Transient HCO/HCOO$^-$ species formation during Fischer-Tropsch over Fe-Co spinel using low Ribblet ratio syngas: A combined operando IR and kinetic study

Shashank Bahri, Shailesh Pathak, Sreedevi Upadhyayula*

Heterogeneous Catalysis and Reaction Engineering Laboratory, Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016, India

*E-mail address: sreedevi@chemical.iitd.ac.in

Supporting Information

Table S1 Parameters for external mass transfer limitations.

Parameter	Value	Unit
Reaction rate of disappearance of A($-r_A$)	2.01×10^{-2}	mol kg_{cat}^{-1} s^{-1}
Order of reaction (n)	1	---
Mass transfer coefficient (k_C)	4.29×10^{-2}	m s^{-1}
Bulk concentration (C_{AB})	112.74	mol m^{-3}
Bulk density of catalyst bed (ρ_b)	546.2	$kg_{cat}m^{-3}$
Particle radius (R_p)	0.42×10^{-3}	m
Mears' Criterion (C_M)	0.9533×10^{-7}	

Table S2 Parameters for internal mass transfer limitations.

Parameter	Value	Unit
Concentration of component A at the surface ($C_{A,i}$)	112.74	mol m^{-3}
Specific surface area (a_c)	7.14×10^{3}	m_p^2 m_p^{-3}
Effective diffusivity (D_e)	1.14×10^{-6}	m^2 s^{-1}
Weisz-Prater Criterion (φ)	5.2×10^{-3}	

Table S3Experimental CO consumption rate at different reaction conditions.

S.No.	Temp (K)	SV$\times 10^{-2}$ (molkg^{-1}sec^{-1})	P_{H2} (bar)	P_{CO} (bar)	CO conversion (%)	$r_{FT}^{exp} \times 10^{-3}$ (molkg^{-1}sec^{-1})	$r_{syngas}^{exp} \times 10^{-3}$ (molkg^{-1}sec^{-1})
1	483	2.04	6.04	4.82	16.90	1.00	4.09
2	483	2.27	5.81	4.70	18.97	1.33	5.08
3	483	2.49	5.72	4.53	21.90	1.61	5.86
4	483	2.72	5.70	4.48	22.76	1.80	7.08
5	483	2.95	5.74	4.50	22.41	2.73	7.76
6	493	2.04	4.93	4.02	30.69	1.81	6.17
7	493	2.27	4.81	3.96	31.72	2.31	7.16
8	493	2.49	4.72	3.88	33.10	2.03	7.69
9	493	2.72	4.69	3.90	32.76	2.59	8.85
10	493	2.95	4.75	4.04	30.34	2.65	9.36
11	503	2.04	4.20	3.45	40.52	1.65	6.76
12	503	2.27	4.09	3.42	41.03	2.18	8.02
13	503	2.49	4.02	3.38	41.72	3.01	8.55
14	503	2.72	4.06	3.46	40.34	3.18	10.27
15	503	2.95	4.15	3.65	37.07	3.22	10.84
16	513	2.04	3.76	3.01	48.10	2.01	6.59
17	513	2.27	3.67	3.07	47.07	2.46	7.90
18	513	2.49	3.68	3.08	46.90	3.02	9.27
19	513	2.72	3.70	3.20	44.83	3.55	10.71
20	513	2.95	3.82	3.41	41.21	3.86	12.19

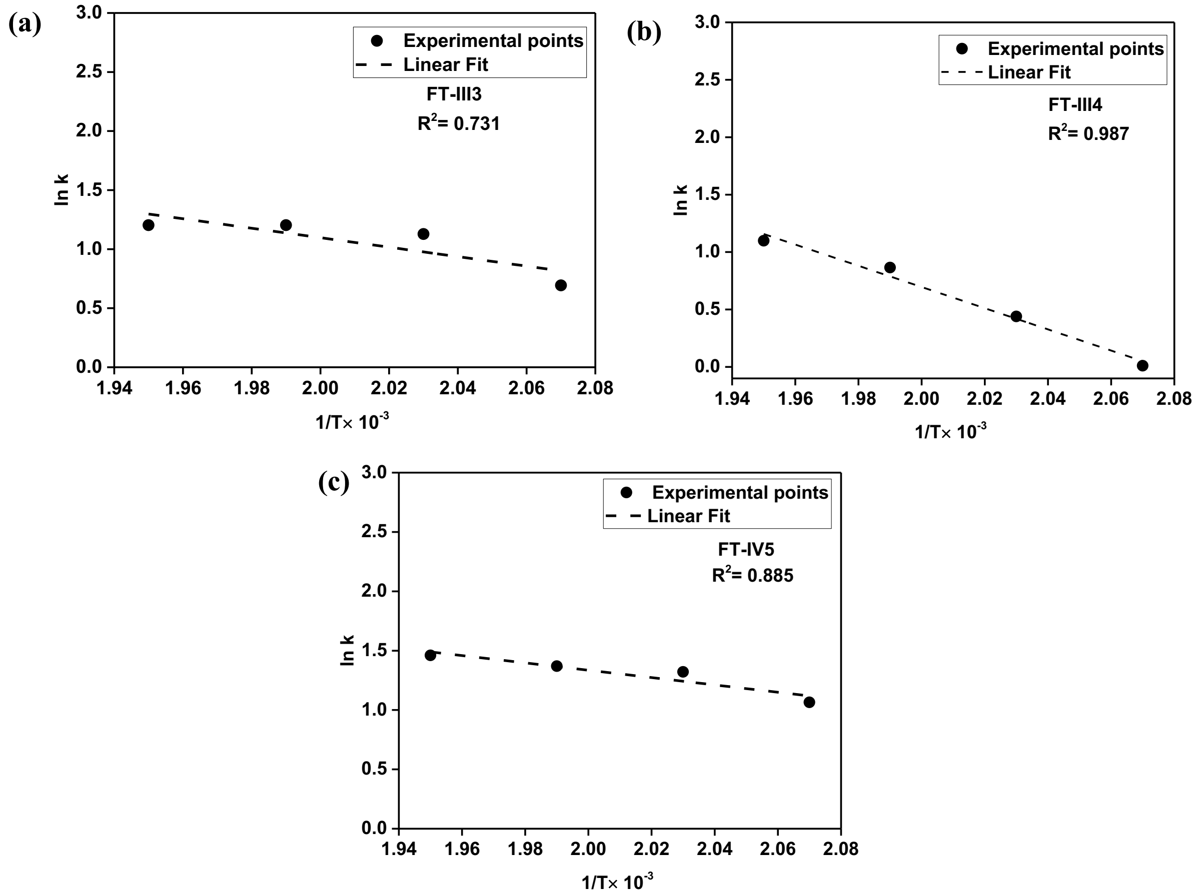

Figure S 1 Arrhenius plot of rate constants (k) of (a) FT-III3, (b) FT-III4 and (c) FT-IV5.

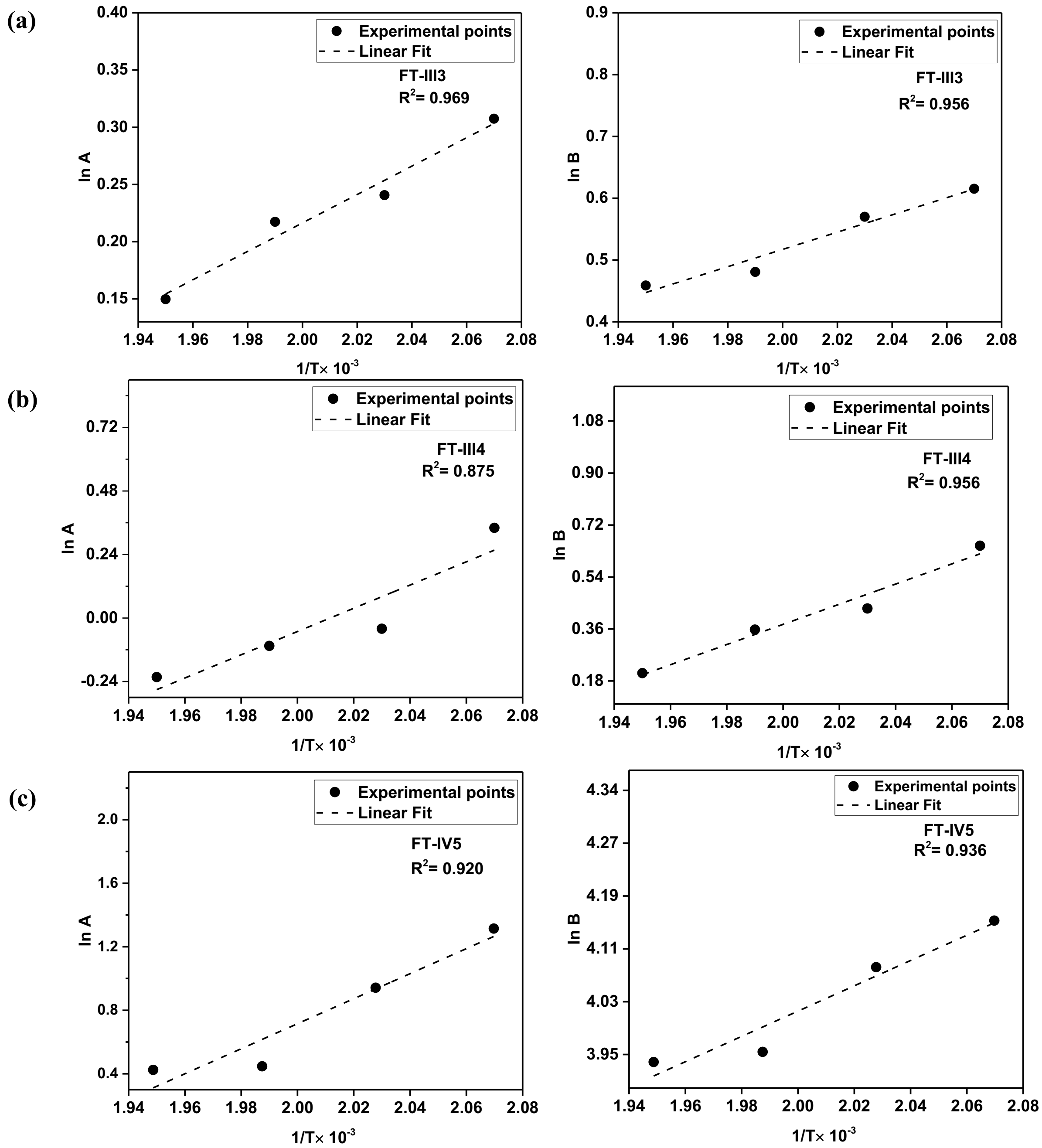

Figure S *2* Van't Hoff plot of adsorption coefficient of (A) of CO molecule and (B) of H_2 molecule based on the (a) FT-III3, (b) FT-III4 and (c) FT-IV-5 models.

Table S *4* MAPD values for literature reported iron and cobalt catalyst

Model	Active metal	Rate Expression	MAPD	Ref.
M1	Co	$r_{FT} = kP_{H_2}^2 P_{CO}$	37.8	(Brötz, 1949)
M2	Fe	$r_{FT} = \frac{kP_{H_2}P_{CO}}{bP_{H_2O} + P_{CO}}$	16.6	(Anderson et al., 1964)
M3	Fe	$-r_{FT} = \frac{aP_{H_2}^2 P_{CO}}{1 + bP_{H_2}^2 P_{CO}}$	15.9	(Anderson et al., 1964)
M4	Fe	$r_{FT} = \frac{kP_{H_2}P_{CO}}{bP_{H_2O} + P_{H_2} + P_{CO}}$	18.5	(Huff and Satterfield, 1984)
M5	Co	$r_{FT} = \frac{aP_{H_2}^{0.5} {P_{CO}}^{0.5}}{(1 + bP_{H_2}^{0.5} + cP_{CO})^2}$	15.1	(Sarup and Wojciechowski, 1989)
M6	Co	$r_{FT} = \frac{aP_{H_2}^{0.5} P_{CO}}{(1 + bP_{CO})^2}$	17.3	(Yates and Satterfield, 1991)
M7	Co	$r_{FT} = \frac{aP_{H2}P_{CO}}{(1{+}cP_{CO})^2}$	15.9	(Yates and Satterfield, 1991)
M8	Co	$r_{FT} = \frac{k{P_{H_2}}^{0.5} P_{CO}}{bP_{H_2O} + P_{CO}}$	17.8	(van Berge, 1994)
M9	Fe	$r_{FT} = \frac{kP_{CO}{P_{H_2}}^{0.5}}{(1 + aP_{CO} + bP_{H2O})^2}$	15.2	(Van Der Laan and Beenackers, 2000)
M10	Co	$r_{FT} = \frac{aP_{H_2}^{0.74} P_{CO}}{(1 + bP_{CO})^2}$	18.6	(Zennaro et al., 2000)
M11	Fe	$r_{FT} = \frac{aP_{H_2}^{0.75} {P_{CO}}^{0.5}}{(1 + b{P_{CO}}^{0.5})^2}$	15.9	(Botes and Breman, 2006)
M12	Co	$r_{FT} = \frac{aP_{H_2}^{0.5} P_{CO}}{(1 + bP_{H_2}^{0.5} + aP_{CO})^2}$	16.2	(Bhatelia et al., 2011)
M13	Co	$r_{FT} = \frac{kP_{CO}P_{H2}}{(1 + bP_{CO_2} + a{P_{CO}}^{0.5})^2}$	44.58	(Fazlollahi et al., 2012)
M14	Fe, Co	$r_{FT} = \frac{aP_{H_2}^{0.75} P_{CO}}{(1 + aP_{CO})^2}$	15.82	(Mousavi et al., 2015)
M15	Fe-Co	$r_{FT} = \frac{aP_{H_2}^{0.5} P_{CO}}{(1 + bP_{H_2}^{0.5} + aP_{CO})^2}$	16.2	(Arsalanfar et al., 2017)