Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information
Utilizing FBR to produce olefins from CO reduction using Fe-Mn nanoparticles on reduced graphene oxide catalysts and comparing the performance with SBR

AL-Hassan Nasser [1, 2*], Hamada ELnaggar [1], Ahmed AbdelMoneim [1*]

[1] Materials Science and Engineering Department, Egypt-Japan University of Science and Technology, New Borg El-Arab, Alexandria 21934, Egypt

[2] Chemical Engineering Department, Faculty of Engineering, Alexandria University, Alexandria 11432, Egypt

* Corresponding authors: codecsubzero@gmail.com; ahmed.abdelmoneim@ejust.edu.eg

1. FBR results

Table S 1: The effect of Mn loading and Temperature on the FBR FTS performance

	Fe	FeMn16	FeMn29	Fe	FeMn16	FeMn29	Fe	FeMn16	FeMn29
T (°C)	**300**			**320**			**340**		
CO conv %	43	60	33	70	93	72	82	98	91
Fraction	**Selectivity C mol%**								
CO_2	14	25	16	29	37	23	38	41	36
CH_4	31	11	10	39	8.3	12	40	17	24
C 2-4 olefin	12	23	20	6.4	20	28	2.6	22	40
C 5-9 olefin	5.8	20	25	2.7	25	28	1.1	14	14
Total olefin	18	47	55	10	49	63	3.8	40	54
C9+ HC	1.7	16	17	0.91	21	5.21	0.29	18	0.32
Total Paraffin	71	33	35	86	26	32	92	39	46
Total iso	11	19	11	4.0	25	5.8	3.8	20	2.5
Total par + iso	82	52	45	90	51	37	96	60	47
O/P	0.22	0.90	1.22	0.11	0.96	1.7	0.04	0.67	1.1
Olefin yield	6.6	21	15	4.6	29	35	1.9	23	31
α	0.55	0.71	0.75	0.51	0.77	0.66	0.42	0.71	0.48
Reaction conditions: H_2/CO = 1, 4.2 l/gh, 2MPa									

Table S 2: Effect of space velocity on the FBR FTS performance

	FeMn16		
GHSV (l/gh)	**4.2**	**6.2**	**8.2**
CO conversion %	92	93	94
Fraction	**Selectivity C mol%**		
CO_2	37	37	44
CH_4	8.3	17	23
C 2-4 olefin	20	27	30
C 5-9 olefin	25	15	14
Total olefin	49	45	46
C9+ HC	21	19	7.4
Total Paraffin	26	39	45
Total iso	25	16	8.9
Total par + iso	51	55	54
O/P	0.96	0.82	0.84
Olefin yield	29	26	24
α	0.77	0.61	0.58
Reaction conditions: H_2/CO = 1, 320°C, 2MPa			

Table S 3: Effect of pressure on the FBR FTS performance

	FeMn16	
P (MPa)	**1**	**2**
CO conversion %	84	93
Fraction	**Selectivity C mol%**	
CO_2	35	37
CH_4	18	8.3
C 2-4 olefin	30	20
C 5-9 olefin	19	25
Total olefin	52	49
C9+ HC	8.58	21
Total Paraffin	40	26
Total iso	11	25
Total par + iso	50	51
O/P	1.0	0.96
-Olefin yield	28	29
α	0.63	0.77
Reaction conditions: H_2/CO=1, 320 °C, 4.2 L/g.h		

2. Calculation scheme

The equations used to calculate the catalyst performance are summarized as follows:

For the inlet conditions the molar rate is calculated by using the Gas Law:

$$F_{0t} = \frac{\dot{V} \times P_r \times 100 \times 60}{10^6 \times 8.314 \times (T_r + 273)} \quad \frac{mol}{h}$$

At any time during the reaction the molar rate is measured by the same law but using the instantaneous flow rate as measured from the bubble flow meter:

$$F_0 or\ F = \frac{P_r \times 100 \times 10 \times 3600}{t_0 or\ t \times 10^6 \times 8.314 \times (T_r + 273)} \quad \frac{mol}{h}$$

Where P_r and T_r are the room temperature and pressure, $\dot{V}$ is the volumetric flow rate of the feed, and t is the time in s/10ml gas (bubble flow meter reading).

The product molar rates for any gas species *i* are calculated as follows utilizing the GC-TCD data:

$$F_i = \frac{F \times EAT_i \times x_i}{SAT_i} \quad \frac{C\ mol}{h} \quad i = CH_4,\ CO\ or\ CO_2,\ TCD\ Area$$

EAT_i is the TCD area for component (*i*) in the exit stream

SAT_i is the TCD area for component (*i*) in the standard gas

The TCD data is used to calculate the CO conversion from the following equation if Ar is used as an internal standard

$$f_{CO}\% = 1 - \frac{EAT_{CO}/EAT_{Ar}}{FAT_{CO}/FAT_{Ar}} \times 100$$

If an external standard is used like CO or CH_4 then the conversion can be calculated as follows

$$f_{CO}\% = 1 - \frac{F_{CO}}{y_{0\,CO}\,F_0} \times 100$$

From the gas FID data we can compute the light hydrocarbon mole rates as follows

$$FG_{N,(o/p/i/t)} = \frac{F \times AG_{N,(o/p/i/t)} \times x_{CH_4}}{SAF_{CH_4}} \frac{C\,mol}{h}$$

$FG_{N,\,(o/p/i/t)}$ is the mole rate of the component N in the exit gas stream

$AG_{N,\,(o/p/i/t)}$ is the FID peak area for component N in the gas product, it can be calculated for olefins, paraffins, iso-paraffins or for the total hydrocarbon fraction, hence the subscript (o/p/i/t).

SAF_{CH4} is the FID peak area for methane in the standard gas

x_{CH4} is the methane mol fraction in the standard gas

And from the liquid FID data the heavy hydrocarbons' molar rate is produced from the following equation

$$FL_{N,(o/p/i/t)} = \frac{AL_{N,(o/p/i/t)} \times W_{12} \times N_{12}}{A_{C12} \times M_{12} \times TOS} \frac{C\,mol}{h}$$

$FL_{N,\,(o/p/i/t)}$ is the mole rate of the component N in the liquid product.

$AL_{N,\,(o/p/i/t)}$ is the FID peak area for component N in the liquid product, it can be calculated for olefins, paraffins, iso-paraffins or for the total hydrocarbon fraction, hence the subscript (o/p/i/t).

W_{12}: is the mass of the n-dodecane external standard used for the FID area calibration.

N_{12} is the number of carbon atoms in n-dodecane

A_{C12} is the FID peak area for theC12 fraction, since the amount of n-dodecane is very big compared to the C-12fraction products in the liquid products, therefore the area can be assumed to represent n-dodecane only.

M_{12}: is the Molecular weight of n-dodecane

TOS: is the total Time On Stream

Then we can calculate the total molar rate in Cmol or mol/h of each carbon number as follows

$$F_{N,t}Cmol = FG_{N,t} + FL_{N,t} \quad \frac{Cmol}{h}$$

$$F_{N,t} = \frac{FG_{N,t} + FL_{N,t}}{N_N} \quad \frac{mol}{h}$$

N_N: is the number of carbon atoms in an alkane of chain length N

The selectivities for the hydrocarbon fractions can be computed from the following equations:

$$S\,Cmol_{N,(o/p/i/t)}\% = \frac{FG_{N,(o/p/i/t)} + FL_{N,(o/p/i/t)}}{\sum_N F_{N,t}} \quad \frac{Cmol\,HC}{Cmol\,CO\,reacted}$$

$$S\,mol_{N,(o/p/i/t)}\% = \frac{FG_{N,(o/p/i/t)} + FL_{N,(o/p/i/t)}}{\sum_N F_{N,t} \times N_N} \quad \frac{mol\,HC}{mol\,THC}$$

If the selectivity are summed up across the carbon numbers by family (paraffins or olefins or isoparaffins), then the total family selectivity can be obtained:

$$S\,Cmol_{(o/p/i)}\% = \sum_N S\,Cmol_{N,(o/p/i)}\%$$

When the total olefin selectivity is divided by the total paraffin and iso paraffins selectivity we get the olefin to paraffin ratio as follows:

$$O/P = \frac{S\,Cmol_o\%}{S\,Cmol_p\% + S\,Cmol_i\%}$$

The total carbon balance of the system must be ≤100% and is calculated as follows:

$$CB\% = \frac{\sum_N F_{N,t}\,Cmol + F_{CO_2}}{F_0 \times y_{CO} \times f_{CO}\%} \times 100$$

The hydrocarbons' molar rate is then used to calculate the mass rates according to the following equation:

$$W_N = F_{N,t} \times M_N \quad \frac{g}{h}$$

From the mass rates the ASF probability factor α can be calculated from the gradient of the plot between log (W_N/N) and (N-1) by using single variable regression.