

Electronic Supplementary Information

Enhanced catalytic performance for toluene combustion via Ce-doped α -MnO₂: efficient balance between toluene adsorption and activation oxidation

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Supplemental Data Items

1. Materials

Manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$, AR) was purchased from Bodi Chemical Co., Ltd., Tianjin, China. Ethanol glycol (AR) was purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Toluene (AR) and potassium permanganate (KMnO_4 , AR) were purchased from Kemiou Chemical Reagent Co. Ltd., Tianjin, China. Ammonium ceric nitrate ($\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$, AR) was purchased from Aladdin, Shanghai, China.

2. Experimental

N_2 adsorption-desorption isothermals were recorded on a Micromeritics Tristar 2420 instrument at 77 K, before measurements, each sample was degassed at 180 °C for 6 h. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas. The pore size distributions were derived from the desorption branches based on Barrett-Joyner-Halenda (BJH) model. Temperature programmed reduction with H_2 (H_2 -TPR) was performed by a TP-5080 adsorption analyzer (Xianquan) equipped with a thermal conductivity detector. Typically, the sample (30 mg) was packed into the reactor and degassed at 300 °C for 1 h with an Ar gas flow, then the sample was cooled down to the room temperature, and the gas flow was shifted to a mixture of 5 vol.% H_2/N_2 (30 mL min^{-1}), then the reactor was carried out by raising the temperature from 30 to 700 °C at a heating rate of 10 °C min^{-1} .

Temperature-programmed desorption of oxygen (O_2 -TPD) was conducted on a TP-5080 adsorption analyzer with a quadrupole mass detector (HIDEN QGA). At first, the MnO_x and Ce- MnO_2 -EG catalyst (30 mg) was packed into the reactor and pre-treated under O_2 atmosphere (30 mL min^{-1}) at 300 °C for 60 min, and then cooled down to 30 °C. Then the reactor was purged by He for 60 min. Finally, the TPD experiment was took under a He flow (30 mL min^{-1}) from 30 to 850 °C upon a rate 10 °C min^{-1} .

Temperature-programmed surface reaction of toluene in He atmosphere (without O₂) (C₇H₈-TPSR (He)) were carried out on a TP-5080 adsorption analyzer with a quadrupole mass detector (HIDEN QGA). At first, the MnO_x and Ce-MnO₂-EG catalyst (30 mg) was packed into the reactor, after the pretreatment in He at 300 °C for 60 min it was cooled to 30 °C. Then the mixture gas of toluene/He was introduced into reactor for 10 min, and then the reactor was purged by He for 60 min. Finally, the TPSR experiment was taken under a He flow (30 mL min⁻¹) from 30 to 850 °C upon a rate 10 °C min⁻¹. The signal was detected by a mass spectrometer (MS) at mass-to-charge (m/z) ratios of 44 (CO₂) and 92 (toluene).

C₇H₈-TPSR (He+O₂) were carried out on a TP-5080 adsorption analyzer with a quadrupole mass detector (HIDEN QGA). At first, the MnO_x and Ce-MnO₂-EG catalyst (30 mg) was packed into the reactor, after the pretreatment in He at 300 °C for 60 min it was cooled to 30 °C. Then the mixture gas of toluene/He was introduced into reactor for 10 min, and then the reactor was purged by He for 30 min. Finally, the TPSR experiment was taken under a O₂/He (20 vol.%) flow (30 mL min⁻¹) from 30 to 850 °C upon a rate 10 °C min⁻¹. The signal was detected by a mass spectrometer (MS) at mass-to-charge (m/z) ratios of 44 (CO₂) and 92 (toluene).

Table S1

The desorption peak areas of O_α-M species, consumption peak areas of O_α-M and CO₂ product peak areas calculated based on the C₇H₈-TPSR curve.

Sample	O _α -M ^a	Consumption of O _α -M ^b	CO ₂ product peak area ^c
MnO ₂ -HT	4370	-	75
MnO ₂ -RP	1055	134	268
MnO ₂ -EG	685	181	422
Ce-MnO ₂ -EG	969	240	769

^a The peak areas of O_α-M species were calculated based on the O₂-TPD curves.

^b The consumption peak areas of O_α-M species were calculated based on the O₂-TPD and C₇H₈-TPSR curves (TCD signal) from 450 to 700 °C.

^c The product peak areas of CO₂ were calculated based on the C₇H₈-TPSR curves (TCD signal) from 200 to 400 °C.

Table S2

Catalytic activities of toluene combustion over different catalysts reported in the literature.

Catalysts	Synthesis method	Oxidation conditions		Toluene conversion		Reference
		Toluene (ppm)	Space velocity	T ₅₀ (°C)	T ₉₀ (°C)	
α -MnO ₂	hydrothermal	1000	50000 mL g ⁻¹ h ⁻¹	215	228	[1]
MnO ₂	H ₂ O ₂ reduction	1000	60000 mL g ⁻¹ h ⁻¹	255	267	[2]
Mn ₂ O ₃	Redox precipitation	1000	20000 mL g ⁻¹ h ⁻¹	241	250	[3]
α -MnO ₂ / δ -MnO ₂	decomposition method	1000	20000 mL g ⁻¹ h ⁻¹	205	213	[4]
Mn ₃ O ₄	solution combustion strategy	1000	19100 h ⁻¹	225	256	[5]
MnO _x -I	redox coprecipitation method	1000	40000 mL g ⁻¹ h ⁻¹	219	223	[6]
MnO _x /AC-0.3	in-situ redox precipitation	1000	20000 mL g ⁻¹ h ⁻¹	184	193	[7]
Mn ₂ O ₃ @MnO ₂	redox-induced H ⁺ /KMnO ₄ treatment method	1000	60000 mL g ⁻¹ h ⁻¹	235	252	[8]
MnO _x	starch paste-assisted method	1000	60000 mL g ⁻¹ h ⁻¹	250	285	[9]
MnCo _x	starch paste-assisted method	1000	60000 mL g ⁻¹ h ⁻¹	203	224	
Ag-MnO ₂	H ₂ O ₂ assisted treatment method	1000	60000 mL g ⁻¹ h ⁻¹	216	225	[10]
Ni-MnO ₂	EG reduction strategy	1000	20000 mL g ⁻¹ h ⁻¹	189	199	[11]
Ce _{0.03} MnO _x	Redox precipitation	1000	20000 mL g ⁻¹ h ⁻¹	215	220	[3]
MnO _x /Co ₃ O ₄	synergistic pyrolysis adsorption-oxidation strategy	1000	120000 mL g ⁻¹ h ⁻¹	237	242	[12]
CuMnO _x	co-precipitation method	1000	20000 mL g ⁻¹ h ⁻¹	210	231	[13]
MnO ₂ -EG	EG reduction strategy	1000	20000 mL g ⁻¹ h ⁻¹	194	214	This work
Ce-MnO ₂ -EG	EG reduction strategy	1000	20000 mL g ⁻¹ h ⁻¹	184	197	This work

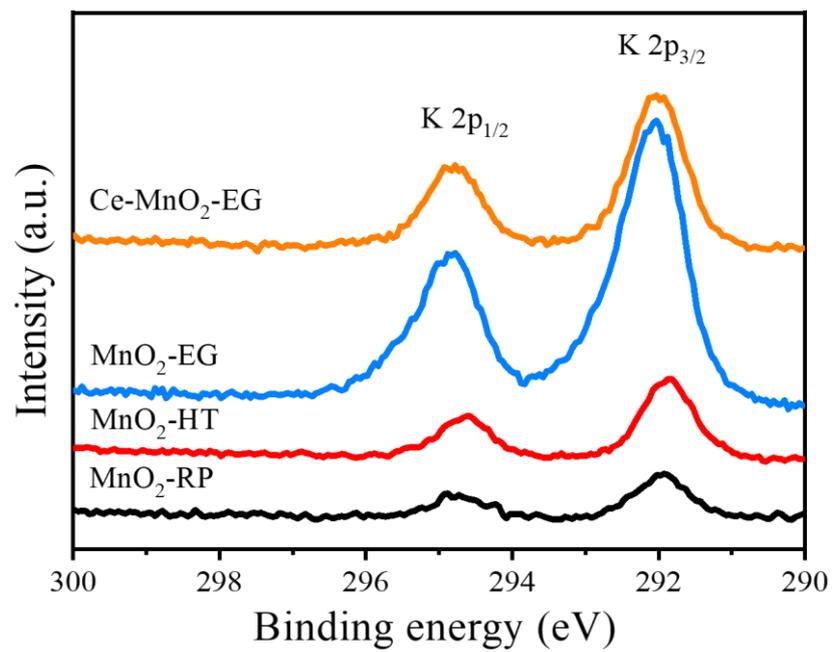


Fig. S1 K 2p XP spectra of various MnO₂ and Ce-MnO₂-EG samples.

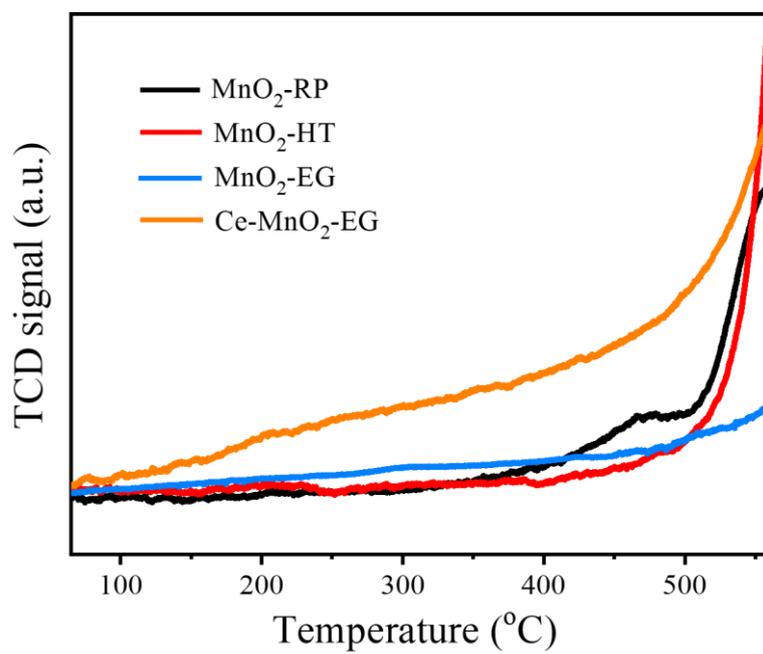


Fig. S2 Enlarged O₂-TPD curves of the various catalysts in the low temperature region.

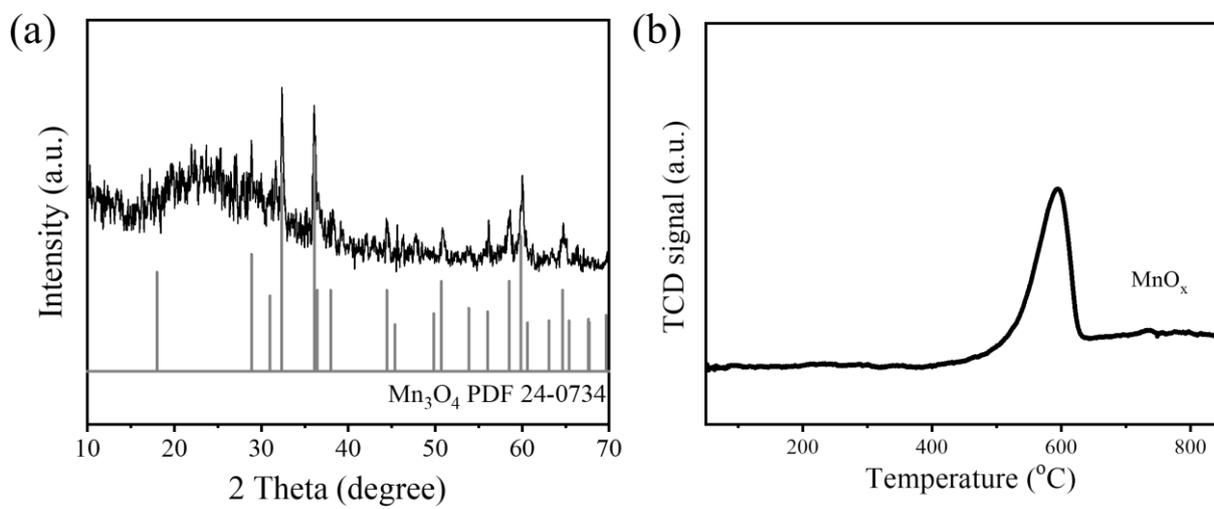


Fig. S3 (a) XRD pattern and (b) O_2 -TPD profile of MnO_x reference sample without K content.

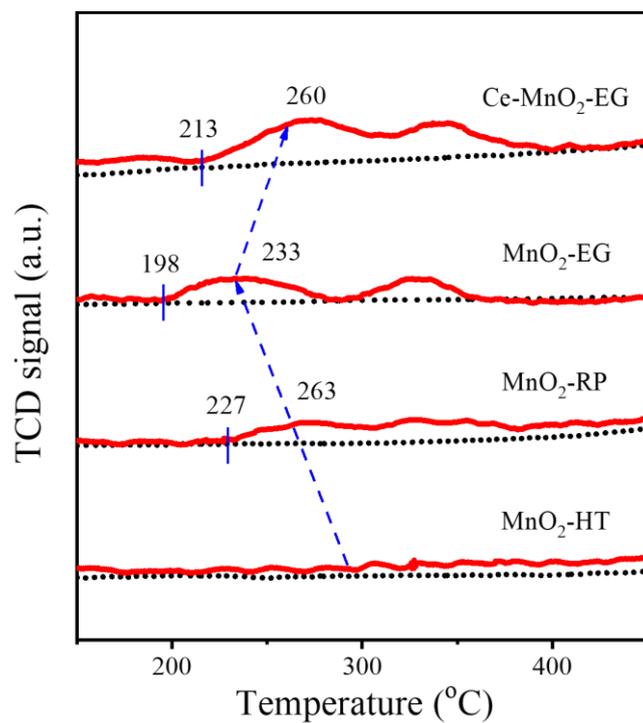


Fig. S4 Activation-oxidation temperature of toluene to CO₂ based the C₇H₈-TPSR testing (without O₂) for various MnO₂ and Ce-MnO₂-EG catalysts under He atmosphere.

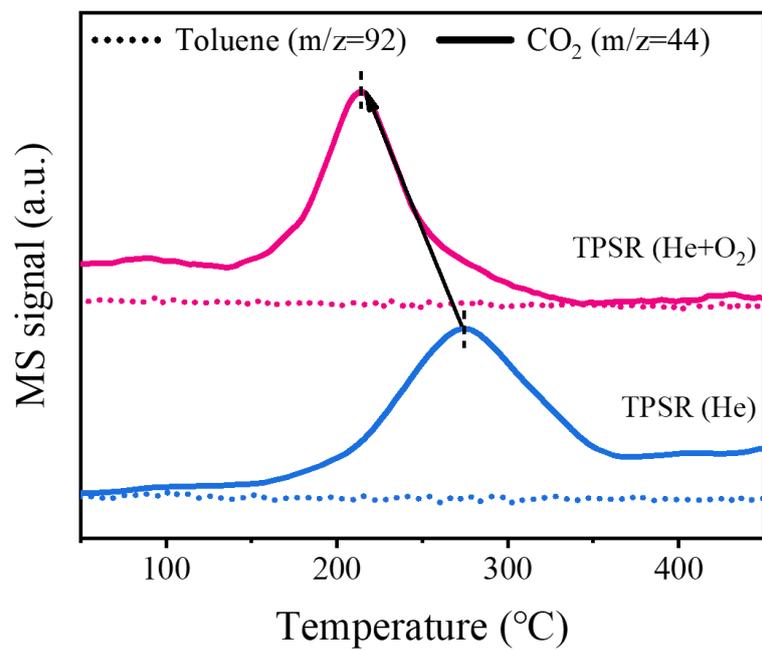


Fig. S5 Comparison curves of toluene signal ($m/z = 92$) and CO_2 signal ($m/z = 44$) for C_7H_8 -TPSR ($\text{He} + \text{O}_2$) and C_7H_8 -TPSR (He) of Ce-MnO_2 -EG.

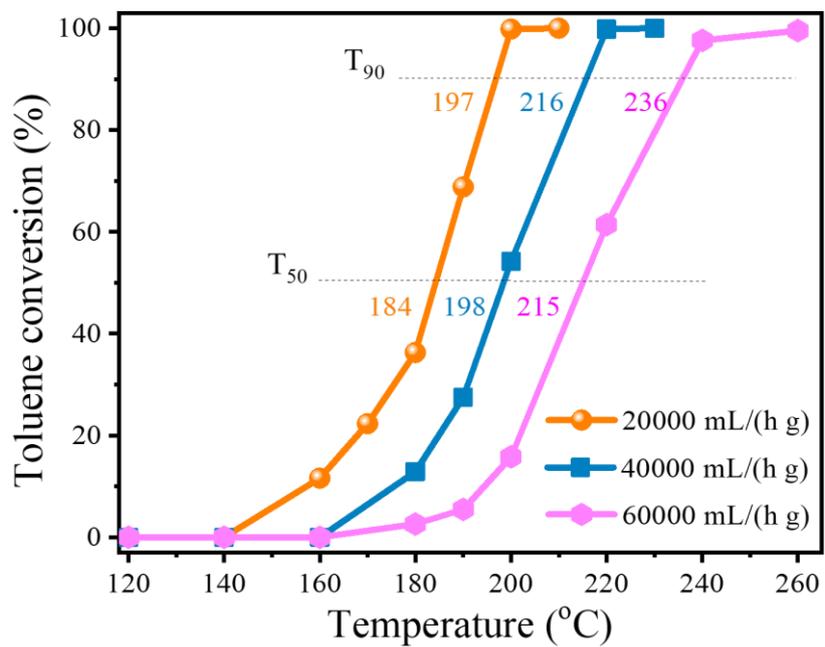


Fig. S6 Catalytic activities of Ce-MnO₂-EG catalyst under different WHSV with [C₇H₈] = 1000 ppm in air.

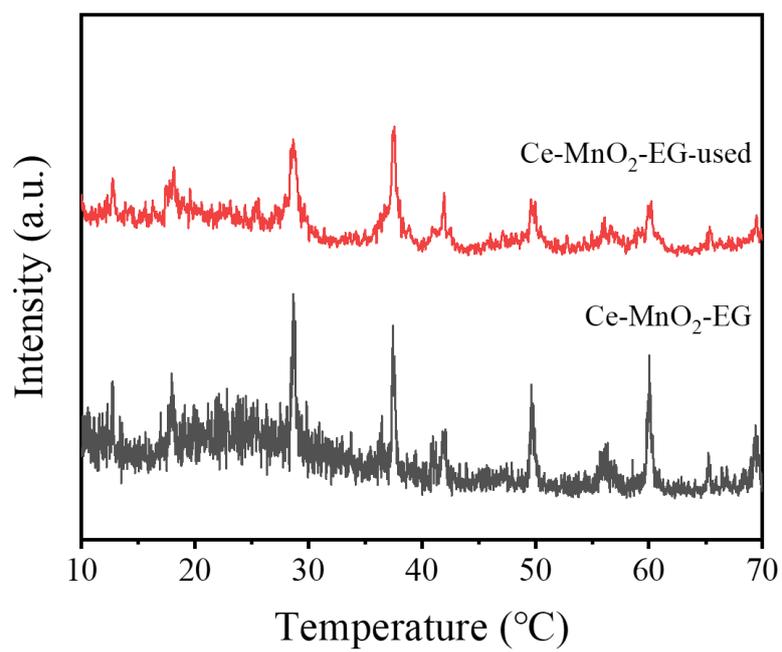


Fig. S7 XRD patterns of fresh Ce-MnO₂-EG and Ce-MnO₂-EG-used samples.

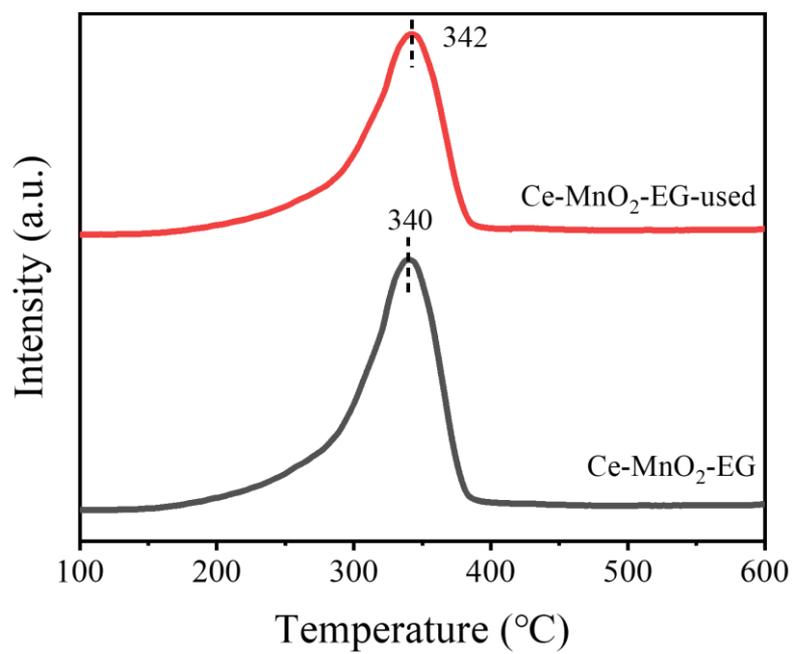


Fig. S8 H₂-TPR curves fresh Ce-MnO₂-EG and Ce-MnO₂-EG-used catalysts.

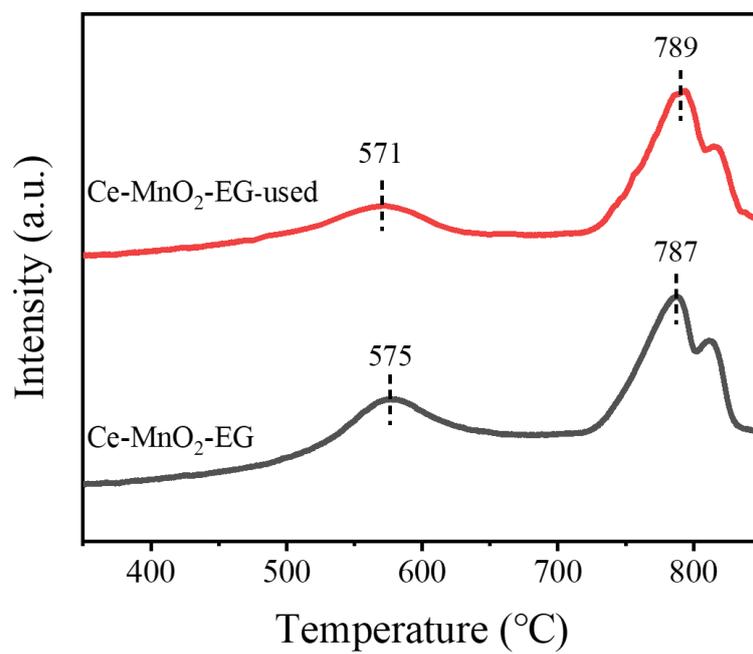


Fig. S9 O₂-TPD profiles of fresh Ce-MnO₂-EG and Ce-MnO₂-EG-used catalysts.

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