Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Size effect of $Co_xMn_{1-x}O$ precursor for Fischer-Tropsch to olefins over Co_2C-based catalysts

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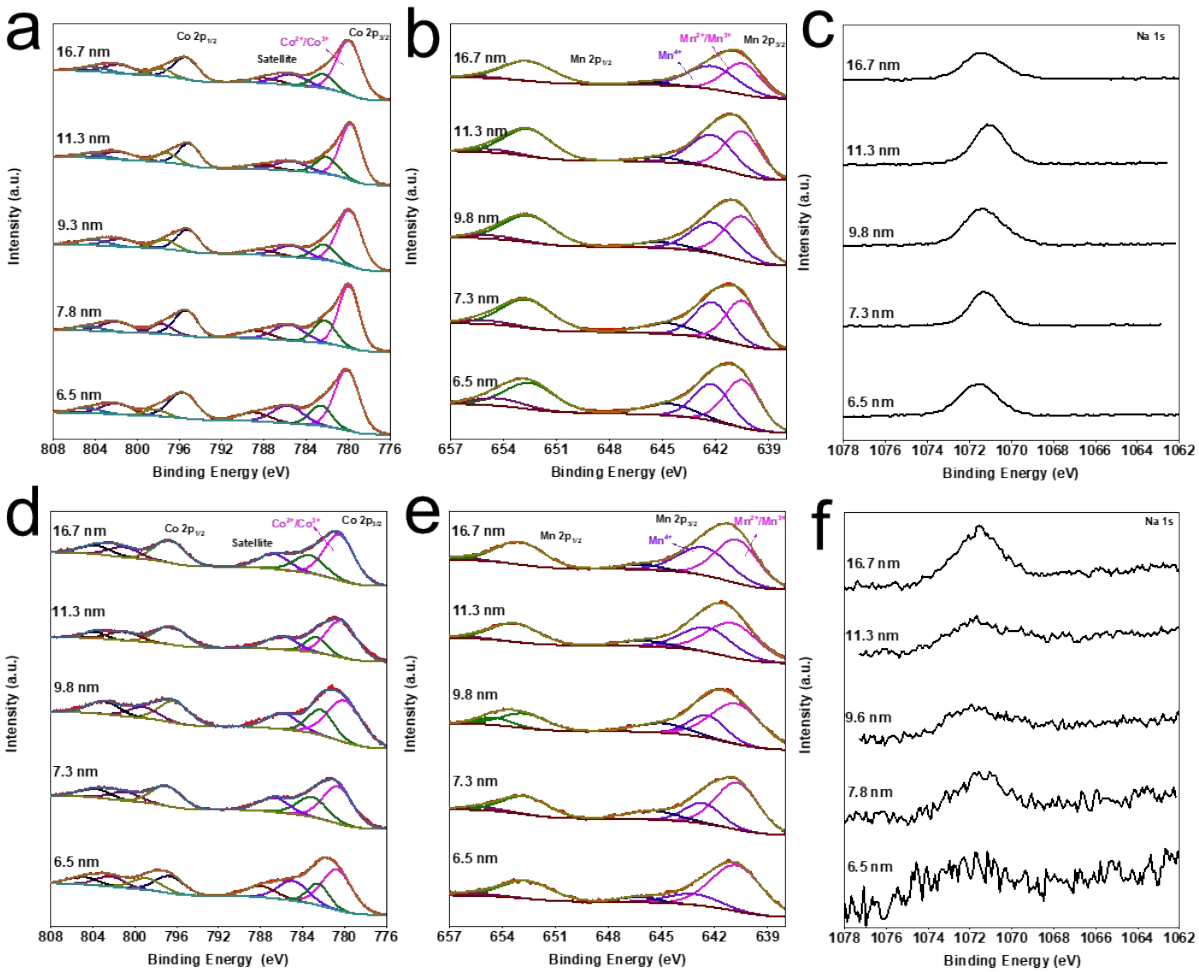

Fig. S1 Co 2p, Mn 2p and Na 1s XPS spectra of $Co_xMn_{1-x}O$ with different size (a, b and c reduced at 300 °C in 10%H_2/Ar atmosphere for 5 h; d, e and f spent at 250 °C, 5 bar, 2000 h^{-1} and a H_2/CO ratio of 0.5).

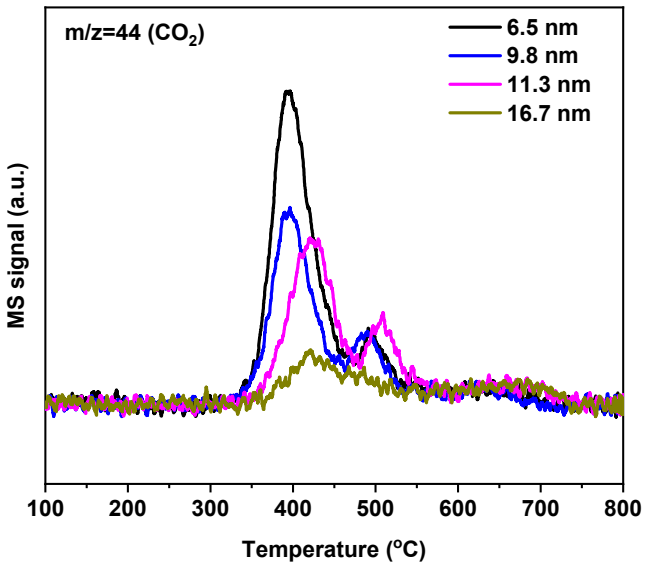

Fig. S2 MS signal of CO_2 during TPSR test over CO pre-absorbed $Co_xMn_{1-x}O$ samples under 5% H_2/Ar flow.

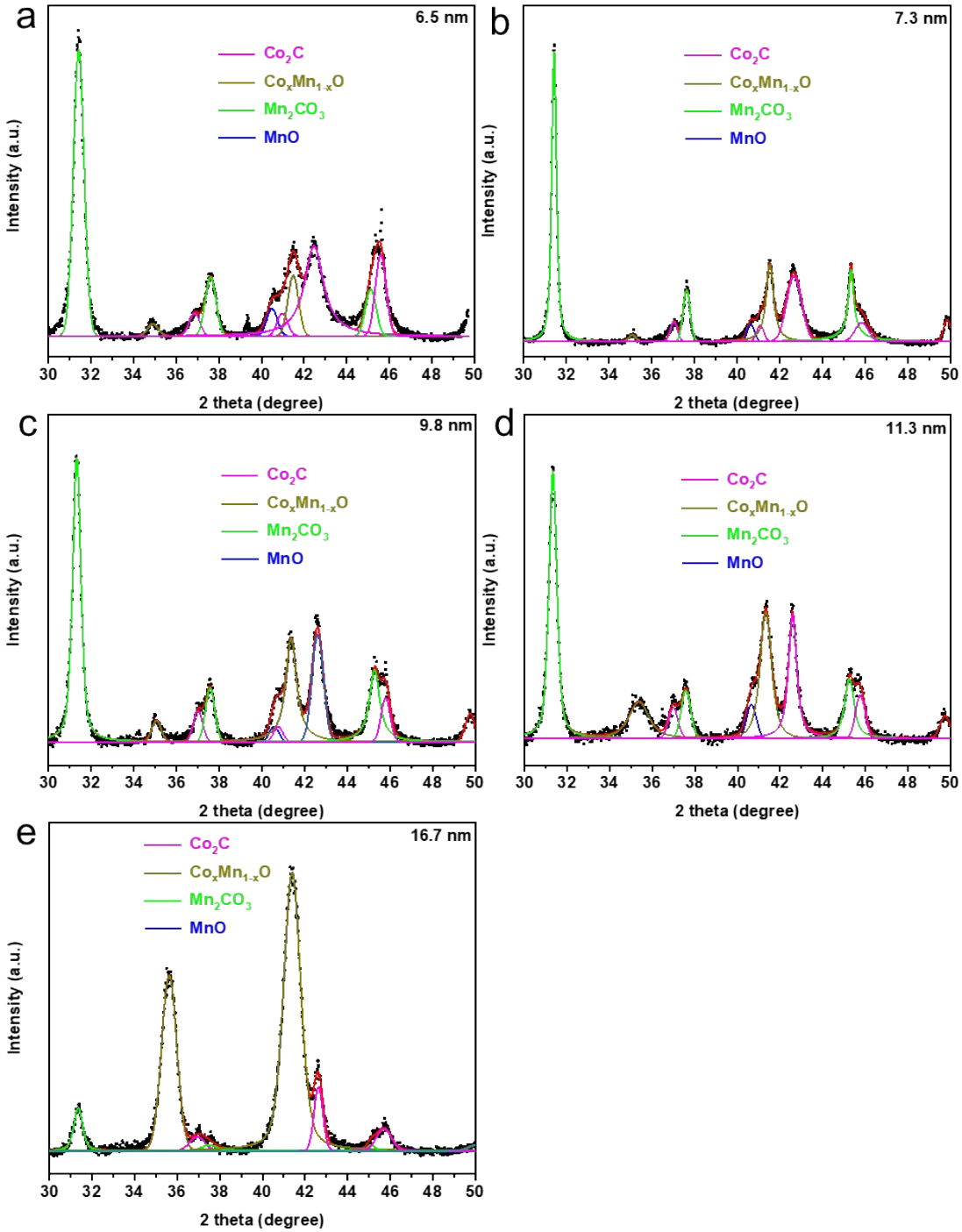

Fig. S3 Peak fitting results of various spent catalysts (a, CM-80; b, CM-300; c, CM-400; d, CM-500; e, CM-600).

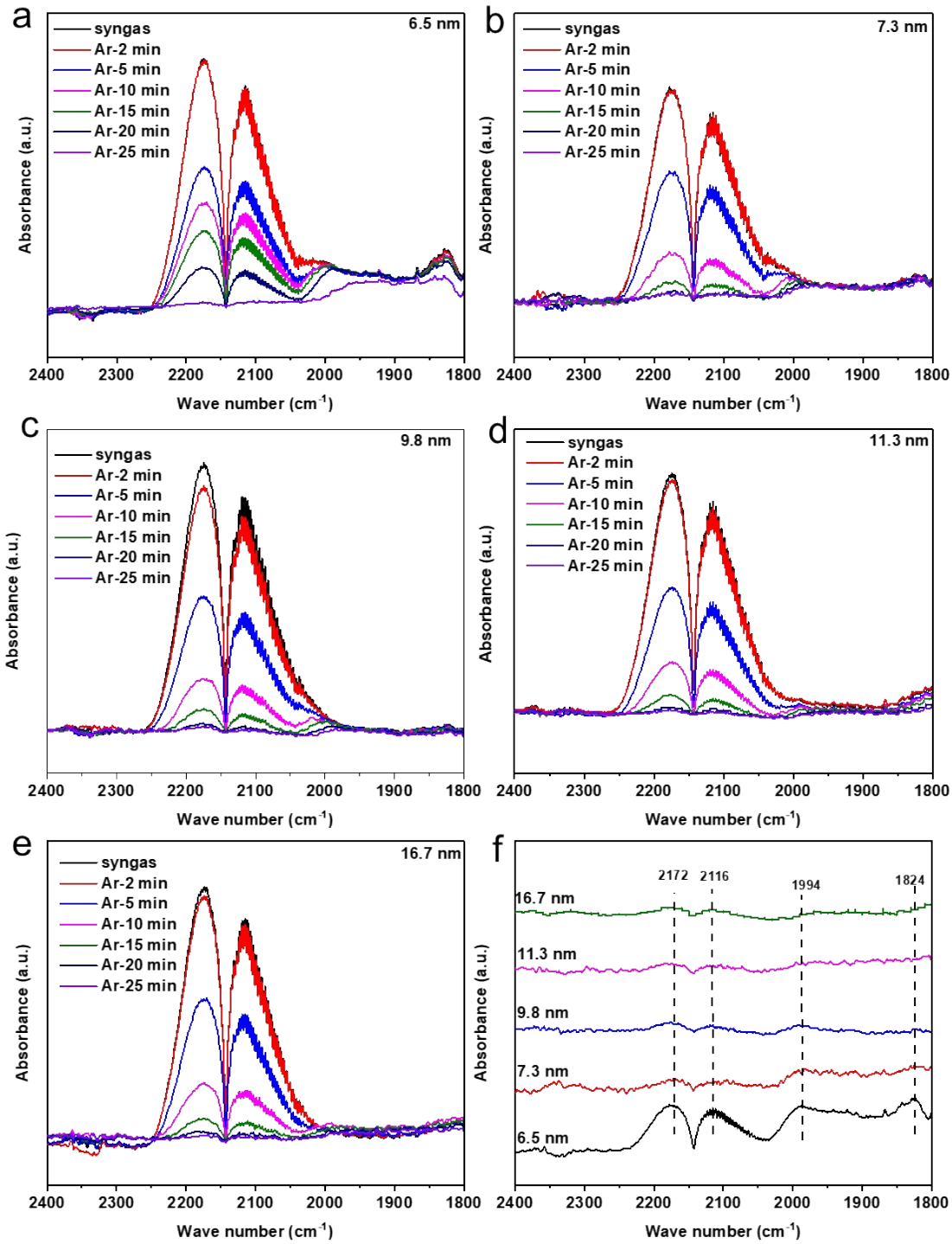

Fig. S4 DRIFTS spectra of various spent samples under syngas (H_2/CO=1) and Ar in the region of 2400-1800 cm^{-1} at 250 ^oC (a, CM-80; b, CM-300; c, CM-400; d, CM-500; e, CM-600) and comparison after flushing with Ar for 20 min (f).

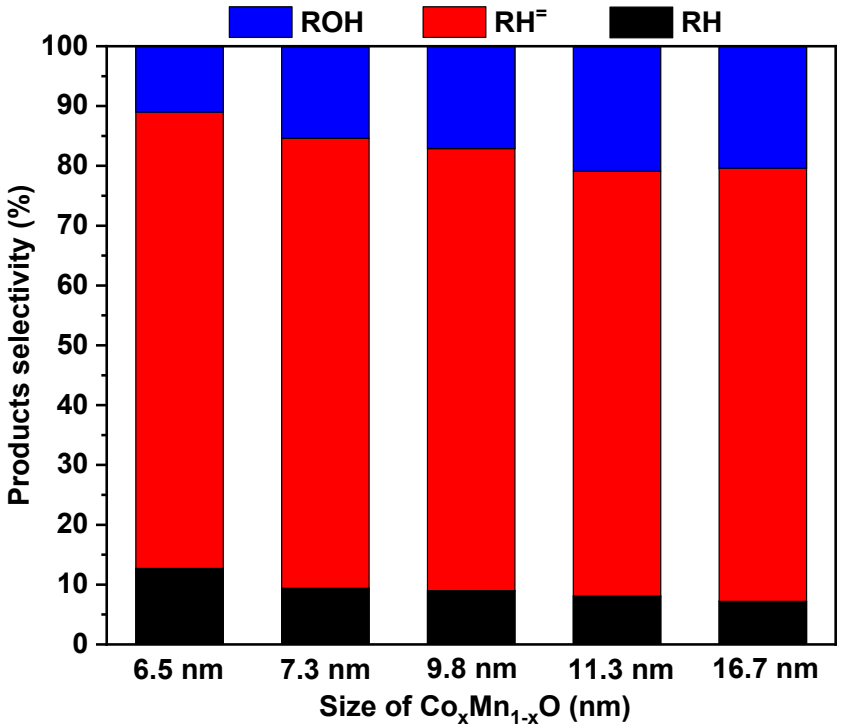

Fig. S5 Products distribution for the catalysts from $Co_xMn_{1-x}O$ precursors with different size at similar CO conversion of ca. 12% via changing space velocity.

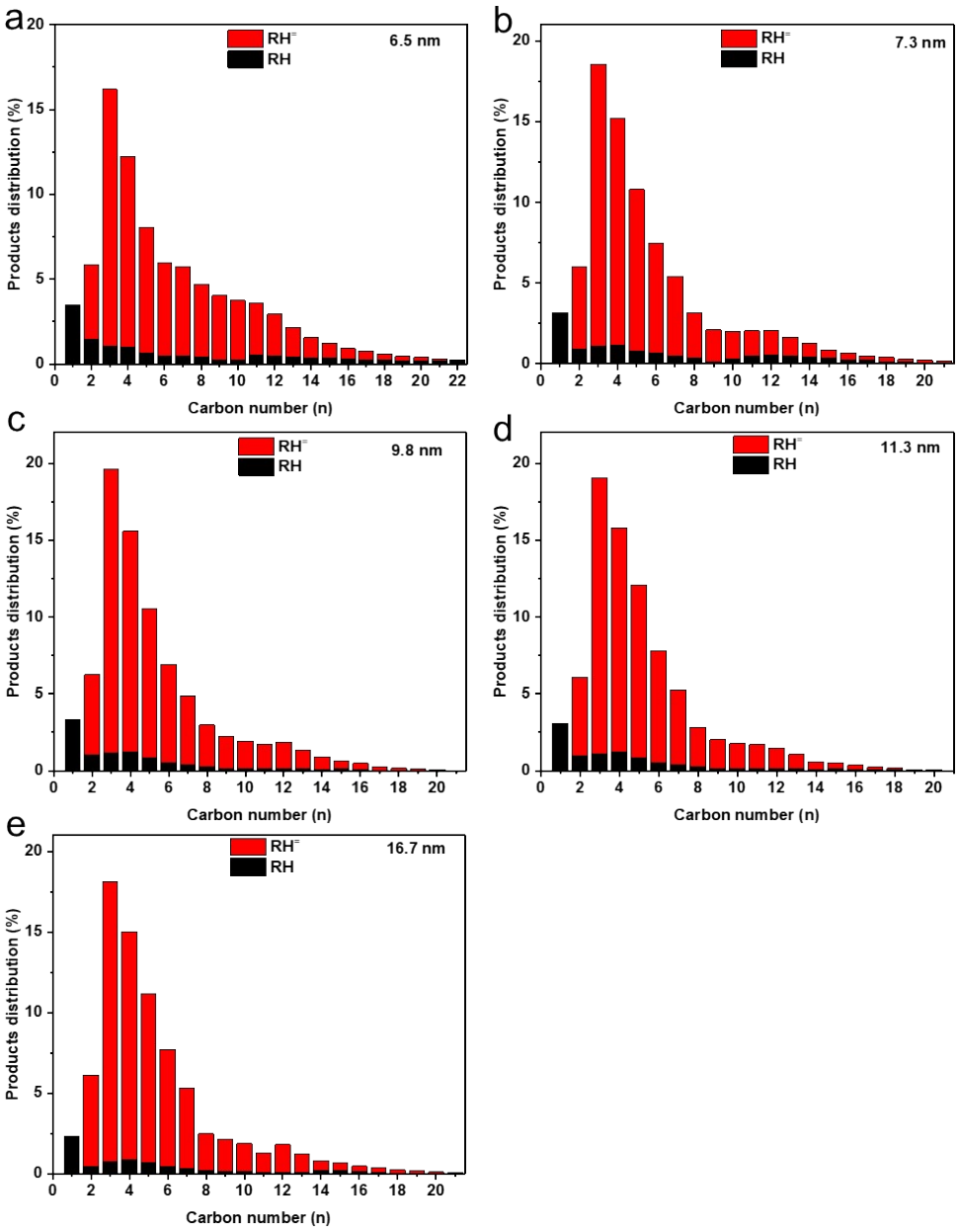

Fig. S6 Detailed hydrocarbons distribution for the catalysts derived from $Co_xMn_{1-x}O$ precursors with different size.

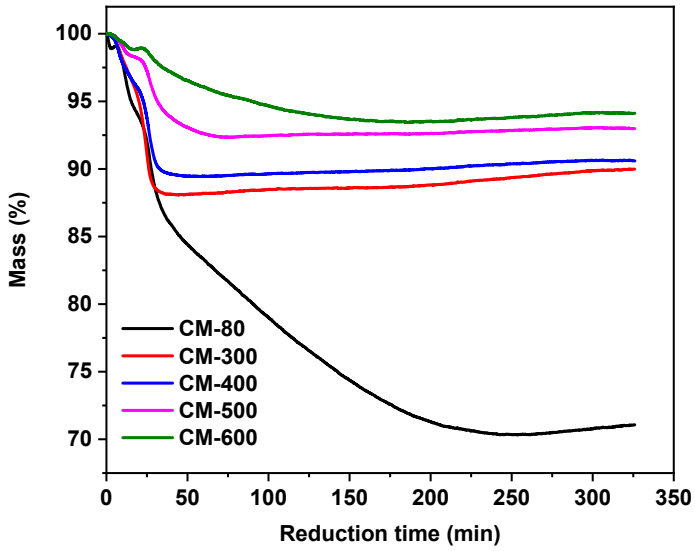

Fig. S7 Thermogravimetric weight loss curve of CoMn samples under reduction conditions (300 ℃, 10%H_2/N_2, 5h).

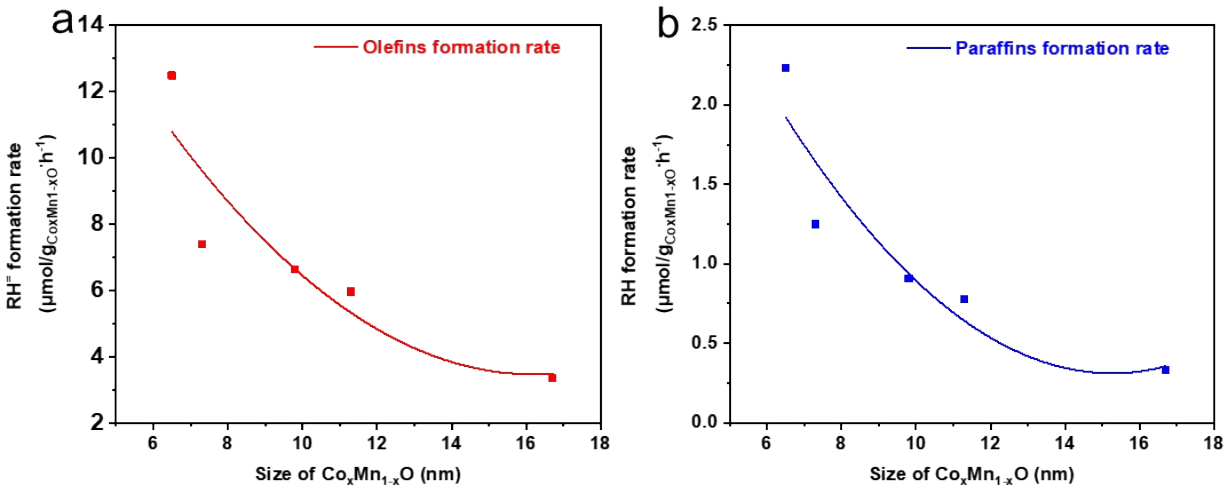

Fig. S8 Olefins formation rate (a) and paraffins formation rate (b) for the catalysts from $Co_xMn_{1-x}O$ precursors with different size.

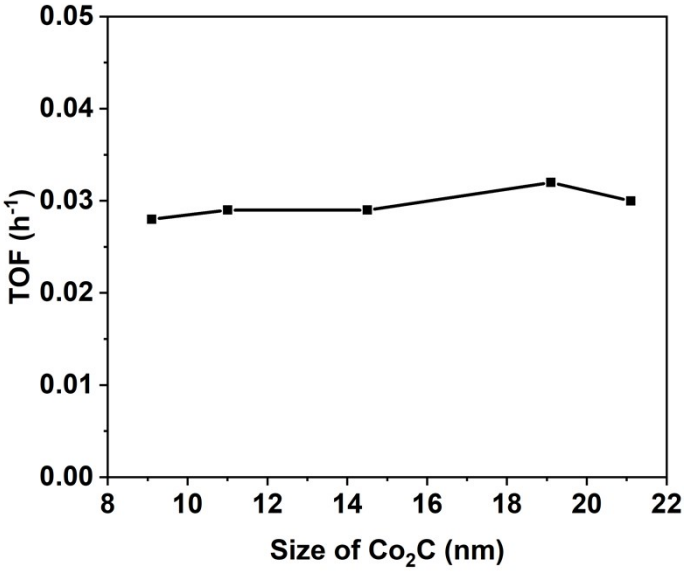

Fig. S9 TOF as a function of the Co_2C particle size.

Table. S1 Phase content and size in spent samples from $Co_xMn_{1-x}O$ precursors with different size.

Size of $Co_xMn_{1-x}O$ (nm)	Relative carbonization rate	Phase content (wt%) [a]		Size of Co_2C (nm) [a]
		$Co_xMn_{1-x}O$	Co_2C	
6.5	4.31	9.6	35.4	9.1
7.3	3.69	11.2	29.0	11.0
9.8	2.83	13.5	26.2	14.5
11.3	2.32	20.3	23.2	19.1
16.7	1.00	76.7	13.2	21.4

[a] measured by XRD.

Table. S2 Catalytic performances of various catalysts from $Co_xMn_{1-x}O$ precursors with different size [a].

Size of $Co_xMn_{1-x}O$	WHGS	CO conv.	CO_2 sele.	Product selectivity (C%, CO_2 free)				Olefin/paraffin ratio			
(nm)	(mL/h/g_{cat})	(C%)	(C%)	$RH^{=}$ [b]	ROH [c]	$RH^{=}$+ROH	RH [d](CH_4) [e]	C_2	C_3	C_4	C_{2-4}
6.5	2000	39.9	48.1	72.2	14.9	87.1	12.9 (3.5)	3.0	14.3	11.6	8.8
	5000	12.7	49.0	76.3	11.0	87.3	12.7 (3.4)	5.8	16.9	12.6	11.7
7.3	2000	30.1	48.4	72.0	15.9	87.9	12.2 (3.2)	5.7	16.1	12.3	11.7
	4000	13.4	51.3	75.2	15.3	90.6	9.4 (3.2)	7.5	17.7	12.7	13.2
9.8	2000	27.9	49.7	72.1	18.1	90.1	9.9 (3.3)	5.2	15.9	11.8	11.2
	4000	12.9	49.6	73.9	17.1	91.0	9.0 (2.9)	8.9	17.6	12.3	13.5
11.3	2000	24.1	47.0	72.7	17.8	90.5	9.5 (3.1)	5.4	16.0	12.2	11.5
	4000	10.1	46.7	71.0	20.8	91.9	8.1 (2.7)	8.5	19.2	13.6	14.4
16.7	2000	13.3	44.9	72.4	20.4	92.8	7.2 (2.3)	12.5	22.9	16.1	17.8

[a] Reaction conditions: 250 °C, 5 bar, H_2/CO=0.5. [b] $RH^{=}$ denotes olefins. [c] ROH denotes oxygenates. [d] RH denotes paraffins. [e] CH_4 denotes methane.

Table. S3 Comparison of catalysts for the direct production of olefins from syngas.

Catalysts	H_2/CO	Temperature (°C)	Pressure (MPa)	WHGS (mL/h/g_{cat})	CO conv. (%)	CO_2 sele. (%)	Products Selectivity (free-CO_2, %)		Ref.
							$RH^=$	CH_4	
$Co_xMn_{1-x}O$	0.5	250	0.5	2000	39.9	48.1	72.2	3.5	this work
CoMn	0.5	250	0.5	2000	23.6	48.0	41.2[a]	4.7	***1***
CoMn/CNT	0.5	265	0.5	2000	12.8	46.1	66.6	2.4	***2***
CoMn-Na_2S	2.0	240	0.5	-	21.0	5.0	27.0[a, b]	6.0	***3***
FeMn@Si	2.0	320	3.0	4000	56.1	13.0	75.0[b]	9.5	***4***
FeMn-Li/CNT	1.0	300	1.0	3000	15.7	39.4	46.0[a]	23.8	***5***
$ZnCrO_x$/SAPO	1.5	400	2.5	7714	17.0	45.0	80.0[a]	2.0	***6***
$ZnZrO_x$/SAPO	2.0	400	1.0	3600	11.0	45	77.0[a]	4.0	***7***

[a] Light olefins ($C_{2-4}^=$); [b] Olefins selectivity in products containing CO_2.

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