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

The reducibility and oxidation states of oxide-supported rhenium: Experimental and theoretical investigations

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Supplementary data

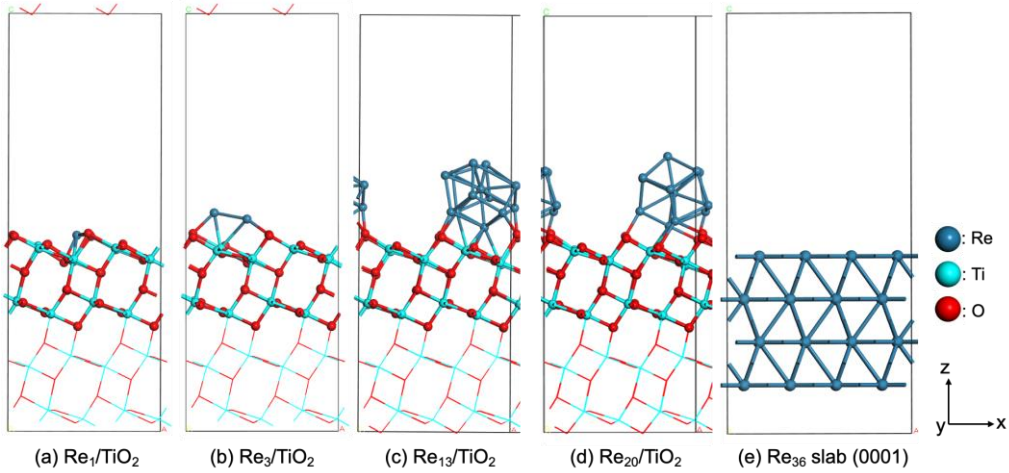

Figure S1. The side view of (a) $Re_1/TiO_2(101)$, (b) $Re_3/TiO_2(101)$, (c) $Re_{13}/TiO_2(101)$, and (d) $Re_{20}/TiO_2(101)$, and (e) Re(0001) slab models used for DFT calculations. The atoms described by ball and stick represent the relaxed layer, and the atoms described by line represent the fixed layer.

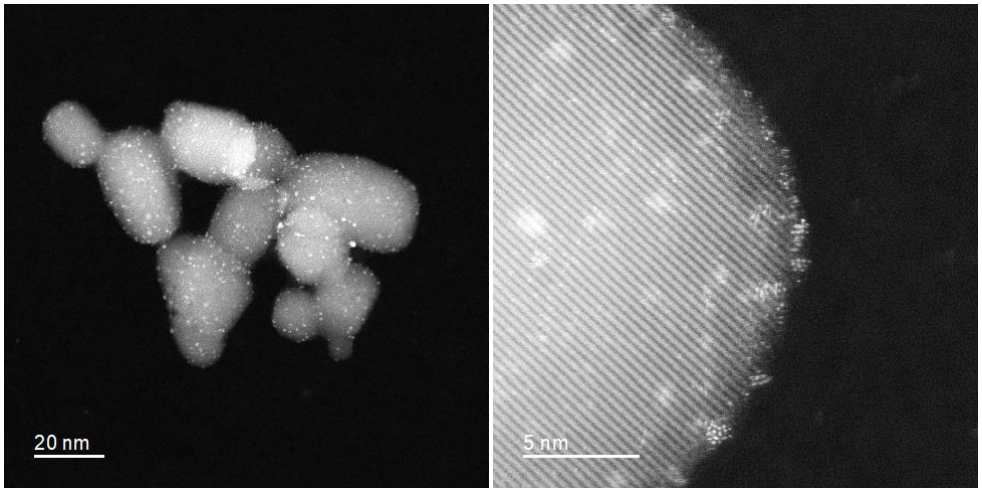

Figure S2. STEM images of Re/TiO_2 after the reduction at 500 °C under a flow of H_2.

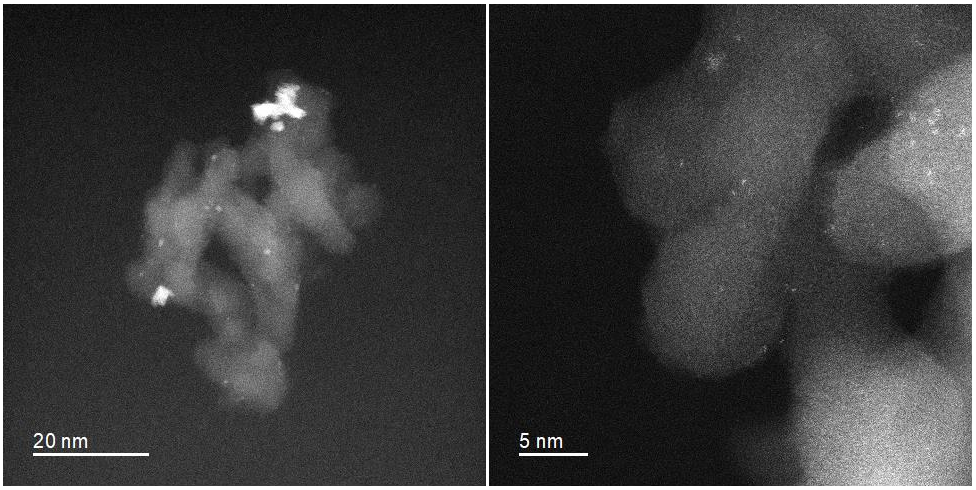

Figure S3. STEM images of Re/SiO_2 after the reduction at 500 °C under a flow of H_2.

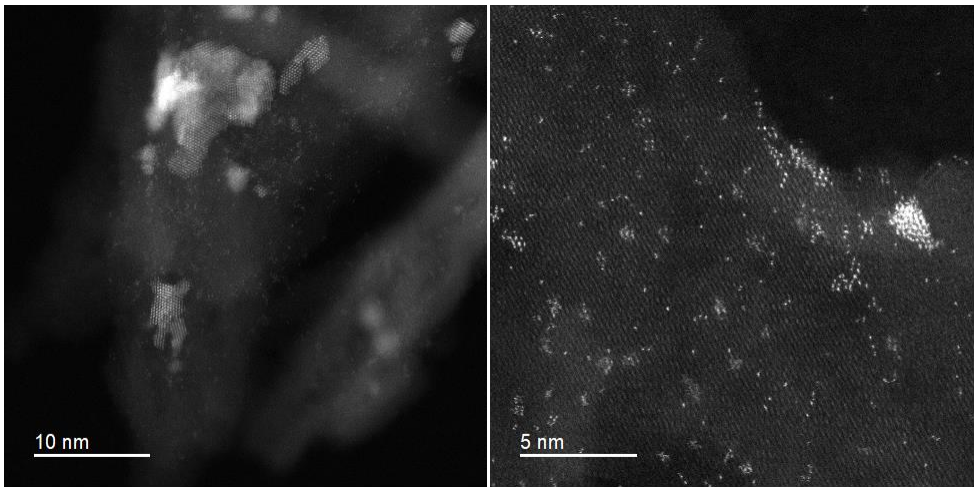

Figure S4. STEM images of Re/Al_2O_3 after the reduction at 500 °C under a flow of H_2.

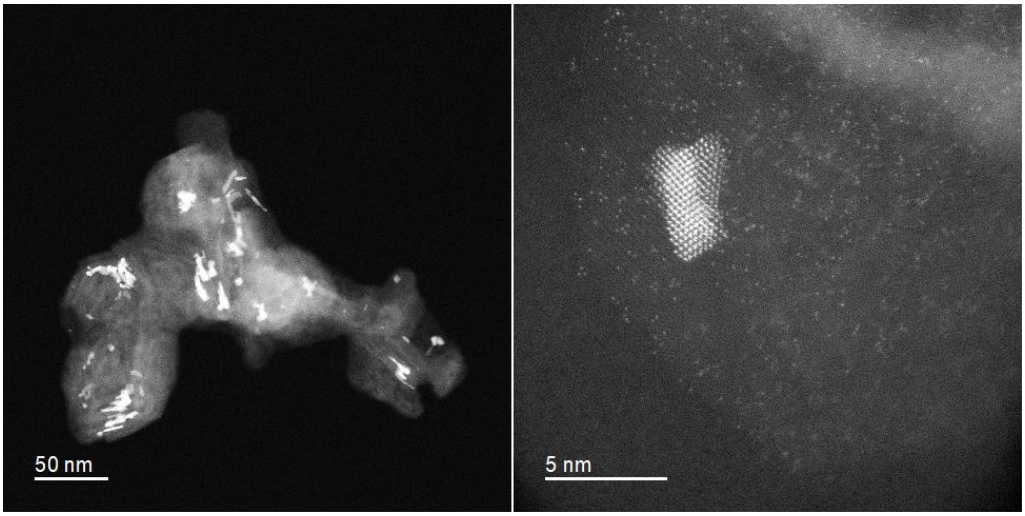

Figure S5. STEM images of Re/MgO after the reduction at 500 °C under a flow of H_2.

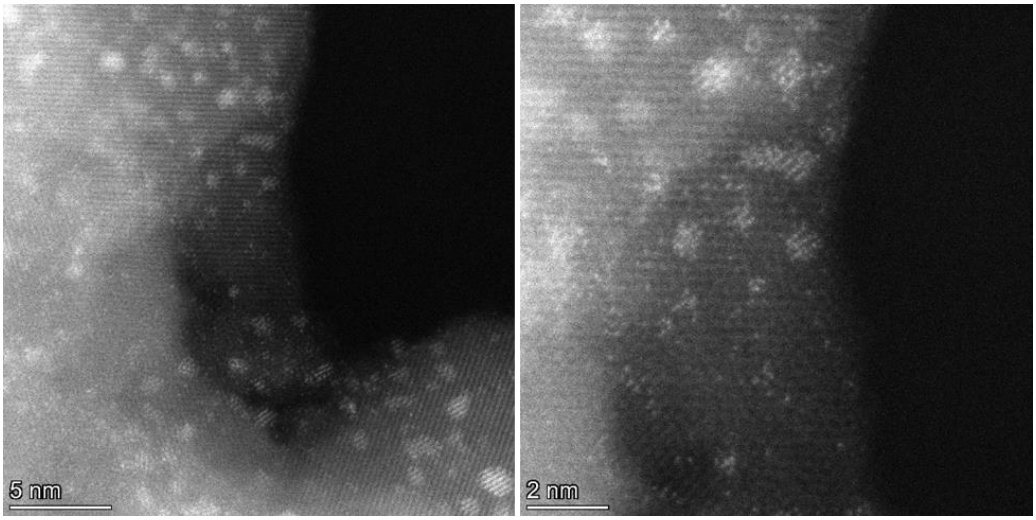

Figure S6. STEM images of Re/V_2O_5 after the reduction at 500 °C under a flow of H_2.

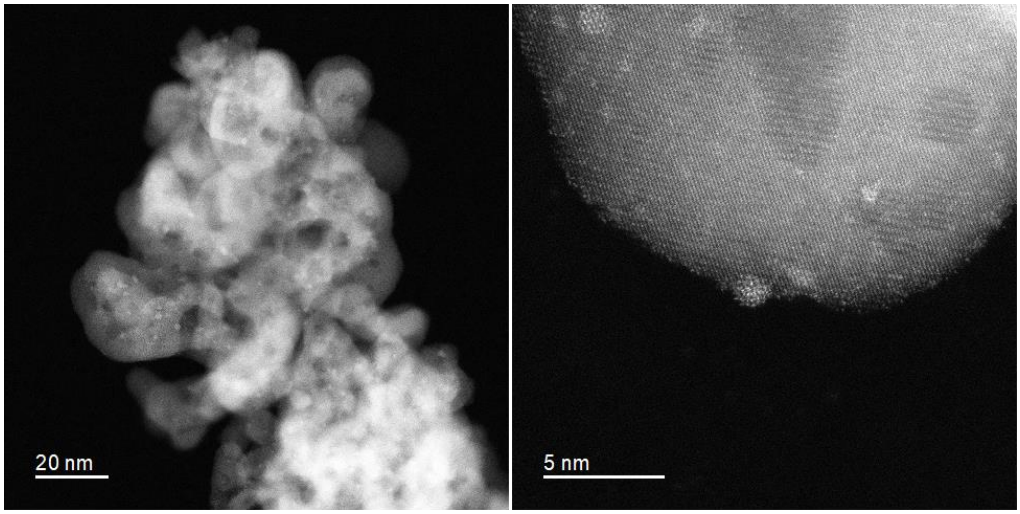

Figure S7. STEM images of Re/ZrO_2 after the reduction at 500 °C under a flow of H_2.

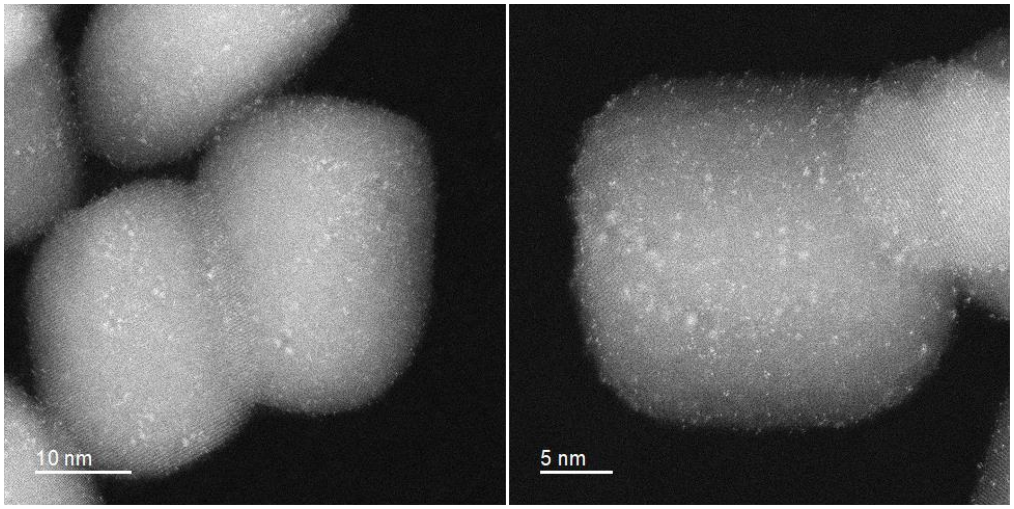

Figure S8. STEM images of Re/TiO_2 without H_2 reduction.

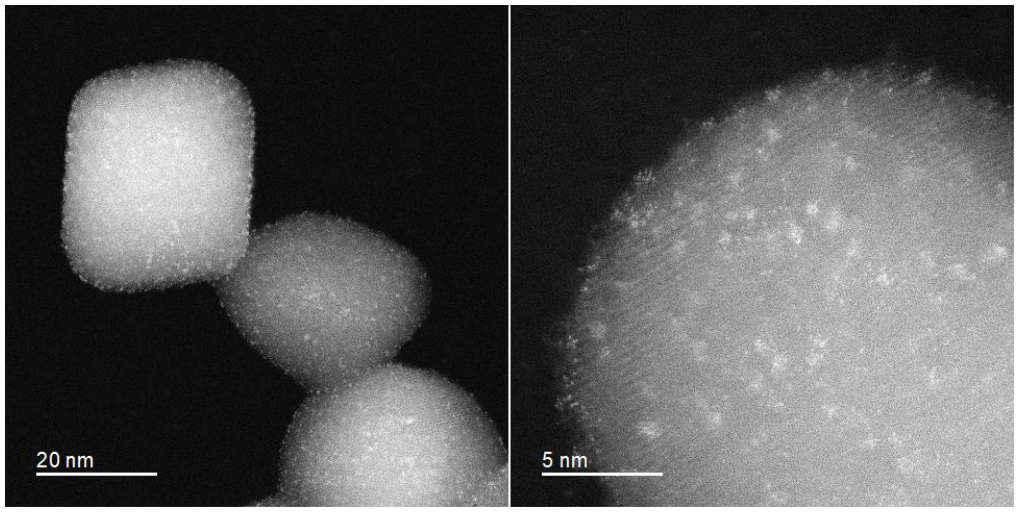

Figure S9. STEM images of Re/TiO_2 after the reduction at 300 °C under a flow of H_2.

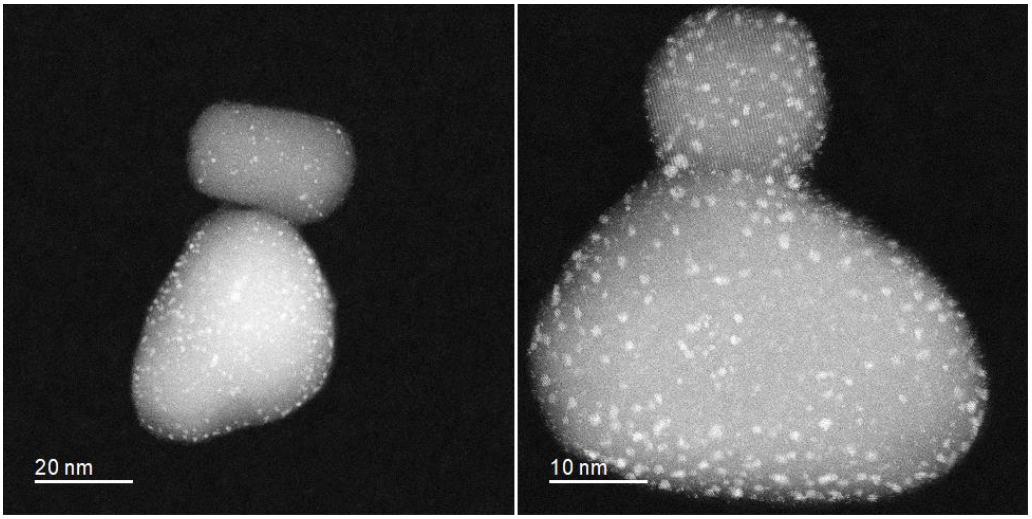

Figure S10. STEM images of Re/TiO_2 after the reduction at 700 °C under a flow of H_2.

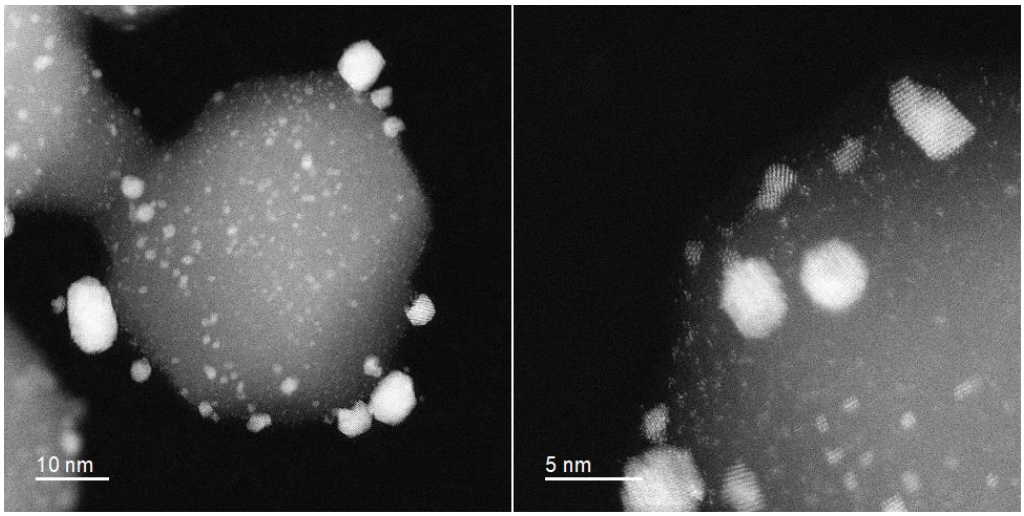

Figure S11. STEM images of Re/TiO_2 after the reduction at 900 °C under a flow of H_2.

Table S1: Data for LCF of *in situ* Re L_1-edge XANES spectra of Re(5)/TiO_2. LCF was performed over a fitting range of −20 to 30 eV relative to the absorption edge (E_0) using Re powder (Re^0), ReO_2 (Re^{4+}), ReO_3 (Re^{6+}), and NH_4ReO_4 (Re^{7+}) as standards.

Reduction temp. (°C)	R-factor	Re^{7+} (%)	Re^{6+} (%)	Re^{4+} (%)	Re^0 (%)
100	0.00299	84 ± 9	8 ± 4.7	< 1	8 ± 2.2
200	0.00232	80 ± 8.1	6 ± 4.2	6 ± 6.6	7 ± 1.9
300	0.00179	1 ± 8.2	< 1	47 ± 6.8	51 ± 2.0
400	0.00204	6 ± 8.6	< 1	23 ± 7.1	72 ± 2.1
500	0.00186	8 ± 8.2	< 1	14 ± 6.8	78 ± 2.0
600	0.00160	7 ± 7.6	< 1	16 ± 6.3	78 ± 1.8
700	0.00095	12 ± 5.7	< 1	5 ± 4.6	83 ± 1.4

Table S2: Data for LCF of *in situ* Re L_1-edge XANES spectra of Re(5)/ZrO_2. LCF was performed over a fitting range of −20 to 30 eV relative to the absorption edge (E_0) using Re powder (Re^0), ReO_2 (Re^{4+}), ReO_3 (Re^{6+}), and NH_4ReO_4 (Re^{7+}) as standards.

Reduction temp. (°C)	R-factor	Re^{7+} (%)	Re^{6+} (%)	Re^{4+} (%)	Re^0 (%)
100	0.00360	59 ± 11	10 ± 5.6	31 ± 8.6	< 1
200	0.00249	60 ± 8.9	17 ± 4.7	23 ± 7.3	< 1
300	0.00116	4 ± 6.9	< 1	71 ± 5.6	25 ± 1.6
400	0.00143	3 ± 7.8	< 1	45 ± 6.3	52 ± 1.8
500	0.00230	3 ± 9.8	< 1	36 ± 8.0	61 ± 2.2
600	0.00373	< 1	< 1	27 ± 10	73 ± 2.9
700	0.00331	2.5 ± 12	< 1	23 ± 9.6	74 ± 2.7

Table S3: Data for LCF of *in situ* Re L_1-edge XANES spectra of Re(5)/SiO_2. LCF was performed over a fitting range of −20 to 30 eV relative to the absorption edge (E_0) using Re powder (Re^0), ReO_2 (Re^{4+}), ReO_3 (Re^{6+}), and NH_4ReO_4 (Re^{7+}) as standards.

Reduction temp. (°C)	R-factor	Re^{7+} (%)	Re^{6+} (%)	Re^{4+} (%)	Re^0 (%)
100	0.00184	87 ± 1.3	1 ± 2.7	< 1	6 ± 1.5
200	0.00153	86 ± 1.1	2 ± 2.4	< 1	7 ± 1.4
300	0.00078	17 ± 0.8	< 1	16 ± 3.0	6 ± 1.0
400	0.00151	2 ± 1.1	< 1	12 ± 4.1	8 ± 1.4
500	0.00119	< 1	< 1	10 ± 3.6	8 ± 1.2
600	0.00155	< 1	< 1	9 ± 4.2	8.4 ± 1.4
700	0.00188	< 1	< 1	9.2 ± 4.6	8.4 ± 1.5

Table S4: Data for LCF of *in situ* Re L_1-edge XANES spectra of Re(5)/V_2O_5. LCF was performed over a fitting range of −20 to 30 eV relative to the absorption edge (E_0) using Re powder (Re^0), ReO_2 (Re^{4+}), ReO_3 (Re^{6+}), and NH_4ReO_4 (Re^{7+}) as standards.

Reduction temp. (°C)	R-factor	Re^{7+} (%)	Re^{6+} (%)	Re^{4+} (%)	Re^0 (%)
100	0.00032	97 ± 0.6	< 1	2 ± 2.4	< 1
200	0.00046	94 ± 0.7	< 1	4 ± 2.9	< 1
300	0.00075	69 ± 0.9	2.7 ± 2.3	12 ± 3.8	16 ± 1.1
400	0.00304	< 1	< 1	< 1	1
500	0.00570	< 1	< 1	< 1	1
600	0.00190	< 1	< 1	< 1	1

Table S5: Data for LCF of *in situ* Re L_1-edge XANES spectra of Re(5)/Al_2O_3. LCF was performed over a fitting range of −20 to 30 eV relative to the absorption edge (E_0) using Re powder (Re^0), ReO_2 (Re^{4+}), ReO_3 (Re^{6+}), and NH_4ReO_4 (Re^{7+}) as standards.

Reduction temp. (°C)	R-factor	Re^{7+} (%)	Re^{6+} (%)	Re^{4+} (%)	Re^0 (%)
100	0.00183	95 ± 1.3	57 ± 2.3	< 1	3 ± 1.4
200	0.00177	90 ± 1.3	78 ± 2.2	< 1	5 ± 1.4
300	0.00156	76 ± 1.2	9 ± 2.1	12 ± 3.5	5 ± 1.3
400	0.00095	3 ± 0.9	< 1	26 ± 2.7	71 ± 0.9
500	0.00220	2 ± 1.4	< 1	25 ± 3.9	72 ± 1.5
600	0.00519	2 ± 2.1	< 1	25 ± 5.9	72 ± 2.2
700	0.00816	2 ± 2.5	< 1	25 ± 7.3	73 ± 2.7

Table S6: Data for LCF of *in situ* Re L_1-edge XANES spectra of Re(5)/MgO. LCF was performed over a fitting range of −20 to 30 eV relative to the absorption edge (E_0) using Re powder (Re^0), ReO_2 (Re^{4+}), ReO_3 (Re^{6+}), and NH_4ReO_4 (Re^{7+}) as standards.

Reduction temp. (°C)	R-factor	Re^{7+} (%)	Re^{6+} (%)	Re^{4+} (%)	Re^0 (%)
100	0.00183	95 ± 1.3	57 ± 2.3	< 1	3 ± 1.4
200	0.00177	90 ± 1.3	78 ± 2.2	< 1	5 ± 1.4
300	0.00156	76 ± 1.2	9 ± 2.1	12 ± 3.5	5 ± 1.3
400	0.00095	3 ± 0.9	< 1	26 ± 2.7	71 ± 0.9
500	0.00220	2 ± 1.4	< 1	25 ± 3.9	72 ± 1.5
600	0.00519	2 ± 2.1	< 1	25 ± 5.9	72 ± 2.2
700	0.00816	2 ± 2.5	< 1	25 ± 7.3	73 ± 2.7

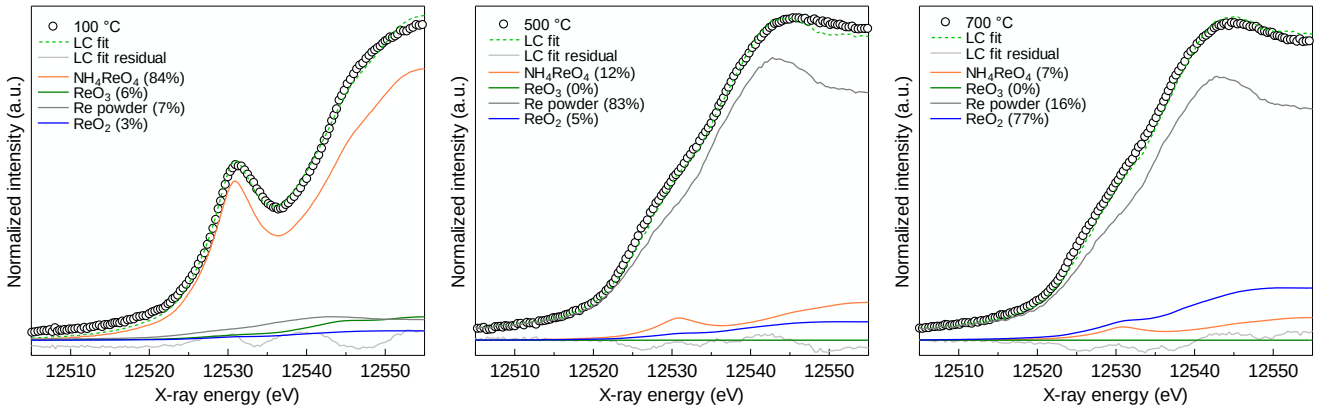

Figure S12: Comparison of experimental and LCF XANES spectra for Re(5)/TiO_2 treated at 100 °C, 500 °C and 700 °C reduction temperature. Component fraction of each standard is also included for ease of reference.

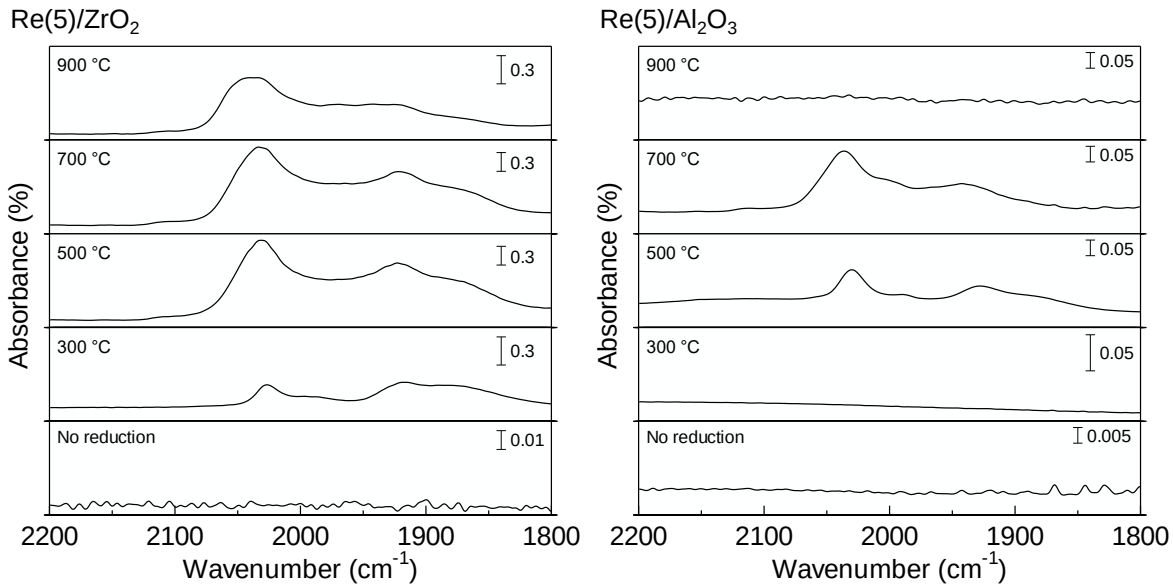

Figure S13. FTIR spectra of CO adsorbed on unreduced and H_2-reduced Re(5)/ZrO_2 and Re(5)/Al_2O_3 catalysts. Each sample was pretreated (if applicable) under a flow of 10% H_2/He (100 mL min^{-1}) for 30 min, exposed to a flow of 1% CO/He (100 mL min^{-1}) for 5 min, and purged with He for 5 min.

Table S7. Summary of formal oxidation states, Bader charges for Re species.

Model	Formal oxidation state of Re	(Average) Bader charge of Re
ReO_2	4	1.85
$Re_1/TiO_2(101)$	0	0.79
$Re_3/TiO_2(101)$	0	0.40
$Re_{13}/TiO_2(101)$	0	0.14
$Re_{20}/TiO_2(101)$	0	0.13
Re(0001)	0	0.00