydrate (8.45 mmol) and benzene-1,3,5-tricarboxylic acid (trimesic acid, 4 mmol) were separately dissolved in the solvent (each in 40 ml) by using ultra sonication. These dissolved solutions were then mixed together in a 100 ml closed vial, followed by heating at 85 °C in an oven for 24 hours. After synthesis, the supernatant was removed by centrifugation (20,000 rpm, 10 minutes). The collected solid was washed by an ethanol/DMF mixture of equal molar ratio, followed by the centrifugation for separation. These steps were repeated for 3 times, and then methanol was used as washing solvent for another three times. The obtained sample was dried in a lyophilizer over-night.

Synthesis of chromium-embedded MOF-199 particles

Similar to the synthesis of MOF-199, the *de novo* synthesis was applied to introduce chromium into MOF. In detail, copper nitrate trihydrate (8.45 mmol) and chromium nitrate nonahydrate with the 0.05:1 molar ratio of chromium/copper (Cr/Cu) was added to 40 ml solvent (H₂O/EtOH/DMF=3:3:4) followed by introducing trimesic acid (4 mmol) dissolved in another 40 ml solvent mixture. Then both solutions were mixed rapidly and kept in an 85 °C-oven for 24 hours. After reaction, same collection methods (centrifugation, washing and drying) were used. In synthesis aspects, several parameters including Cr/Cu molar ratio and synthesis temperature were studied. To investigate the Cr/Cu molar ratio, 0.2:1 and 0.1:1 of chromium/copper molar ratio was adjusted for the reaction at 85 °C. On the other hand, temperatures of 45 °C and 65 °C were utilized with a synthetic Cr/Cu molar ratio fixed at 0.2:1. The chromium embedded MOF-199 with the reaction conditions of 0.2:1 Cr/Cu ratio and 85 °C were denoted as “Cr-MOF-199”.

Calcination process for derived MOFs

As-synthesized Cr-MOF-199 was further pyrolyzed in a tubular furnace in N₂ atmosphere with a gas flow rate of 80 cc/min. The samples were loaded in a ceramic crucible boat and then heated to 600 °C with a heating rate of 3 °C/min. After calcination for 4 hours, the samples were calcined in air atmosphere for another 3 hours with the same temperature and heating rate. The obtained product after calcination at 600 °C was denoted as “CuO/CuCr₂O₄ composites”, and used as catalyst for phenol hydroxylation. To realize the effect of calcination temperature, Cr-MOF-199 were calcined in the range of 300 °C – 800 °C with the same heating rate in N₂ followed by air atmosphere. To realize the effect of different Cr/Cu ratio, chromium containing MOF-199 with different Cr/Cu ratio (0:1, 0.05:1, 0.1:1, 0.2:1) were calcined at 600 °C.

CuO/CuCr₂O₄ composites for phenol hydroxylation

Before we studied the effectiveness of the catalyst in the phenol hydroxylation, optimization had done by controlling several factors including amount of catalyst and oxidant, species of solvent, reaction temperature and time. In the optimization procedure, CuO/CuCr₂O₄ composites (synthesis temperature = 85 °C, synthetic Cr/Cu ratio = 0.2:1, calcination temperature = 600 °C) were chosen for further investigations. Typically, a phenol solution (0.1M) was prepared by sonication in H₂O and loaded in a 20 ml closed vial with stir bar. After that, a certain amount of the catalyst (0mg-30mg) was given into the phenol solution and then a certain amount of hydrogen peroxide as oxidant was added (with the H₂O₂/phenol ratio from 0 to 10:1). After adding the oxidant, the vial was closed and the reaction mixture was stirred in a preheated oil bath at a certain temperature (50-80 °C) for a certain time (10-360 minutes). The optimized conditions (20 mg catalyst, oxidant/reactant = 5/1, water as solvent, 70 °C and 30 minutes) were used for evaluating our materials. In the aspect of catalytic performance of phenol hydroxylation, CuO/CuCr₂O₄ composites with different synthetic Cr/Cu ratio (from 0 to 0.2:1) and calcination temperature (from 300-800 °C) were investigated. Commercial copper oxide was also tested in our study.

CHARACTERIZATION TECHNIQUES

The morphology and structure of the synthesized materials (i.e. MOF-199, Cr-MOF-199 and CuO/CuCr₂O₄ composites) were investigated by scanning electron microscope (SEM, Nova™ NanoSEM 230) with energy-dispersive X-ray spectroscopy (EDS), X-ray diffractometer (XRD, Rigaku Ultima IV), and scanning transmission electron microscope (STEM, JEOL 2010F). The sample for STEM analysis had been treated with focused ion beam and electron beam system (FIB, FEI Helios 600i) beforehand. Energy-dispersive X-ray fluorescence spectrometer (XRF, JEOL JSX-3100RII) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific K α X-ray photoelectron spectrometer) were utilized for analyzing the composition of our materials. The surface properties of MOF materials were analyzed with N₂ adsorption/desorption measurements by ASAP 2020 micrometrics, and the properties of CuO/CuCr₂O₄ composites were analyzed by mercury porosimeter (micromeritics AutoPore® IV 9520). The thermal stability of MOF was measured by differential thermal analysis thermoanalyzer (TG-DTA) under N₂ environment.

In the analysis of phenol hydroxylation, high performance liquid chromatography (HPLC) with UV/Visible detector was used to measure the concentration of reactant (phenol) and products (dihydroxybenzenes). All samples were diluted by a factor of at least 25 by deionized water. For the calculation of the conversion, selectivity and yield of this reaction, calibration curves were firstly determined by analyzing commercial phenol and dihydroxybenzenes as standards. The definition of conversion of phenol, selectivity of dihydroxybenzenes, yield of dihydroxybenzenes and selectivity between dihydroxybenzenes are listed in **Table S5**.

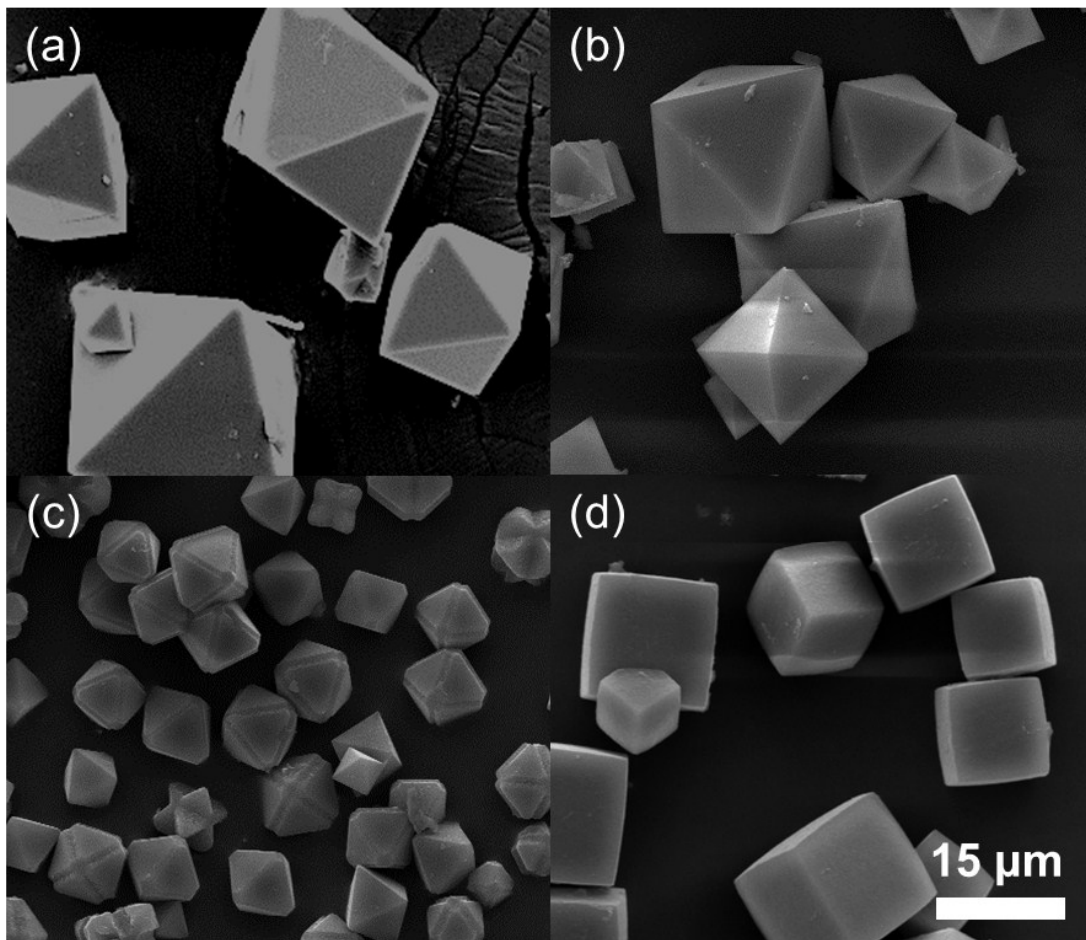


Figure S1. SEM images of a) MOF-199 and MOF-199 embedded with different Cr content at the Cr/Cu ratio of b) 0.05/1, c) 0.1/1 and d) 0.2/1.

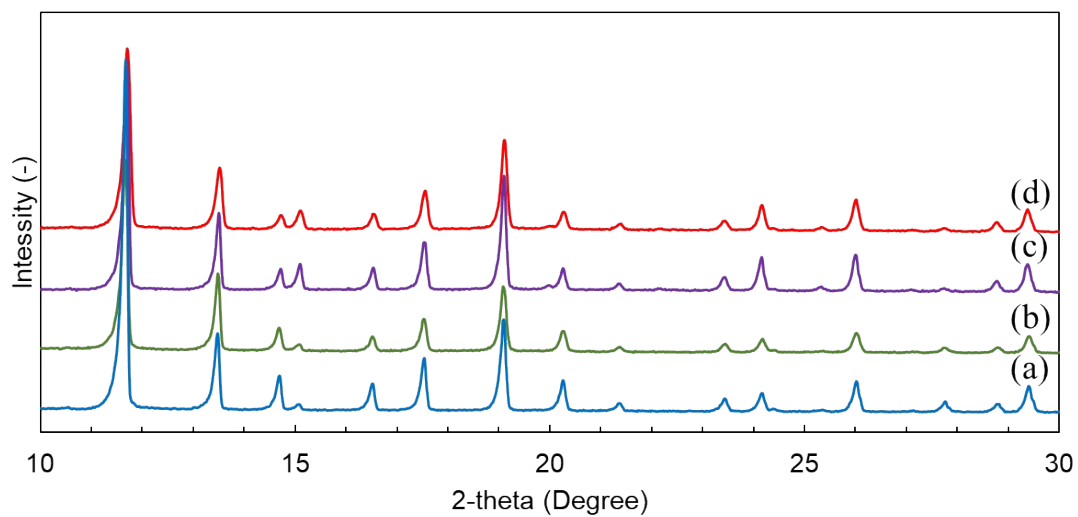


Figure S2. XRD patterns of a) MOF-199 and MOF-199 embedded with different Cr amounts with Cr/Cu ratio of b) 0.05/1, c) 0.1/1 and d) 0.2/1.

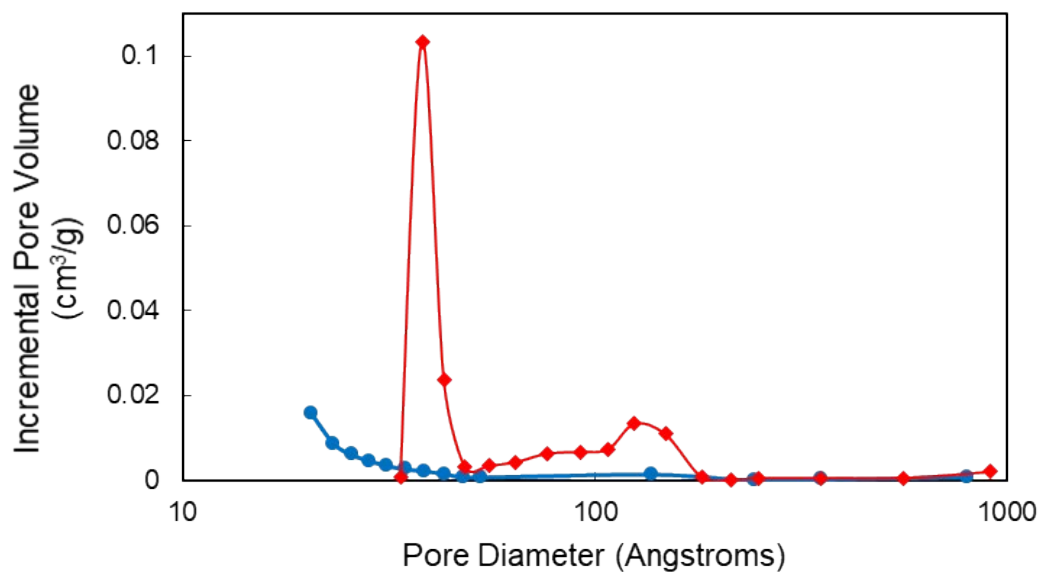


Figure S3. Pore size distribution of MOF-199 (blue) and Cr-MOF-199 (red) from BJH desorption method.

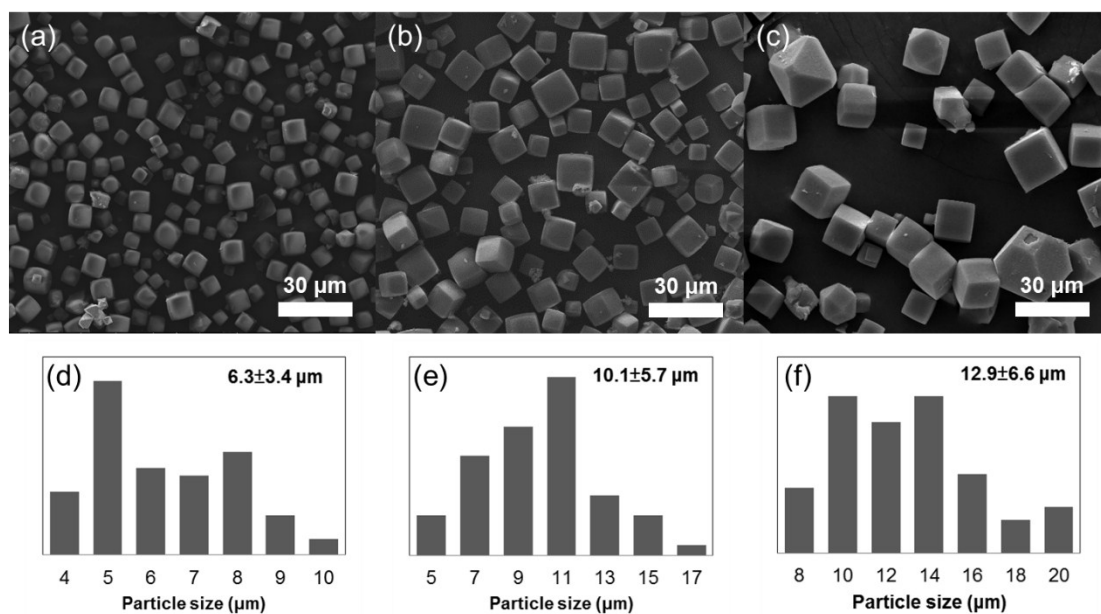


Figure S4. SEM images and corresponding particle size distribution of Cr-MOF-199 with different temperature at a, d) 45 °C, b, e) 65 °C and c, f) 85 °C. Particle size distributions were calculated from the SEM images ($n > 100$).

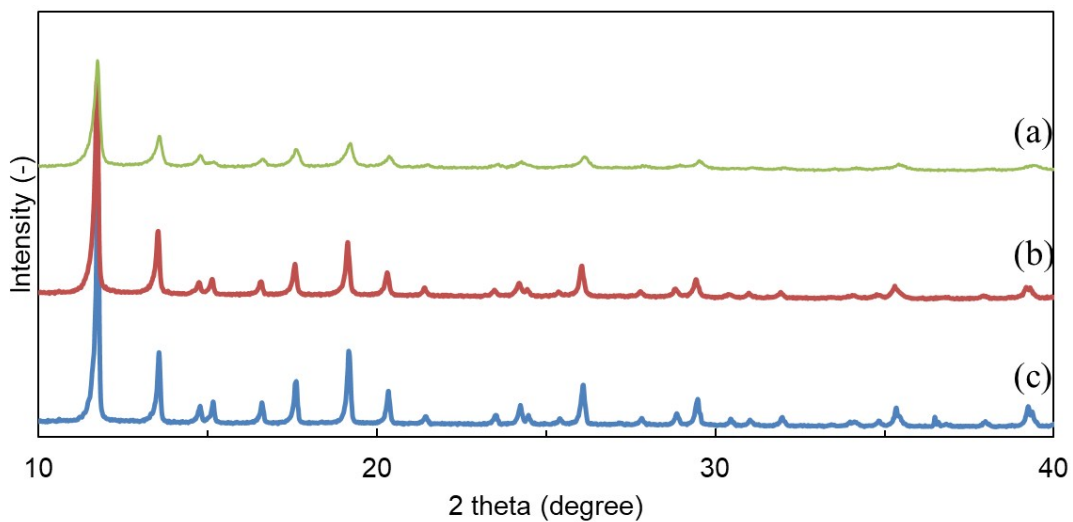


Figure S5. XRD patterns of Cr-MOF-199 with synthesis temperatures at a) 45 °C, b) 65 °C and c) 85 °C.

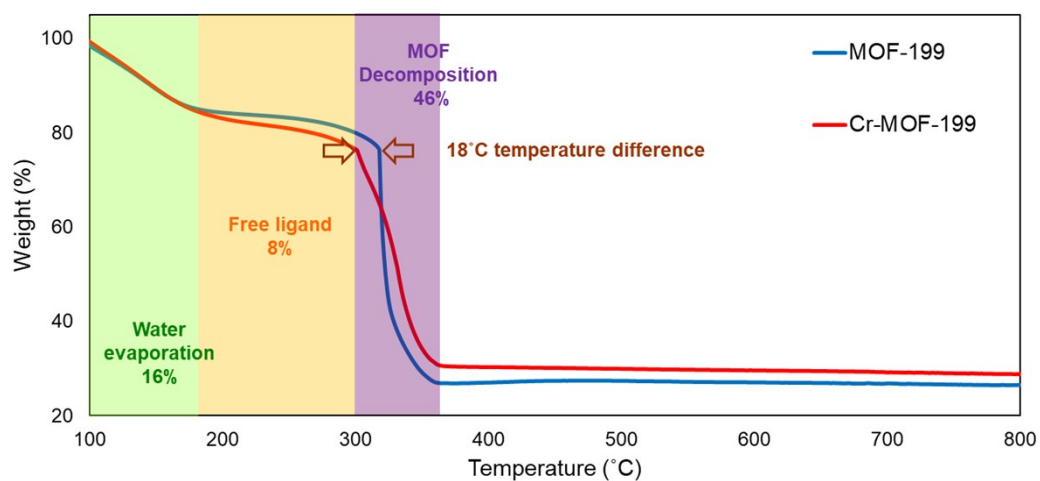


Figure S6. TGA N₂ analysis of MOF-199 and Cr-MOF-199.

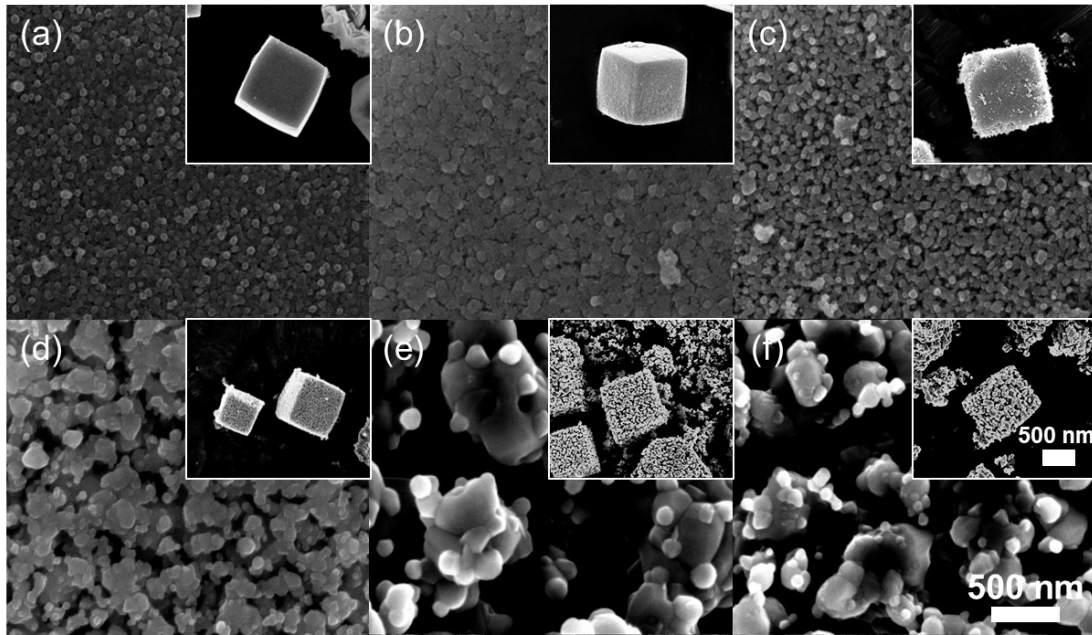


Figure S7. SEM images of CuO/CuCr₂O₄ composites with different calcination temperatures. The calcination temperature is a) 300 °C, b) 400 °C, c) 500 °C, d) 600 °C, e) 700 °C and f) 800 °C, respectively.

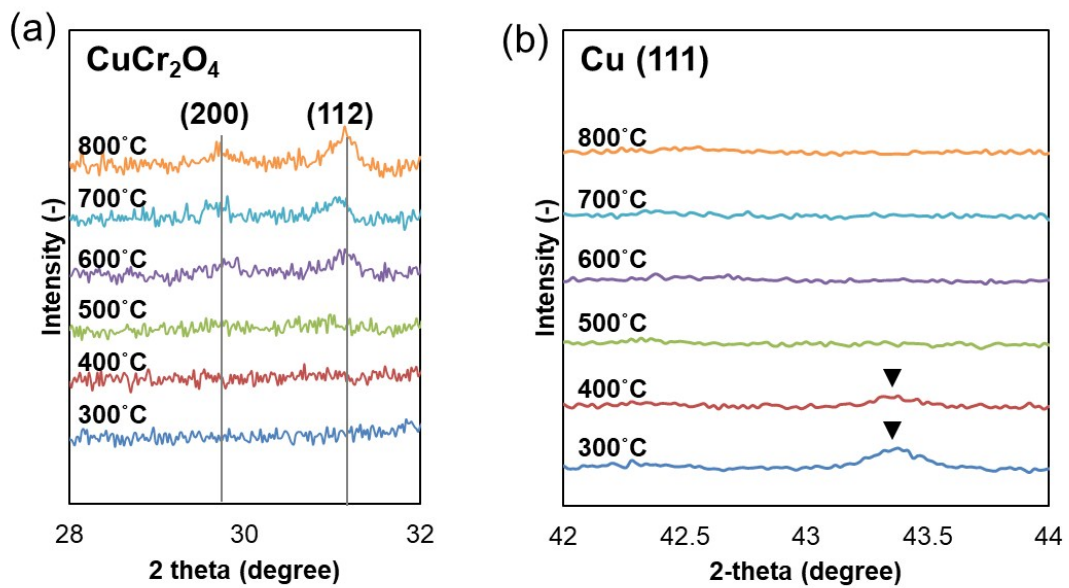


Figure S8. XRD patterns of CuO/CuCr₂O₄ as a function of different calcination temperatures. The diffractograms in figure a) compare the CuCr₂O₄ (200) and (112) phases and the diffractograms in figure b) compare the Cu (111) phases.

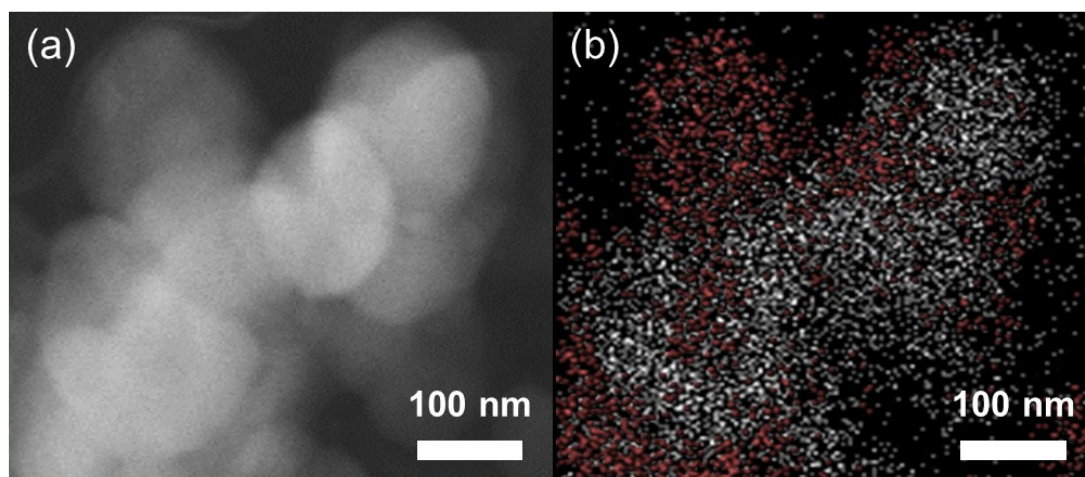


Figure S9. TEM images of CuO/CuCr₂O₄ composites and corresponding elemental distribution of chromium (red) and copper (white). The elemental distribution was analyzed by EDS.

Table S1. Porous characteristics of the samples.

Sample	BET specific surface area (m ² /g) ^a	Micropore volume (g/cm ³) ^b	Porosity (-) ^c
MOF-199	1060.54±16.40	0.37	
Cr-MOF-199	519.10±7.40	0.19	
CuO/CuCr ₂ O ₄ composites	7.00±0.08		33.08%

a. The calculation of the specific surface area was based on BET theory.

b. The calculation of the total pore volume and micropore volume were based on the t-plot method.

c. The calculation of the porosity was measured from Hg porosimetry.

Table S2. Comparison of the detected Cr/Cu ratio with the Cr/Cu ratio used during the synthesis of the composite material

Synthetic Cr/Cu ratio ^a	0.05/1	0.10/1	0.20/1
Detected Cr/Cu ratio ^b	0.03/1	0.14/1	0.10/1

a. All reaction temperatures are fixed at 85 °C.

b. The Cr/Cu ratio are analyzed by XRF.

Table S3. Comparison of the detected Cr/Cu ratio with different synthesis temperatures.

Synthetic temperature ^a	45°C	65°C	85°C
Detected Cr/Cu ratio ^b	0.03/1	0.05/1	0.10/1

a. All synthetic Cr/Cu ratio are fixed at 0.20/1.

b. The Cr/Cu ratio are analyzed by XRF.

Table S4. Optimization of the phenol hydroxylation reaction.

Entry	Catalyst amount (mg)	H ₂ O ₂ /Phenol ratio (-)	Solvent	Reaction temperature (°C)	Reaction time (min)	X _{Ph} (%)	S _{DHB} (%)	Y _{DHB} (%)
1	0	1.25/1	H ₂ O	65°C	60	0	0	0
2	5	1.25/1	H ₂ O	65°C	60	31	76	23
3	10	1.25/1	H ₂ O	65°C	60	36	66	24
4	20	1.25/1	H ₂ O	65°C	60	43	67	29
5	30	1.25/1	H ₂ O	65°C	60	45	59	26
6	20	0.7/1	H ₂ O	65°C	60	34	31	11
7	20	2.5/1	H ₂ O	65°C	60	58	52	30
8	20	5/1	H ₂ O	65°C	60	77	49	38
9	20	8/1	H ₂ O	65°C	60	93	29	27
10	20	10/1	H ₂ O	65°C	60	98	18	18
11	20	5/1	H ₂ O	70°C	30	71	55	40
12	20	5/1	Acetonitrile	70°C	30	58	34	20
13	20	5/1	Acetic acid	70°C	30	40	6	2
14	20	5/1	MeOH	70°C	30	21	0	0
15	20	5/1	EtOH	70°C	30	20	0	0
16	20	5/1	H ₂ O	50°C	30	35	52	18
17	20	5/1	H ₂ O	50°C	60	49	51	25
18	20	5/1	H ₂ O	50°C	120	70	53	37
19	20	5/1	H ₂ O	50°C	240	89	33	29
20	20	5/1	H ₂ O	50°C	360	94	24	23
21	20	5/1	H ₂ O	60°C	30	43	62	26
22	20	5/1	H ₂ O	60°C	60	64	59	37
23	20	5/1	H ₂ O	60°C	120	86	40	34
24	20	5/1	H ₂ O	60°C	240	97	18	18
25	20	5/1	H ₂ O	60°C	360	98	17	16
26	20	5/1	H ₂ O	70°C	10	33	54	18
27	20	5/1	H ₂ O	70°C	20	53	56	29
28	20	5/1	H ₂ O	70°C	30	71	55	40
29	20	5/1	H ₂ O	70°C	40	77	47	36
30	20	5/1	H ₂ O	70°C	50	84	42	35
31	20	5/1	H ₂ O	70°C	60	86	41	35
32	20	5/1	H ₂ O	70°C	120	98	15	15
33	20	5/1	H ₂ O	70°C	240	98	18	17
34	20	5/1	H ₂ O	70°C	360	98	17	16
35	20	5/1	H ₂ O	80°C	30	83	45	38
36	20	5/1	H ₂ O	80°C	60	95	28	26
37	20	5/1	H ₂ O	80°C	120	97	21	21
38	20	5/1	H ₂ O	80°C	240	98	19	18
39	20	5/1	H ₂ O	80°C	360	98	16	16
40 ^a	20	5/1	H ₂ O	70°C	30	0	0	0

^aThe radical scavenger 2,6-di-tert-butyl-4-methylphenol was added to the reaction.

Table S5. Definition of abbreviations used in the phenol hydroxylation reaction.

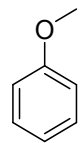
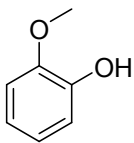
Expression (Symbol)	Definition
Conversion of phenol (X_{Ph})	moles of phenol reacted/initial moles of phenol used
Selectivity of dihydroxybenzene (S_{DHB})	moles of dihydroxybenzene/ moles of phenol reacted
Yields of dihydroxybenzene (Y_{DHB})	moles of dihydroxybenzene/ initial moles of phenol used
Selectivity between dihydroxybenzene (CAT/HQ)	moles of catechol/ moles of hydroquinone

Table S6. Summary of the catalytic performance of different catalysts.

Catalysts	Conversion (%)	Selectivity (%)		Yield of diphenols (%)	CAT/HQ	Ref.
		Diphenols (CAT+HQ)	Others			
CuCl ₂	7.5	74.9	25.1	5.6	1.1	1
Cu ₂ (OH)PO ₄	21.4	82.3	17.7	17.9	1.1	2
CuNiAl ternary hydrotalcites	23.7	47.4	52.6	11.2	1.5	3
Cu/MCM-41-H	25.0	63.9	37.1	15.72	1.7	4
Cu nanoparticles	56.0	70.0	30.0	39.20	1.3	5
CuCr ₂ O ₄ /CuO	71.4	55.4	44.6	39.6	1.8	This study

1. F.-S. Xiao et al., *Appl. Catal., A*, **2001**, 207, 267
2. F.-S. Xiao et al., *Journal of Catalysis*, **2001**, 199, 273
3. Dubey, A et al., *J. Mol. Catal. A Chem.*, **2002**, 181, 1, 151
4. G. Y. Zhang et al., *Langmuir*, **2010**, 26, 1362
5. E.A. Karakhanov et al. *Appl. Catal., A*, **2010**, 385, 62

Table S7. Substrate screening of different aromatic compounds.

Entry	Substrate	Conversion [%]	Product	Yield[%]
1		91		1

Reaction conditions: catalyst amount CuO/CuCr₂O₄ composite: 20 mg, 0.5 mmol substrate, H₂O₂/substrate ratio = 5/1, H₂O, 70 °C, 30 min.

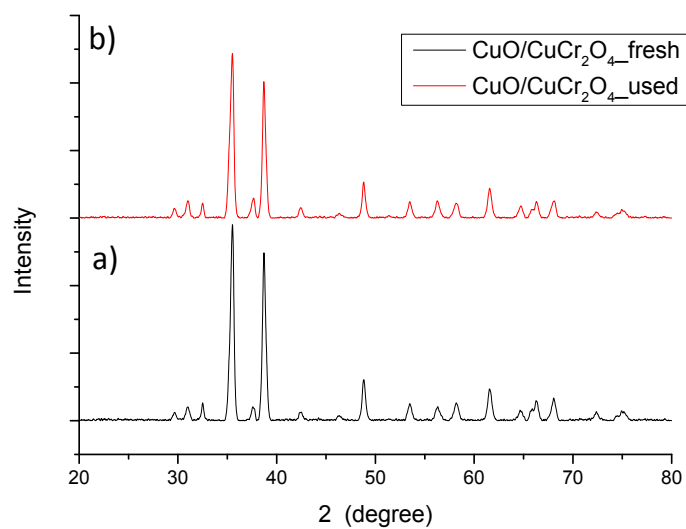


Fig. S10. XRD pattern of (a) the fresh $\text{CuO/CuCr}_2\text{O}_4$ composite and (b) the used catalyst $\text{Cu/CuCr}_2\text{O}_4$ after catalysis.

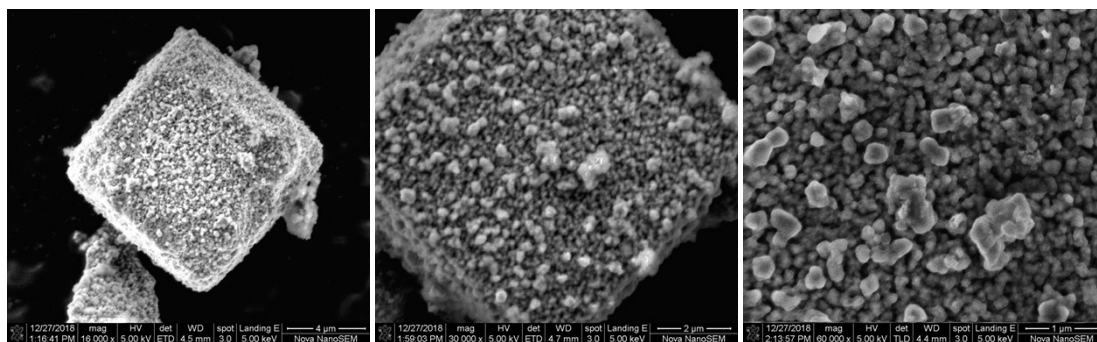
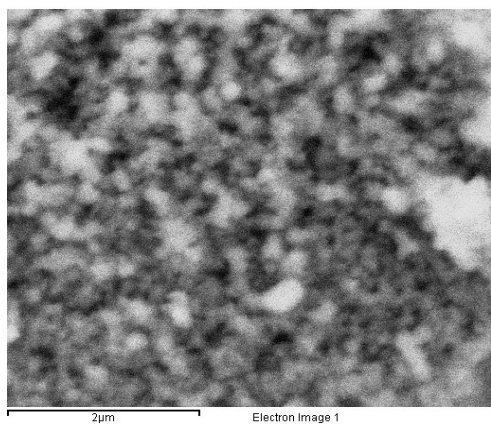
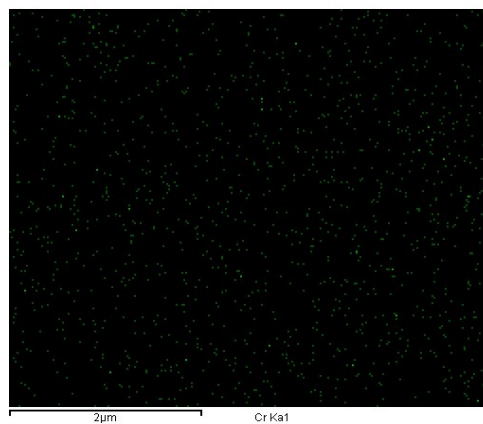


Fig. S11. SEM images of $\text{CuO/CuCr}_2\text{O}_4$ composite after catalysis.

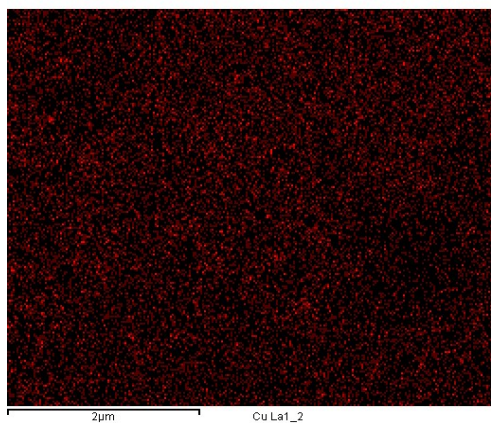
a)



b)



c)



d)

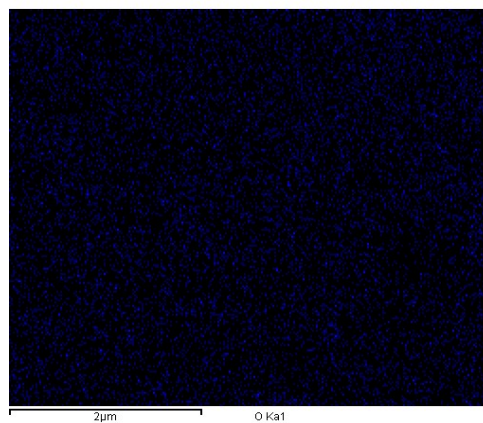


Fig. S12. SEM images of CuO/CuCr₂O₄ composites after catalysis a) and corresponding elemental distribution of b) chromium, c) copper and d) oxygen.

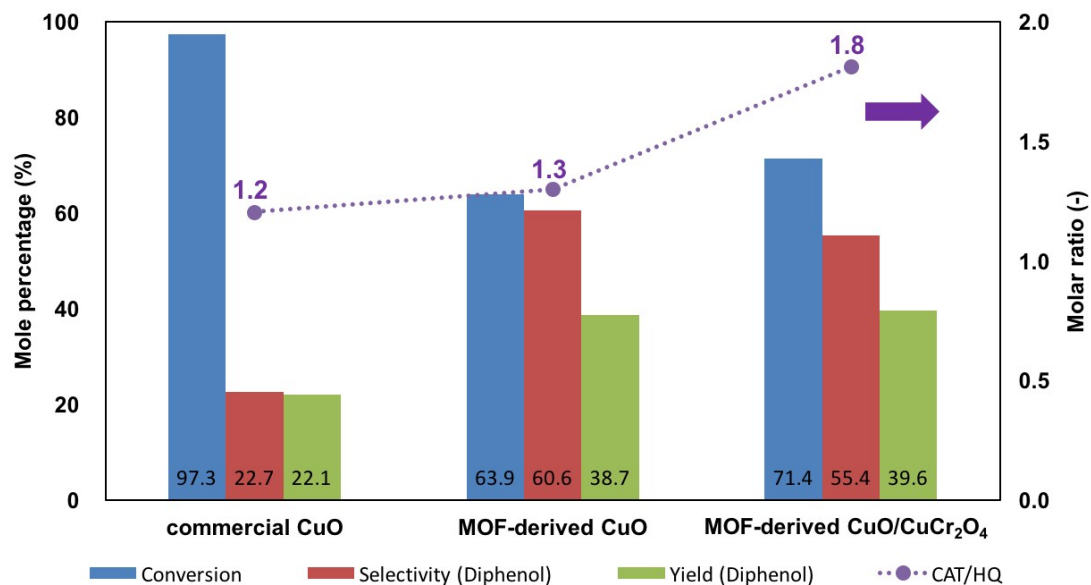


Figure S13. Comparison of the catalytic performance of different catalysts.

REFERENCE

1. Rowsell, J. L. C.; Yaghi, O. M., Effects of functionalization, catenation, and variation of the metal oxide and organic linking units on the low-pressure hydrogen adsorption properties of metal-organic frameworks. *Journal of the American Chemical Society* **2006**, *128* (4), 1304-1315.