Supporting Information:

Computational Mechanistic Investigation of the $Fe + CO_2 \rightarrow FeO + CO$ Reaction [†]

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Table S1: Cartesian coordinates for CO

2			
CO	Eopt	−113.362525624	
C	0.000000	0.000000	0.002554
O	0.000000	0.000000	1.127446

Table S2: Cartesian coordinates for CO_2

3			
co2	Eopt	−188.669937	
C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.159724
O	0.000000	0.000000	−1.159724

Table S3: Cartesian coordinates for FeO

2			
FeO	Eopt	−1338.95079640	
Fe	0.000000	0.000000	−0.000003
O	0.000000	0.000000	1.607903

Table S4: Cartesian coordinates for 12

4			
TS12	Eopt	−1452.35825483	
O	1.010187	−0.000401	−0.828551
C	−0.075422	−0.000037	−1.329520
O	−0.953515	0.000258	−2.088556
Fe	−0.000004	−0.000074	1.120963

Table S5: Cartesian coordinates for 2

4			
2	Eopt	−1452.36103272	
O	1.047844	0.000028	−0.734835
C	−0.149457	0.000003	−1.074320
O	−0.935743	−0.000023	−1.951245
Fe	0.000119	0.000015	1.000514

Table S6: Cartesian coordinates for 23

4			
TS23	Eopt	−1452.32312222	
O	1.184810	0.000025	−0.360631
C	−0.551393	−0.000027	−0.954381
O	−0.770911	0.000079	−2.081379
Fe	0.000228	−0.000217	0.904801

Table S7: Cartesian coordinates for 3

4			
3	Eopt	−1452.35227223	
O	1.313574	−0.000065	1.487807
C	−0.646843	0.000077	−1.292090
O	−0.827014	−0.000144	−2.410217
Fe	−0.000900	0.000279	0.542397

Table S8: Cartesian coordinates for 34

4			
TS34	Eopt	−1452.31964786	
O	1.164893	−0.004181	1.521390
C	−0.148967	−0.407562	−1.673877
O	−1.054230	0.303432	−1.667863
Fe	0.000786	0.006379	0.402159

Table S9: Cartesian coordinates for 4

4			
4	Eopt	−1452.31972066	
O	1.221301	0.000307	1.450780
C	−0.236952	−0.467063	−1.683342
O	−1.043177	0.350760	−1.555630
Fe	−0.000211	−0.000387	0.392101

Table S10: Cartesian coordinates for 45

4			
TS45	Eopt	−1452.31629208	
O	0.475700	0.013674	1.965354
C	0.178543	0.382121	−2.258433
O	−0.600604	−0.279934	−1.759030
Fe	−0.010762	−0.021133	0.428198

Table S11: Cartesian coordinates for 5

4			
5	Eopt	−1452.32284074	
O	0.054401	−0.000256	2.093920
C	−0.054968	0.000338	−2.803456
O	−0.029427	0.000209	−1.670107
Fe	0.018493	−0.000057	0.481868

Table S12: Cartesian coordinates for 56

4			
TS56	Eopt	−1452.319565390389	
O	0.062066	−0.000178	2.353130
C	−0.055670	0.000487	−2.988109
O	−0.037125	0.000134	−1.858897
Fe	0.022575	−0.000230	0.741918

Table S13: Cartesian coordinates for 17

4			
TS17	Eopt	−1452.33201193	
O	1.131483	−0.000265	−1.066575
C	−0.001085	−0.000102	−1.496429
O	−1.132556	0.000139	−1.063691
Fe	0.001983	0.000094	0.932056

Table S14: Cartesian coordinates for 7

4			
7	Eopt	−1452.33596351	
O	1.309713	−0.052375	−0.309774
C	0.461265	−0.905226	0.037996
O	−0.740244	−0.653153	0.285125
Fe	−0.247735	1.313654	−0.163547

Table S15: Cartesian coordinates for 75

4			
TS75	Eopt	−1452.29853760	
O	1.140197	−0.000571	−1.119423
C	0.117965	−0.000431	−1.709677
O	−1.228736	0.000350	−0.383991
Fe	0.000007	0.000381	0.798312

Table S16: Cartesian coordinates for 16

4			
TS16	Eopt	−1452.29527504	
O	−0.499982	−0.065459	0.440933
C	0.478267	0.066922	1.027030
O	0.388556	0.053206	2.757736
Fe	−0.366841	−0.054669	4.270352

Table S17: Rate constants for the elementary reactions involved on the $Fe + CO_2$ reaction in the 1000–3000 K temperature range.

T (K)	k_1 [b]	k_2 [b]	k_3 [a]	k_4 [a]	k_5 [a]	k_6 [a]	k_7 [b]
1000	5.25×10^{-16}	1.94×10^{-12}	1.63×10^{9}	1.44×10^{8}	1.68×10^{14}	1.56×10^{15}	6.56×10^{-14}
1100	1.94×10^{-15}	2.91×10^{-12}	3.83×10^{9}	4.30×10^{8}	1.35×10^{14}	2.97×10^{15}	1.36×10^{-13}
1200	5.75×10^{-15}	4.09×10^{-12}	7.84×10^{9}	1.08×10^{9}	1.13×10^{14}	5.08×10^{15}	2.49×10^{-13}
1300	1.45×10^{-14}	5.47×10^{-12}	1.44×10^{10}	2.35×10^{9}	9.77×10^{13}	8.01×10^{15}	4.18×10^{-13}
1400	3.19×10^{-14}	7.02×10^{-12}	2.43×10^{10}	4.59×10^{9}	8.63×10^{13}	1.19×10^{16}	6.52×10^{-13}
1500	6.34×10^{-14}	8.74×10^{-12}	3.82×10^{10}	8.22×10^{9}	7.77×10^{13}	1.69×10^{16}	9.60×10^{-13}
1600	1.16×10^{-13}	1.06×10^{-11}	5.69×10^{10}	1.37×10^{10}	7.10×10^{13}	2.22×10^{16}	1.35×10^{-12}
1700	1.96×10^{-13}	1.26×10^{-11}	8.09×10^{10}	2.16×10^{10}	6.57×10^{13}	2.81×10^{16}	1.82×10^{-12}
1800	3.15×10^{-13}	1.46×10^{-11}	1.11×10^{11}	3.24×10^{10}	6.14×10^{13}	3.49×10^{16}	2.38×10^{-12}
1900	4.79×10^{-13}	1.68×10^{-11}	1.47×10^{11}	4.66×10^{10}	5.78×10^{13}	4.26×10^{16}	3.04×10^{-12}
2000	7.00×10^{-13}	1.90×10^{-11}	1.89×10^{11}	6.47×10^{10}	5.49×10^{13}	5.12×10^{16}	3.77×10^{-12}
2100	9.87×10^{-13}	2.13×10^{-11}	2.38×10^{11}	8.71×10^{10}	5.24×10^{13}	6.07×10^{16}	4.60×10^{-12}
2200	1.35×10^{-12}	2.37×10^{-11}	2.94×10^{11}	1.14×10^{11}	5.03×10^{13}	7.11×10^{16}	5.51×10^{-12}
2300	1.79×10^{-12}	2.60×10^{-11}	3.56×10^{11}	1.47×10^{11}	4.85×10^{13}	8.26×10^{16}	6.50×10^{-12}
2400	2.32×10^{-12}	2.84×10^{-11}	4.24×10^{11}	1.85×10^{11}	4.70×10^{13}	9.50×10^{16}	7.56×10^{-12}
2500	2.95×10^{-12}	3.08×10^{-11}	4.99×10^{11}	2.28×10^{11}	4.56×10^{13}	1.08×10^{17}	8.70×10^{-12}
2600	3.68×10^{-12}	3.32×10^{-11}	5.80×10^{11}	2.77×10^{11}	4.45×10^{13}	1.23×10^{17}	9.90×10^{-12}
2700	4.51×10^{-12}	3.56×10^{-11}	6.67×10^{11}	3.33×10^{11}	4.34×10^{13}	1.38×10^{17}	1.12×10^{-11}
2800	5.46×10^{-12}	3.80×10^{-11}	7.59×10^{11}	3.94×10^{11}	4.25×10^{13}	1.55×10^{17}	1.25×10^{-11}
2900	6.51×10^{-12}	4.04×10^{-11}	8.57×10^{11}	4.62×10^{11}	4.17×10^{13}	1.72×10^{17}	1.39×10^{-11}
3000	7.67×10^{-12}	4.28×10^{-11}	9.60×10^{11}	5.36×10^{11}	4.10×10^{13}	1.90×10^{17}	1.53×10^{-11}

[a] s^{-1}

[b] cm^3 $molecule^{-1}$ s^{-1}

T (K)	k_8[a]	k_{-2}[a]	k_{-3}[a]	k_{-4}[a]	k_{-5}[a]	k_{-7}[a]	k_{-8}[a]
1000	6.31×10^{10}	9.70×10^{8}	6.53×10^{9}	4.97×10^{12}	3.96×10^{17}	3.91×10^{12}	1.73×10^{14}
1100	1.10×10^{11}	2.37×10^{9}	1.27×10^{10}	5.24×10^{12}	6.14×10^{17}	4.56×10^{12}	4.91×10^{14}
1200	1.76×10^{11}	5.01×10^{9}	2.23×10^{10}	5.50×10^{12}	8.98×10^{17}	5.20×10^{12}	1.19×10^{15}
1300	2.61×10^{11}	9.46×10^{9}	3.59×10^{10}	5.74×10^{12}	1.25×10^{18}	5.82×10^{12}	2.54×10^{15}
1400	3.68×10^{11}	1.63×10^{10}	5.42×10^{10}	5.97×10^{12}	1.69×10^{18}	6.41×10^{12}	4.94×10^{15}
1500	4.95×10^{11}	2.63×10^{10}	7.77×10^{10}	6.20×10^{12}	2.21×10^{18}	6.99×10^{12}	8.87×10^{15}
1600	6.42×10^{11}	3.98×10^{10}	1.07×10^{11}	6.41×10^{12}	2.81×10^{18}	7.55×10^{12}	1.49×10^{16}
1700	8.08×10^{11}	5.76×10^{10}	1.41×10^{11}	6.62×10^{12}	3.51×10^{18}	8.09×10^{12}	2.39×10^{16}
1800	9.93×10^{11}	8.01×10^{10}	1.82×10^{11}	6.83×10^{12}	4.30×10^{18}	8.61×10^{12}	3.64×10^{16}
1900	1.19×10^{12}	1.08×10^{11}	2.28×10^{11}	7.02×10^{12}	5.18×10^{18}	9.11×10^{12}	5.35×10^{16}
2000	1.41×10^{12}	1.41×10^{11}	2.80×10^{11}	7.21×10^{12}	6.17×10^{18}	9.60×10^{12}	7.60×10^{16}
2100	1.64×10^{12}	1.79×10^{11}	3.37×10^{11}	7.40×10^{12}	7.26×10^{18}	1.01×10^{13}	1.05×10^{17}
2200	1.89×10^{12}	2.23×10^{11}	4.00×10^{11}	7.58×10^{12}	8.45×10^{18}	1.05×10^{13}	1.41×10^{17}
2300	2.14×10^{12}	2.74×10^{11}	4.68×10^{11}	7.76×10^{12}	9.74×10^{18}	1.10×10^{13}	1.86×10^{17}
2400	2.40×10^{12}	3.30×10^{11}	5.41×10^{11}	7.93×10^{12}	1.11×10^{19}	1.14×10^{13}	2.41×10^{17}
2500	2.68×10^{12}	3.92×10^{11}	6.19×10^{11}	8.10×10^{12}	1.27×10^{19}	1.18×10^{13}	3.06×10^{17}
2600	2.96×10^{12}	4.60×10^{11}	7.01×10^{11}	8.27×10^{12}	1.43×10^{19}	1.22×10^{13}	3.83×10^{17}
2700	3.24×10^{12}	5.33×10^{11}	7.87×10^{11}	8.43×10^{12}	1.60×10^{19}	1.26×10^{13}	4.74×10^{17}
2800	3.53×10^{12}	6.12×10^{11}	8.77×10^{11}	8.59×10^{12}	1.78×10^{19}	1.30×10^{13}	5.78×10^{17}
2900	3.83×10^{12}	6.96×10^{11}	9.71×10^{11}	8.74×10^{12}	1.98×10^{19}	1.33×10^{13}	6.97×10^{17}
3000	4.13×10^{12}	7.86×10^{11}	1.07×10^{12}	8.90×10^{12}	2.18×10^{19}	1.37×10^{13}	8.32×10^{17}

[a] s^{-1}

[b] cm^3 $molecule^{-1}$ s^{-1}

Table S18: Fitting parameters and root-mean square residuals (RMRS) for the modified Arrhenius equation, $k_{\text{fit}}(T) = AT^n e^{-B/T}$, for the elementary reactions involved on the $Fe + CO_2$ reaction.

Rate constant	A	B (K)	n	RMSR
k_1	$1.018\,460 \times 10^{-9}$ [b]	$1.440\,961 \times 10^{4}$	$-1.036\,047 \times 10^{-2}$	$1.970\,685 \times 10^{-3}$
k_{-2}	$1.140\,089 \times 10^{12}$ [a]	$9.472\,284 \times 10^{3}$	$3.478\,232 \times 10^{-1}$	$1.263\,559 \times 10^{-3}$
k_2	$1.721\,995 \times 10^{-11}$ [b]	$4.169\,444 \times 10^{3}$	$2.873\,889 \times 10^{-1}$	$1.174\,592 \times 10^{-3}$
k_{-3}	$1.930\,910 \times 10^{11}$ [a]	$6.827\,475 \times 10^{3}$	$4.979\,307 \times 10^{-1}$	$1.159\,706 \times 10^{-3}$
k_3	$3.331\,095 \times 10^{12}$ [a]	$9.196\,665 \times 10^{3}$	$2.275\,497 \times 10^{-1}$	$1.079\,980 \times 10^{-3}$
k_{-4}	$1.764\,592 \times 10^{11}$ [a]	$6.178\,540 \times 10^{1}$	$4.922\,439 \times 10^{-1}$	$3.925\,445 \times 10^{-4}$
k_4	$6.609\,193 \times 10^{11}$ [a]	$1.158\,314 \times 10^{4}$	$4.561\,314 \times 10^{-1}$	$1.348\,313 \times 10^{-3}$
k_{-5}	$6.204\,955 \times 10^{12}$ [a]	$2.725\,220 \times 10^{3}$	$1.996\,166$	$1.653\,085 \times 10^{-3}$
k_5	$4.022\,807 \times 10^{11}$ [a]	$-2.870\,626 \times 10^{3}$	$4.579\,550 \times 10^{-1}$	$6.523\,817 \times 10^{-4}$
k_6	$3.110\,506 \times 10^{16}$ [a]	$6.295\,689 \times 10^{3}$	$4.833\,389 \times 10^{-1}$	$2.607\,927 \times 10^{-2}$
k_{-7}	$1.702\,237 \times 10^{12}$ [a]	$1.357\,358 \times 10^{3}$	$3.169\,325 \times 10^{-1}$	$1.376\,503 \times 10^{-3}$
k_7	$1.813\,413 \times 10^{-11}$ [b]	$7.689\,179 \times 10^{3}$	$2.992\,003 \times 10^{-1}$	$1.245\,185 \times 10^{-3}$
k_{-8}	$8.981\,567 \times 10^{11}$ [a]	$9.253\,766 \times 10^{3}$	$2.101\,322$	$1.241\,104 \times 10^{-3}$
k_8	$5.144\,236 \times 10^{12}$ [a]	$5.912\,667 \times 10^{3}$	$2.187\,396 \times 10^{-1}$	$1.356\,674 \times 10^{-3}$

[a] $K^n\ s^{-1}$

[b] $K^n\ cm^3\ molecule^{-1}\ s^{-1}$

Table S19: Global rate constants for the $Fe + CO_2$ reaction for temperatures between 1000 and 3000 K.

Temperature	Rate Constant [a]
1000	5.89×10^{-16}
1100	2.47×10^{-15}
1200	6.31×10^{-15}
1300	1.64×10^{-14}
1400	4.40×10^{-14}
1500	7.25×10^{-14}
1600	1.25×10^{-13}
1700	2.98×10^{-13}
1800	5.43×10^{-13}
1900	7.22×10^{-13}
2000	9.72×10^{-13}
2100	1.39×10^{-12}
2200	1.70×10^{-12}
2300	2.15×10^{-12}
2400	2.98×10^{-12}
2500	3.43×10^{-12}
2600	4.29×10^{-12}
2700	5.15×10^{-12}
2800	6.14×10^{-12}
2900	7.47×10^{-12}
3000	8.74×10^{-12}

[a] cm^3 $molecule^{-1}$ s^{-1}

Table S20: Unscaled harmonic vibrational frequencies of the molecular species involved on the $Fe + CO_2$ reaction.

System	Vibrational Frequencies (cm^{-1})					
CO_2	677.24	677.24	1372.25	2411.12		
CO	2214.52					
FeO	910.26					
2	208.71	285.97	497.10	621.36	1151.12	1995.93
3	83.76	318.10	327.12	376.06	933.10	2141.03
4	75.23	123.44	150.73	269.68	919.17	1937.05
5	67.44	135.24	168.12	176.62	934.60	2114.58
7	243.79	264.87	372.04	75.40	1238.80	1521.93
12	207.57i	145.80	440.65	536.02	1238.70	2239.19
16	650.25i	64.25	125.15	361.46	643.11	1997.45
17	361.14i	122.56	405.11	477.78	1196.39	1864.69
23	377.43i	287.85	307.35	454.10	820.87	2040.29
34	120.16i	80.71	126.66	256.59	917.75	1966.47
45	132.65i	54.00	86.18	167.18	932.24	2080.64
75	347.44i	203.53	207.13	501.85	787.41	1771.13
56	52.11i	52.82	110.97	116.34	920.65	2171.78