# **Supporting Information**

# Role of an intermediate $Co_xMn_{1-x}O$ (x=0.6-0.85) nanocrystals in the formation of active species for the direct production of lower

# olefins from syngas

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## Experimental

## 1. Preparation of the catalysts

Synthesis of CoMn(HT) and CoMn(LT): The samples were prepared using urea and glucose as precursors via an in-situ self-assembly process. 3.0 g of glucose was mixed with 5.0 g of urea at 120 °C, forming a transplant solution. Then, 1.34 g of 50%  $Mn(NO_3)_2$  solution, 2.18 g of Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (Co/Mn=2) , 0.018 g of NaNO<sub>3</sub> were added into the above solution. The resulting compounds were melted to homogenous liquid phase after stirring for 10 min. After drying at 180 °C for 24 h, a black solid was obtained. The CoMn(HT) nanocomposites were obtained from the above black solid calcined at 650 °C for 2 hours in N<sub>2</sub>, then at 300 °C for 3 hours in air. The CoMn(LT) nanocomposites were obtained from by calcining the above black solid at 300 °C for 3 hours in air. CoMn(HT) reduced in H<sub>2</sub> at 300°C was designated as CoMn(LT)-R250 and CoMn(LT)-R300 respectively. CoMn(HT) and CoMn(LT) after 100h reaction were designated CoMn(HT)-Used and CoMn(LT)-Used.

### 2. Characterizations

Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 powder diffractometer using Cu-K $\alpha$  radiation operated at 40 kV and 40 mA and a Vantec-1 detector. The size and morphology of samples were determined using a FEI Tecnai G20 transmission electron microscope (TEM) operated at 200 kV and SU8000 field emission scanning electron microscope (FESEM, Hitachi, Japan) at an accelerating voltage of 15 kV. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a VG Multilab 2000 (VG Inc.) photoelectron spectrometer using Al K $\alpha$  radiation as the excitation source under vacuum at 2 × 10–6 Pa. All the binding energy (BE) values were calibrated by the C 1s peak at 284.6 eV of the surface adventitious carbon. Thermogravimetric analysis (TGA) was carried out on a NETZSCH TG 209F3 instrument. About 10 mg of the samples was placed in a ceramic crucible and heated from 30 to 900 °C at 10 °C/min in air at a flow rate of 50 mL/min. The physical properties including pore volume, specific surface area and pore size were

measured by Nitrogen physical sorption with an ASAP-2020 Micromeritics instrument at liquid nitrogen temperature.

H<sub>2</sub>-temperature programmed reduction (H<sub>2</sub>-TPR) measurements were performed in a Zeton Altamira AMI-200 unit. Prior to the H<sub>2</sub>-TPR measurements, the sample (0.05 g) was first purged with Ar (30 mL/min) at 150 °C for 1 h, and then cooled down to 50 °C. Subsequently, the gas was switched to 10% H<sub>2</sub>/Ar (30 mL/min). Then, the temperature was increased to 800 °C at a rate of 10 °C/min and held at 800 °C for 30 min. The H<sub>2</sub> consumption was monitored by a TCD detector.

#### 3. Catalytic test

Fischer-Tropsch synthesis was performed in a fixed-bed reactor (stainless steel, I.D.=12 mm). Typically, 0.3 g catalyst was diluted with 3 g of inert SiC pellets. Prior to reaction test, the catalyst was reduced in pure H<sub>2</sub> at 300 °C for 5 h. After reduction, the catalyst was cooled to 100 °C in H<sub>2</sub>. Then, after the syngas (H<sub>2</sub>/CO=2) was introduced, the temperature was slowly increased (1 °C/min) to the target reaction temperature, 250 °C. During reaction, outlet gas composition including H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub> etc. were measured online by Agilent GC7890B equipped with molecular sieves, Plot-Q and Al<sub>2</sub>O<sub>3</sub> capillary columns. The oil and water products were collected in a cold trap (271 K). These products were separated into different fractions (oil and aqueous) for quantification. The oil was analyzed by an Agilent GC6890N with a FID detector and a HP-5 column, and the aqueous fraction was analyzed by an Agilent GC4890 equipped with a FID detector and a HP-Innowax column. The product selectivity was calculated based on the carbon mass balance. The calculated carbon balance is ~95.7 % and the mass balance is ~96.2 %. The olefin/paraffin ratio was calculated from the respective chromatogram peak areas.

#### 4. Computational details

Density functional theory calculations were performed using meta-GGA M06L functional and projector-augmented wave (PAW) method as implemented in Vienna ab initio simulation package (VASP). Gaussian electron smearing scheme (sigma = 0.05

eV) was used for modeling the semi-conductor systems. Spin polarization effects was considered using plane wave energy cutoff of 400 eV and Monkhorst-Pack  $5 \times 5 \times 5$  k-point scheme. All three lattices and atoms in a p(2×2×2) supercell were fully optimized in the cubic symmetry constraint with energy (10-6 eV) and force convergences (0.02 eV/Å).



**Fig. S1** Deconvolution of XPS (a) Co 2*p* and (b) Mn 2*p* spectra of CoMn(HT) and CoMn(LT) samples.

Samples	Binding energy (eV)				$C_{2}^{3+1}$	<b>M</b> == 4+ /	
	$2p_{3/2}$		$2p_{3/2}$		$(C_{0}^{2+}+C_{0}^{3+})^{a}$	$VIII^{+}$	
	Co <sup>3+</sup>	Co <sup>2+</sup>	Mn <sup>4+</sup>	Mn <sup>3+</sup>	(00-+00-)*	(IVIII <sup>2</sup> +IVIII <sup>2</sup> ) <sup>2</sup>	
CoMn(HT)	779.6	781.2	642.9	641.1	0.53	0.51	
CoMn(LT)	779.5	781.1	643.1	641.3	0.49	0.54	

Table S1 XPS characterization results of CoMn(HT) and CoMn(LT) samples.

<sup>a</sup> Peak area ratio of  $Co^{3+}/(Co^{2+}+Co^{3+})$ .

<sup>b</sup> Peak area ratio of  $Mn^{4+}/(Mn^{3+}+Mn^{4+})$ .



Fig. S2 TG curves of CoMn(HT) and CoMn(LT) samples.



Fig. S3 Nitrogen adsorption-desorption isotherms of CoMn(HT) and CoMn(LT) samples.

Samulas	Surface area	Total pore volume	Average Pore size	
Samples	(m²/g)	$(cm^{3}/g)$	(nm)	
CoMn(HT)	50.2	0.18	5.6	
CoMn(LT)	64.9	0.41	30.6	

Table S2 Physicochemical property of the as-synthesized samples.



Fig. S4 Powder XRD patterns of CoMn(HT) and CoMn(LT).



Fig. S5 Product distribution of normal Co<sub>2</sub>C (Na 0.4% wt) and MnO.



**Fig. S6** Distribution of products according to the Anderson-Schulz-Flory (ASF) model over a) CoMn(HT)-300 catalyst, b) Co<sub>2</sub>C sphere catalyst, c) MnO catalyst.



Fig. S7 TEM images of CoMn(HT)-R300 and CoMn(LT)-R300 samples.

.11	ing to experimental results.								
	Ma doming notio	calcu	ulation	experiment					
	Min-doping ratio	lattice <sup>a</sup>	expansion	lattice <sup>b</sup>	expansion				
	0.000%	8.416	0.000%	4.253	0.000%				
	3.125%	8.431	0.178%	4.257	0.094%				
	6.250%	8.442	0.309%	4.277	0.564%				
	9.375%	8.450	0.404%	4.312	1.387%				
	12.500%	8.455	0.463%						
	15.625%	8.467	0.606%						
	25.000%	8.477	0.725%						
	50.000%	8.581°	1.961%						

**Table S3** Calculation of the lattice (Å) and its expansion (%) of CoO with different Mn-doping ratio referring to experimental results.

<sup>a</sup> A p(2×2×2) supercell is used for the calculation; <sup>b</sup> the experimental lattice obtained according to the XRD is averaged over all diffraction peaks; <sup>c</sup> average result is given because the optimized unit cell is not cubic for Co<sub>0.50</sub>Mn<sub>0.50</sub>O (a = c = 8.545 Å, b = 8.617 Å).

Catalysta	Reduction	CO Conv. –	Hydro	O/P			
Catalysis	Temp./°C		CH <sub>4</sub>	C <sub>2-4</sub> °	C <sub>2-4</sub> =	C <sub>5</sub> <sup>+</sup>	(C <sub>2-4</sub> )
CoMn(HT)	200	-	-	-	-	-	-
CoMn(HT)	250	20.7	5.0	4.0	60.8	30.2	15.2
CoMn(HT)	300	35.9	12.1	5.8	61.9	20.2	10.7
CoMn(HT)	350	25.5	4.3	2.7	27.8	65.2	10.3
CoMn(HT)	450	9.5	3.7	3.5	32.6	60.2	9.3

**Table S4** Catalytic performances of the CoMn catalysts at different reducing conditions in a fixed bed reactor. <sup>a</sup>

<sup>a</sup> Reaction Condition: P=0.1 MPa, H<sub>2</sub>/CO=2, T=250 °C, GHSV=4 SL·h<sup>-1</sup>·g<sup>-1</sup>.



Fig. S8 Powder XRD patterns of reduced CoMn(HT) catalysts with different reduced temperature.

Catalanta	Т	GHSV	СО	Hydroca	Hydrocarbon selectivity (C. %)			O/P
Catalysts	/°C	$(SL \cdot h^{-1} \cdot g^{-1})$	Conv.	CH <sub>4</sub>	C <sub>2-4</sub> °	C <sub>2-4</sub> =	$C_{5}^{+}$	(C <sub>2-4</sub> )
CoMn(HT)-R300	250	4	32.0	14.7	11.6	52.6	21.1	4.5
CoMn(HT)-R300	250	8	27.3	2.5	9.2	49.7	28.6	5.4
CoMn(LT)-R250	250	4	26.1	15.3	12.1	48.7	23.9	4.0
CoMn(LT)-R250	250	8	29.0	14.7	12.4	46.7	26.2	3.8
CoMn(HT)-R300	230	4	16.0	10.0	10.1	47.6	32.3	4.7
CoMn(HT)-R300	230	8	9.0	9.8	9.5	43.5	37.2	4.6

**Table S5** Catalytic performances of the CoMn catalysts at different reaction conditions in a fixed bed reactor. <sup>a</sup>

<sup>a</sup> Reaction Condition: P=1 MPa,  $H_2/CO=2$ 



Fig. S9 Powder XRD patterns of CoMn(HT)-R300-Used and CoMn(LT)-R300-Used.



Fig. S10 TEM and HRTEM images of CoMn(LT)-R250-Used sample.



Fig. S11 TEM images and the size distributions (inset) of a) CoMn(HT)-R300-Used, b)



CoMn(LT)-R300-Used samples.

**Fig. S12** Product distribution of Fischer-Tropsch synthesis over CoMn(HT) catalysts. Reaction condition: P = 0.1 MPa, T = 250 °C,  $H_2/CO = 1$ , GHSV = 4 SL • h<sup>-1</sup> •  $g_{cat}^{-1}$ .