

Supporting Information
**Mn-Fe nanoparticles on reduced graphene oxide catalysts for enhanced
olefins production from syngas in slurry reactor**

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1 **1 Experimental**

2 **1.1 Graphite oxide preparation**

3 Graphite oxide (GtO) was prepared by the modified Hummers method, the details of which
4 are mentioned elsewhere [1,2]. Basically 10 g of graphite powder (general purpose grade,
5 Fischer Scientific) was oxidized by the strong oxidizing mixture of 160 ml sulfuric acid (99
6 wt%), and 500 ml fuming nitric acid which was added to the graphite in a three neck round
7 bottom flask put in an ice bath, followed by 60 g potassium permanganate which was added
8 gradually over a one hour period. The mixture as purplish-brown slurry was ultrasonicated for 15
9 min and then magnetically stirred for another 15 min, this cycle was repeated 5 times. The
10 mixture was then left on magnetic stirring for 4 days to complete the oxidation stage. The
11 resulting slurry was then added to 500 g of frozen distilled water (DW) to remove acid dilution
12 heat. Afterwards H₂O₂ 70% vol was added drop wise to the stirred mixture to complete the
13 reduction of any remaining traces of KMnO₄ until all effervescence halted. The mixture was then
14 washed with concentrated HCl 35% wt thrice, then with DW thrice, each time followed by
15 settling and decantation. When the slurry would take a very long time to settle after DW washing,
16 it was more practical to use centrifugation to separate the solids whilst washing with warm (>80
17 °C) DW. When the conductivity of the supernatant was lower than 200 μS as measured by a
18 conductivity meter the washing was stopped and the slurry was introduced into Petri dishes and
19 dried, and the resulting GtO dark brown solid was stored in an air tight plastic box for later use.

20 **1.2 Fe/rGO preparation by solvothermal coprecipitation**

21 The Fe/rGO catalyst was prepared by coprecipitation method [3,4], in which 1 g of GtO was
22 reslurried by ultrasonication in 200 ml DW for 2 h, after ultrasonication a black brown

1 suspension of graphene oxide (GO) was obtained. Then $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 1.14 g (Wako
 2 chemicals) dissolved in 50 ml DW was added drop wise whilst stirring. The viscous brownish-
 3 black mixture was then allowed to homogenize for 8 h by stirring. It was then heated to 80 °C in
 4 an oil bath, then 22 ml of 80 wt % hydrazine hydrate (HH, Acros Organics) solution was added
 5 drop wise to convert GO into reduced graphene oxide (rGO) and to reduce the Fe precursor salt.
 6 The pH of the mixture increased from 2.5 to about 9.2 upon HH addition. The mixture was
 7 further refluxed at 80 °C, then filtered off and washed with distilled water to a neutral pH of 7-8
 8 then vacuum dried at 60 °C for 12 h. The dried black powder was collected at a yield of 0.7 g
 9 and stored in an air tight glass vial and labeled as Fe. The amount of Fe loading (Fe wt %) was
 10 determined by averaging three XRF measurements as shown in Table S1 and using the result (31
 11 wt %) as a basis for promoter amount calculations.

12 Table S1: XRF elemental analysis results

Catalyst	wt%				mol Mn/100 mol Fe
	C	O	Fe	Mn	
Fe	52.4	16.7	30.9	-	-
FeMn16	49.6	23.5	23.9	3.8	16
FeMn29	43.4	26.2	23.7	6.7	29

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 14 **2 Mn Promotion by Impregnation**

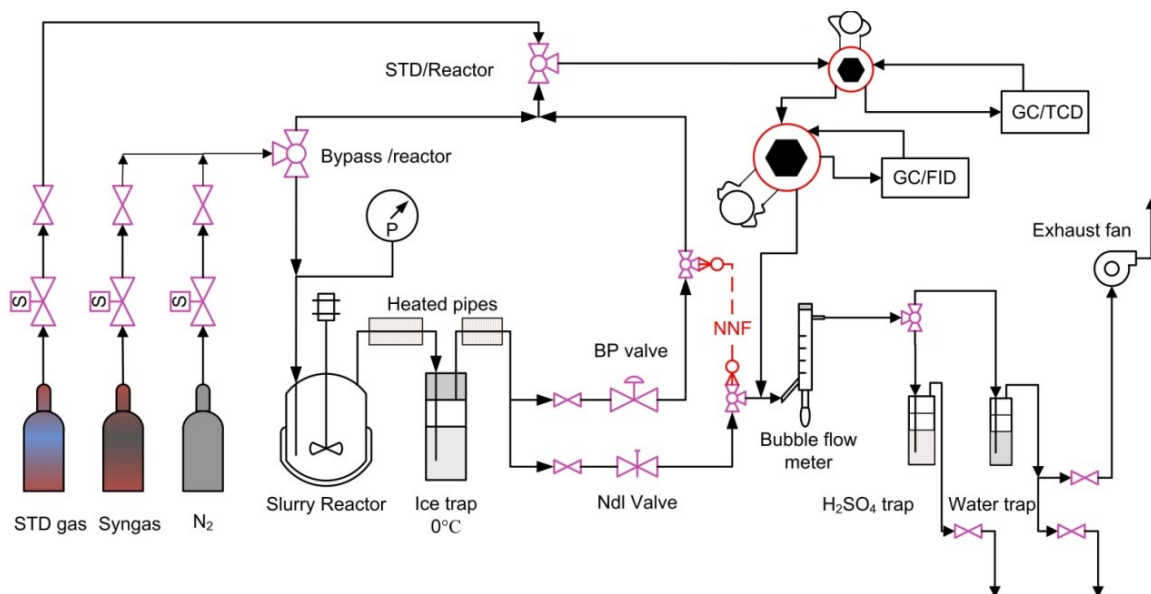
15 The Fe/rGO was decorated with Mn promoters by ultrasonic assisted impregnation. 1 g of
 16 Fe/rGO was reslurried by ultrasonication in a ceramic crucible for 30 min in a 20 ml ethanol
 17 solution of the weighed amount of promoter nitrate salt precursor $\text{MnNO}_3 \cdot 6\text{H}_2\text{O}$ (Wako
 18 chemicals). The slurry was dried by steam heating over a beaker of boiling water, then vacuum
 19 dried at 60 °C for 6 h. The resulting black powder was collected and stored in a glass vial. It was
 20 labeled FeMny where y represented the molar ratios of Mn per 100 mol Fe as calculated from the

1 XRF elemental analysis of the catalyst (for example FeMn16 indicates a molar ratio of 16 moles
2 Mn per 100 moles Fe). The XRF data of all the samples prepared are shown in Table S1.

3 **3 FTS Slurry bed reactor performance evaluation**

4 The as-prepared catalysts (1 gram) was first loaded into an offline reduction reactor, the
5 catalysts were first heated from room temperature to 300 °C in 30 min then kept at 300 °C for 3
6 h, under a flow of 50 ml/min of N₂ gas to conduct calcination of the precursor salts under inert
7 atmosphere to prevent any graphene from burning. After that the temperature was ramped up to
8 450 °C and kept constant for 16 h while the gas flow was switched to pure H₂ to reduce the
9 catalyst. After reduction and cooling to room temperature, the catalyst was passivated by
10 introducing a very slow stream of 1% vol O₂/ Ar balance gas to prevent severe oxidation of the
11 reduced catalyst on air exposure. During passivation, the temperature of the catalyst was closely
12 monitored and the temperature rise due to surface oxidation was kept at all time below 5 °C, by
13 reducing the flow of passivation gas when temperature rise was significant.

14 The passivated catalyst (0.5 gram) was then transferred to an agate mortar to which 20 ml of
15 Polyalphaolefin fluid (PAO, SpectraSyn 10 ExxonMobil) was added. Then the solid catalyst was
16 crushed thoroughly to form homogeneous black slurry. This was then transferred to a semi-batch
17 slurry bed reactor (SBR) of 80 ml internal capacity. The reactor was then operated with a feed of
18 syngas 1:1 CO:H₂ volume ratio and 2.99 vol% Ar as an internal standard. The values of
19 temperature, pressure and space velocity were adjusted before starting the run. The reactor unit
20 flow diagram is shown in Figure S1.



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Figure S1: Process flow diagram of the slurry bed reactor unit

3 The gas exiting from the reactor was first cooled in an ice trap that contains 2g n-Octane to

4 collect the condensables at this temperature. The exit gas was then analyzed by online GC/TCD

5 system (Shimadzu GC-14B) equipped with ShinCarbon column to measure Ar, CO and CH₄.

6 Then after 8 hours operation a sample of the gas was collected in a gas bag, and analyzed in

7 offline GC/FID system Shimadzu GC-14B equipped with a J&W Scientific Alumina capillary

8 column 30 m×0.53 mm, an olefin free gas sample was also collected in a gas bag after passing

9 the exit gas through a sulfuric acid trap to remove any olefins present. The liquid product

10 collected after the reaction from the ice trap was first mixed with 0.2 g of n-dodecane as external

11 standard and then analyzed in an offline GC/FID system (Shimadzu GC-2014) equipped with an

12 Agilent DB-1 column 30 m × 0.25 mm. An olefin free liquid sample was also prepared by

13 sulfuric acid treatment, separation of spent acid and neutralization by 10 wt% Na₂CO₃ solution

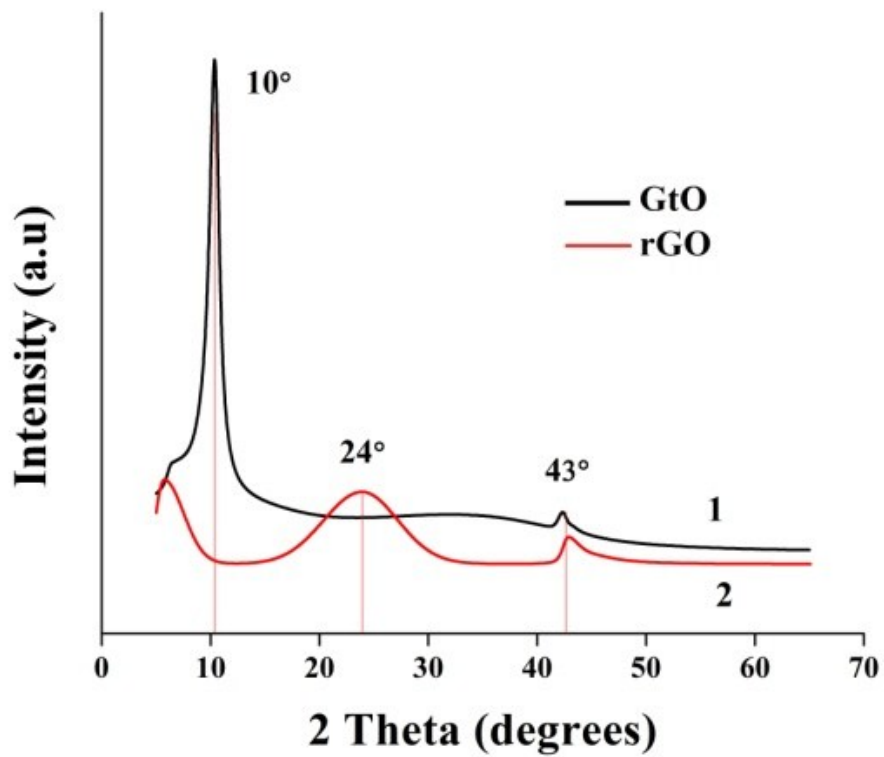
14 and analyzed by GC/FID. After the FTS reaction, the slurry phase consisting of PAO and the

15 carburized catalyst was collected in a glass bottle (150 ml) and mixed with an equal volume of n-

16 hexane to reduce its viscosity, and make it suitable for fast filtration in a Buchner vacuum

1 assembly. The filtered solid was then washed three times with n-hexane (100 ml each time) and
2 stored in glass vial for further analysis. There was no any change of catalytic activity and
3 products selectivity within six-hour reaction process. Besides that, the data of carbon balance is
4 between 90% and 100%.

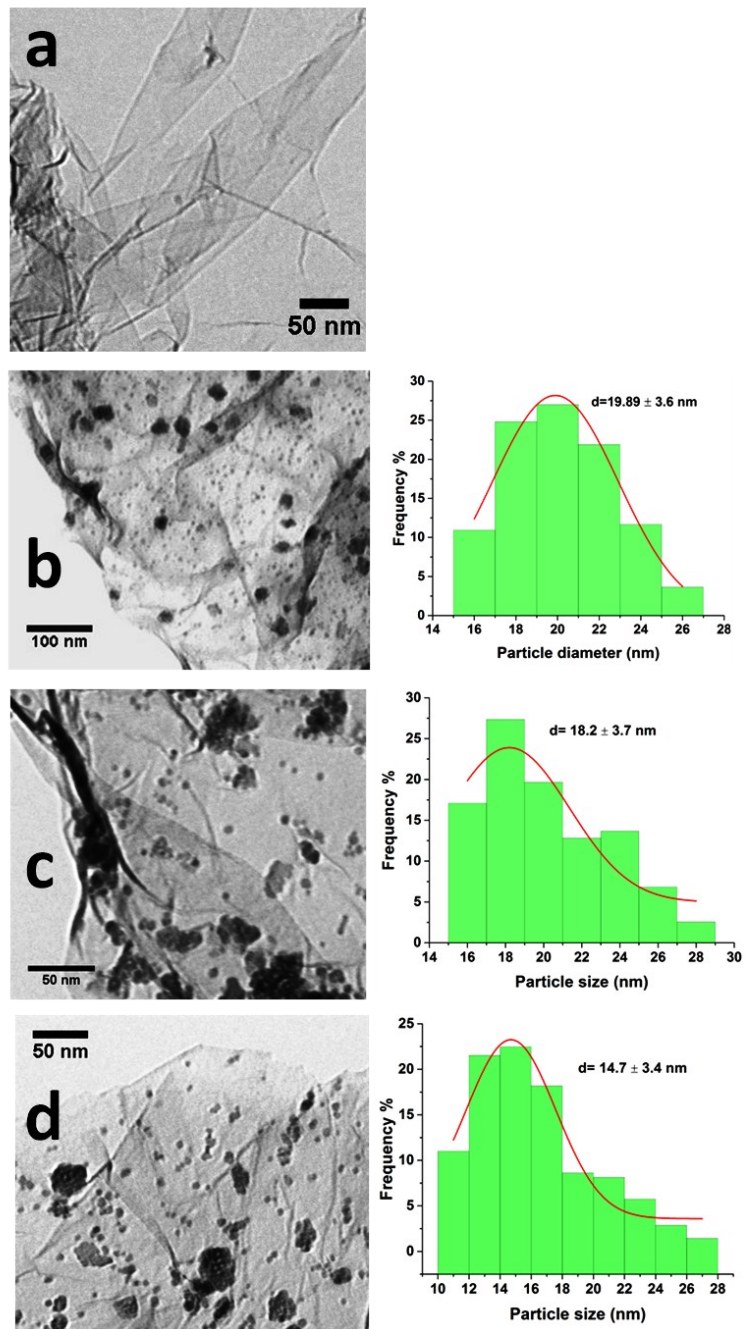
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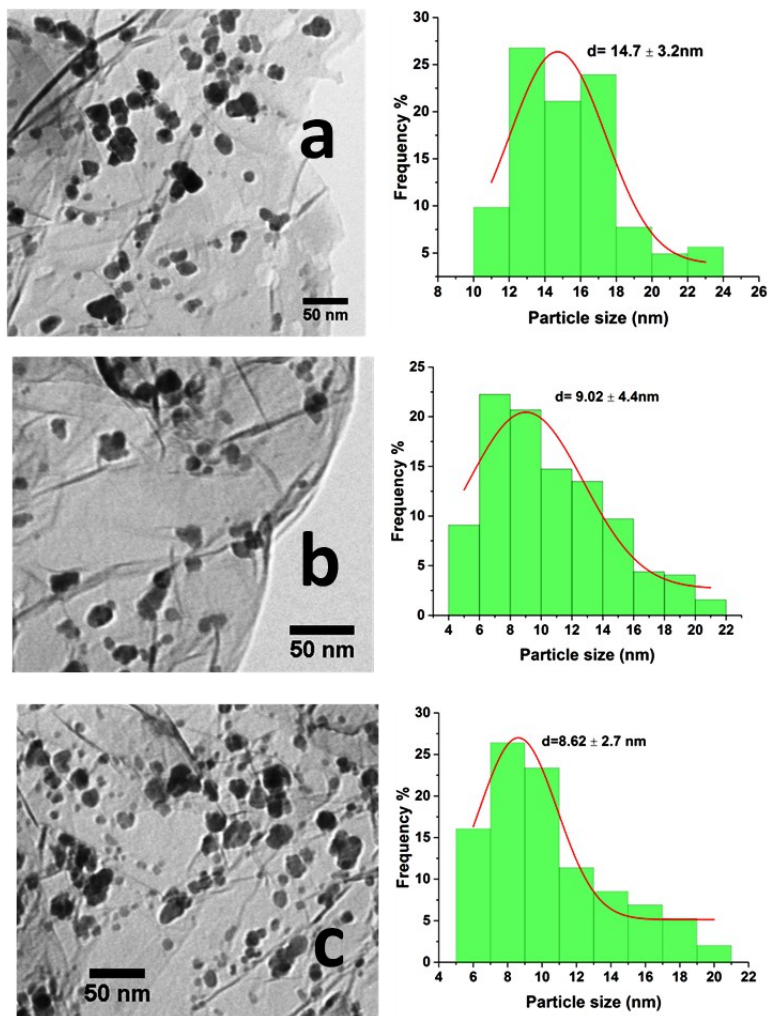
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Figure S2: XRD spectra of (1) GtO and (2) rGO



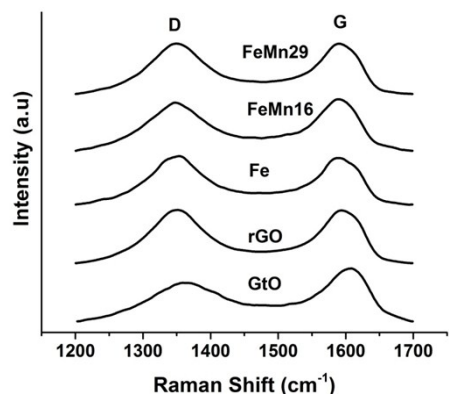
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2 Figure S3: TEM images of (a) rGO, (b) Fe as prepared, (c) calcined FeMn16, (d) calcined
 3 FeMn29; and the PSD histograms of the hematite nanoparticles.



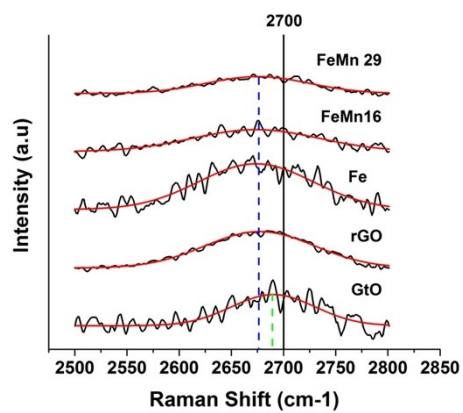
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2 Figure S4: TEM images and PSD histograms of the carburized catalysts (a) FeC, (b) FeMn16C,
 3 and (c) FeMn29C. The C stands for carburized catalysts.



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2 Figure S5: Raman D and G bands of GtO, rGO and the catalysts Fe, FeMn16, and FeMn29
3 before the FTS reaction



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2 Figure S6: The Raman 2D band peaks for GtO, rGO and the catalysts Fe, FeMn16, and FeMn29
3 before the FTS reaction

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Table S2: The effect of space velocity on the FTS reaction performance

GHSV (ml/g h)	FeMn16		
	4200	8400	12600
CO conversion %	84	73	72
Fraction	Selectivity C mol%		
CO ₂	34	34	31
CH ₄	24	23	27
C ₂₋₄ olefin	12	11	16
C ₄₋₈ olefin	9	9	8
Total olefin	21	20	24
C ₉₊ HC	5	15	9
Total Paraffin	72	67	68
Total iso	7	13	9
Total par + iso	79	80	76
O/P	0.271	0.246	0.312
Olefin yield	12	9	12
α	0.55	0.60	0.56
Reaction conditions: H ₂ /CO = 1, 340 °C, 2MPa, TOS =8h			

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Table S3: The effect of pressure on the FTS reaction performance

FeMn16		
P (MPa)	2	1
CO conversion %	84	62
Fraction	Selectivity C mol%	
CO ₂	34	25
CH ₄	24	38
C ₂₋₄ olefin	12	16
Total olefin	21	22
C ₉₊ HC	5	6
Total Paraffin	72	72
Total iso	7	6
Total par + iso	79	78
O/P	0.271	0.275
Olefin yield	12	10
α	0.55	0.49

H₂/CO=1, 340 °C, 4.2 L/g· h, TOS =8h

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Table S4: The effect of temperature on the FTS reaction performance

FeMn16				
T (°C)	340	320	300	280
CO conversion %	84	67	64	35
Fraction	Selectivity C mol%			
CO ₂	34	34	33	16
CH ₄	24	25	15	18
C ₂₋₄ olefin	12	11	25	19
Total olefin	21	20	44	31
C ₉₊ HC	5	7	6	23
Total Paraffin	72	73	49	59
Total iso	7	7	7	10
Total par + iso	79	80	56	69
O/P	0.271	0.257	0.770	0.447
Olefin yield	12	9	19	9
α	0.55	0.55	0.57	0.57

Reaction conditions: H₂/CO=1, 2 MPa, 4.2 L/g·h, TOS =8h

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1 4 References

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