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Supplementary Information

Thermodynamic assessment of Gd-doped CeO_2 for microwave-assisted thermochemical reduction

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S1. Microwave power transfer from source to sample-loaded cavity

In typical electric circuit analysis, lumped elements are used. This means that the components are not affected by the physical size of the circuit. However, suppose the wavelength of the high-frequency (such as RF, microwave) power source is smaller or similar to the physical size of the circuit (considered distributed elements). In that case, the voltage and current can vary significantly in amplitude and phase along the line length. Therefore, if these characteristics are not considered, the microwave signal will be reflected from the load, resulting in a decrease in the power reaching the load. Transmission line theory is utilized for the efficient delivery of microwave power to load.[1]

$$Return\ Loss = -20\log(|\Gamma|) = -S_{11}(f) \tag{S1}$$

$$P_{eff}(f) = P(1 - |S_{11}(f)|^2) \tag{S2}$$

$$f_0 \equiv f_{nml} = \frac{c}{2\pi\sqrt{\varepsilon_r \mu_r}}\sqrt{\left(\frac{P_{nm}^{TE}}{r}\right)^2 + \left(\frac{l\pi}{h}\right)^2} \tag{S3}$$

Equation (**S1**) shows the expression for the return loss of the reflection coefficient Γ, where Γ corresponds to the voltage ratio of reflected voltage (V_{ref}) divided by incident voltage (V_{inc}). $-S_{11}$ expressed as a function of frequency is equivalent to return loss and can be measured with a network analyzer. Additionally, this value can be obtained from a spectrum analyzer for a single frequency used in this paper. The effective microwave power $P_{eff}(f)$ delivered to the sample-loaded cavity can be expressed as **equation** (**S2**), where P represents the amplified microwave output power. Meanwhile, the resonant frequency f_0 for the cylindrical cavity is defined only in TE (Transverse Electric) mode in this work, as shown in **equation** (**S3**). The term c is the speed of light, ε_r is the relative permittivity of the filled medium inside the cavity, μ_r is the relative permeability of the filled medium inside the cavity, and P_{nm}^{TE} is m^{th} zero of the n^{th} Bessel function. The values r and h represent the radius and height of the cavity, respectively. Due to the nature of the resonance mode, when a driving frequency f_d different from f_0 is applied to the cavity, the reflection ratio of power increases ($|S_{11}(f)|$ increases), resulting in a decrease in the power transfer ratio $(1 - |S_{11}(f)|^2)$ to the cavity. For the case of literature[2,3] and our work, when the temperature of the metal oxides is increased via microwave heating, f_0 of the sample-loaded cavity decreases. Therefore, $P_{eff}(f)$ is maximized by tracking the continuous shift of f_0 and matching f_d to f_0.

δ	1000/T	$ln(P(O_2))$	Slope	ΔH_O (kJ/mol_O)
0.0045	1.45	-8.52		
	1.38	-5.00	-45.86	190.64
	1.34	-4.49	-14.45	60.08
	1.19	-2.28	-14.66	60.93
0.0065	1.40	-8.52		
	1.30	-5.00	-34.89	145.03
	1.25	-4.49	-11.05	45.92
	1.09	-2.28	-13.70	56.95
0.0085	1.35	-8.52		
	1.23	-5.00	-29.21	121.53
	1.18	-4.49	-9.38	39.00
	1.01	-2.28	-13.19	54.82
0.0105	1.30	-8.52		
	1.17	-5.00	-25.79	107.20
	1.11	-4.49	-8.42	35.02
0.0125	1.26	-8.52		
	1.11	-5.00	-23.54	97.85
	1.05	-4.49	-7.83	32.53
0.0145	1.22	-8.52		
	1.06	-5.00	-21.98	91.37
	0.99	-4.49	-7.43	30.89

Table S1 Enthalpy changes based on slope analysis between consecutive data points in Figure 7 of the main text. The slope represents the $\Delta \ln\left(P(O_2)\right)/\Delta(1000/T)$ obtained from the data points of the previous and the corresponding rows.

References

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