Supporting Information

Application two morphologies of Mn_2O_3 for efficient catalytic ortho-methylation of 4-chlorophenol

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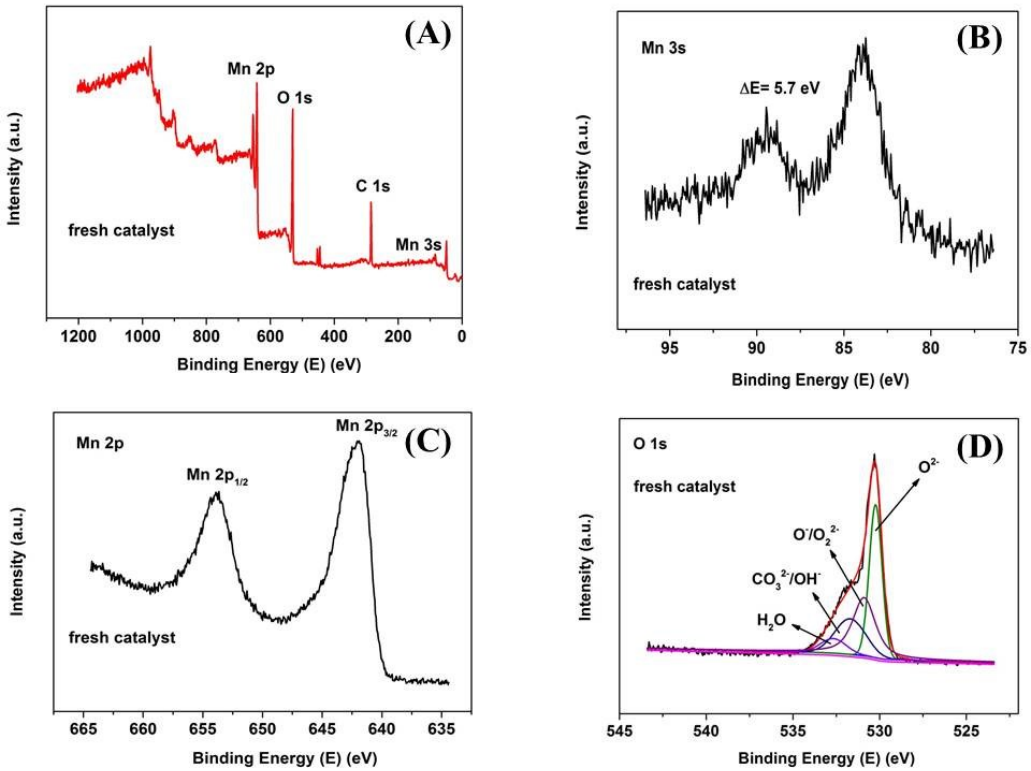

Fig S1 XPS spectrum of fresh Mn_2O_{3NW} samples: (A) survey scan XPS spectra; (B) Mn 3s detailed XPS spectra; (C) Mn 2p detailed XPS spectra; (D) O 1s detailed and fitted XPS spectra.

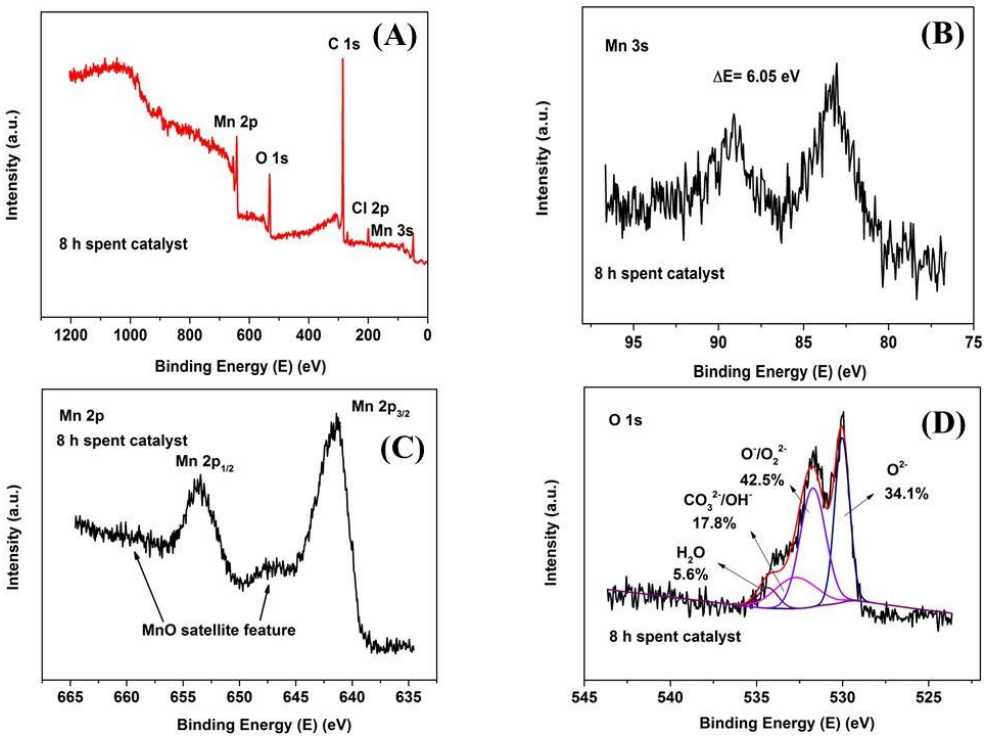

Fig S2 XPS spectrum of 8 h spent Mn_2O_{3NW} samples: (A) survey scan XPS spectra; (B) Mn 3s detailed XPS spectra; (C) Mn 2p detailed XPS spectra; (D) O 1s detailed and fitted XPS spectra.

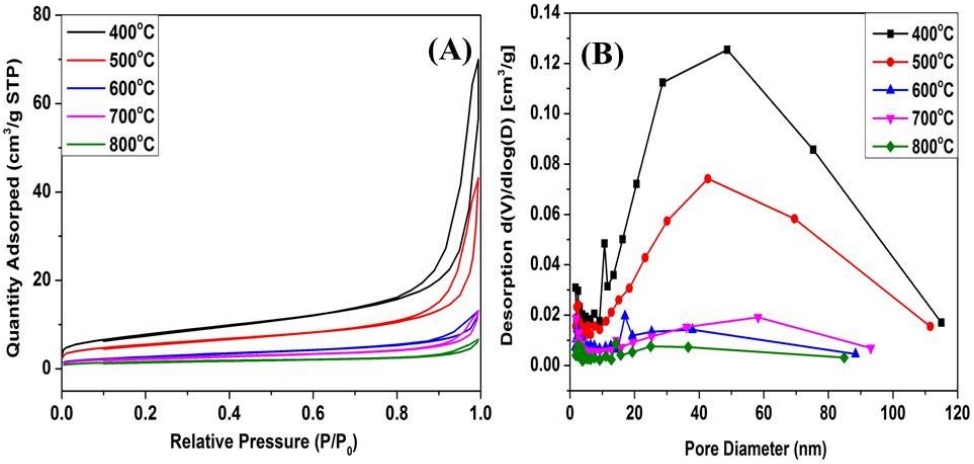

Fig S3 (A) N_2 adsorption/desorption isotherms of Mn_2O_{3NW} catalysts; (B) BJH pore distribution curves of Mn_2O_{3NW} catalysts.

Table S1 Porosity of Mn_2O_{3NP} samples under different calcination temperatures.

Calcination temperature(^oC)	S_{BET}[a] (m^2/g)	Pore volume[b] (cm^3/g)	Average pore diameter[c] (nm)
400	11.9	0.068	22.1
500	7.1	0.030	21.9
600	6.5	0.016	12.3
700	4.6	0.008	9.0
800	3.6	0.005	9.0

[a]S_{BET} (total surface area) calculated by applying the BET equation using the linear part ($0.07 < P/P_0 < 0.20$) of the adsorption isotherm. [b]Pore volume calculated using the BJH method (from desorption cumulative pore volume of pores between 1.7 and 300 nm diameter). [c]Average pore diameter calculated by 4V/A (V means total pore volume and A stands for total pore surface area) applying BJH method (desorption) .

Table S2 Porosity of Mn_2O_{3NW} samples under different calcination temperatures.

Calcination temperature(^oC)	S_{BET}[a] (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
400	27.9	0.109	15.1
500	19.6	0.068	14.1
600	10.0	0.021	7.8
700	8.4	0.021	10.6
800	5.6	0.010	8.9

[a]S_{BET} (total surface area) calculated by applying the BET equation using the linear part ($0.07 < P/P_0 < 0.25$) of the adsorption isotherm.

Table S3 Summary of activity and selectivity of Mn_2O_{3NP} catalyst in the different calcination temperature

Calcination Temperature(°C)	4-CP[a] Conversion(%)	Selectivity (%)					
		4-C-2-C[b]	P[c]	O[d]	2,6-X[e]	4-C-2,6-X[f]	Others
400	51.2	43.9	19.4	13.3	11.0	4.8	7.6
500	45.0	54.0	11.1	17.3	6.4	6.2	5.0
600	27.2	56.1	10.7	16.2	6.2	6.1	4.7
700	21.1	57.4	10.2	17.4	5.8	5.1	4.1
800	13.5	55.9	11.5	17.0	5.4	6.1	4.1

a: 4-chlorophenol; b: 4-chloro-2-cresol; c: phenol; d: 2-cresol; e: 2,6-xylenol; f: 4-chloro-2,6-xylenol; Others are stand for 2,4-xylenol and 2,4,6-trimethylphenol.

Reaction conditions: catalyst, 0.5 g; reaction temperature= 390 °C; n(methanol)/n(4-chlorophenol)=10:1; LHSV=0.75 h^{-1}; P=101 kPa; nitrogen flow rate= 3.5 mL/min; reaction time= 2~3 h.

Table S4 Summary of activity and selectivity of Mn_2O_{3NW} catalyst in the different calcination temperature

Calcination Temperature(°C)	4-CP Conversion(%)	Selectivity (%)					
		4-C-2-C	P	O	2,6-X	4-C-2,6-X	Others
400	53.7	52.8	11.9	16.0	7.8	6.5	5.0
500	51.2	51.2	13.0	16.4	7.1	6.7	5.6
600	33.7	53.2	11.7	17.2	6.9	6.1	4.9
700	27.4	50.5	12.2	17.3	7.5	6.2	6.3
800	25.0	52.1	12.8	16.8	6.5	6.0	5.8

Reaction conditions: catalyst, 0.5 g; reaction temperature= 390 °C; n(methanol)/n(4-chlorophenol)=10:1; LHSV=0.75 h^{-1}; P=101 kPa; nitrogen flow rate= 3.5 mL/min; reaction time= 2~3 h.

Table S5 Summary of activity and selectivity of Mn_2O_{3NP} catalyst in the different reaction temperature

Reaction Temperature(°C)	4-CP Conversion(%)	Selectivity (%)					
		4-C-2-C	P	O	2,6-X	4-C-2,6-X	Others
350	28.3	63.6	5.7	16.1	4.9	6.5	3.2
370	42.1	59.6	8.1	17.1	5.6	6.3	3.3
390	45.0	54.0	11.1	17.3	6.4	6.2	5.0
410	48.7	45.8	16.6	18.8	7.1	5.8	5.9
430	59.3	35.6	19.1	26.1	7.6	4.4	7.2
450	53.7	24.2	21.9	34.3	8.9	3.1	7.6

Reaction conditions: catalyst, 0.5 g; calcination temperature of catalyst: 500 °C; n(methanol)/n(4-chlorophenol)=10:1; LHSV=0.75 h^{-1}; P=101 kPa; nitrogen flow rate= 3.5 mL/min; reaction time= 2~3 h.

Table S6 Summary of activity and selectivity of Mn_2O_{3NW} catalyst in the different reaction temperature

Reaction Temperature(°C)	4-CP Conversion(%)	Selectivity (%)					
		4-C-2-C	P	O	2,6-X	4-C-2,6-X	Others
350	24.4	61.6	8.5	13.4	7.4	6.9	2.2
370	37.7	57.6	9.9	14.2	7.4	6.5	4.4
390	53.7	52.8	11.9	16.0	7.8	6.5	5.0
410	56.4	50.9	13.6	17.5	8.5	4.1	5.4
430	63.3	39.1	20.0	23.2	9.8	2.2	5.7
450	74.9	18.7	29.5	31.7	13.3	0.4	6.4

Reaction conditions: catalyst, 0.5 g; calcination temperature of catalyst: 400 °C; n(methanol)/n(4-chlorophenol)=10:1; LHSV=0.75 h^{-1}; P=101 kPa; nitrogen flow rate= 3.5 mL/min; reaction time= 2~3 h.

Table S7 Summary of activity and selectivity of Mn_2O_{3NP} catalyst in different 4-chlorophenol/methanol molar ratio

4-chlorophenol : methanol	4-CP Conversion(%)	Selectivity (%)					
		4-C-2-C	P	O	2,6-X	4-C-2,6-X	Others
1:1	21.2	44.4	29.2	18.3	4.6	1.4	2.1
1:2	28.5	51.0	21.0	18.6	5.1	1.9	2.4
1:5	39.8	52.0	16.1	18.5	6.1	4.1	3.2
1:10	45.0	54.0	11.1	17.3	6.4	6.2	5.0
1:20	67.3	43.3	5.3	17.4	14.8	13.7	5.5

Reaction conditions: catalyst, 0.5 g; calcination temperature of catalyst: 500 ^oC; reaction temperature= 390 ^oC; LHSV=0.75 h^{-1}; P=101 kPa; nitrogen flow rate= 3.5 mL/min; reaction time= 2~3 h.

Table S8 Summary of activity and selectivity of Mn_2O_{3NW} catalyst in different 4-chlorophenol/methanol molar ratio

4-chlorophenol : methanol	4-CP Conversion(%)	Selectivity (%)					
		4-C-2-C	P	O	2,6-X	4-C-2,6-X	Others
1:1	22.7	31.9	41.5	18.7	4.8	1.0	2.1
1:2	43.9	39.8	31.6	18.1	6.9	1.2	2.4
1:5	47.0	44.5	22.5	18.2	7.7	2.4	4.7
1:10	56.4	50.9	13.6	17.5	8.5	4.1	5.4
1:20	65.3	50.6	7.6	17.5	11.6	5.1	7.6

Reaction conditions: catalyst, 0.5 g; calcination temperature of catalyst: 400 ^oC; reaction temperature= 410 ^oC; LHSV=0.75 h^{-1}; P=101 kPa; nitrogen flow rate= 3.5 mL/min; reaction time= 2~3 h.

Table S9 Summary of activity and selectivity of Mn_2O_{3NP} catalyst in different liquid hourly space velocity (LHSV)

LHSV	4-CP	Selectivity (%)					
(h^{-1})	Conversion(%)	4-C-2-C	P	O	2,6-X	4-C-2,6-X	Others
0.75	45.0	54.0	11.1	17.3	6.4	6.2	5.0
1.50	36.6	54.7	11.9	17.0	6.4	5.9	4.1
2.25	24.6	60.0	12.2	16.5	5.6	3.1	2.6
3.00	15.5	60.9	13.0	16.7	4.3	3.0	2.1
3.75	13.0	59.8	17.8	17.1	2.2	2.1	1.0
4.50	10.9	59.8	19.7	16.7	1.5	1.2	1.1

Reaction conditions: catalyst, 0.5 g; calcination temperature of catalyst: 500 ^oC; reaction temperature= 390 ^oC; n(methanol)/n(4-chlorophenol)=10:1; P=101 kPa; nitrogen flow rate= 3.5 mL/min; reaction time= 2~3 h.

Table S10 Summary of activity and selectivity of Mn_2O_{3NW} catalyst in different liquid hourly space velocity

LHSV	4-CP	Selectivity (%)					
(h^{-1})	Conversion(%)	4-C-2-C	P	O	2,6-X	4-C-2,6-X	Others
0.75	56.4	50.9	13.6	17.5	8.5	4.1	5.4
1.50	54.0	51.7	14.3	17.2	8.3	3.6	4.9
2.25	56.8	52.8	14.7	17.7	7.2	3.3	4.3
3.00	34.6	54.7	16.5	16.6	6.3	2.1	3.8
3.75	30.1	56.8	18.6	16.1	4.9	1.7	1.9
4.50	21.2	57.8	20.7	16.5	2.3	1.3	1.4

Reaction conditions: catalyst, 0.5g; calcination temperature of catalyst: 400 ^oC; reaction temperature= 410 ^oC; n(methanol)/n(4-chlorophenol)=10:1; P=101 kPa; nitrogen flow rate= 3.5 mL/min; reaction time= 2~3 h.

Table S11 Vapor-phase methylation of 4-chlorophenol under different conditions.

Different	4-CP	Selectivity (%)					
Conditions:	Conversion(%)	4-C-2-C	P	O	2,6-X	4-C-2,6-X	Others
1	0.3	90.8	0	0	0	9.2	0
2	0.3	49.5	50.5	0	0	0	0
3	40.6	51.1	6.6	18.6	10.6	6.2	6.9
4	14.3	53.5	3.8	10.5	13.6	12.5	6.1
5	45.3	60.5	7.8	10.7	6.7	10.5	3.8
6	58.1	65.5	5.3	9.6	5.1	11.4	3.1

Reaction conditions: catalyst, 0.5 g; calcination temperature of catalyst: Mn_2O_{3NP}, 500 ^oC; Mn_2O_{3NW}, 400 ^oC； reaction temperature= 390 ^oC; n(methanol)/n(4-chlorophenol)=10:1; P=101 kPa; carrier gas flow rate= 3.5 mL/min; reaction time= 2~3 h.

Specific details of different conditions:

1. Reaction without catalyst.
2. Reaction without catalyst and 10% H_2/Ar mixture as carrier gas.
3. Mn_2O_{3NP} as catalyst and 10% H_2/Ar mixture as carrier gas.
4. Mn_2O_{3NW} as catalyst and 10% H_2/Ar mixture as carrier gas.
5. Mn_2O_{3NP} as catalyst , the formalin solution as methylation reagent (traces of methanol) and nitrogen as carrier gas.
6. Mn_2O_{3NW} as catalyst , the formalin solution as methylation reagent (traces of methanol) and nitrogen as carrier gas.