Supporting Information

Solvent- and additive-free liquid-phase oxidation of toluene using molecular oxygen catalyzed by CeO_2-MnO_x/C_3N_4

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1. Experimental

1.1. Reagents and instruments

Manganese chloride (AR, ≥99.5%) and manganese nitrate (AR, 50% solution) were purchased from Xiangtan Electric Technology Co., Ltd. Toluene (AR, ≥99.5%) was supplied by Petroleum Chemical Corporation. Sodium hydroxide (AR, ≥99.5%) was obtained from Tianjin Bohua Group Co. Ltd. Ethanol (AR, ≥99.7%) was obtained from Jiangsu Sopo Group Co. Ltd. Melamine (AR, ≥99.5%) and cerium nitrate (AR, ≥99.0%) were acquired from Jinan Yuanlian Chemical Co., Ltd. All other additional reagents were commercially available and used without further purification.

1.2. Catalyst characterization

Textural properties of the samples were determined through N_2 physisorption measurements at 77 K using a Micromeritics ASAP 2020 system. X-ray diffraction (XRD) analysis was conducted with a Rigaku Ultima IV X-ray powder diffractometer (Rigaku Corporation, Japan). X-ray photoelectron spectroscopy (XPS) analyses were recorded on a 250Xi analyzer, using Al Kα radiation (1486.6 eV). Morphological observations were performed via a Sigma HD scanning electron microscope (SEM). Fourier transform infrared (FT-IR) spectra were acquired on a Nicolet 6700 FT-IR spectrophotometer using the KBr pellet method, covering the

spectral range of 400-4000 cm^{-1}. Thermogravimetric (TG/DTG) analyses were carried out with a Waters TGA 55 thermogravimetric analyzer, over a temperature range of 30-800 °C. Hydrogen/Oxygen Temperature-Programmed Reduction (H_2-TPR/O_2-TPD) spectra were collected on an Auto Chem II 2920 and Micromeritics TriStar II 3Flex, respectively.

1.3. Toluene oxidation reaction procedure

Toluene catalytic oxidation was conducted in a stainless steel high-pressure reactor. First, 0.1 g solid catalyst and 21.0 g toluene were placed in the reactor, which was then sealed. The stirring rate and target reaction temperature were set. When the reactor temperature reached 20 °C below the target, oxygen was introduced, with strict temperature control to maintain stability. After reaction completion, oxygen supply was stopped. The reactor was cooled naturally to room temperature, and the product was weighed. Finally, solid-liquid separation was done via centrifugation, and each product's content was determined by gas chromatography internal standard method.

Toluene conversion and the selectivity to different products were obtained as follows:

$$\text{Conversion of toluene (\%)} = \frac{\text{The mole of toluene converted}}{\text{The mole of toluene added}} \times 100\% \quad (1)$$

$$\text{Selectivity of Bz-OH/Bz-CHO/Bz-COOH (\%)} = \frac{\text{The mole of Bz-OH/Bz-CHO/Bz-COOH}}{\text{The mole of toluene reacted}} \times 100\% \quad (2)$$

Table S1 Textural properties of two samples.

Sample	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
Fresh	40.88	0.96	94.27
Regenerative	29.52	0.61	82.99

Fig. S1 H_2-TPR (A) and O_2-TPD (B) profiles of fresh and regenerative samples.

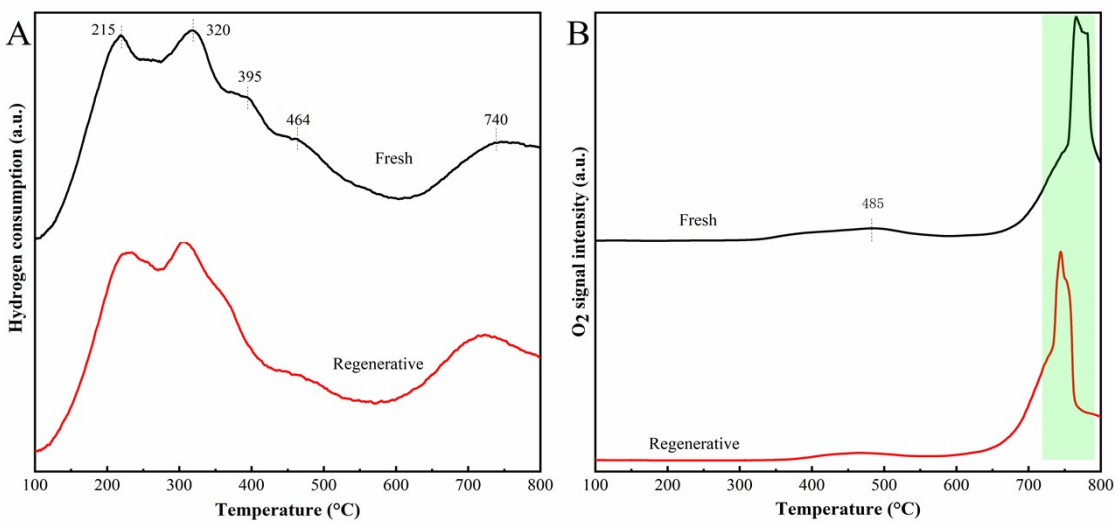

Fig. S2 Repeatability experiments of CeO_2-MnO_x/C_3N_4-catalyzed toluene

oxidation.

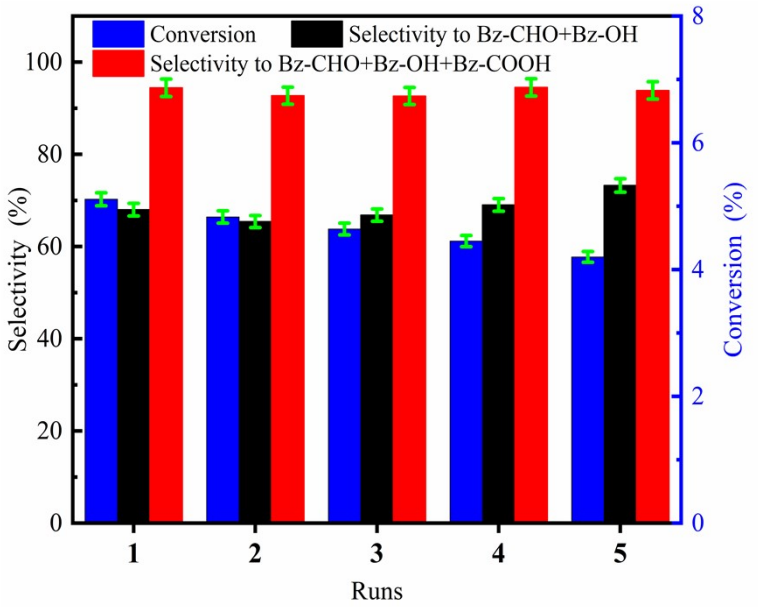

Table S2 Comparison on the catalytic performances of several catalysts reported in previous literatures.

Catalyst	Solvent/ (Initiator)	Oxidizer	Tem. (°C)	Time (h)	Con. (%)	Sel. (%) Bz-CHO	Bz-OH	Bz-COOH	Ref.
$VO(acac)_2$	Glacial acid	H_2O_2	90	4.0	19.8	50	6.1	22.2	[1]
Mn_3O_4/CNTs-3	(TBHP)	O_2	90	12.0	24.6	43.5	47.0	-	[2]
$[TPPFeIII]_2O$	-	molecular oxygen	165	3.75	7.4	59.1			[3]
[Co(II)TPP/CTS	-	air	160	4.5	8.8	37.0	28.0	34.0	[4]
Pd@C-GluA-550	-	oxygen	160	7.0	-	51.0	-	-	[5]
Pt/ZrO_2	-	oxygen	90	3.0	37.2	19.6	6.5	70.4	[6]
Mn@ZIF-8	-	molecular oxygen	180	2.5	6.5	31.6	38.7	24.8	[7]
MnO_x/g-C_3N_4@ZIF-8	-	molecular oxygen	180	2.0	4.7	36.2	38.1	18.2	[8]
$CeMnO_x$	-	molecular oxygen	180	4.0	7.0	26.3	24.8	44.5	[9]
Mn-TiO_2	-	molecular oxygen	160	4.0	6.4	36.7	21.9	40.4	[10]
CeO_2-MnO_x/C_3N_4	-	molecular oxygen	180	2.0	5.1	30.1	37.8	26.5	this work

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