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

Ceria-based Oxide Catalysts Supported on Metal-organic Frameworks: The Selective Oxidation Toluene to CO_2 and Doped metals − Activity Relationship

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1 Experimental section

1.1 *Preparation of catalysts*

First, 12 ml of aqueous cerium ammonium nitrate solution (0.533 mol·L^{-1}) was poured into a precipitate formed by mixing 1.062 g terephthalic acid and 24 mL N, N-dimethylformamide (DMF). Then, an organic solvent is produced by stirring the previous solution for 30 minutes in a glass reactor. The organic solvents are heated for 15 minutes at 100°C with stirring in an oil bath. After natural cooling, the pale-yellow precipitates are washed twice with DMF, and three times with acetone, then dried overnight in the air at 70°C to obtain UiO-66-Ce precursor.

$CeMO_x$/UiO-66-Ce (M=Cu, Co, Mn, Fe, Zr) precursors are prepared by applying the same method. 12 ml of aqueous cerium ammonium nitrate solution and other metals nitrate solution (0.533 mol·L^{-1}) was poured into a precipitate formed by mixing 1.062 g terephthalic acid and 24 mL N, N-dimethylformamide (DMF). Then, an organic solvent is produced by stirring the previous solution for 30 minutes in a glass reactor. The organic solvents are heated for 15 minutes at 100°C with stirring in an oil bath. The molar ratio of the obtained sample (Ce/M) is 3/1.

All precursors are achieved by calcination at 350℃ for 4 h in the air (heating rate of 2℃ /min). Later, the collected samples are expressed as CeO_2/U and CeM/U (M=Ce, Cu, Co, Mn, Fe, Zr).

1.2 Material characterizations

The crystalline structure of the samples was analyzed by X-ray diffraction ***(XRD)*** spectrometry with Rigaku Ultimate IV Powder X-Ray (Japan) Cu Ka Diffractometer Wavelength 1.5418A Voltage 40KV Current 40mA, the spectra obtained from 5°-30° at a scan speed of 2°·min^{-1}.

A Mike ASAP2460 (USA) analyzer was used to test the Brunauer-Emmet-Teller ***(BET)*** at a temperature of 77 K.

The actual metal contents were determined using Inductively Coupled Plasma Mass spectrometry ***(ICP-MS)*** with a PerkinElmer NexION 300X spectrometer (USA).

Transmission electron microscopy ***(TEM)*** was performed on the FEI talos F200x G2 transmission electron microscope operated at an accelerating voltage of 80 kV.

The oxygen vacancy structure of UiO-66-Ce-M (M=Cu, Co, Mn, Fe, Zr) was measured by Electron Paramagnetic Resonance ***(EPR)*** using Bruker EMXPLUS (Germany), and the performance of 20 mg catalyst powder was analyzed at 30℃. Besides, UiO-66-Ce-Cu was also analyzed by EPR at 250 ℃.

The hydrogen temperature programmed reduction ***(H_2-TPR)*** and oxygen temperature programmed desorption ***(O_2-TPD)*** measurements were conducted on FINSORB3010 (China). The hydrogen temperature programmed reduction (H_2-TPR) corresponding samples (70 mg) placed in a quartz reactor was pre-heated in 5% H_2/Ar flow from room temperature to 200 °C and held for 1 h (10 mL min^{-1}), and then cooled to room temperature. The catalysts were heated from room temperature to 800 °C with a constant rate of 10 °C min^{-1} under a gas flow (5% H_2/Ar, 10 mL min^{-1}).

The temperature-programmed desorption of O_2 (**O_2-TPD**) with 50 mg catalysts was pre-heated in 5% O_2/He flow from room temperature to 200 °C and held for 1 h (10 mL min^{-1}), and then cooled to room temperature. The catalysts were heated from room temperature to 800 °C at 10 °C min^{-1} in pure He (10 mL min^{-1}).

Thermo Fisher Nexsa (USA) electronic spectrometer was used for X-ray photoelectron spectroscopy ***(XPS),*** which was corrected with C 1s = 284.8 eV.

Raman was tested by Invia Reflex LabRam HR Evolution (UK) with the Laser wavelength 532nm.

FTIR spectra were measured on a Nicolet 6700 spectroscopy using an MCT detector. The spectra were measured in the range from 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans.

In situ DRIFT (diffuse reflectance infrared Fourier transform) spectra of Toluene/O_2 adsorption was measured by Nicolet 6700 spectroscopy (Thermo Fisher Scientific, USA), and the background was collected at the required temperature). The catalyst (20 mg) was put into a sample cup and set inside a DRIFT cell fitted with a ZnSe window.

In a typical experiment, the powder samples were pretreated in pure N_2 (100 mL min^{-1}) at 350 °C for 1 h to remove the residuals. After cooling down to 30 °C, a background spectrum was collected at 4 cm^{-1} resolution for 32 scans in N_2 atmosphere. Then, the reactant gas (500 ppm toluene/N_2 or toluene/Air) with 100 mL min^{-1} was continuously introduced into the in-situ reaction chamber. The DRIFTS spectra (4000–900 cm^{-1}) were collected and continuously recorded for 3 h to realize the adsorption equilibrium at different temperatures (30, 100, 150, and 200°C).

1.3 Catalytic activity measurements

The toluene oxidation performance of the prepared catalysts was examined in a fixed-bed tubular quartz reactor (with a temperature-regulated electric furnace) in the temperature range of 100 - 300°C, with the temperature measured by a thermocouple placed in the middle. At a weight-hourly space velocity (WHSV) of 60,000 $ml \cdot g^{-1} \cdot h^{-1}$, the total flow rate of the experimental atmosphere (containing 500 ppm toluene, 21% O_2 and 79% N_2) was controlled at 100 $mL \cdot min^{-1}$ through a reactor by Teflon pipe. In a quartz tube reactor, 100 mg of catalyst powder (40 -60 mesh) was filled (outer diameter 6 mm, inside diameter 4 mm). As the reaction proceeded, the effluent gas was measured by a flame gas chromatograph (GC-9860-5CNJ, China) with a flame ionization detector (FID) to record continuously. To study the effect of water vapor on the catalytic activity, the on-stream toluene oxidation experiment was carried out in the presence and absence of 10.0 vol.% water vapor obtained by bubbling.

2 Structure and Texture of Catalysts

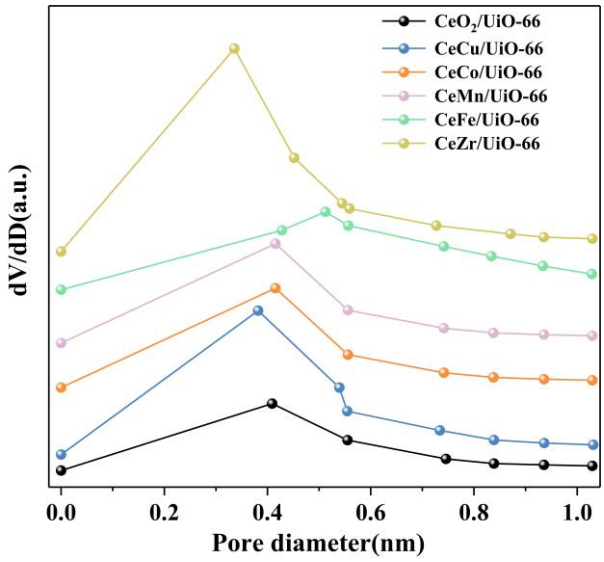

Figure S1. Microporous pore size distribution derived from the desorption branch of the isotherms.

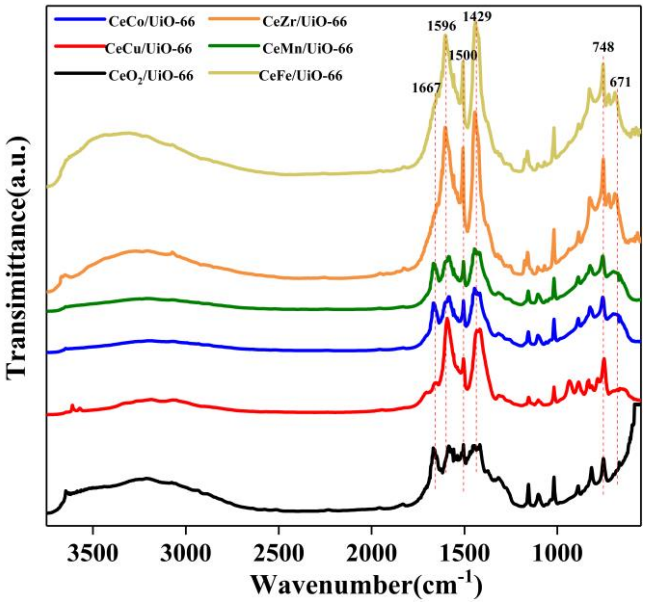

Figure S2. The infrared spectrum of $CeMO_x$/UiO-66

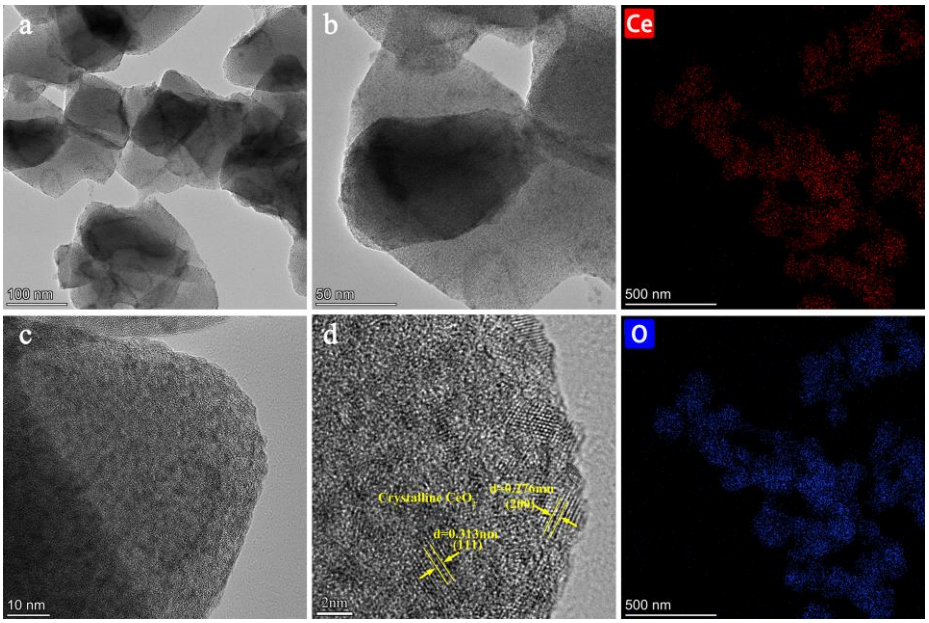

Figure S3. TEM images of CeO_2/UiO-66 at (a-b) low resolution and (c) high resolution. (d) Enlarged high-resolution images taken from the selected areas indicated by rectangles in (c).and EDS elemental maps of Ce, O in the right, respectively

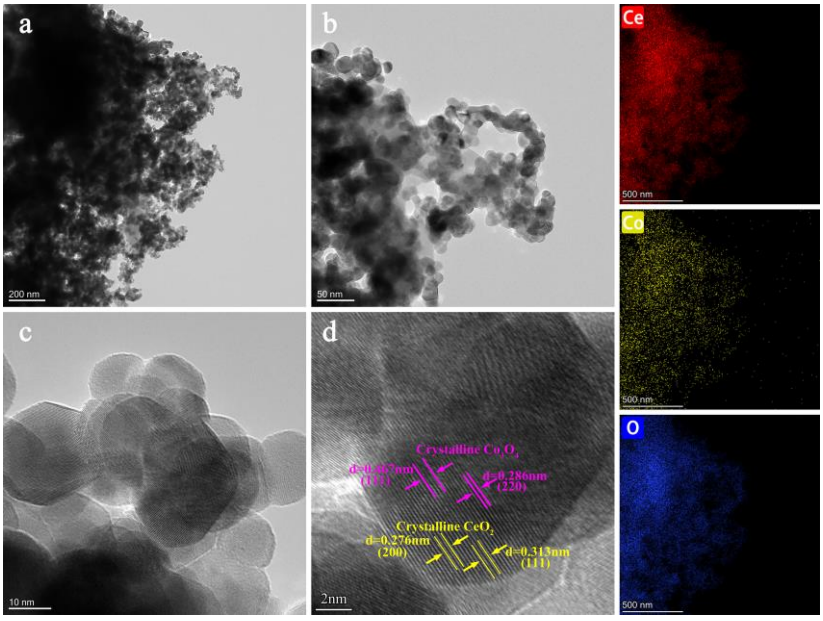

Figure S4 TEM images of CeCo/UiO-66 at (a-b) low resolution and (c) high resolution. (d) Enlarged high-resolution images taken from the selected areas indicated by rectangles in (c).and EDS elemental maps of Ce, Co, and O in the right, respectively

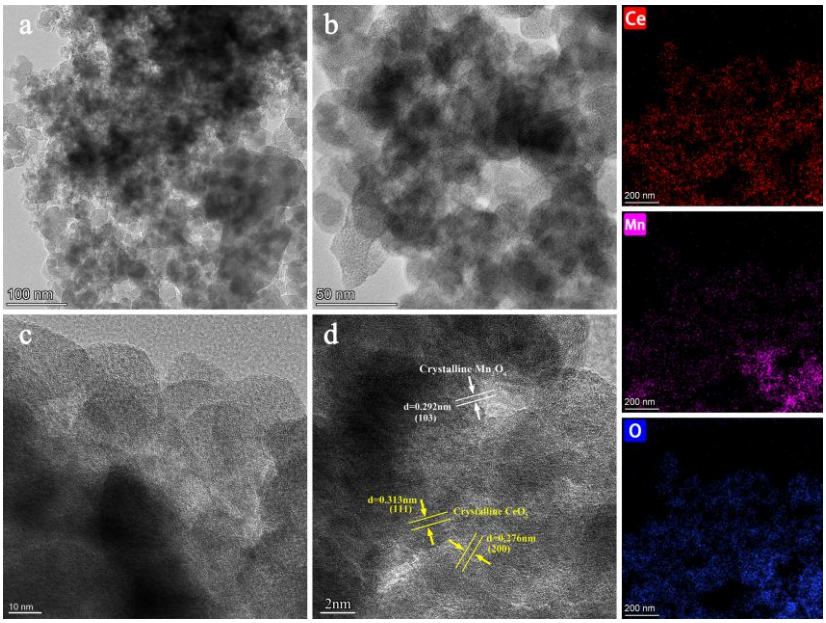

Figure S5 TEM images of CeMn/UiO-66 at (a-b) low resolution and (c) high resolution. (d) Enlarged high-resolution images taken from the selected areas indicated by rectangles in (c).and EDS elemental maps of Ce, Mn, and O in the right, respectively

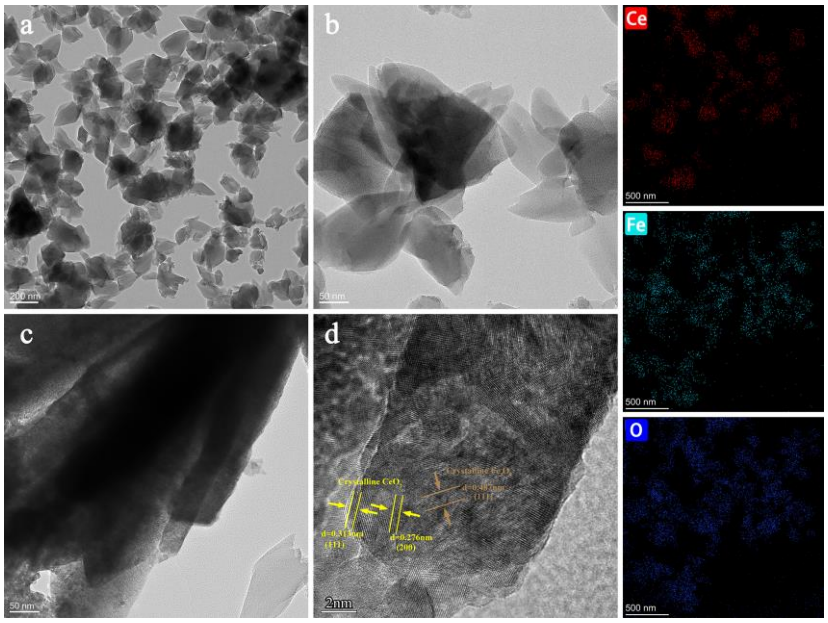

Figure S6 TEM images of CeFe/UiO-66 at (a-b) low resolution and (c) high resolution. (d) Enlarged high-resolution images taken from the selected areas indicated by rectangles in (c).and EDS elemental maps of Ce, Fe, and O in the right, respectively

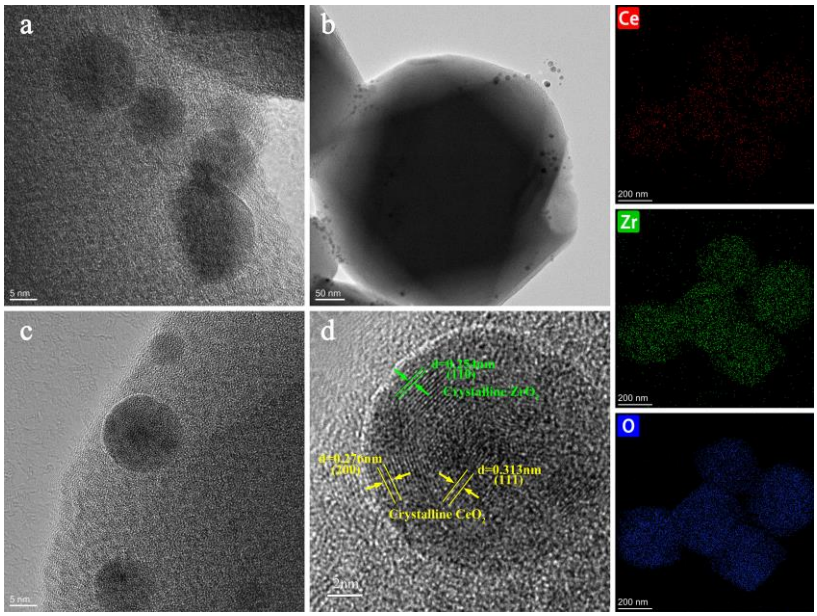

Figure S7 TEM images of CeZr/UiO-66 at (a-b) low resolution and (c) high resolution. (d) Enlarged high-resolution images taken from the selected areas indicated by rectangles in (c).and EDS elemental maps of Ce, Zr, and O in the right, respectively

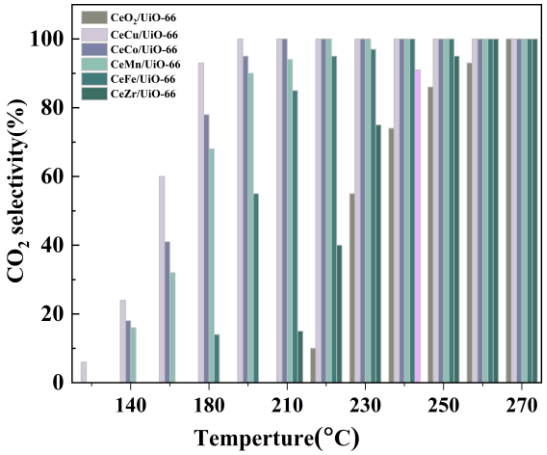

Figure S8 CO_2 selectivity of the samples

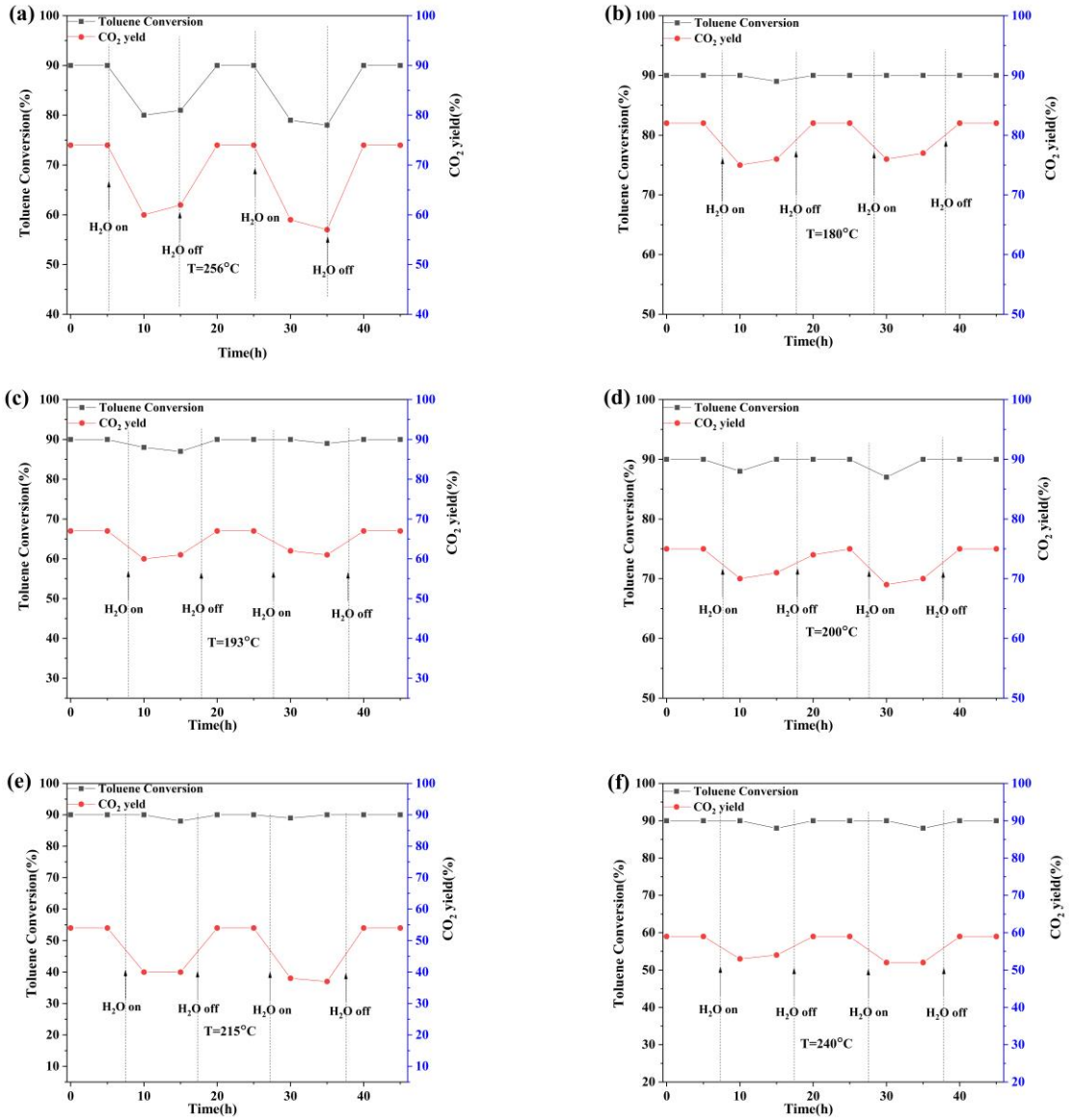

Figure S9. The effect of water vapor on catalytic oxidation at T90 over: (a) CeO_2/UiO-66, (b) CeCu/UiO-66 (c) CeCo/UiO-66 (d) CeMn/UiO-66 (e) CeFe/UiO-66 (f) CeZr/UiO-66 at WHSV = 60, 000 $mL \cdot g_{cat}^{-1} \cdot h^{-1}$

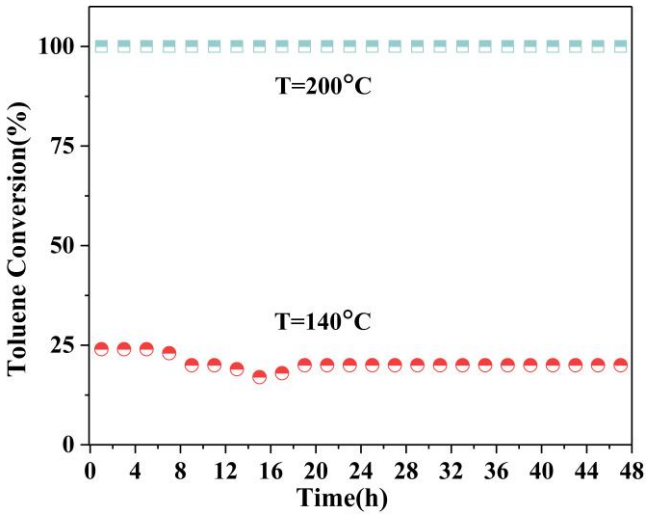

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Figure S10. Thermal stability of CeCu/UiO-66. Reaction conditions:500 ppm toluene balanced air, WHSV = 60, 000 mL·g_{cat}^{-1}· h^{-1}

Table S1 The percentage of surface element valence and acidity for CeMOx/UiO-66 samples.

Samples	Ce^{3+} (%)	Cu^{2+} (%)	Co^{3+} (%)	Mn^{4+} (%)	Fe^{3+} (%)	Zr^{4+} (%)	O_{latt} (%)	O_{ads} (%)	Weak acid (%)
CeO_2/UiO-66	18.11						19.64	56.96	53.11
CeCu/UiO-66	55.87	77.46					73.42	17.18	79.28
CeCo/UiO-66	47.78		52.18				54.13	24.67	71.73
CeMn/UiO-66	33.85			44. 41			48.65	31.85	62.76
CeFe/UiO-66	25.76				62.28		32.19	47.18	59.68
CeZr/UiO-66	21.02					100	27.66	47.54	57.49