## Supplementary Materials for Reverse Water-Gas Shift Iron Catalyst

## Derived from Magnetite

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Figure S1. XRD pattern of Fe<sub>3</sub>O<sub>4</sub> after the reduction in H<sub>2</sub>.



**Figure S2.** Ion current at m/z = 18 (H<sub>2</sub>O), 28 (CO), and 44 (CO<sub>2</sub>) during H<sub>2</sub>/CO<sub>2</sub> switching experiments on Fe<sub>3</sub>O<sub>4</sub>. Arrows with a label indicate a change in gas composition to the indicated gas. Reaction conditions: T = 773 K, F<sub>He</sub> = 36 sccm, F<sub>H2</sub> or F<sub>CO2</sub> = 4 sccm. The figure is a modification of Figure 6.



**Figure S3.** Ion current at m/z = 2 (H<sub>2</sub>), 3 (HD), 4 (D<sub>2</sub>), and 28 (CO) during flow of 7.5 kPa H<sub>2</sub> + 7.5 kPa D<sub>2</sub> +15 kPa CO<sub>2</sub> and 7.5 kPa H<sub>2</sub> +15 kPa CO<sub>2</sub> on Fe<sub>3</sub>O<sub>4</sub>. Reaction conditions: T = 753 K, F<sub>tot</sub> = 75 sccm.



**Figure S4.** (a) Ion current at m/z = 28 (CO) and m/z = 18 (H<sub>2</sub>O) during H<sub>2</sub>/CO<sub>2</sub> switching experiments on Fe<sub>3</sub>O<sub>4</sub>. Arrows with a label indicate a change in gas composition to the indicated gas. The catalysts were in flowing H<sub>2</sub> for 2 h followed by the reaction in CO<sub>2</sub>+H<sub>2</sub> for 2 h before the first admission of H<sub>2</sub> (relative time: 31 min) and CO<sub>2</sub> (relative time: 46 min). Reaction conditions: T = 753 K, F<sub>tot</sub> = 75 sccm, P<sub>H2</sub> or P<sub>CO2</sub> = 15kPa. (b) is the modification of (a).



**Figure S5**. XPS O1s spectra of Fe<sub>3</sub>O<sub>4</sub> and post-reaction Fe<sub>3</sub>O<sub>4</sub>. The curves under the fitted envelope and above the background are contributions of estimated components from peak fitting. The peak deconvolution and their atomic % are listed on the right of the spectra for each sample.

| Period                                      | Magnitude of H <sub>2</sub> O Initial Slope<br>(10 <sup>-11</sup> A min <sup>-1</sup> ) | H <sub>2</sub> O Area<br>(10 <sup>-9</sup> A min) |
|---|---|---|
| 1st CO <sub>2</sub>                         | 6.46  | 1.71  |
| 2nd CO <sub>2</sub><br>(after 5 min purge)  | 0.70  | 0.47  |
| 3rd CO <sub>2</sub><br>(after 10 min purge) | 0.38  | 0.33  |
| 4th CO <sub>2</sub><br>(after 15 min purge) | 0.19  | 0.29  |
| 5th CO <sub>2</sub><br>(after 20 min purge) | 0.11  | 0.22  |

**Table S1.** Fitted initial slopes and area of H<sub>2</sub>O in H<sub>2</sub>/CO<sub>2</sub> switching experiment with different He purging time in Figure S4.