Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Dissecting the steps of CO_2 reduction: 1. The interaction of CO and CO_2 with γ-Al_2O_3: *an in situ FTIR study*

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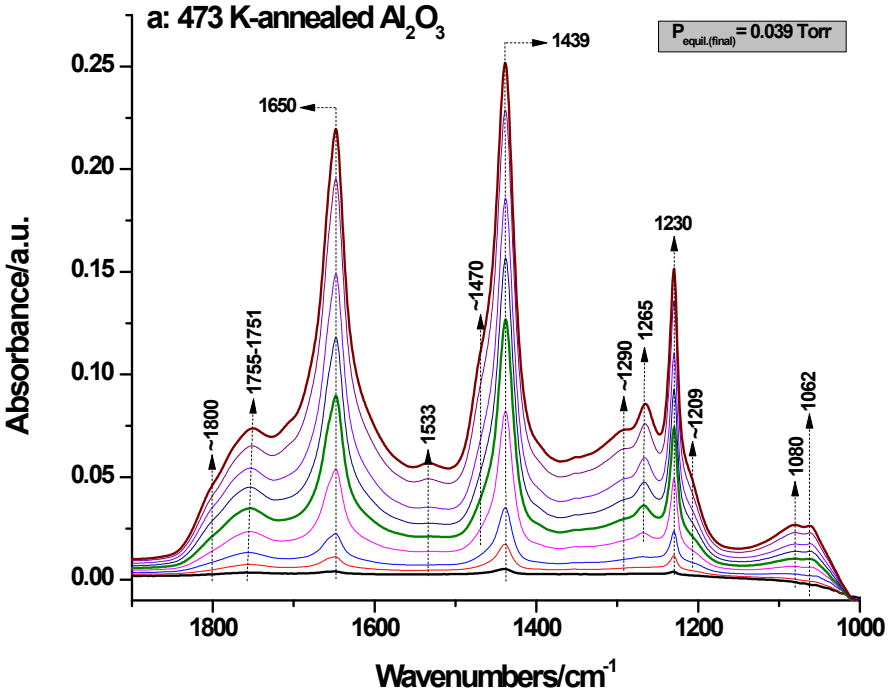
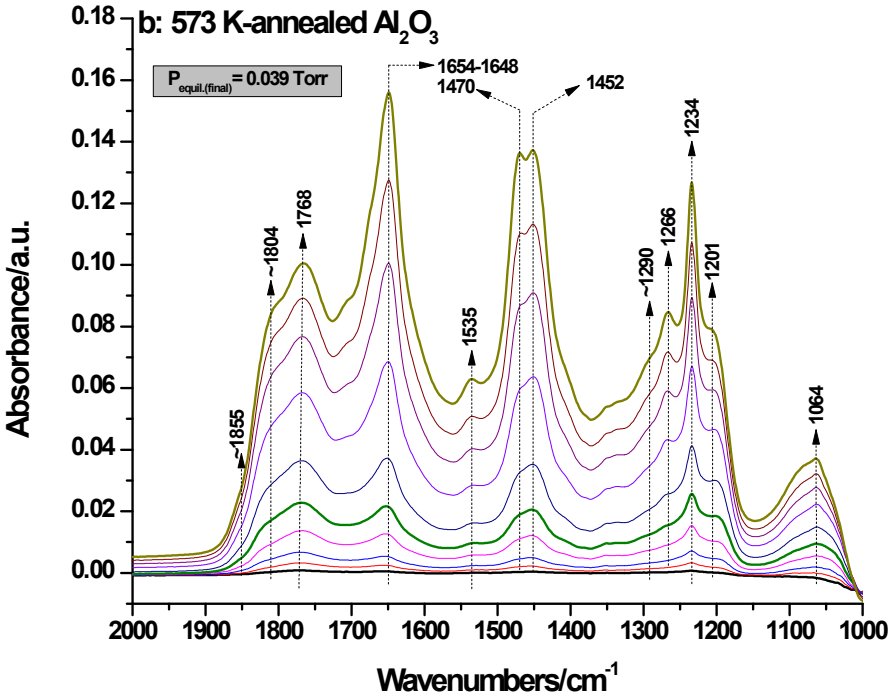
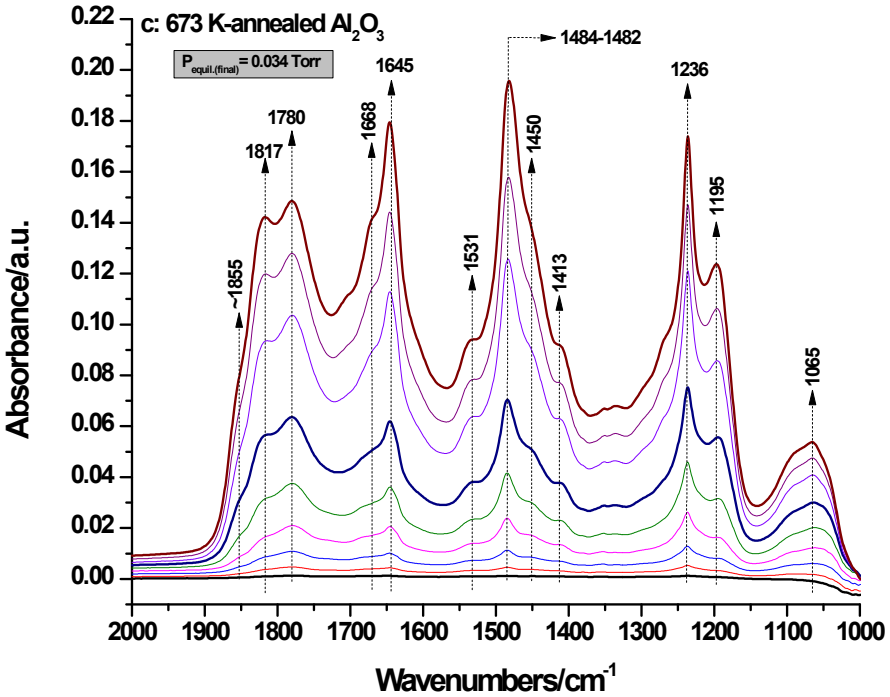
Supplementary Information:

Figure S1: IR spectra collected at 295 K during stepwise CO_2 adsorption on γ-Al_2O_3 samples calcined at 473 (a), 573 (b), 673 (c) and 773 K (d).




b: 573 K-annealed Al2O3
P equil.(final) = 0.039 Torr
1654-1648
1470
1452
1234
1768
~1804
1266
~1290
1201
1535
~1855
1064
Absorbance/a.u.
Wavenumbers/cm-1


c: 673 K-annealed Al2O3
P equil.(final) = 0.034 Torr
1484-1482
1645
1236
1780
1668
1817
1450
1195
1531
~1855
1413
1065
Absorbance/a.u.
Wavenumbers/cm-1

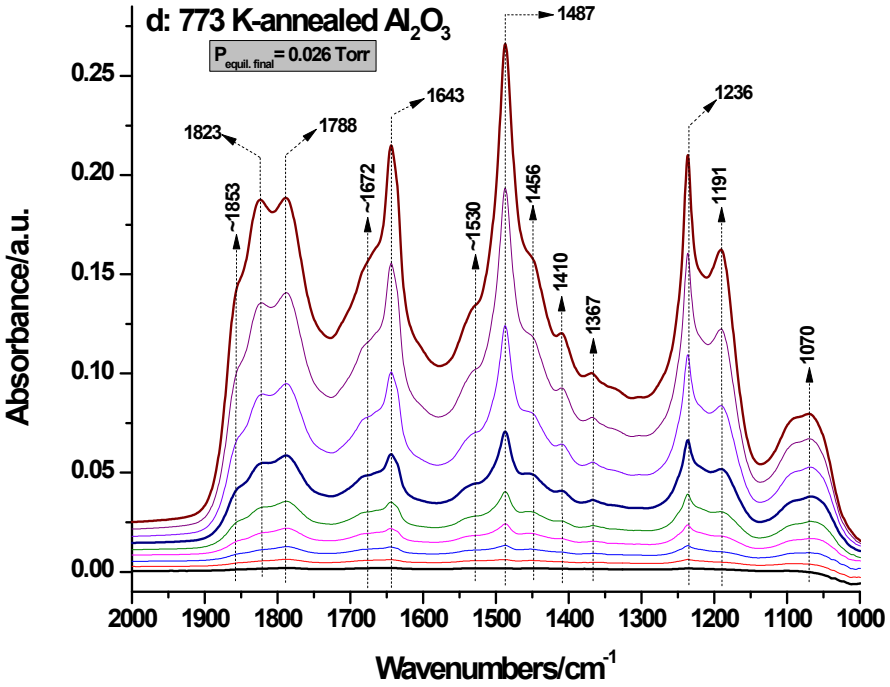

d: 773 K-annealed Al2O3
P equil. final = 0.026 Torr
1823
1788
1643
1487
1236
~1853
~1672
~1530
1456
1410
1367
1191
1070
Absorbance/a.u.
0.25
0.20
0.15
0.10
0.05
0.00
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
Wavenumbers/cm-1

Figure S2. IR spectra collected during the stepwise annealing (in vacuum) of the CO_2-saturated, 773 K-annealed γ-Al_2O_3 sample. (IR spectra were collected at 295 K. Temperature increment between 300 and 500 K was 25 K, and above that 50 K.)

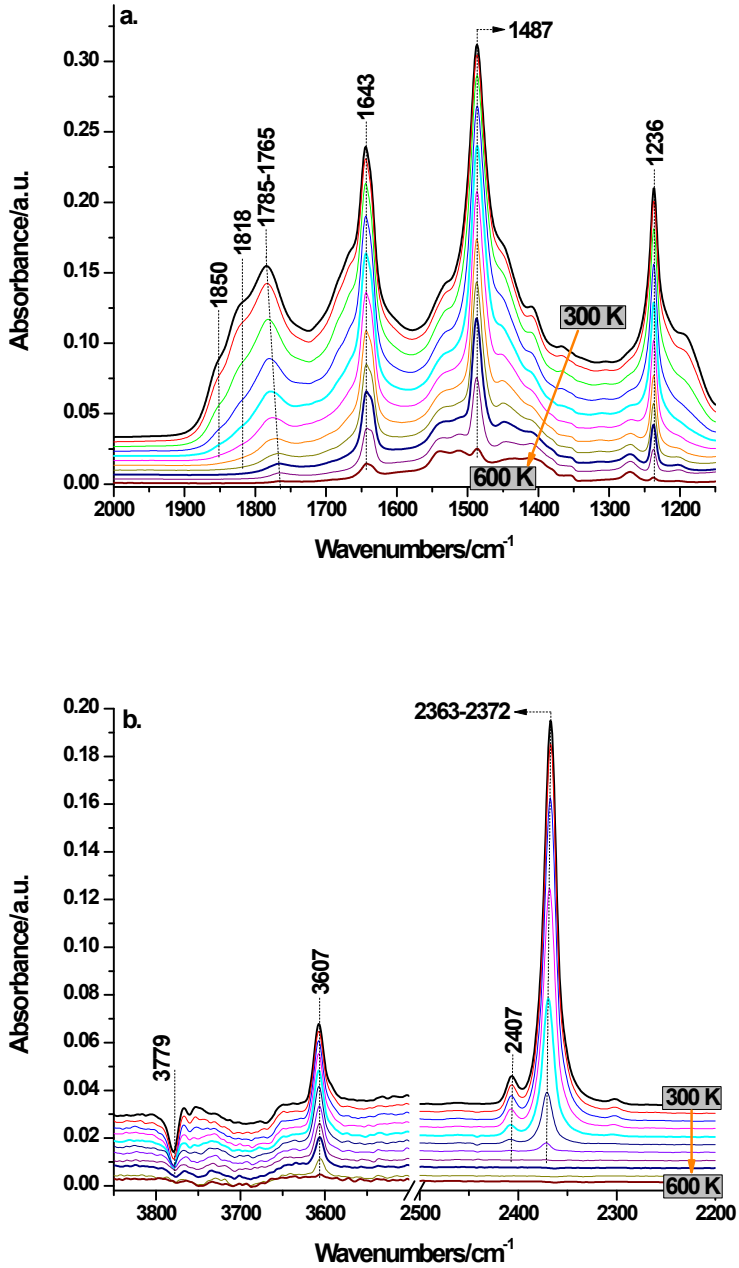


Figure S3. Five series of IR spectra collected from γ-Al_2O_3 annealed at different temperatures (from 473 to 973 K) during stepwise CO exposure at 100 K sample temperature.

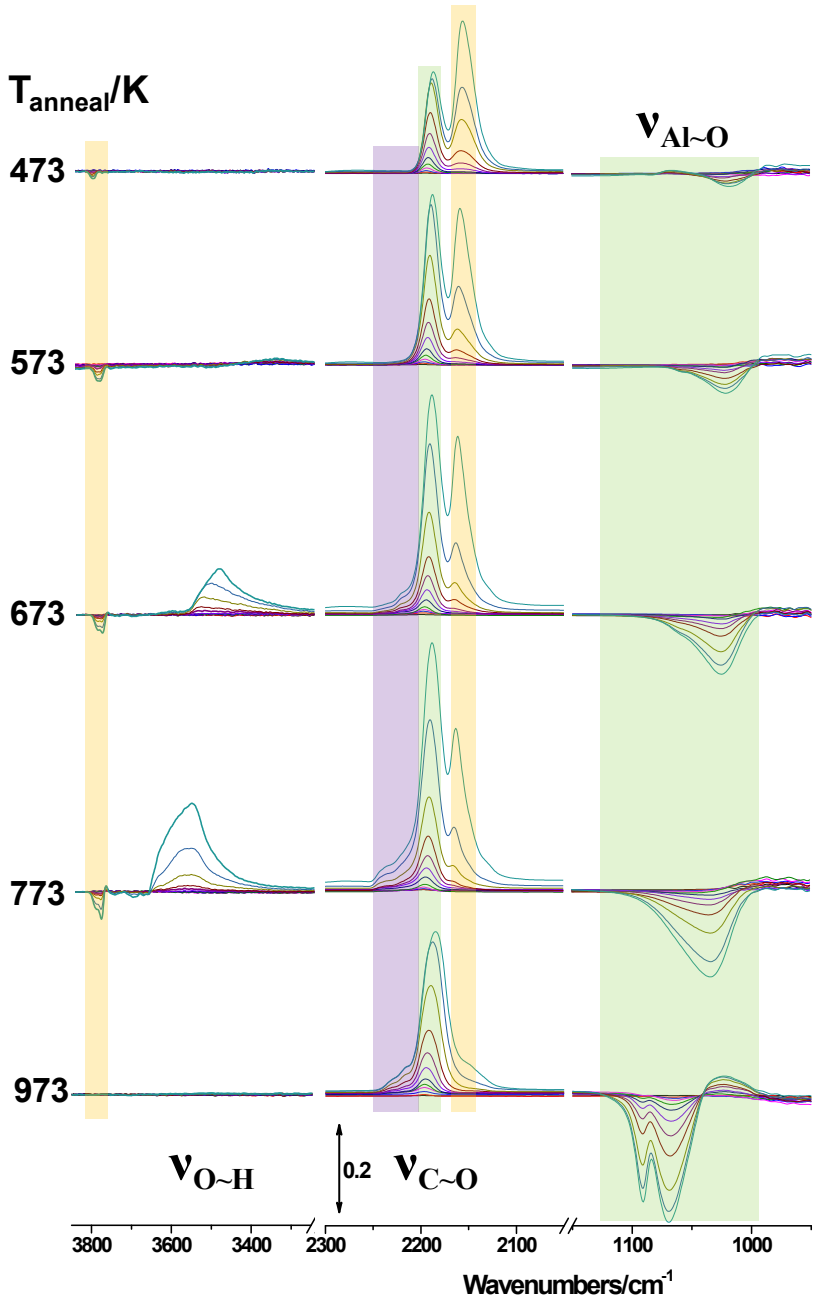


Figure S4. Series of IR spectra collected after step-wise H_2O exposure of a CO_2-saturated, 773 K-annealed Al_2O_3 sample at 295 K in the 1150-2000 cm^{-1} (a) and 2150-3850 cm^{-1} (b) regions.

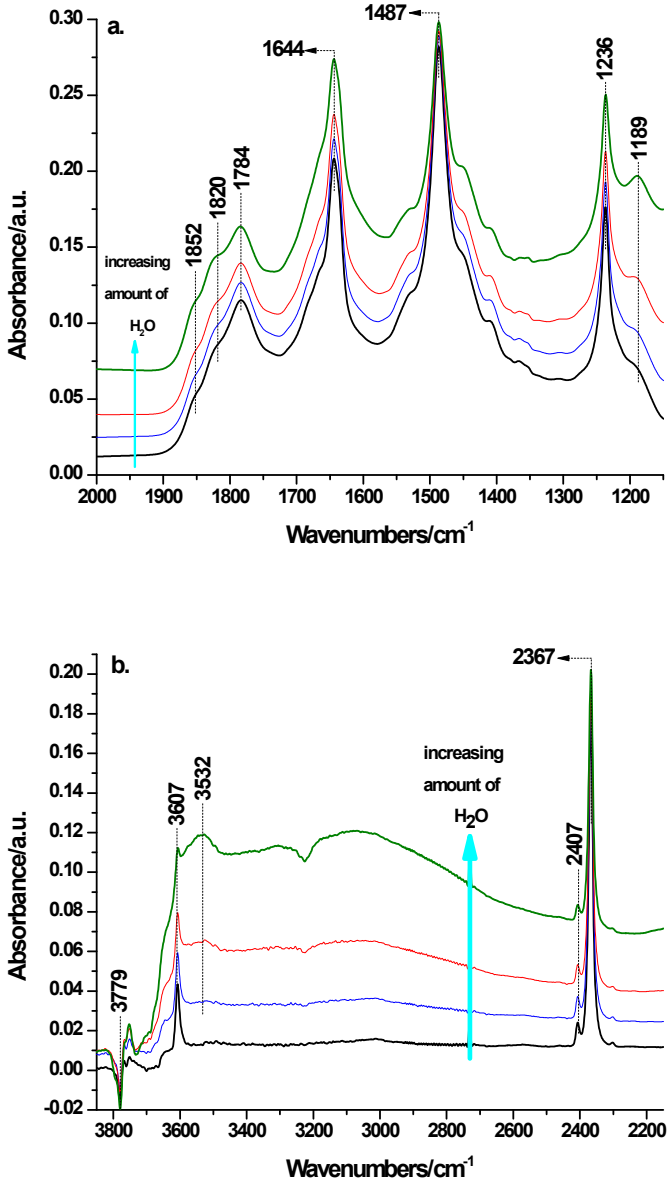


Figure S5. Series of IR spectra collected after the exposure of a 773 K-annealed, H_2O-exposed γ-Al_2O_3 sample to CO_2 at 295 K. (P_{H2O}= 2 Torr and P_{CO2}= 5 Torr in the gas manifold)

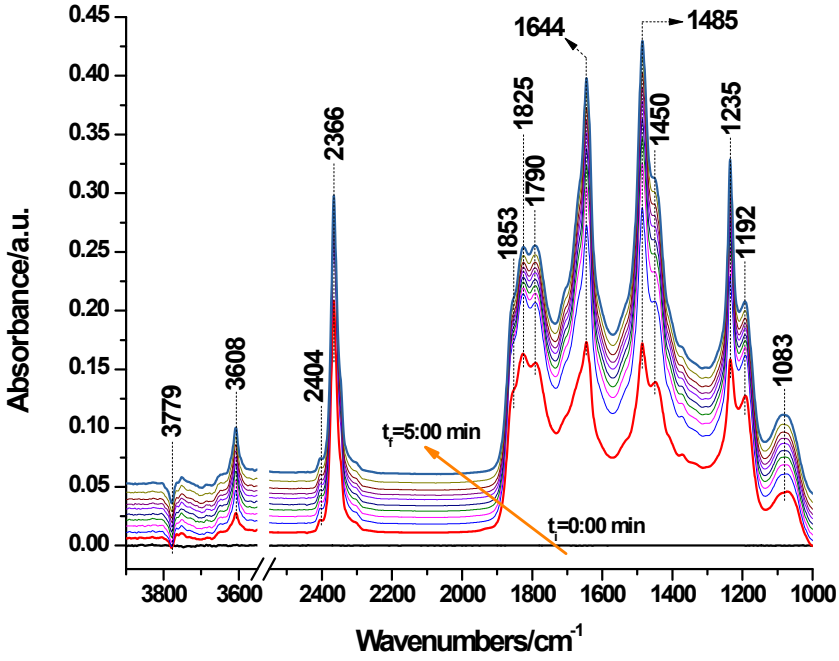

Absorbance/a.u.
Wavenumbers/cm-1
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3800
3600
2400
2200
2000
1800
1600
1400
1200
1000
3779
3608
2404
2366
1853
1825
1790
1644
1485
1450
1235
1192
1083
tf=5:00 min
t=0:00 min

Table. S1. Assignment of IR features observed after CO_2 and CO adsorption on γ-Al_2O_3

CO_2/γ-Al_2O_3

Wavenumbers/cm^{-1}	Assignment		Reference
	chemisorbed CO_2 on		12;16;17
2360-2366	Al^{3+}_{VI}		
2405	Al^{3+}_{IV}		
	Bridged and bidentate carbonates		9;12;15;17
1067	γ_{COO}		
1206-1191	ν_{as}		
1720-1870	ν_{sym}		
	Bicarbonates		7;8;12;17
1228-1236	γ_{OH}		
1438	ν_{sym}	B1	
1469-1486	ν_{sym}	B2	
1644-1650	ν_{as}		
3621-3607	ν_{OH}		
	Free carbonates		5;12;17
1409	ν_{as}		

CO/γ-Al_2O_3

2155-2166	**H-bonded CO**	12
2186-2208	**Lewis site-bound on low index planes**	12
2220-2223, 2230-2245	**Lewis site-bound on defects (step edges, corners, etc.)**	12
1050-1090	**CO adsorption-relaxed Al-O vibration**	12