Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information for

Photodegradation of volatile organic compounds catalyzed by MCr–LDHs and hybrid MO@MCr–LDHs (M=Co, Ni, Cu, Zn): The comparison of activity, kinetics and photocatalytic mechanism

Yue Meng[a], Tiantian Dai[b], Xiaobo Zhou[c], Guoxiang Pan[a], Shengjie Xia[b]*

[a] *School of Life Science, Huzhou University, 759 East Erhuan Road, Huzhou 313000, P R China*

[b] *Department of Chemistry, College of Chemical Engineering, Zhejiang University of Technology, 18 Chaowang Road, Hangzhou 310014, P R China*

[c] *Entegris, Inc., 129 Concord Road, Billerica, MA 01821, USA*

---

* Corresponding author.

E–mail: xiasj@zjut.edu.cn (S.J. Xia)

Telephone number: +86–0571–88320373

1. Experimental Instruction

1.1 Materials and Characterization

1.1.1 Materials

Chloroauric acid ($HAuCl_4$) and sodium borohydride ($NaBH_4$) were guarantee reagent (GR) and purchased from Aladdin Chemistry Co. Ltd. Zinc nitrate ($Zn(NO_3)_2\cdot6H_2O$), chromic nitrate ($Cr(NO_3)_3\cdot9H_2O$), sodium hydroxide (NaOH) and sodium carbonate ($Na(CO_3)_2$) were analytical reagent (AR) and all purchased from Guoyao Fine Chemical Co. Ltd. In addition, ultrapure water was used in all synthetic process.

1.1.2 Characterizations

Powder X–ray diffraction (XRD) was recorded on a Rigaku UltimaIV powder diffractometer with the testing of Cu Kα radiation (λ = 1.54 Å) at 40 kV and 178 mA and scanning rate of 5 °/min in the range of 5–70 °. C, H and N elemental microanalyses were obtained on a ThermoFisher Italia S.P.A elemental analyzer; the analysis of Au, Zn and Cr elements was conducted using inductively coupled plasma atomic emission spectrometry (ICP–AES) on a IRIS Intrepid II XSP instrument. Solid state UV–vis diffuse reflectance spectra was recorded at room temperature in the air by means of a Shimadzu UV–2600 spectrometer equipped with an integrating sphere attachment. $BaSO_4$ was used as background. The TEM with EDS was recorded on a Hitachi HT–7700 to examine the morphologies, lattice fringes and crystal boundaries of the samples.

1.2 Photodegradation of gaseous *p*-xylene under visible light irradiation

1.2.1 Instruction for experimental setup and operational procedures

Schematic diagram of experimental setup for photocatalytic degradation of gaseous *p*-xylene is shown in **Fig. S1.** In this experiment, standard air is introduced into gas washing bottle by going through reducing valve and flow meter, and then carrying gaseous *p*-xylene into the mixing tank. The gaseous *p*-xylene concentration is regulated by flow meter and the temperate box. The other stream of air goes into steam generator to carry vapor into the mixing tank. Mixing tank is a 5L stainless steel cylinder with a blast fan to mix different components. A hygrothermograph meter can measure the relative humidity, and the sampling hole on top of the mixing tank is used to sample and measure the initial concentration of the reaction gases.

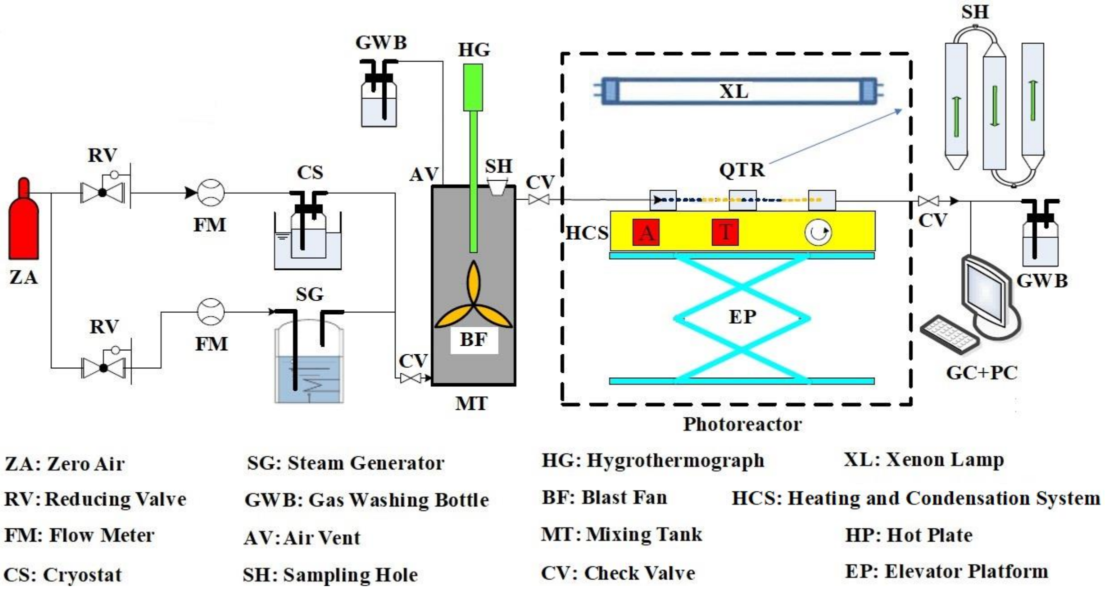


Figure S1 Schematic diagram of experimental setup for photocatalytic degradation of gaseous *p*-xylene.

The photocatalytic reaction box is composed of elevator platform, hot plate, quartz tube reactor and xenon lamp. Elevator platform is used to adjust the distance between the lamp and the quartz tube reactor; hot plate is used to control the reaction temperature. Quartz reactor has 3 connected quartz tubes with the size of 500×100×25 mm. The quartz tubes are attached to the hotplate and evenly distributed inside the quartz reactor unit. There are sampling holes on the reaction system to sample the gas inside the reactor for GC–MS analysis. The xenon lamp on the top of reaction box is adjustable with a capacity of 150–1000 W.

1.2.2 Instruction for products analysis

Gaseous *p*-xylene concentration is measured by Agilent 7890A equipped with FID detector. The column is INNOWAX capillary column (30 m×0.25 mm×0.25 μm). The temperature is programmed as follows: it increases to 50 ^{o}C and then kept there for 1 min, then increase to 180 ^{o}C with a rate of 10 ^{o}C /min.

The reaction intermediate at the surface of the catalyst is rinsed off from the catalyst by *p*-xylen*e* solution and then refluxed for 2 hours before analysis. They analysis is done on Trace DSQ II GC–MS (Thermo Fisher) with a DB–WAX column. The temperature ramp is set as: keep at 40 ^{o}C for 1 min, then increase up to 200 ^{o}C with the rate of 10 ^{o}C/min, the temperature keeps going up to 240 ^{o}C at 8 ^{o}C/min and stay for 5 min. The ion source temperature is set at 200 ^{o}C with total ion scanning mode, the m/z value is in the range of 35–450 with 5 scan/second. The analysis result of VOCs mapping is compared with NIST05 database to determine the products.

1.3 Instruction for electrochemical measurements

For the electrochemical measurement, the conductive glass prepared by this method, ultrasonic cleaning with acetone, ethanol and deionized water (the volume ratio is 1:1:1) 30 min, respectively. All sample powders were fabricated as the film electrodes by dip-coating: typically, 20 mg of photocatalyst was suspended in 0.3 mL ethanol to produce suspension, which was then dip-coated onto a 5 cm × 0.6 cm ITO conductive glass electrode with a sheet resistance of 20 Ω. When the films were dried at room temperature, and then dried at 65 °C for 2 h.

The electrochemical experiments were performed with a Metrohm Autolab 302N electrochemical workstation with a conventional three-electrode cell. The resultant electrode served as the working electrode, with a graphite rod as the counter electrode and a saturated calomel electrode (SCE) electrode as the reference electrodes. Electrochemical impedance measurements were performed in a 0.50 mol/L Na_2SO_4 solution containing 2.5 mmol/L $K_3[Fe(CN)_6]$ + 2.5 mmol/L $K_4[Fe(CN)_6]$ (1:1). The conduction band (CB) potentials were determined from Mott–Schottky plots by electrochemical method. The Mott–Schottky measurements were performed at a fixed frequency of 1000 Hz with 5 mV amplitude at various applied potentials, the electrolyte was 0.50 mol/L Na_2SO_4 solution.

2. Supplements for Results and Discussion

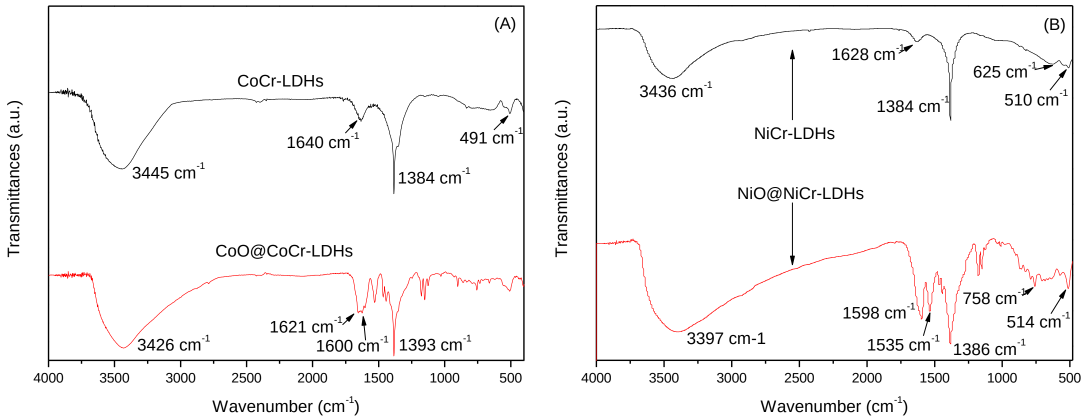


Figure S2 FT–IR spectrums of layered double hydroxides contained different cobalt components (A) and different nickel components (B).

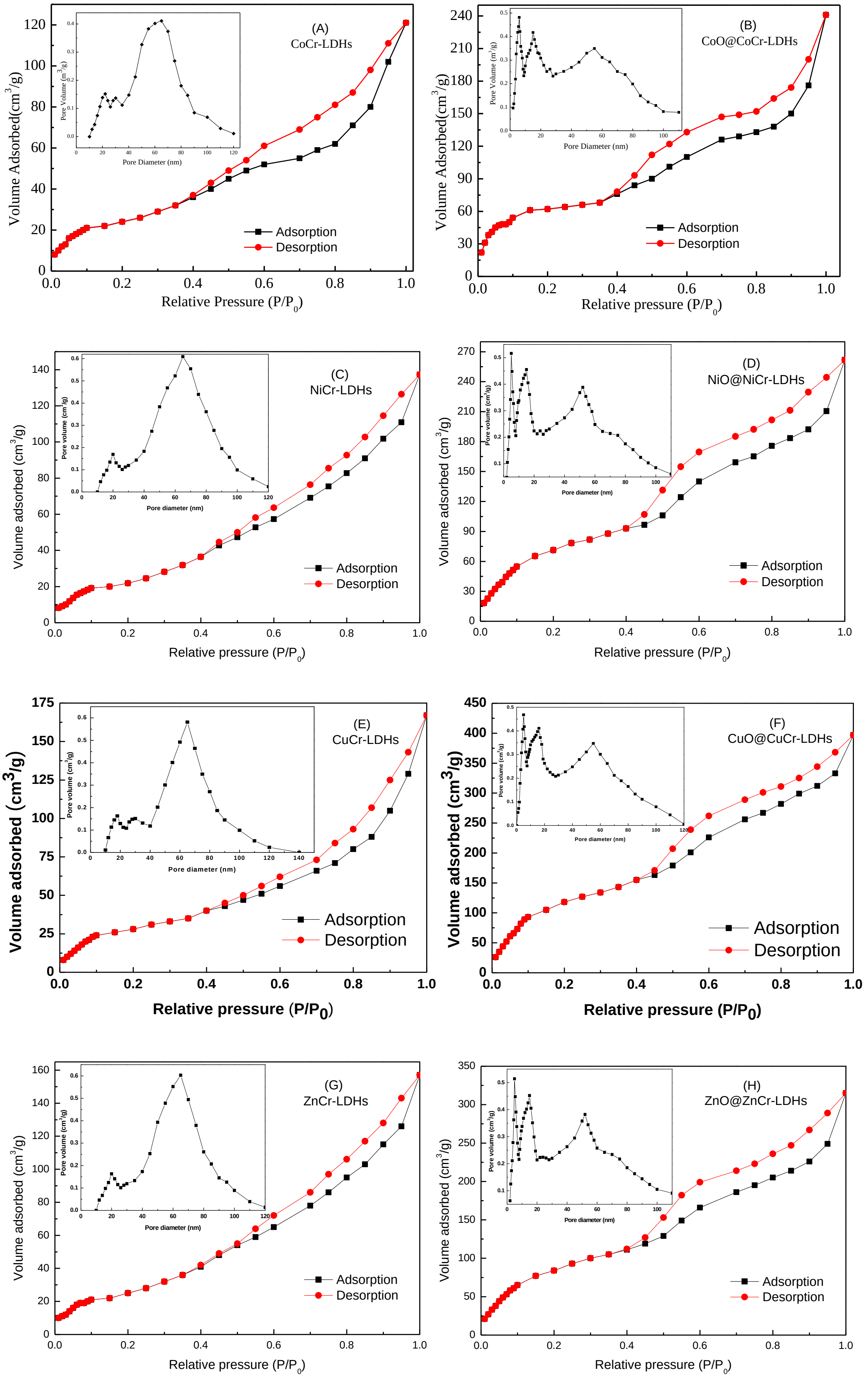


Figure S3 N_2 sorption isotherms and pore size distribution for MCr–LDHs and hybrid

MO@MCr–LDHs (M=Co, Ni, Cu, Zn).

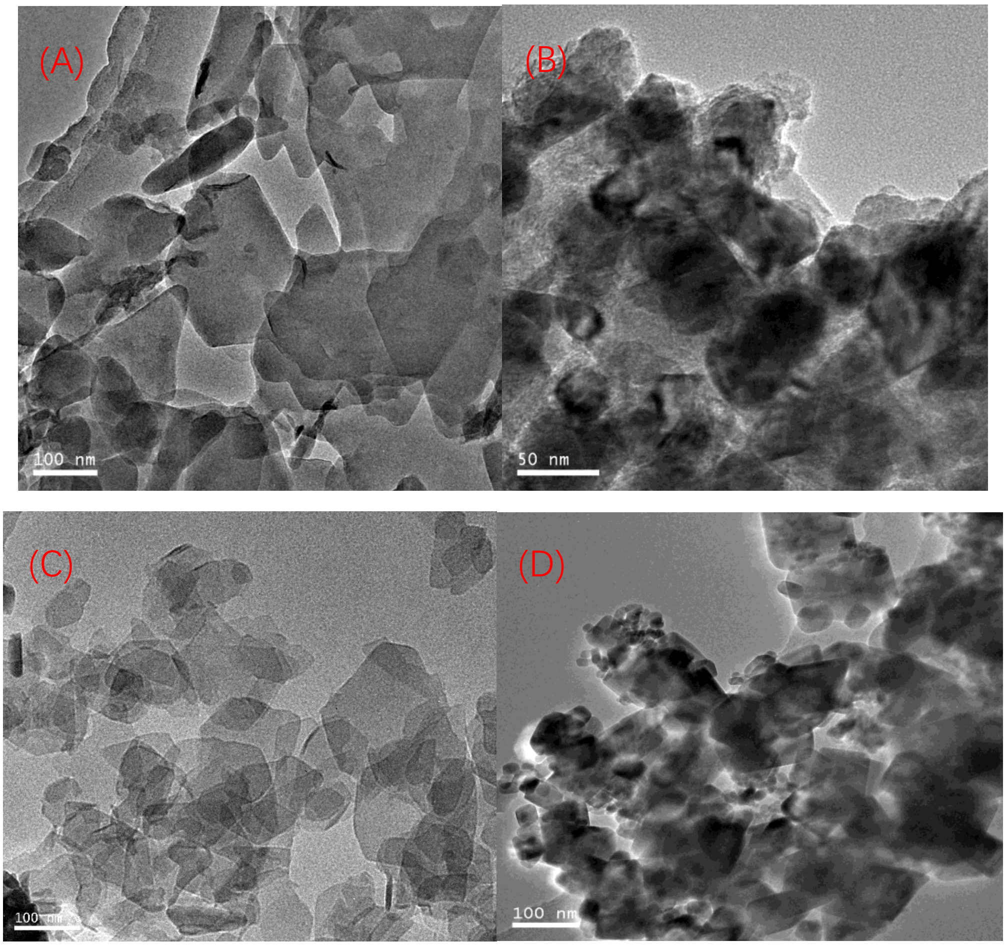


Figure S4 TEM images of CoCr-LDHs (A), CoO@CoCr-LDHs (B), NiCr-LDHs (C) and NiO@NiCr-LDHs (D).

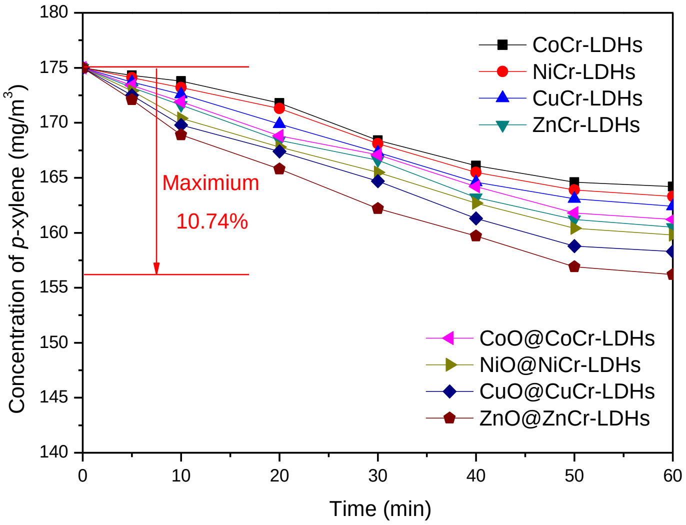


Figure S5 Adsorption results of gaseous *p*-xylene in dark using different samples.

Table S1 Kinetic parameters of different catalyst dosage [A].

Catalyst	Catalyst dosage (g)	ln[A]	Kinetic equation	K	R^2	lnK
CuCr–LDHs	0.5	–0.69315	y=0.0005x+0.0015	0.0005	0.9984	–7.60090
	1.0	0	y=0.0009x–0.0005	0.0009	0.9979	–7.01312
	1.5	0.405465	y=0.0013x+0.0062	0.0013	0.9841	–6.64539
	2.0	0.693147	y=0.0015x+0.0082	0.0015	0.9942	–6.50229
	2.5	0.916291	y=0.0016x+0.0162	0.0016	0.9876	–6.43775
CuO@CuCr–LDHs	0.5	–0.69315	y=0.0042x–0.0085	0.0042	0.9904	–5.47267
	1.0	0	y=0.0067x–0.0231	0.0067	0.9954	–5.00565
	1.5	0.405465	y=0.0088x+0.0153	0.0088	0.9989	–4.73300
	2.0	0.693147	y=0.0117x–0.0041	0.0117	0.9942	–4.44817
	2.5	0.916291	y=0.0121x+0.0128	0.0121	0.9954	–4.41455

Table S2 Kinetic parameters of different irradiation intensity [B].

Catalyst	Irradiation intensity (W)	ln[B]	Kinetic equation	K	R^2	lnK
CuCr–LDHs	200	5.298317	y=0.0010x+0.0060	0.0010	0.9717	–6.90776
	300	5.703782	y=0.0012x+0.0044	0.0012	0.9855	–6.72543
	400	5.991465	y=0.0014x+0.0058	0.0014	0.9911	–6.57128
	500	6.214608	y=0.0015x+0.0082	0.0015	0.9942	–6.50229
	600	6.39693	y=0.0016x+0.0171	0.0016	0.9808	–6.43775
CuO@CuCr–LDHs	200	5.298317	y=0.0049x+0.0241	0.0049	0.9910	–5.31852
	300	5.703782	y=0.0066x+0.0051	0.0066	0.9998	–5.02069
	400	5.991465	y=0.0083x–0.0107	0.0083	0.9945	–4.79150
	500	6.214608	y=0.0117x–0.0041	0.0117	0.9942	–4.44817
	600	6.39693	y=0.0123x–0.0069	0.0123	0.9958	–4.39816

Table S3 Kinetic parameters of different relative humidity [C].

Catalyst	Relative humidity (%)	ln[C]	Kinetic equation	K	R^2	lnK
CuCr–LDHs	20	2.995732	y=0.0008x+0.0009	0.0008	0.9927	–7.13090
	30	3.401197	y=0.0011x+0.0034	0.0011	0.9894	–6.81245
	40	3.688879	y=0.0013x+0.0057	0.0013	0.9943	–6.64539
	50	3.912023	y=0.0015x+0.0082	0.0015	0.9942	–6.50229
	60	4.094345	y=0.0016x+0.0134	0.0016	0.9847	–6.43775
CuO@CuCr–LDHs	20	2.995732	y=0.0047x–0.0331	0.0047	0.9951	–5.36019
	30	3.401197	y=0.0067x–0.0582	0.0067	0.9921	–5.00565
	40	3.688879	y=0.0086x–0.0208	0.0086	0.9953	–4.75599
	50	3.912023	y=0.0117x–0.0041	0.0117	0.9942	–4.44817
	60	4.094345	y=0.0121x–0.0203	0.0121	0.9941	–4.41455

Table S4 Kinetic parameters of different reaction temperature [T].

Catalyst	Temperature (°C)	1/T	Kinetic equation	K	R^2	–lnK
CuCr–LDHs	10	0.003532	y=0.0004x+0.0036	0.0004	0.9708	7.824046
	20	0.003411	y=0.0007x–0.0027	0.0007	0.9978	7.264430
	30	0.003299	y=0.0011x+0.0068	0.0011	0.9846	6.812445
	40	0.003193	y=0.0015x+0.0082	0.0015	0.9942	6.502290
	50	0.003095	y=0.0017x+0.0020	0.0017	0.9859	6.377127
CuO@CuCr–LDHs	10	0.003532	y=0.0061x–0.0216	0.0061	0.9957	5.099467
	20	0.003411	y=0.0073x–0.0220	0.0073	0.9965	4.919881
	30	0.003299	y=0.0088x–0.0225	0.0088	0.9960	4.733004

	40	0.003193	y=0.0117x–0.0041	0.0117	0.9942	4.448166
	50	0.003095	y=0.0124x+0.0022	0.0124	0.9908	4.390059

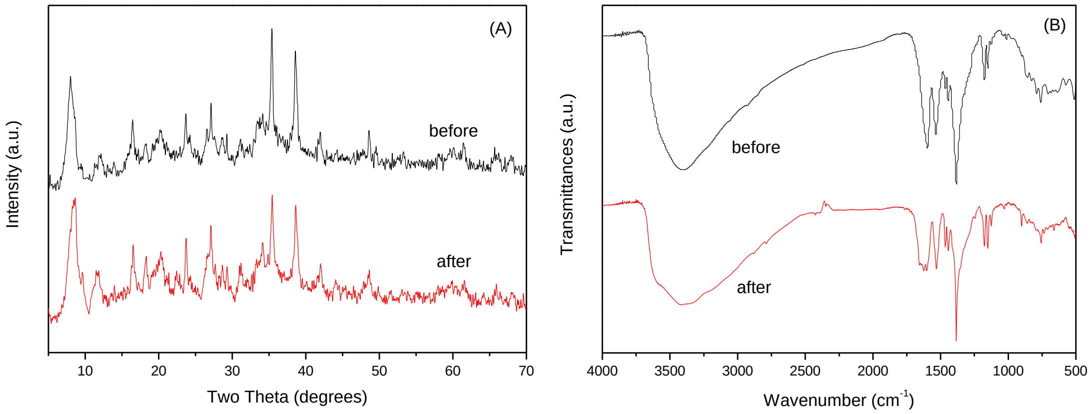


Figure S6 Contrast of XRD and FT-IR results for CuO@CuCr–LDHs before and after photodegradation.

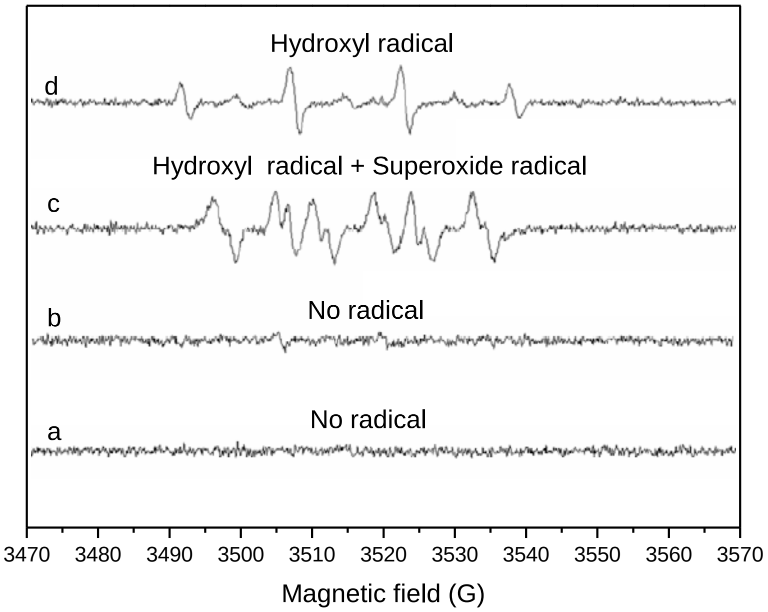


Figure S7 ESR spectrum of CuCr–LDHs (*a* is dark, *d* is visible light irradiation) and CuO@CuCr–LDHs (*b* is dark, *c* is visible light irradiation).

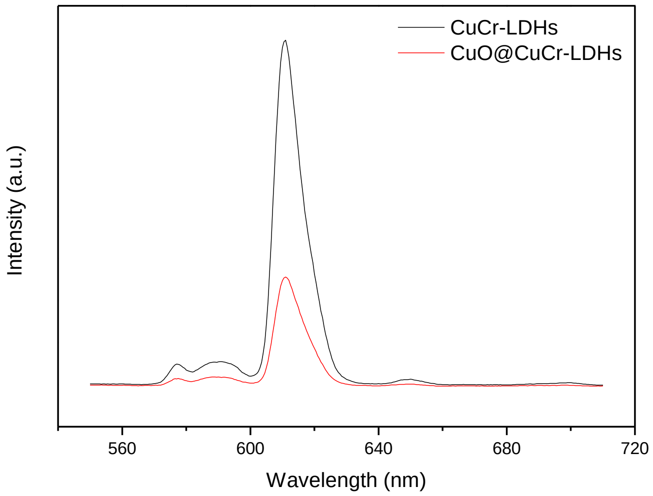


Figure S8 PL spectra of CuCr–LDHs and CuO@CuCr–LDHs.

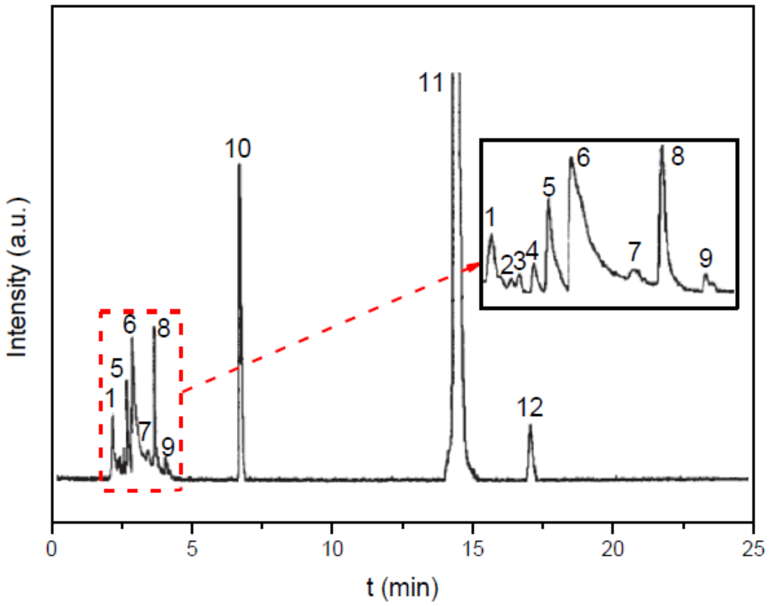
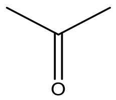
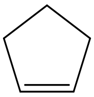
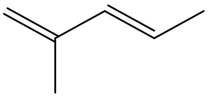
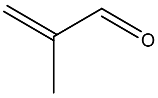
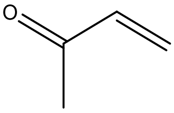
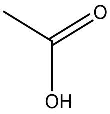
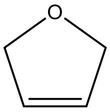
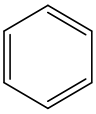
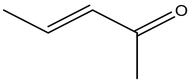
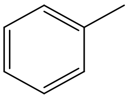
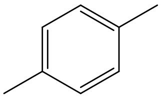
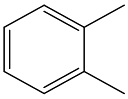


Figure S9 GC curves of photodegradation of gaseous *p*-xylene catalyzed by CuCr–LDHs.

Table S5 Photodegradation intermediates of gaseous *p*-xylene catalyzed by CuCr-LDHs.

No	Name	Molecular formula	Molecular weight	Structural formula	Remarks
1	acetone	C_3H_6O	58		

2	cyclopentene	C_5H_8	68		small quantity
3	2,4-dimethyl-1,3-butadiene	C_6H_{10}	82		small quantity
4	2-methyl propenal	C_4H_6O	70		small quantity
5	methyl vinyl ketone	C_4H_6O	70		
6	Acetic acid	$C_2H_4O_2$	97		
7	2,5-dihydrofuran	C_4H_6O	70		small quantity
8	benzene	C_6H_6	78		
9	3-penten-2-one	C_5H_8O	84		small quantity
10	toluene	C_7H_8	98		
11	*p*-xylene	C_8H_{10}	106		original sample
12	*o*-xylene	C_8H_{10}	106		

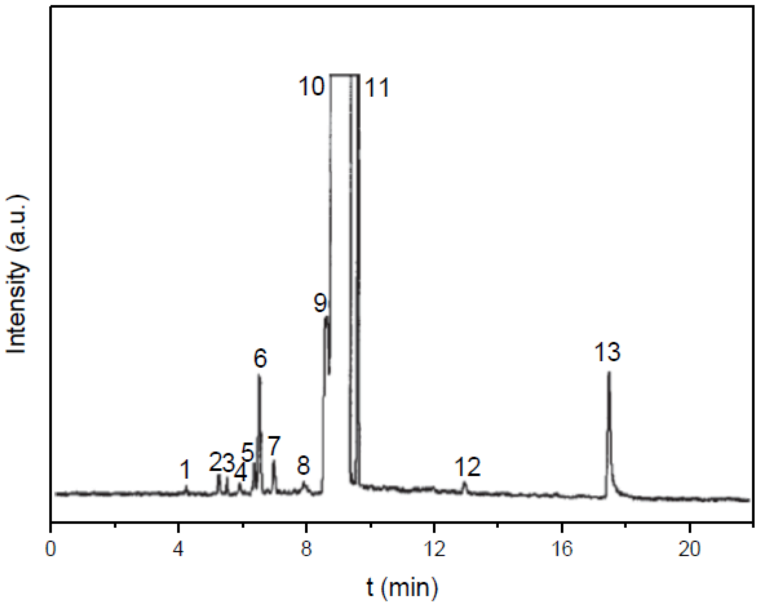
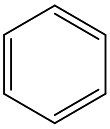
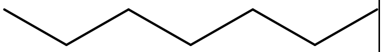
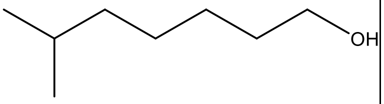
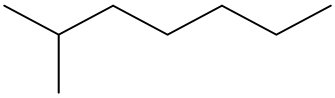
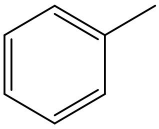
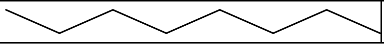
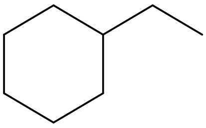
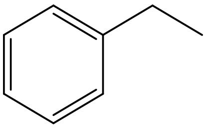
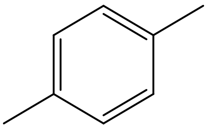
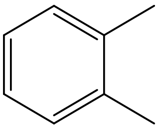
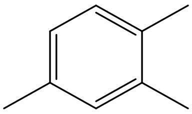


Figure S10 GC curves of photodegradation of gaseous *p*-xylene catalyzed by CuO@CuCr–LDHs.

Table S6 Photodegradation intermediates of gaseous *p*-xylene catalyzed by CuO@CuCr-LDHs.

No	Name	Molecular formula	Molecular weight	Structural formula	Remarks
1	methanol	CH_4O	32	H_3C-OH	small quantity
2	benzene	C_6H_6	78		
3	heptane	C_7H_{16}	100		
4	2-methylheptanol	$C_8H_{18}O$	130		small quantity
5	2-methylheptane	C_8H_{18}	114		
6	toluene	C_7H_8	92		
7	octane	C_8H_{18}	114		

8	ethylcyclohexane	C_8H_{16}	112		small quantity
9	ethylbenzene	C_8H_{10}	106		
10	*p*-xylene	C_8H_{10}	106		original sample
11	*o*-xylene	C_8H_{10}	106		
12	1,2,4-trimethylbenzene	C_9H_{12}	120		small quantity
13	4-methylbenzaldehyde	C_8H_8O	120