Supporting Information

Microreactor-assisted synthesis of surface-active oxygen-rich Mn–Ce oxide particles and their catalytic activity in the wet air oxidation process

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Materials

Manganese(II) nitrate hexahydrate ($Mn(NO_3)_2 \cdot 6H_2O$, >98%), cerium(III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, >98%), potassium permanganate ($KMnO_4$, 99.3%), potassium hydroxide (KOH, 0.2 M aqueous solution), and phenol (>99%) were purchased from Kishida Chemical Co., Ltd. (Japan). All chemicals were used without further purification. Aqueous solutions of the desired concentrations were prepared by dissolving the above chemicals in distilled deionized water obtained using an RFD240NC system (Advantec, Japan). Oxygen and nitrogen gases were purchased from Iwatani Fine Gas Inc. (Japan) and used without further purification.

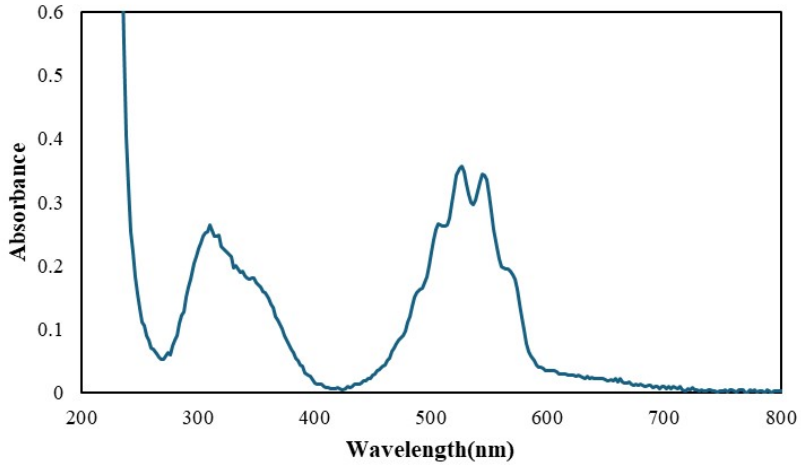
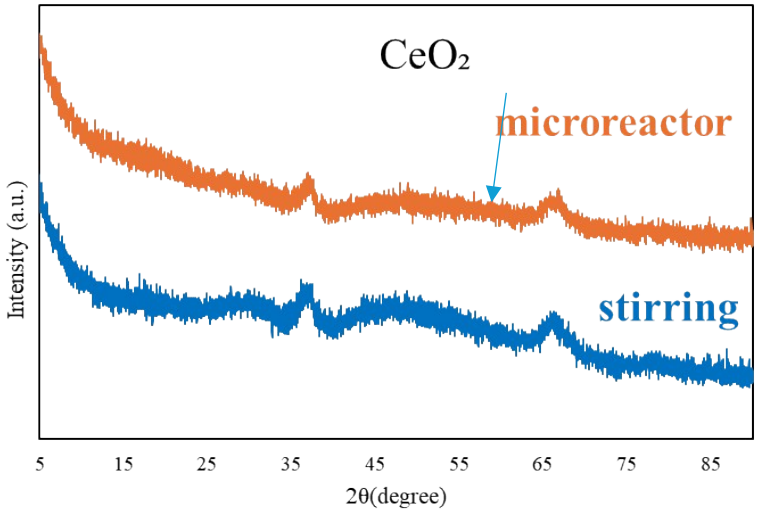
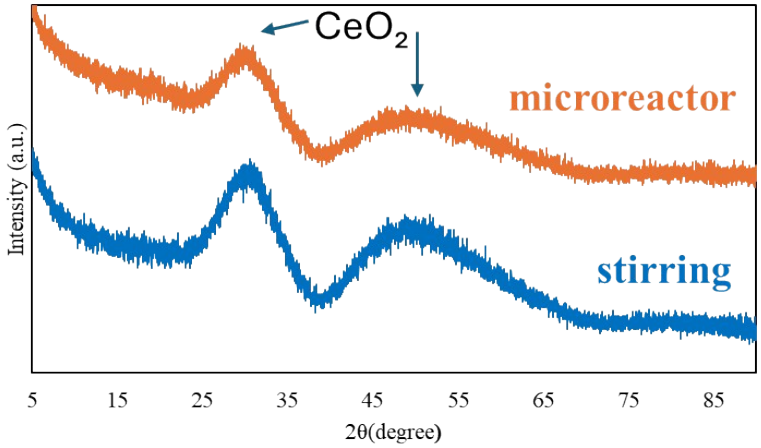


Figure. S1 UV–Vis spectrum of the filtrate obtained after the catalyst synthesis by the stirring–mixing method.

□□□□□□(a)Mn:Ce=5:1



(b)Mn:Ce=1:1



(c)Mn only

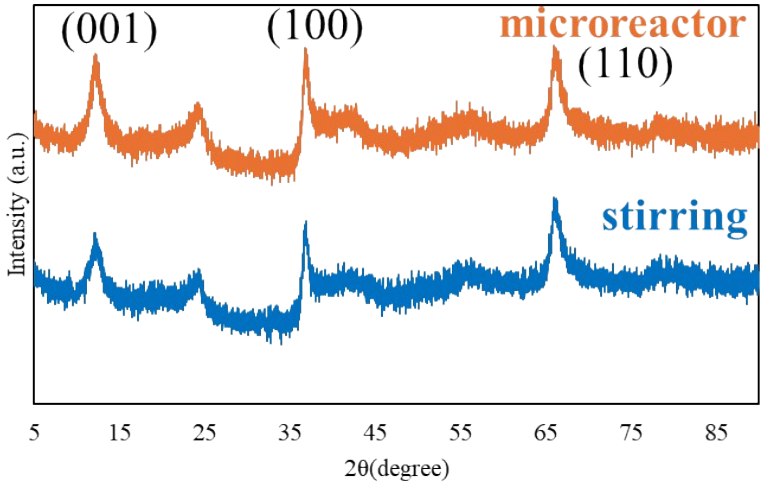


Figure. S2 XRD patterns of the catalysts synthesized with different Mn:Ce molar ratios.

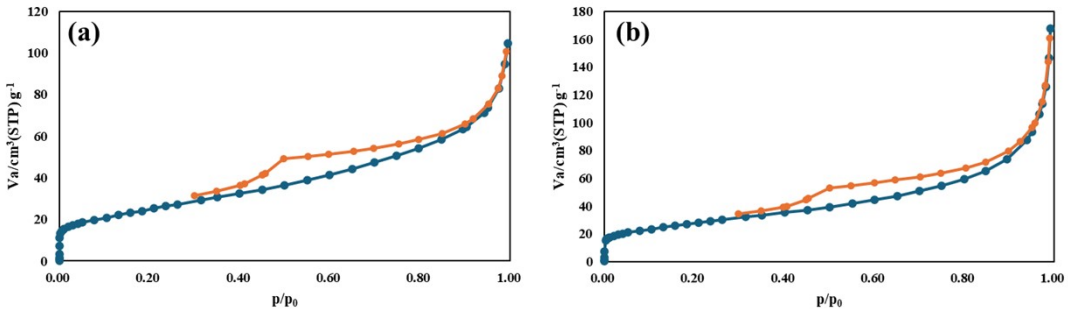


Figure S3. (a) N_2 adsorption–desorption isotherms of the catalyst synthesized by the stirring–mixing method and (b) N_2 adsorption–desorption isotherms of the catalyst synthesized using the microreactor.

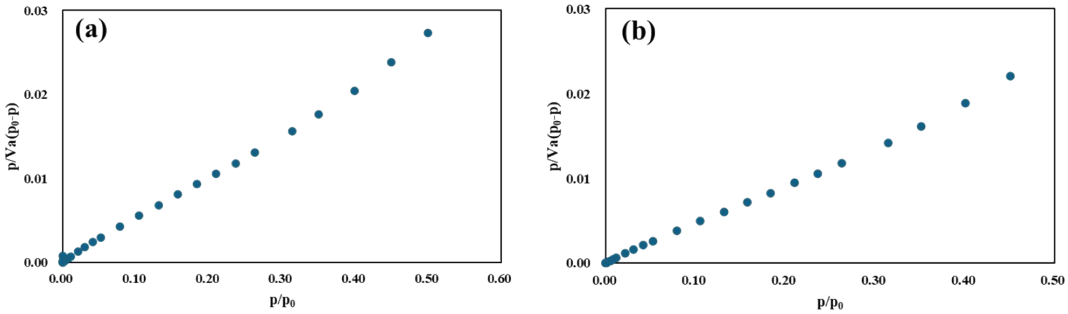


Figure S4. (a) BET plot derived from the N_2 adsorption–desorption isotherm of the catalyst synthesized by the stirring–mixing method. (b) BET plots derived from N_2 adsorption–desorption isotherms of catalysts synthesized using the microreactor.

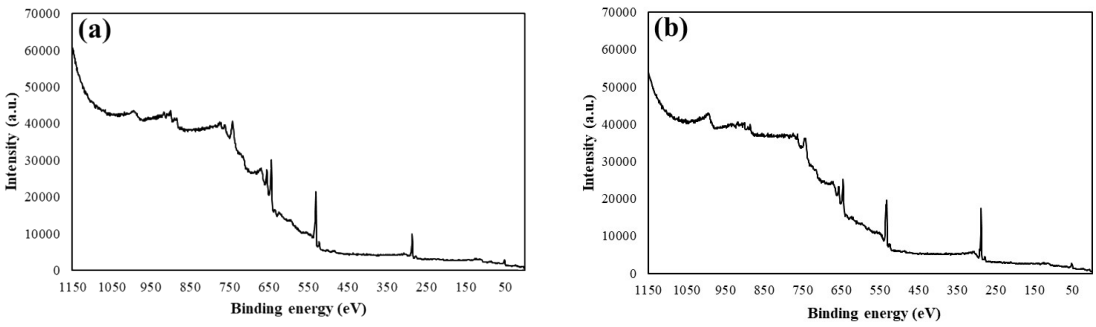


Figure S5. (a) XPS wide spectra of the catalyst synthesized by the conventional stirring-mixing method and (b) that synthesized using the microreactor.

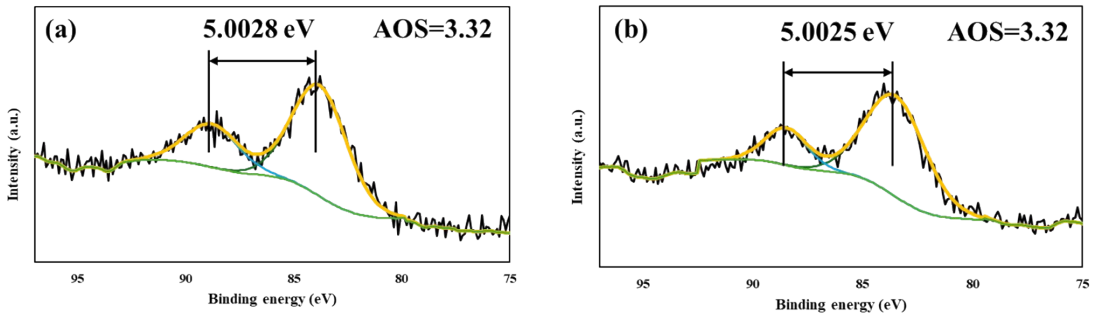


Figure S6. (a) Mn 3s XPS spectrum of the catalyst synthesized by the stirring–mixing method and (b) Mn 3s XPS spectrum of the catalyst synthesized using the microreactor. The surface average oxidation state (AOS) was calculated using the equation AOS = 8.956 – 1.126ΔE_s as reported in ref 39. The slight deviation from the AOS estimated based on the Mn^{3+}/Mn^{4+} ratio in the Mn 2p spectra is attributed to the presence of a small amount of Mn^{2+}, which was not considered in the calculation.

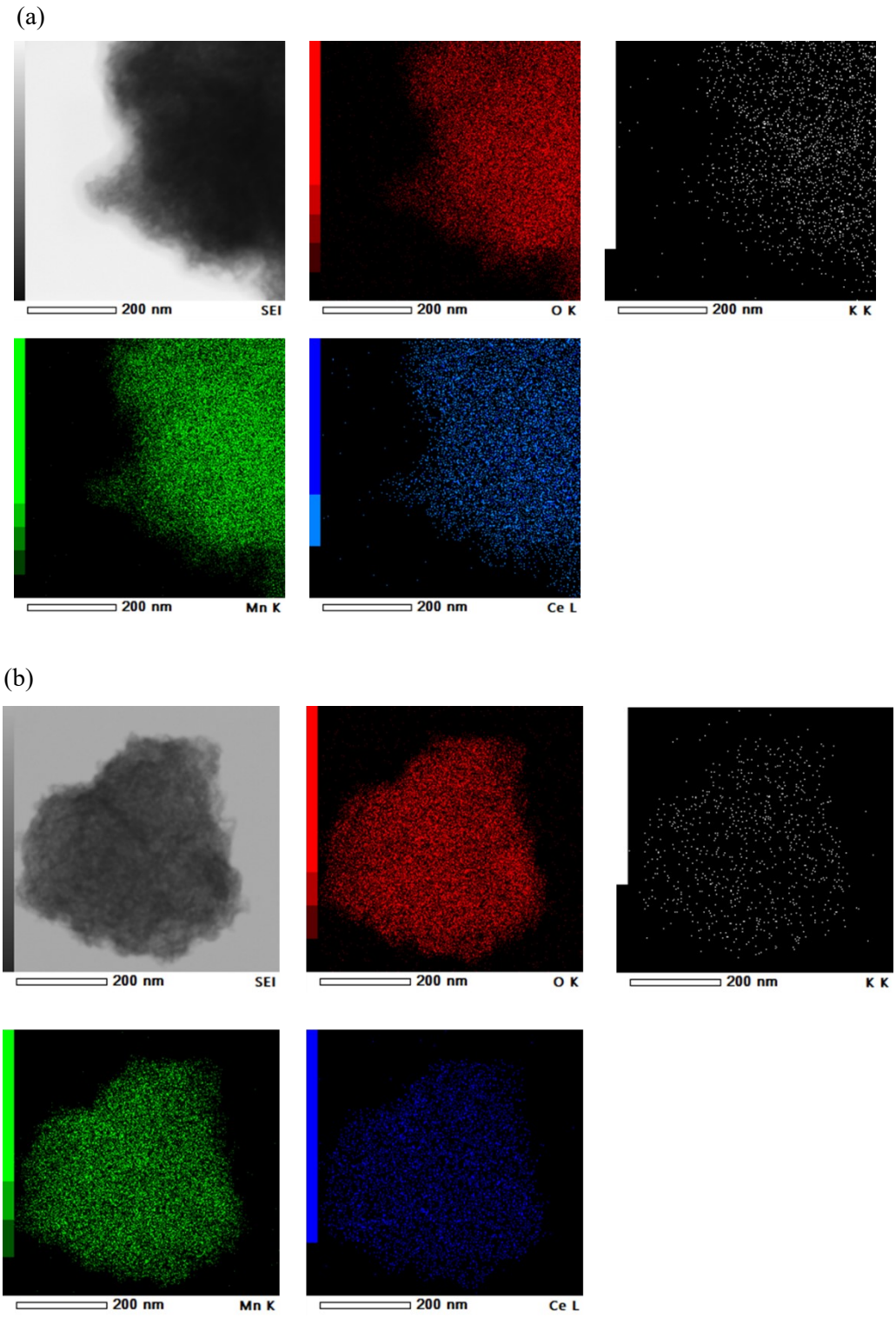
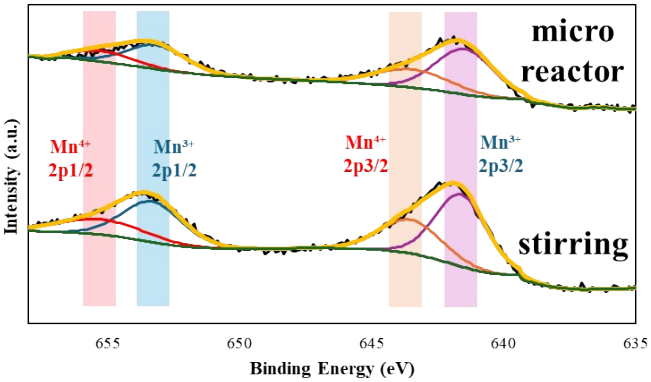


Figure S7. (a) STEM–EDS elemental maps of catalysts prepared by the conventional stirring-mixing method and (b) those of catalysts synthesized using the microreactor.



Mn 2p	Mn^{3+}(%)	Mn^{4+}(%)
stirring	60.72	39.28
microreactor	65.94	34.06

Figure S8. Mn 2p XPS spectra of the catalysts synthesized by the conventional stirring-mixing method and using the microreactor after phenol degradation experiments under an N_2 atmosphere. The corresponding Mn^{3+}/Mn^{4+} ratios are shown in the right table.

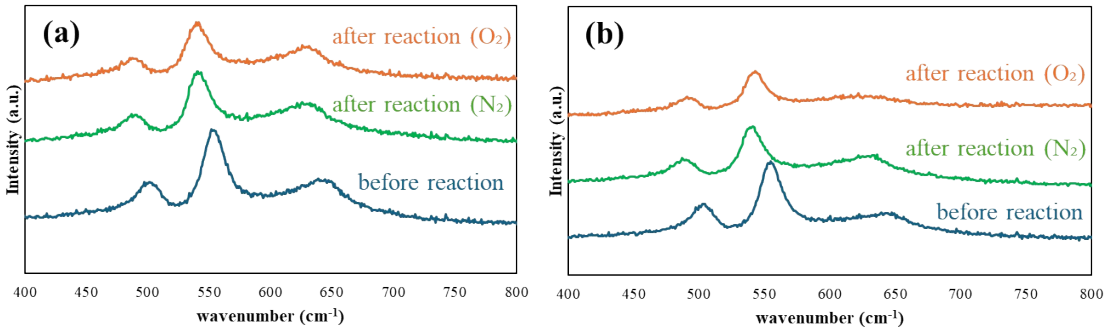


Figure S9. Raman spectra of the catalysts synthesized (a) by the conventional stirring-mixing method and (b) using the microreactor, before and after 2 h of the degradation experiments under each condition.

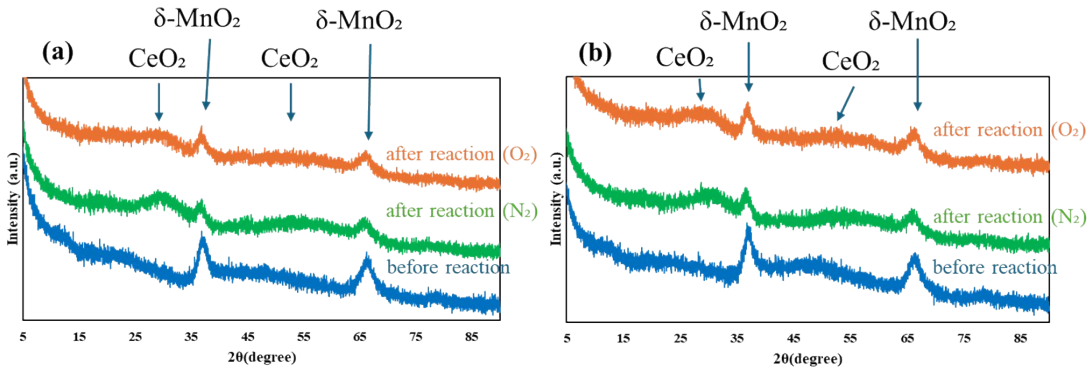
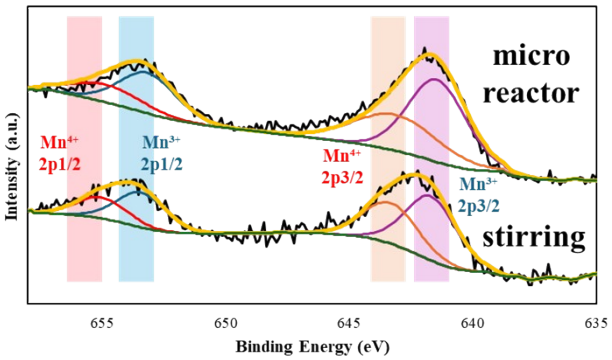


Figure S10. XRD patterns of the catalysts synthesized (a) by the stirring-mixing methods and (b) using the microreactor before and after 2 h of the degradation experiments under each condition.

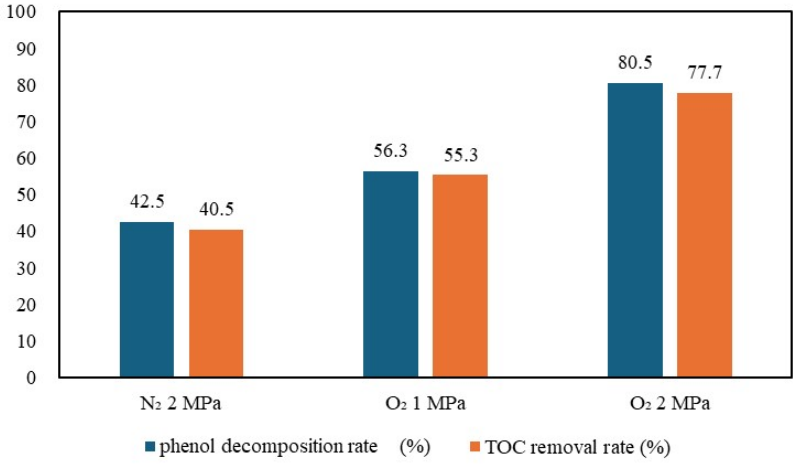


stirring (%)	before	after O_2	after N_2
Mn^{3+}	55.52	60.39	60.72
Mn^{4+}	44.49	39.61	39.28

microreactor (%)	before	after O_2	after N_2
Mn^{3+}	55.72	62.15	65.94
Mn^{4+}	44.28	37.85	34.06

Figure S11. Mn 2p XPS spectra of the catalysts synthesized by the conventional stirring-mixing method and using the microreactor after 2 h of phenol degradation experiments under an O_2 atmosphere and the corresponding Mn^{3+}/Mn^{4+} peak area ratios.

(a) stirring



(b) microreactor

Figure S12. Phenol decomposition ratios (%) and TOC removal ratios (%) under different atmospheres and different O_2 pressure conditions for catalysts synthesized by (a) the stirring-mixing method and using (b) the microreactor (reaction time = 2h; reaction temperature = 150℃; phenol concentration = 100 ppm).

Table S1. The Mn-to-Ce ratios for catalysts synthesized by each method before and after 2 h of the phenol decomposition experiments, as determined by XRF measurements.

stirring	Before reaction	After reaction
Mn	71.3	66.2
Ce	28.7	33.8

microreactor	Before reaction	After reaction
Mn	71.3	68.4
Ce	28.7	31.6