Supporting Information

Effect of pretreatment conditions on Fe-ZSM-5 properties and performance for Fischer-Tropsch synthesis

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Table S1. CO conversion and selectivity averaged between 9-12 hours on stream of Fe-Na-ZSM-5 pretreated in H_2 or CO at temperatures ranging from 300 -770 °C.

		CO	Selectivity (%)					
Catalyst	Reduction Gas	Conversion (%)	C_2-C_4 Olefins	C_{5+}	C_2-C_4 Paraffins	CH_4	CO_2	Carbon Balance
H_2-350	H_2	10.6	19.0	14.0	13.4	22.5	31.1	97.2
H_2-450	"	9.6	21.9	17.8	15.0	19.1	26.2	97.4
H_2-550	"	8.8	24.1	26.1	5.3	19.6	24.9	98.4
H_2-770	"	3.4	28.2	25.4	3.5	20.0	22.9	99.2
CO-300	CO	10.8	21.1	17.6	8.9	37.6	14.8	98.0
CO-490	"	8.0	15.3	36.0	11.3	28.1	9.3	99.2
CO-750	"	5.5	10.0	18.8	12.3	48.8	10.1	99.0

Reaction conditions: catalyst mass = 50 mg, temperature = 300 °C, pressure = 300 psig, H_2/CO = 2, H_2 = 20 ml/min, CO = 10 ml/min, and Ar = 15 ml/min as internal standard.

Table S2. Hydrocarbon product selectivity averaged between 9-12 hours on stream of Fe-Na-ZSM-5 pretreated in H_2 or CO at temperatures ranging from 300 -770 °C.

Catalyst	Selectivity (%)												
	Ethylene	**Propylene**	**Isobutylene**	**Cis & Trans-2-butene**	**1-3-butadiene**	**Ethane**	**1-butene**	**Propane**	**Butane**	**Pentane**	**iso-pentane**	**Hexane**	**Unspecified C_{5+}**
H_2-350	3.1	9.4	0.4	1.9	4.1	7.8	-	2.9	2.6	1.1	0.2	1.0	11.7
H_2-450	4.5	10.7	0.8	4.3	1.6	6.6	-	3.4	5.1	2.5	-	1.3	14.0
H_2-550	7.2	10.2	-	5.7	0.7	2.2	0.3	1.1	2.0	5.5	0.3	2.0	18.3
H_2-770	8.8	10.9	-	7.7	0.7	1.7	0.1	1.0	0.8	10.7	0.2	3.0	11.5
CO-300	6.1	9.3	-	5.0	0.6	6.0	0.1	1.7	1.1	5.6	0.3	1.6	10.1
CO-490	1.7	7.3	0.5	1.1	4.4	5.4	0.3	2.7	3.2	3.3	0.6	1.2	30.9
CO-750	1.8	5.0	-	2.6	0.4	6.5	0.2	3.1	2.5	2.1	0.5	0.6	15.6

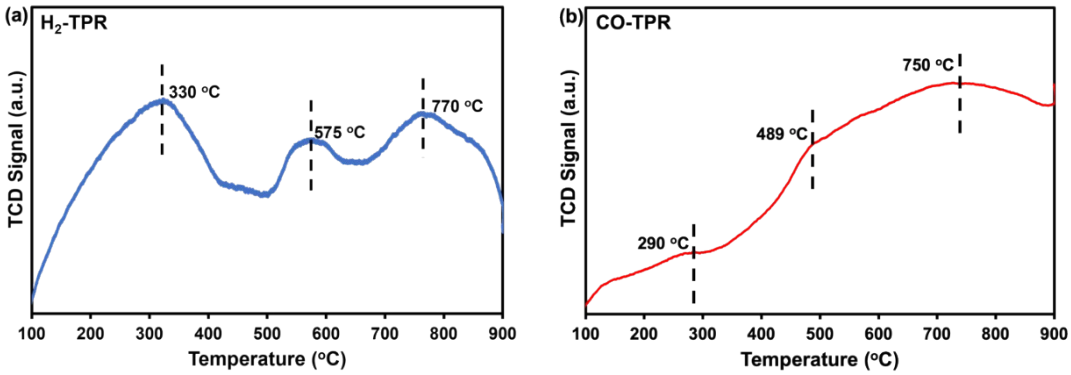

Figure S1. Hydrogen temperature programmed reduction, H_2-TPR (a), and carbon monoxide temperature programmed reduction, CO-TPR (b) of the Fe-Na-ZSM-5 catalyst.

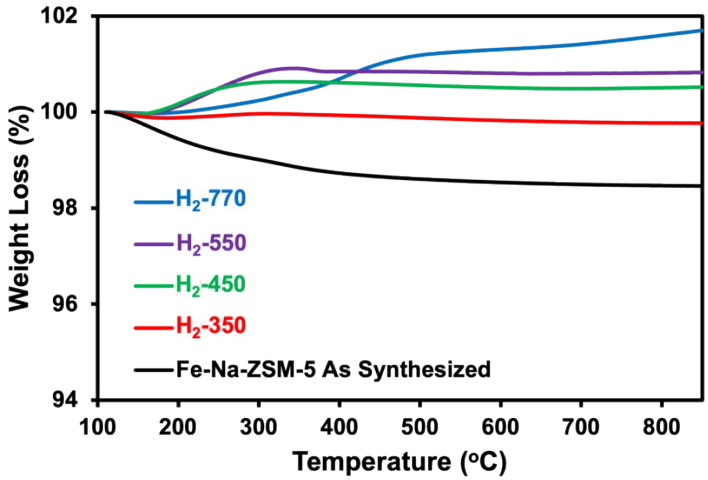

Figure S2. Thermogravimetric analysis (TGA) of Fe-Na-ZSM-5 pretreated in H_2.

Table S3. CO Uptake of the Pretreated Fe-Na-ZSM-5 Samples

Sample	CO Uptake (μmol/g)
H_2-350	12.0
H_2-450	21.5
H_2-550	27.8
H_2-770	10.0
CO-300	13.2
CO-490	2.3
CO-750	7.8

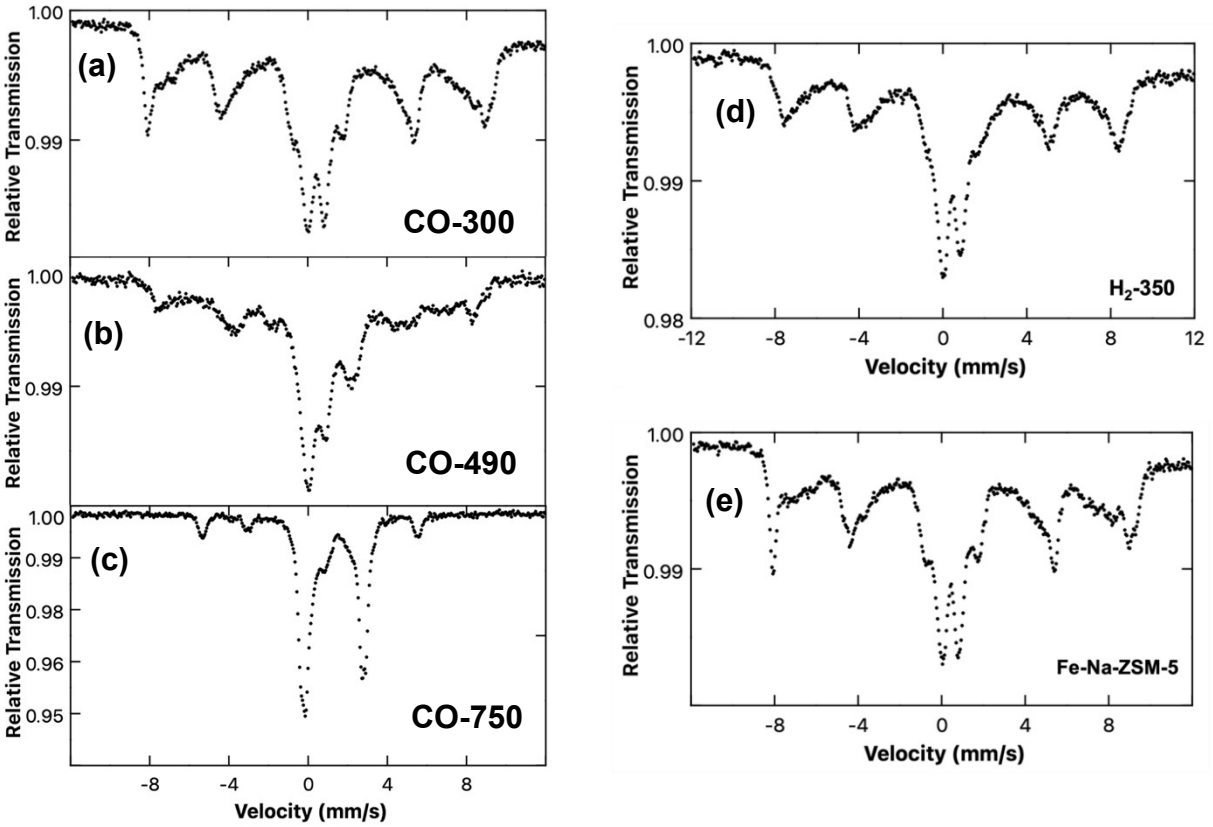

Figure S3. Mossbauer spectra of Fe-Na-ZSM-5 pretreated in CO at 300 °C (a), 490 °C (b), 750 °C (c), in H_2 at 350 °C (d), and fresh Fe-Na-ZSM-5 (e).

Table S4. Summary of ^{57}Fe Mössbauer Parameters of Fe-Na-ZSM-5 pretreated in CO at 750 °C.[1-3]

	Fe^{2+}	α-Fe	Fe_2O_3	Fe-ZSM-5: Fe^{2+} oxo
δ	1.00	0.00	0.48	1.26
ΔE_Q	1.88	0.23	0.88	3.04
FWHM	0.50	0.41	0.45	0.49
H int (kG)	-	337	-	-
Area (%)	7	57	12	21

Table S5. Summary of ^{57}Fe Mössbauer Parameters of Fe-Na-ZSM-5 pretreated in H_2 at 770 °C.

	Fe^{2+}	α-Fe	Fe_2O_3	Fe-ZSM-5: Fe^{2+} oxo
δ	1.00	0.00	0.48	1.26
ΔE_Q	1.88	0.23	0.88	3.04
FWHM	0.50	0.41	0.45	0.49
H int (kG)	-	337	-	-
Area (%)	9	12	20	65

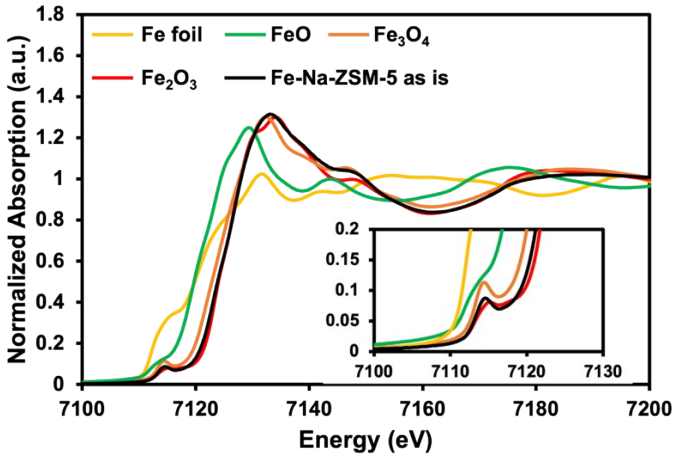

Figure S4. Fe K-edge X-ray absorption near-edge structure (XANES) spectra of iron standards: Fe foil, FeO, Fe_3O_4, Fe_2O_3, and as-synthesized Fe-Na-ZSM-5.

Table S6. CO conversion and selectivity averaged between 9-12 hours on stream of Fe-Na-ZSM-5 pretreated in H_2 or CO at a similar temperature of 300 °C.

Activation Temp (C)	Activation Gas/flowrate (mL/min)	CO Conversion (%)	Selectivity (%)					Carbon Balance
			C_2-C_4 Olefins	C_{5+}	C_2-C_4 Paraffins	CH_4	CO_2	
300	CO/20	10.8	21.1	17.6	8.9	37.6	14.8	98.0
300	H_2/40	4.7	18.7	17.8	15.4	25.2	22.9	98.8

References

1. Agwara, J. N.; Bakas, N. J.; Neidig, M. L.; Porosoff, M. D., Challenges and Opportunities of Fe - based Core - Shell Catalysts for Fischer - Tropsch Synthesis. *ChemCatChem* **2022,** *14* (19), e202200289.
2. Yang, X.; Wang, R.; Yang, J.; Qian, W.; Zhang, Y.; Li, X.; Huang, Y.; Zhang, T.; Chen, D., Exploring the reaction paths in the consecutive Fe-based FT catalyst–zeolite process for syngas conversion. *ACS Catalysis* **2020,** *10* (6), 3797-3806.
3. Fierro, G.; Moretti, G.; Ferraris, G.; Andreozzi, G. B., A Mössbauer and structural investigation of Fe-ZSM-5 catalysts: Influence of Fe oxide nanoparticles size on the catalytic behaviour for the NO-SCR by C3H8. *Applied Catalysis B: Environmental* **2011,** *102* (1-2), 215-223.