

Supporting Information

Fe/ γ -Al₂O₃ and Fe-K/ γ -Al₂O₃ as Reverse Water-Gas Shift Catalysts

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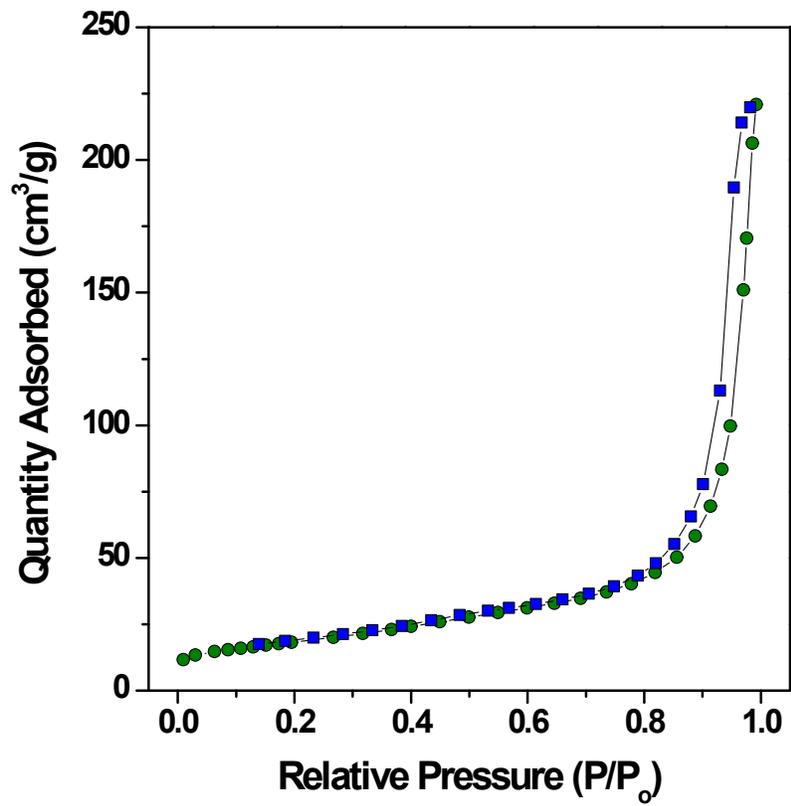


Figure S1. N₂ adsorption isotherm for 10% Fe – 2.5% K/Al₂O₃.

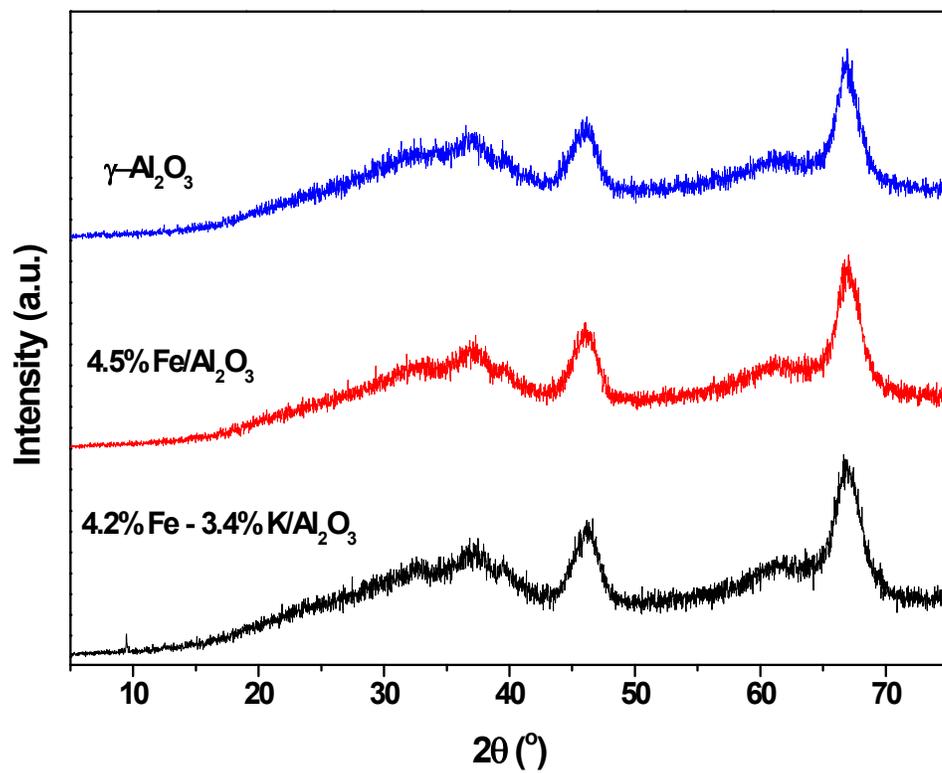


Figure S2. Powder XRD patterns of 4.2% Fe – 3.4% K/Al₂O₃, 4.5% Fe/Al₂O₃ and $\gamma\text{-Al}_2\text{O}_3$.

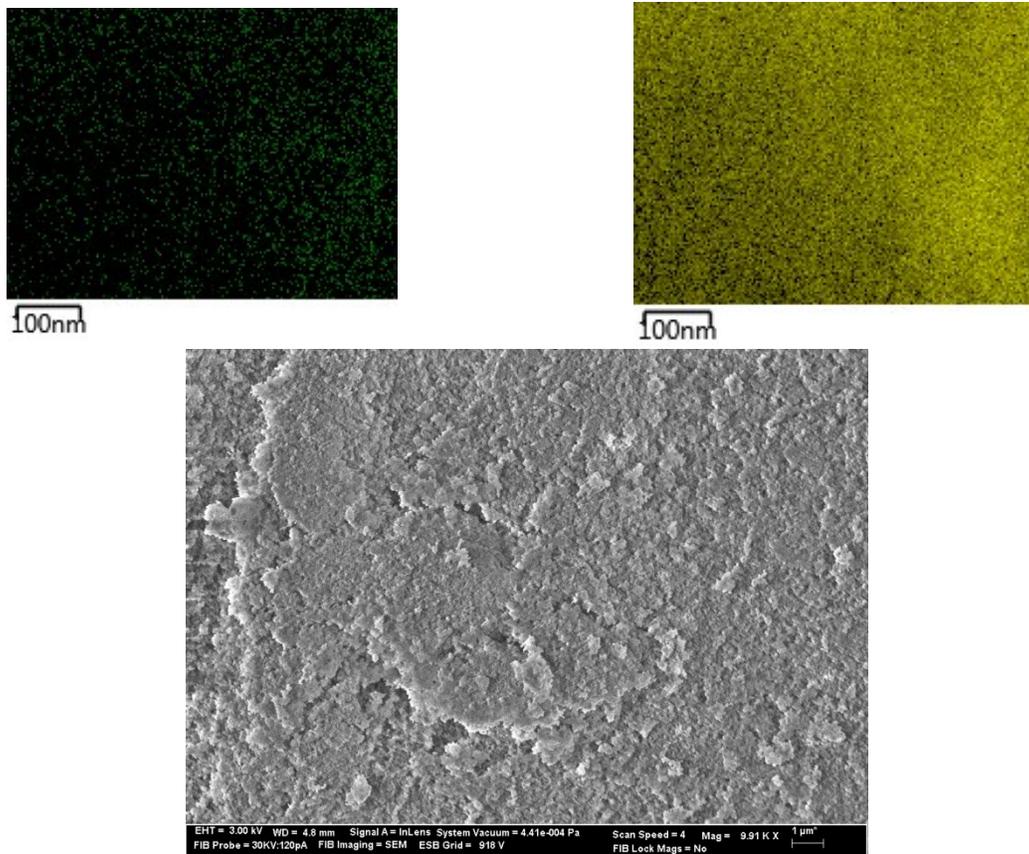


Figure S3. Elemental mapping images of 4.5% Fe/Al₂O₃. Iron highlighted (green, top left), oxygen highlighted (yellow, top right), and regular SEM image (bottom).

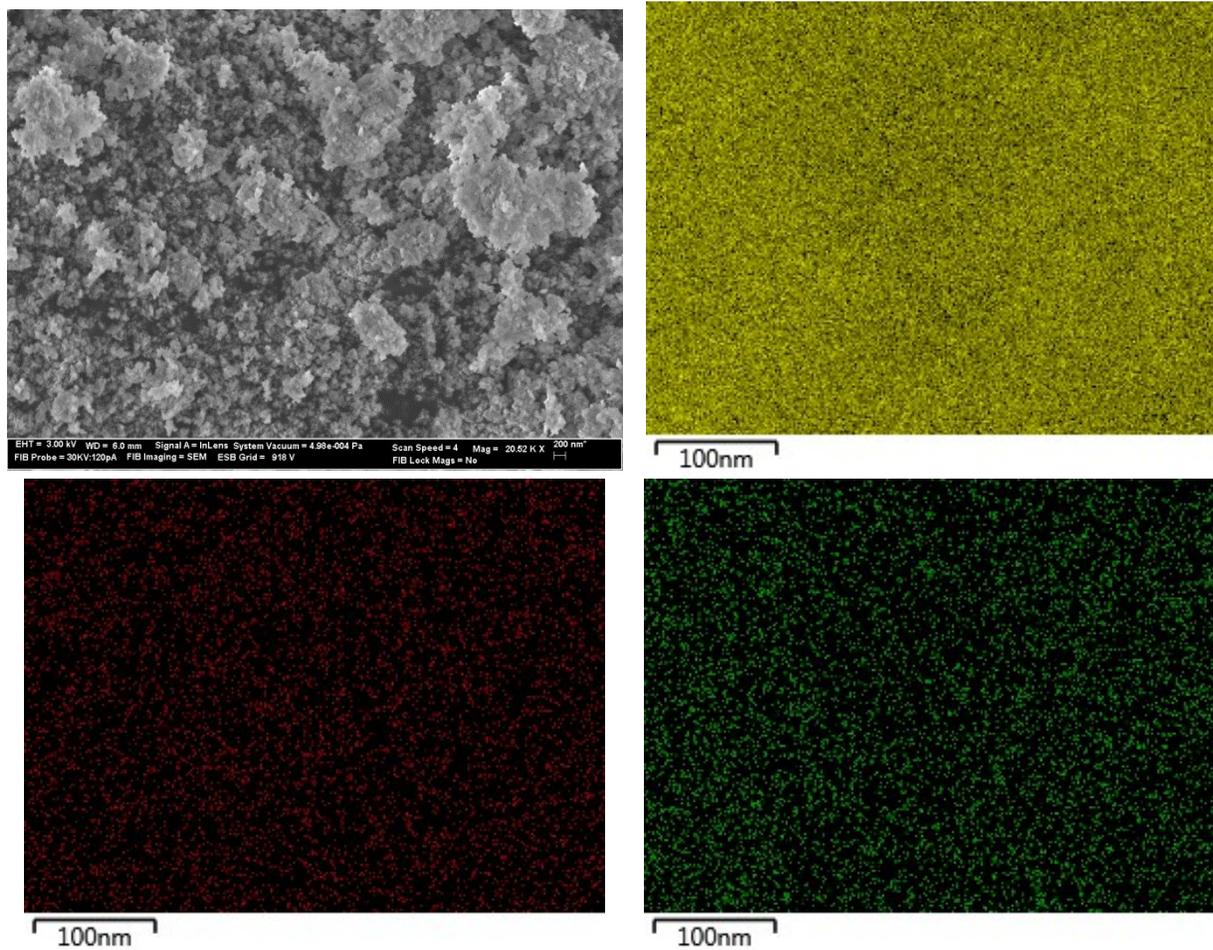


Figure S4. Elemental mapping images of 4.2% Fe – 3.4% K/Al₂O₃. Regular SEM image (top left), oxygen highlighted (yellow, top right), potassium highlighted (red, bottom right), and iron highlighted (green, bottom right).

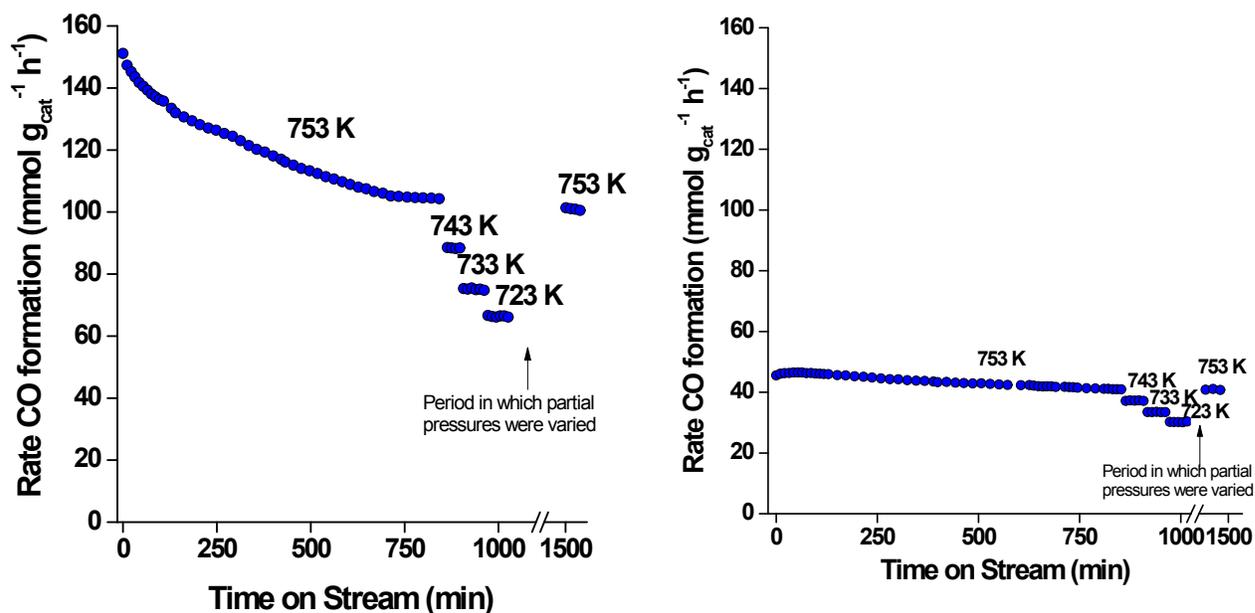


Figure S5. CO formation rates on 4.2% Fe -3.4% K/Al₂O₃ (left) and 4.5% Fe/Al₂O₃ (right) during experiments in which kinetic parameters were determined with equimolar concentrations of CO₂ and H₂ in the feed. Temperatures are indicated in the figure, and the partial pressures of CO₂ and H₂ were 15 kPa.

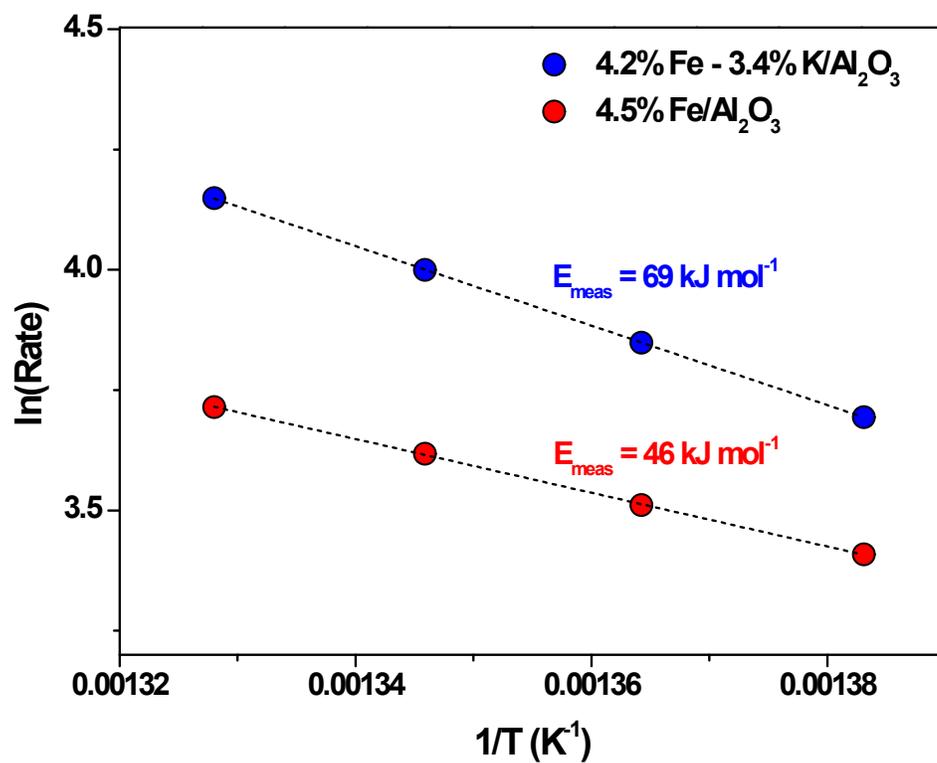


Figure S6. Arrhenius plots from conversion of CO₂ on 4.5% Fe/Al₂O₃ and 4.2% Fe - 3.4% K/Al₂O₃. Reaction conditions: T = 723-753 K, P_{CO₂} = 15 kPa, P_{H₂} = 15 kPa, F_{tot} = 75 sccm.

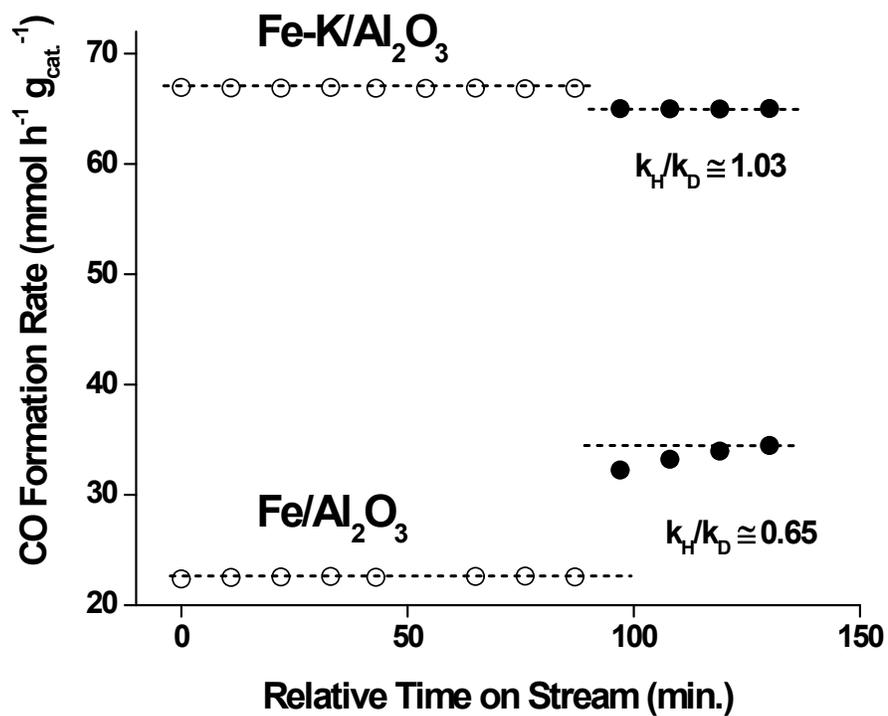


Figure S7. CO formation rates on 4.5% Fe/Al₂O₃ and 4.2% Fe – 3.4% K/Al₂O₃ while flowing H₂ (open circles) or D₂ (filled circles). Reaction conditions: T = 723 K, P_{CO2} = 15 kPa, P_{H2} or P_{D2} = 15 kPa, F_{tot.} = 75 scfm.

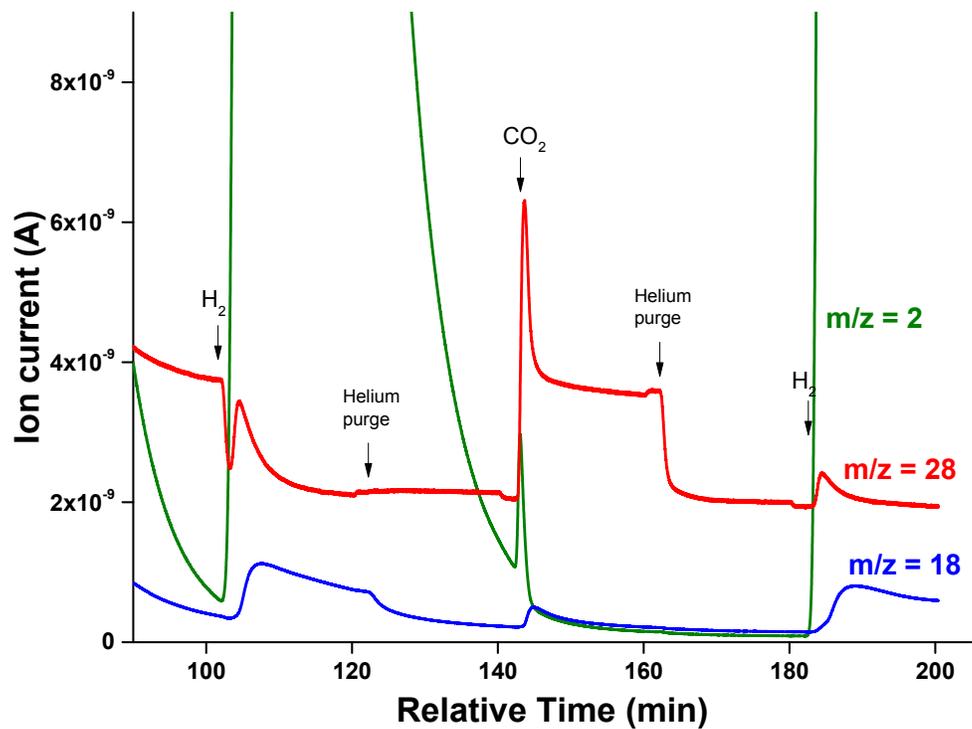


Figure S8. Ion currents at $m/z = 2$ (H_2), 18 (H_2O), and 28 (CO) during H_2/CO_2 switching experiments on 4.2% Fe – 3.4% K/ Al_2O_3 . Arrows with a label indicate a change in gas composition to the indicated gas. Reaction conditions: $T = 773 \text{ K}$, $F_{\text{He}} = 36 \text{ sccm}$, F_{H_2} or $F_{\text{CO}_2} = 4 \text{ sccm}$. The figure is a modification of Figure 2.

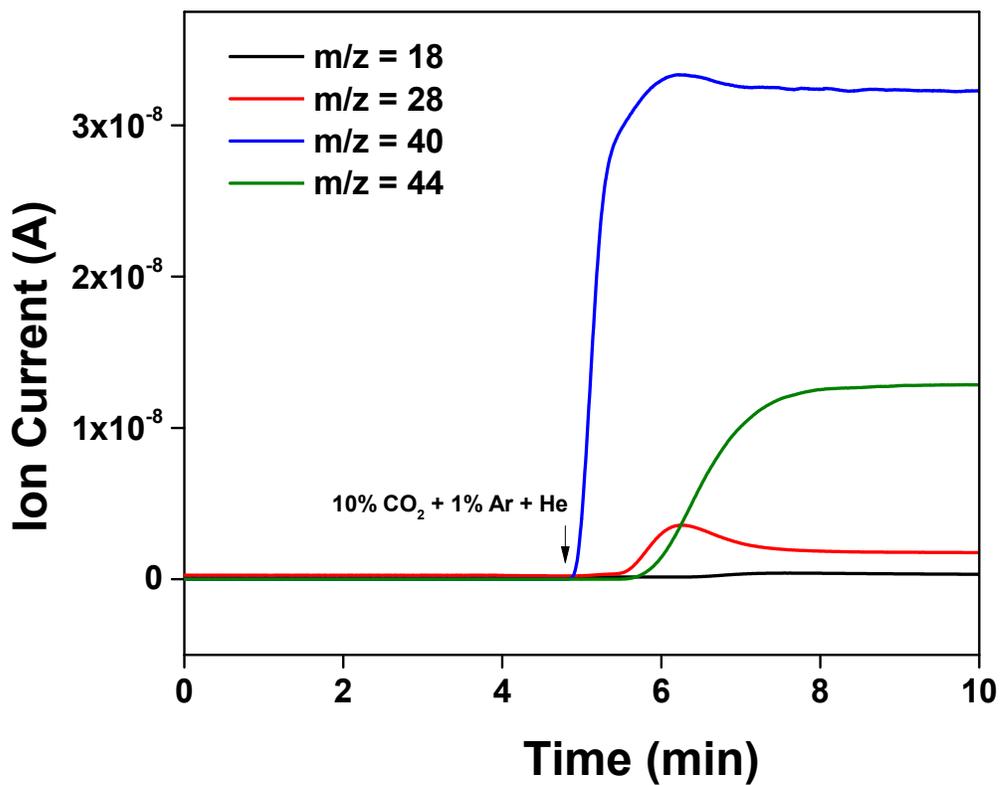


Figure S9. Transient response curves for Ar ($m/z = 40$), CO₂ ($m/z = 28, 44$), CO ($m/z = 28$), and H₂O ($m/z = 18$) during gas switching experiments over Fe-K/Al₂O₃. Gas flow was switched from 10% H₂/He to 10% CO₂/1% Ar/He. Reaction conditions: $T = 773$ K, total flow rate = 40 sccm.

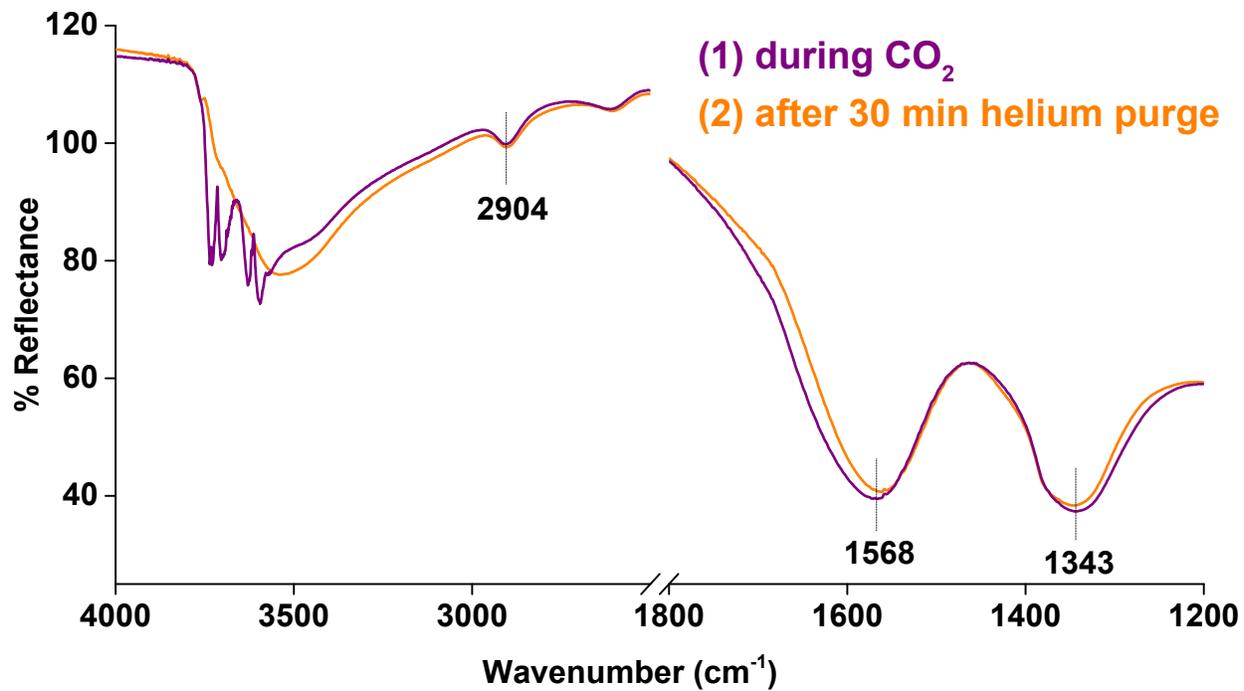


Figure S10. Diffuse reflectance IR spectra collected *in situ* of 7.7% Fe – 3.4% K/Al₂O₃ after 30 min of CO₂ flow (purple) and after purging the chamber for 30 min with helium. The temperature was 723 K.

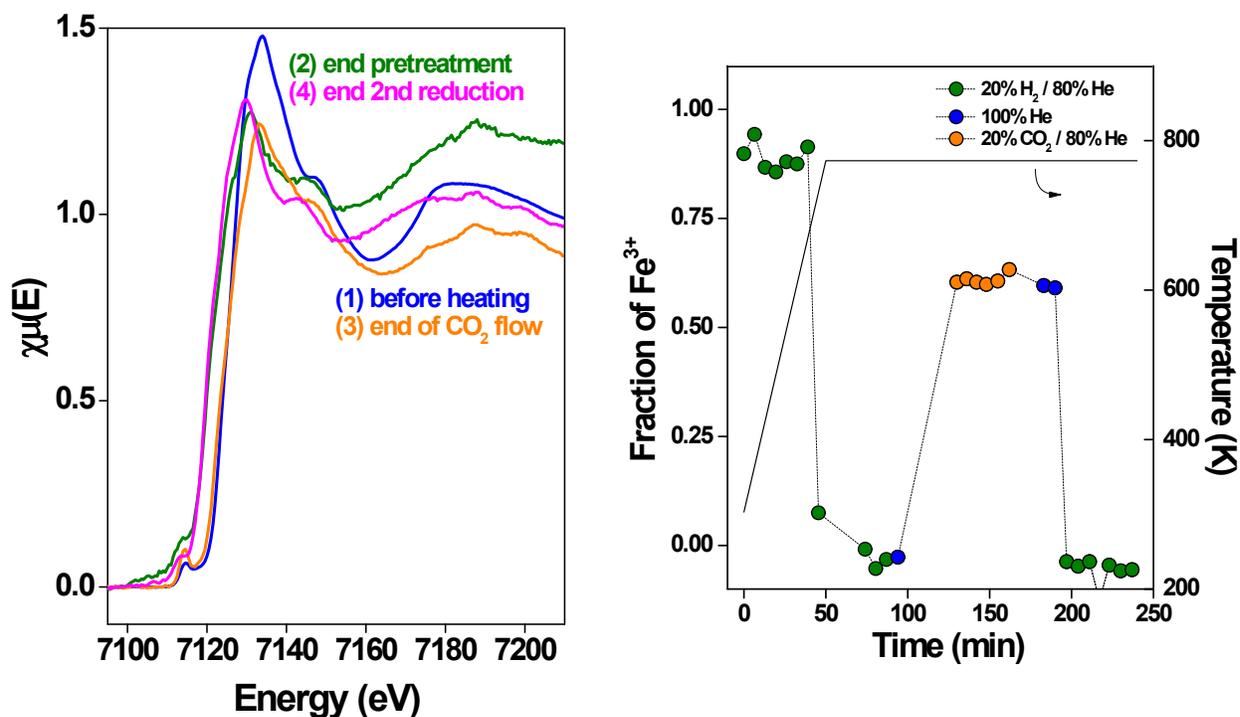


Figure S11. XANES spectra collected *in-situ* (left) during a gas switching experiment on 4.5% Fe/Al₂O₃ and fraction of Fe³⁺ (right) over the duration of the experiment. The catalyst was pretreated in H₂, and the H₂ flow was then stopped while CO₂ was added simultaneously. The catalyst was then re-reduced in H₂ after the period in CO₂. $T_{\text{rxn}} = 773 \text{ K}$, P_{CO_2} or $P_{\text{H}_2} = 20 \text{ kPa}$, $F_{\text{tot}} = 10 \text{ sccm}$.

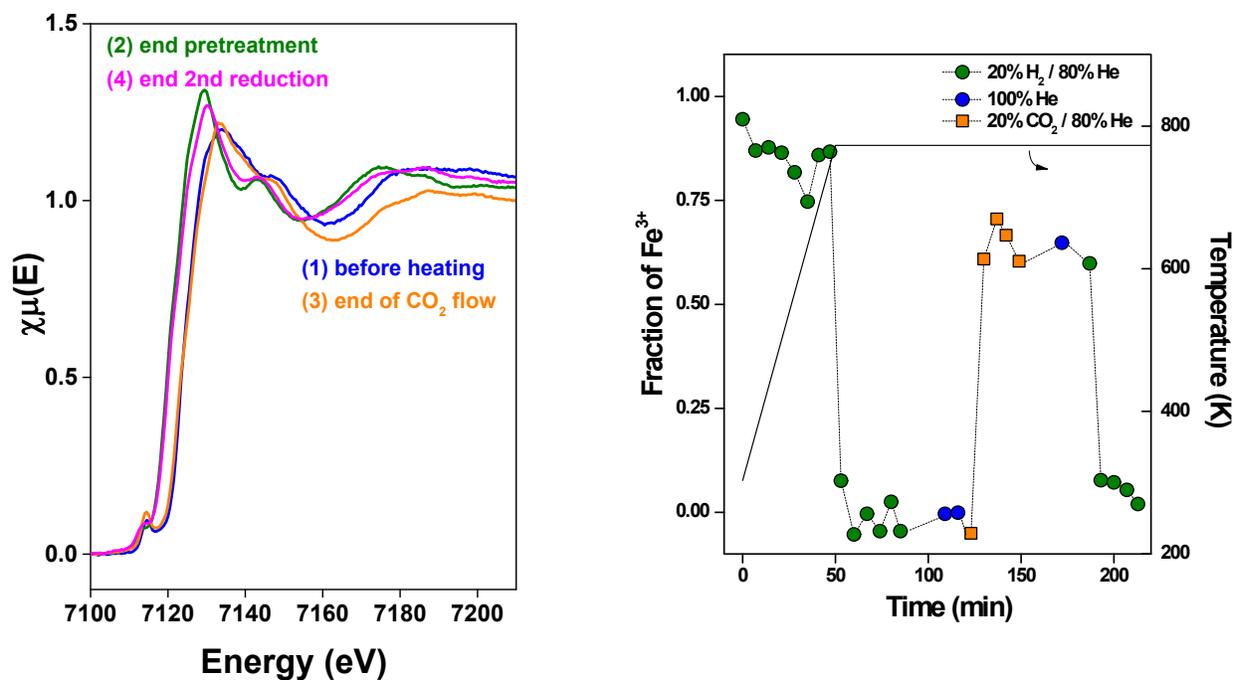


Figure S12. XANES spectra collected *in situ* (left) during a gas switching experiment on 4.2% Fe – 3.4% K/Al₂O₃ and fraction of Fe³⁺ (right) over the duration of the experiment. The catalyst was pretreated in H₂, and the H₂ flow was then stopped while CO₂ was added simultaneously. The catalyst was then re-reduced in H₂ after the period in CO₂. Reaction conditions: $T_{\text{rxn}} = 773 \text{ K}$, P_{CO_2} or $P_{\text{H}_2} = 20 \text{ kPa}$, $F_{\text{tot}} = 10 \text{ sccm}$.

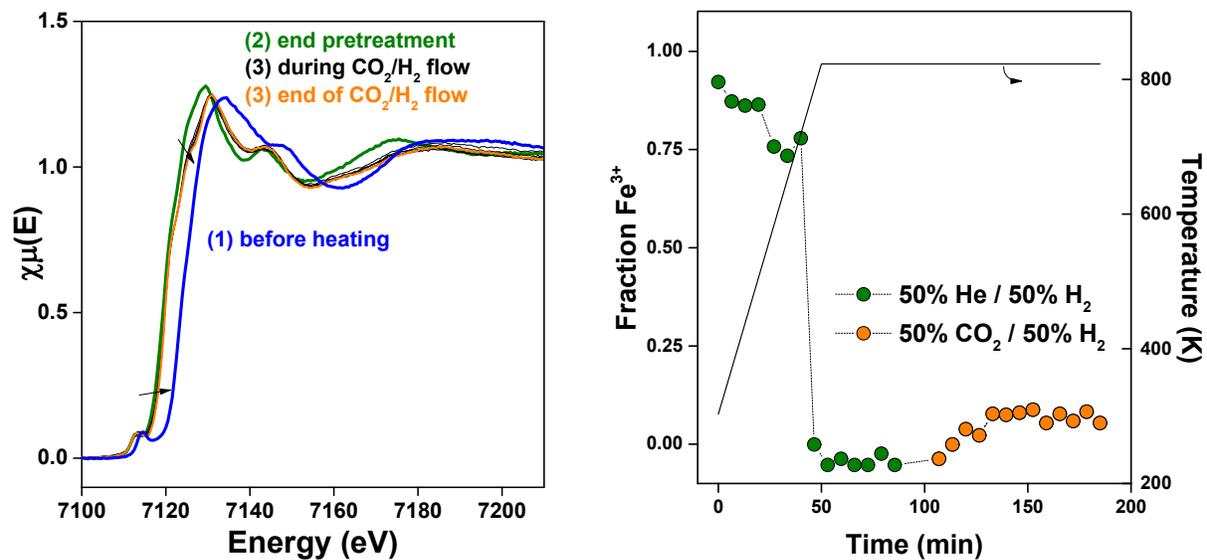


Figure S13. XANES spectra collected *in situ* before and during flow of CO_2/H_2 on 4.2% Fe – 3.4% K/ Al_2O_3 (left) and fraction of Fe^{3+} determined from XANES spectra over the duration of the experiment (right). $T_{\text{rxn}} = 823 \text{ K}$, $F_{\text{tot}} = 10 \text{ sccm}$.

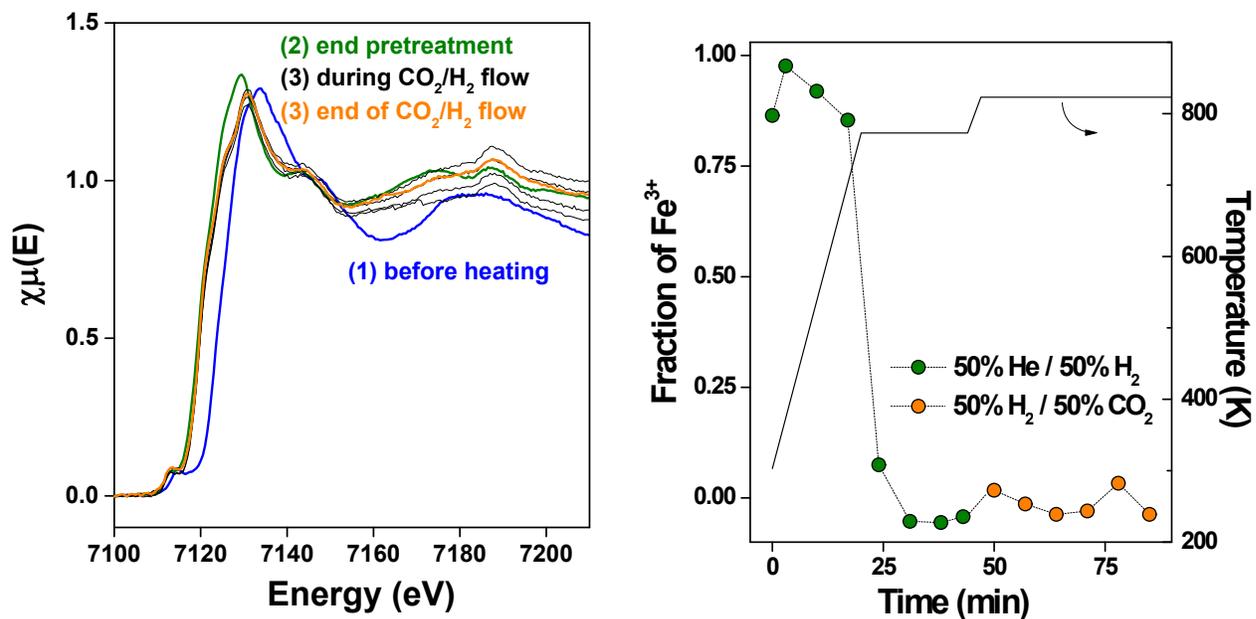


Figure S14. XANES spectra collected *in situ* before and during flow of CO_2/H_2 on 4.5% $\text{Fe}/\text{Al}_2\text{O}_3$ (left) and fraction of Fe^{3+} determined from XANES spectra over the duration of the experiment (right). $T_{\text{rxn}} = 823 \text{ K}$, $F_{\text{tot}} = 10 \text{ sccm}$.

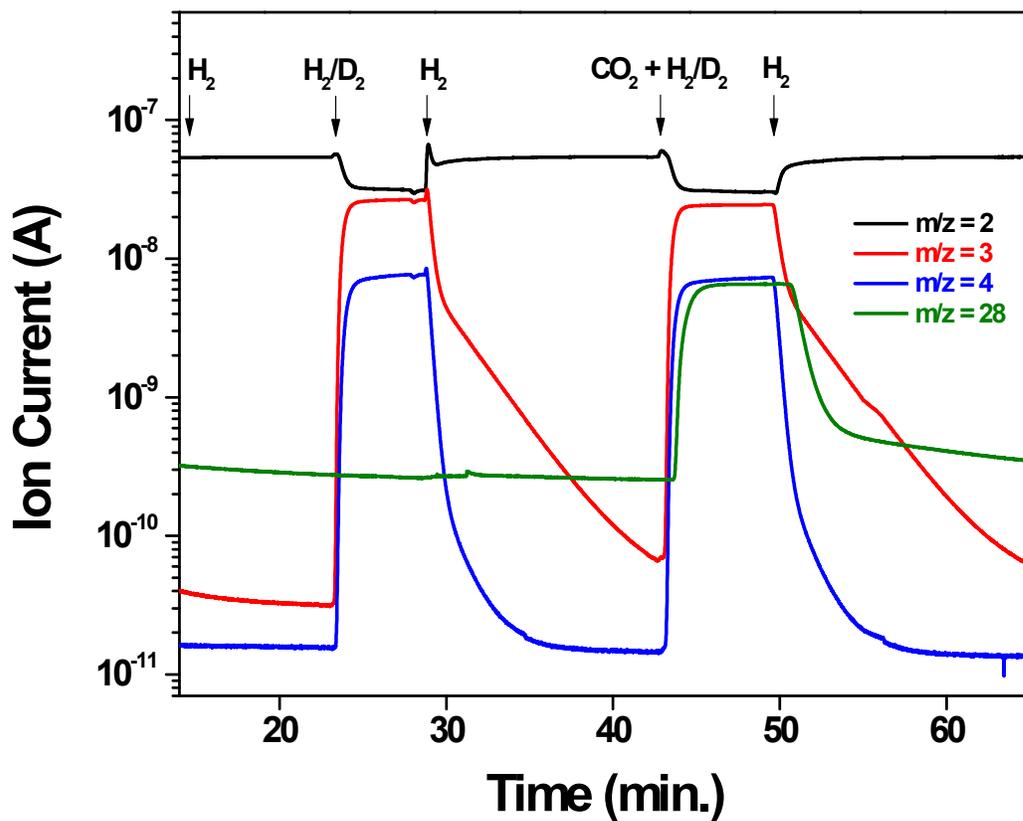


Figure S15. Ion currents at $m/z = 2$ (H_2), 3 (HD), 4 (D_2), and 28 (CO) during flow of 7.5 kPa H_2 , 7.5 kPa $\text{H}_2 + 7.5$ kPa D_2 , and 7.5 kPa $\text{H}_2 + 7.5$ kPa $\text{D}_2 + 15$ kPa CO_2 on $\text{Fe}/\text{Al}_2\text{O}_3$. Arrows with a label indicate a change in gas composition to the indicated gas. Reaction conditions: $T = 753$ K, $F_{\text{tot}} = 75$ sccm.

Table S1. Catalyst precursor amounts, nominal weight loadings, and actual weight loadings.

Catalyst	Mass Fe Precursor / g	Mass K Precursor / g	Mass Al ₂ O ₃ / g	Nominal Fe Loading / wt %	Nominal K Loading / wt %	Actual Fe Loading / wt %	Actual K Loading / wt %
1Fe 3K	0.22	0.19	2.75	1.05	3.7	0.9	3.5
4Fe	0.994	--	2.75	4.8	--	4.5	-
10Fe	1.99	--	2.75	9.1	--	9.1	-
8Fe 3K	1.99	0.243	2.75	8.7	4.3	7.7	3.4
5Fe 1K	1.50	0.10	2.75	6.9	1.9	6.7	2.3
4Fe 4K	0.994	0.243	2.75	4.5	4.6	4.2	3.4