Supporting Information

Two-dimentional manganese oxide on ceria for the catalytic partial

oxidation of hydrocarbons

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Experimental Section:

1. Materials

All chemicals were of analytical grade and used as purchased without further purification. Cerium nitrate hexahydrate [Ce(NO₃)₃·6H₂O], citric acid monohydrate, acetophenone, DL-1-phenylethyl alcohol, benzaldehyde, bromobenzene, biphenyl, propylbenzene, propiophenone, 4-acetylbiphenyl, diphenylmethane, benzophenone, benzhydrol, 1,2-dihydrostilbene, and benzoic acid were obtained from Aladdin Chemical Reagent Company, 50 *wt*% manganese nitrate solution, ethanol, glycerol, and ethylbenzene were obtained from Shanghai Lingfeng Chemical Reagent Co. Ltd, 4-ethylbiphenyl, isobutylbenzene, and isobutyrophenone were obtained from J&K China Chemical Ltd.

2. Characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku D/MAX 2550 diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å). Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) characterizations were carried out on a Cs-corrected JEM-ARM300F Grand ARM electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. The FT-IR spectra were collected using a Nicolet *is50* FT-IR spectrometer equipped with an MCT/A detector and ZeSe windows and a high temperature reaction chamber. The X-ray photoelectron spectroscopy (XPS) was used to test the Ce *3d*, Mn *2p*, and O *1s* binding energy values of surface cerium, manganese, and oxygen species on AXIS Supra (Kratos, England). The binding energy values were calibrated against the C *1s* signal (BE = 284.6 eV) of contaminant carbon. The mercury-intrusion curves were performed on AutoPore IV 9510 (Micromeritics, America). Raman spectra were recorded using a HR800 Raman spectrometer equipped with an Ar excitation source ($\lambda = 514.532$ nm). More details of *in-situ* IR and Raman characterizations are shown in the Supporting Information.







Figure S1. ¹³C NMR spectra of (a) the polyester synthesized from esterification of critic acid and glycerol, (b) critic acid, (c) glycerol. Compared with glycerol and critic acid, the ¹³C NMR spectra gives typical peals assigning to the ester species, demonstrating esterification occur to form high molecule species [1-4].

Figure S2. SEM images of CeO₂.

Figure S3. SEM images of the (a) external and (b) internal view of the $MnO_x/CeO_2(0.05)$.

Figure S4. (a,c) SEM images and (b,d) the corresponding EDS spectrum of red square in (a,c) for $MnO_x/CeO_2(0.05)$.

Note: As shown in the scanning electron microscope (SEM) images in Figure S4, the samples exhibited a smooth surface with an internal coral morphology, which is typical structure constructed from the gaseous template during the foaming step, leading to the formation of metal oxide with rich porosity. The existence of Mn species on CeO_2 support was evidenced by the energy dispersive spectroscopy (EDS) analysis (Figure S4).

Figure S5. SEM images of various samples. (a,b) $MnO_x/CeO_2(0.025)$, (c,d) $MnO_x/CeO_2(0.1)$, and (e,f) $MnO_x/CeO_2(0.3)$.

Figure S6. Scanning transmission electron microscopy (STEM) images of $MnO_x/CeO_2(0.05)$ taken under different modes.

Figure S7. Raman spectra of various samples.

Figure S8. XRD patterns of MnO_2 , MnO_x/CeO_2 , and MnO_x/SiO_2 prepared by the conventional impregnation method.

Figure S9. (a) Mn2p XP spectra of $MnO_x/CeO_2(0.05)$ and MnO_2 .

Figure S10. In-situ (a) O1s, (b) Mn2p, and (c) Ce3d XP spectra of MnO_x/CeO₂(0.05) under different redox conditions.

Figure S11. In-situ Raman spectra of $MnO_x/CeO_2(0.05)$ recorded under different conditions.

Note: Raman characteristic band at ~460 cm⁻¹ was detected in $MnO_x/CeO_2(0.05)$ catalyst, which can be assigned as the oxygen breathing frequency around the Ce⁴⁺ ions (F_{2g} mode) [5-7]. During the *in-situ* Raman test with induced Ar, as the temperature increased from 140 °C to 350 °C, slight down-shifts, increase in bandwidth, and decrease of the band intensity of the 465 cm⁻¹ band were observed, which can be explained by the inhomogeneous strain effects associated with dispersion in particle size and by phonon confinement [8-13]. However, the shape of the band recovers when temperature drops back to room temperature (rt) in O₂ atmosphere, suggesting that lattice thermal expansion in CeO₂ is reversible.

Figure S12. (a) *In-situ* Raman spectra of $MnO_x/CeO_2(0.05)$ and CeO_2 . (b) An enlargement of the top two curves in (a).

Note: Figure S12 shows the *in-situ* Raman spectroscopy in CO atmosphere, the broadening and red shift of F_{2g} mode, and the disappearance of band at 649-656 cm⁻¹ also occurred, because the CO acted as reductant to remove the active oxygen species associated with MnO_x species. When oxygen was introduced to the sample, the band at 653 cm⁻¹ is regenerated again, confirming the reversibility of the active oxygen.

Figure S13. O₂-TPD profiles of commercial CeO₂, MnO₂, CeO₂, and MnO_x/CeO₂(0.05) samples.

Figure S14. GC traces of the gaseous composition after ethylbenzene oxidation over $MnO_x/CeO_2(0.05)$ catalyst (entry 21 in Table 1 in the maintext). The broad signal at 2.5-4.0 min is oxygen.

Figure S15. Recycling runs for the aerobic oxidation of ethylbenzene by $MnO_x/CeO_2(0.05)$ catalyst, reaction conditions: 47 mmol of substrate, 100 mg of catalyst, oxygen pressure at 2.0 MPa, 6 h. Conv.: conversion for ethylbenzene; Sel.: selectivity to acetophenone and 1-phenylethanol.

sample	$O_{surf}/(O_{ads} + O_{latt} + O_{surf})$ (%)	$Ce^{3+}/(Ce^{3+}+Ce^{4+})$	
		(%)	
CeO ₂	26.8	19.8	
MnO ₂	28.4	-	
$MnO_x/CeO_2(0.05)$	46.1	22.0	

Table S1. Surface element compositions parameters of CeO₂, MnO₂ and MnO_x/CeO₂(0.05) with different calcination temperature.

Entry	redox conditions	$O_{surf} / (O_{ads} + O_{latt} + O_{surf}) (\%)$
1	as-synthesized	46.4
2	H ₂ -RT	37.9
3	H ₂ -50 °C	32.7
4	H ₂ -80 °C	28.4
5	H ₂ -120 °C	27.1
6	air-50 °C	44.3

Table S2. In-situ XPS parameters of $MnO_x/CeO_2(0.05)$ under different redox conditions.

Catalyst	Reaction condition	Conv. (%)	Ref
Ce _{0.5} Mn _{0.5} O _x @500	10 bar of O ₂ , 120 °C, CH ₃ CN solvent	20.3	[14]
0.5%Pd@C-Glu _A -550	1 atm of air, 120 °C	14.2	[15]
Mn-N-C@HS (IM)	0.8 MPa of O ₂ , 120 °C	15.7	[16]
GSCN-20	10 bar of O ₂ , 150 °C, CH ₃ CN solvent	12	[17]
Au/LDH hybrid	3 MPa of O ₂ , 140 °C, <i>t</i> -butyl hydroperoxide (initiator)	40	[18]
Au/LDH hybrid	3 MPa of O ₂ , 140 °C (initiator-free)	trace	[18]
Au-Pd/MIL-101	1.5 MPa of O ₂ , 150 °C	38.5	[19]
TiO ₂ (Degaussa P25)	13 ml deionized H ₂ O, 5-W UV-vis Pen Ray lamp	6.71	[20]
S-CoAPO-11	3.0 MPa of O ₂ , 140 °C, <i>t</i> -butyl hydroperoxide,	14.8	[21]
MnSBA-15	80 °C, <i>t</i> -butyl hydroperoxide	25	[22]
5 wt% Ag/SiO ₂	120 °C, <i>t</i> -butyl hydroperoxide, chlorobenzene solvent	38	[23]
Co-N-C/SN	0.8 MPa of O ₂ , 120 °C	15.7	[24]
NiAl-hydrotalcite	oxygen flow = 5 mLmin ⁻¹ , 135 °C	47	[25]
Graphene	H ₂ O ₂ (20 equiv.), 60°C , CH ₃ CN solvent	0.5	[26]
Co/AC-salen-400	TBHP (0.4 equiv.), 80°C, CH ₃ CN solvent	20.8	[27]

 Table S3. The performances of various catalysts in the oxidation of ethylbenzene reported in literatures.

Table S4. Selective oxidation of various hydrocarbons over $MnO_x/CeO_2(0.05)$ catalyst under solvent- and initiator-free conditions.

Note: Compared with the aromatic hydrocarbons, the aliphatic ones are more inert [14,18]. Notably, the $MnO_x/CeO_2(0.05)$ catalyst is even active for the oxidation of hexane. Although the conversion is only 2%. In contrast, the Mn-Ce catalyst synthesized from the conventional impregnation method and the two-dimensional Au nanosheet catalyst (an efficient noble metal catalyst for hydrocarbon oxidation in

literature) [18] are completely inactive for the reaction under equivalent conditions. These data, again, confirms the high activity of $MnO_x/CeO_2(0.05)$.

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