

Supplementary Information

Temperature-dependent CO₂ Sorption and Thermal-reduction without Reactant Gases on BaTiO₃ Nanocatalysts by Low Temperatures at 300–1000 K

Takumi Watanabe and Tomonori Ohba*

Graduate School of Science, Chiba University, 1-33 Yayoi, Inage, Chiba 263-8522,
Japan

**Corresponding author.* E-mail: ohba@chiba-u.jp (T. Ohba)

Table S1

Figure S1–S15

Table S1 Structural properties of 10, 20, and 200 nm-nanocatalysts.

Sample	Crystal size / nm	Particle size / nm	Surface area / m² g⁻¹	Total Pore volume / cm³ g⁻¹
10 nm- nanocatalysts	7.4 ± 0.4	10–11	96	0.07
20 nm- nanocatalysts	18 ± 1.0	19–21	52	0.12
200 nm- nanocatalysts	190 ± 20	1600–2010	1	0.00

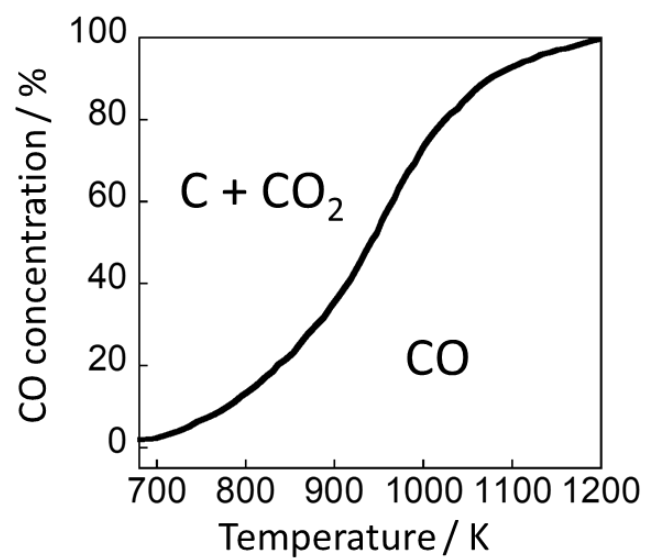


Fig. S1 CO concentration dependence on temperature during the CO disproportionation reaction.

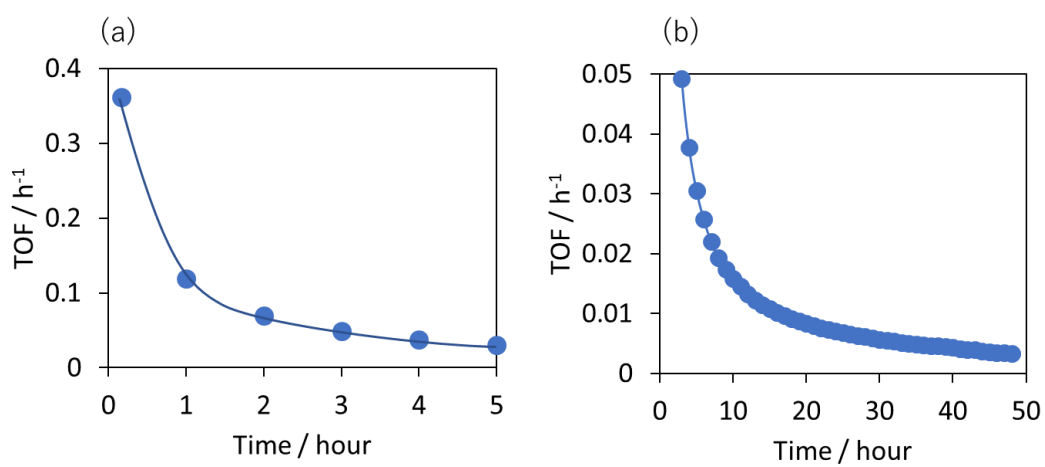


Fig. S2 TOF changes of CO_2 reduction using BaTiO_3 nanocatalysts in short-term (a) and long-term (b) at 700 K.

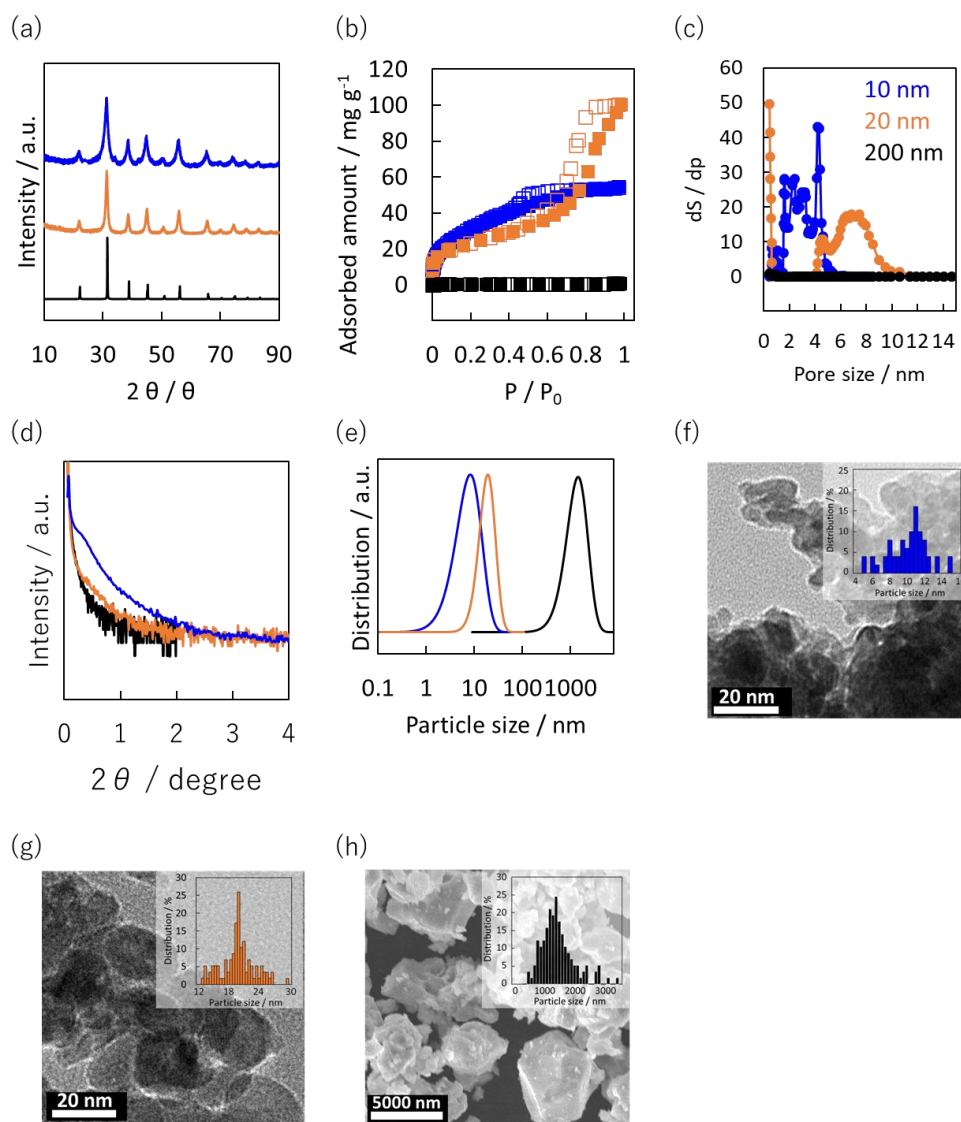


Fig. S3 (a) XRDs, (b) N_2 adsorption isotherms at 77 K, (c) pore size distribution calculated from comparison of the N_2 adsorption isotherms with grand canonical Monte Carlo simulations, (d) small angle X-ray scatterings, and (e) particle size distributions of the 10 nm (blue), 20 nm (orange) and 200 nm-nanocatalysts (black), obtained from the small angle X-ray scatterings. The closed and open symbol represent adsorption and desorption, respectively. TEM and SEM observation with the particle size distribution of the (f) 10 nm, (g) 20 nm, and (h) 200 nm-nanocatalysts.

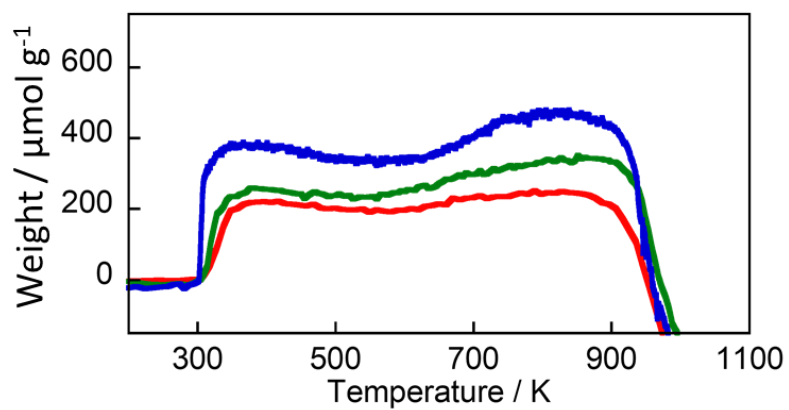


Fig. S4 Temperature-sweep weight changes of the 10 nm-nanocatalysts at 1 (blue), 5 (dark green), and 10 K min^{-1} (red).

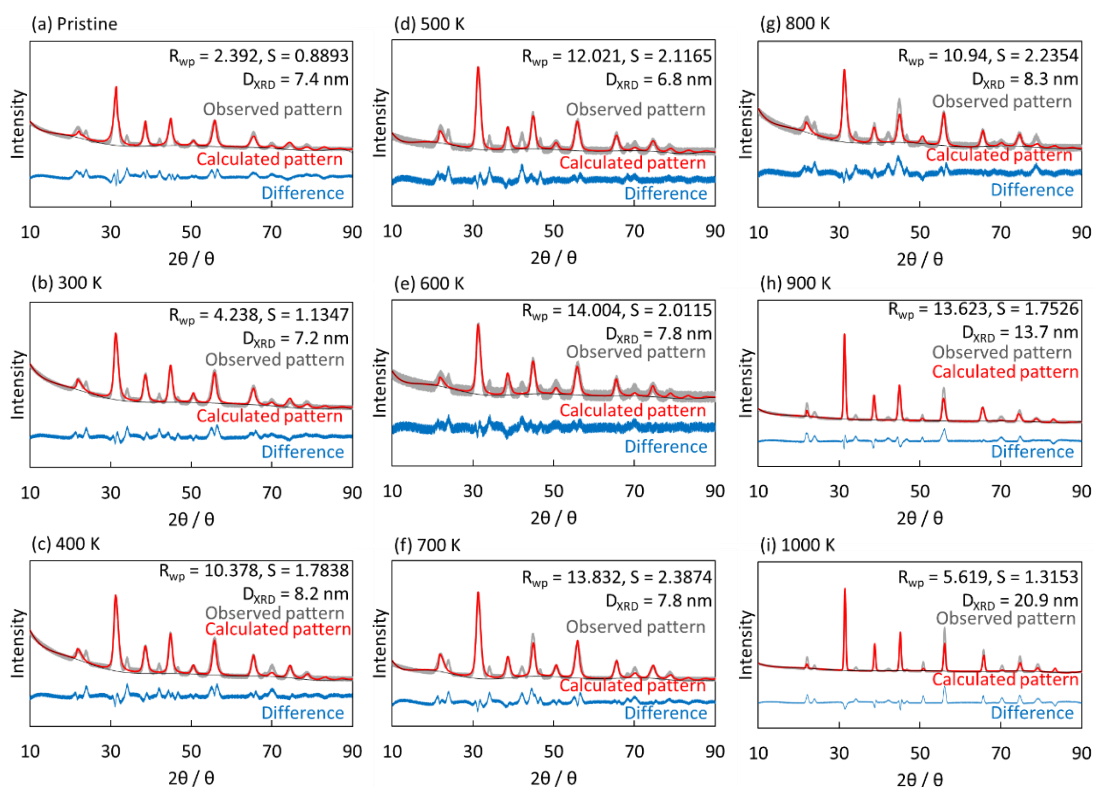


Fig. S5 X-ray diffraction patterns of the 10 nm-nanocatalysts heated at 300–1000 K and the results of the Rietveld analysis performed to determine the crystallite size. The figure illustrates the observed patterns (gray), calculated patterns (red), and differences between them (blue). D_{XRD} is the crystallite size determined using the Scherrer equation.

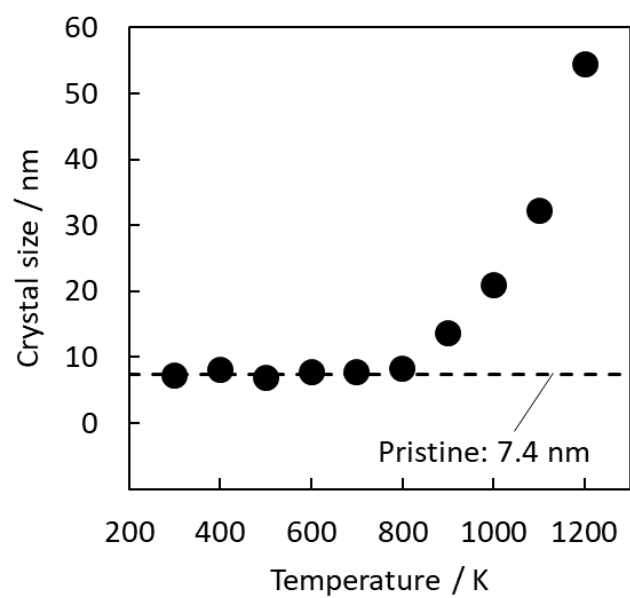


Fig. S6 Crystal size dependence on the calcination temperature.

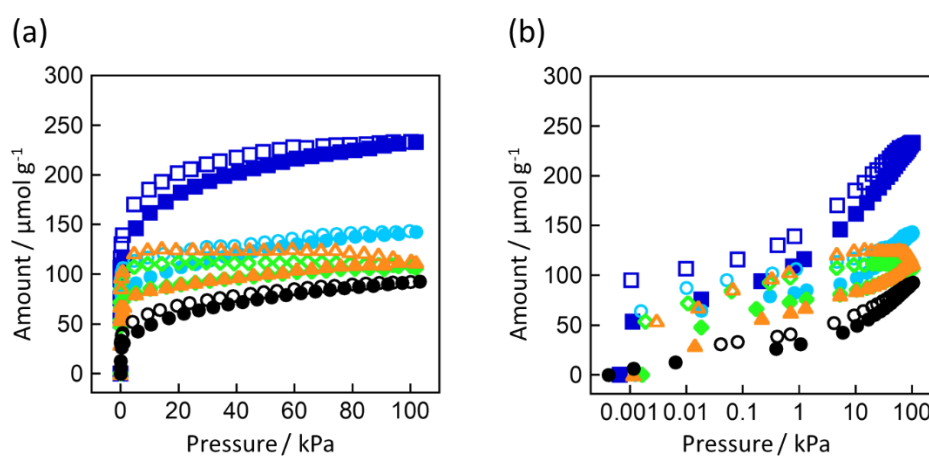


Fig. S7 (a) Adsorption isotherms of CO₂ by the 10 nm-nanocatalysts at 300 K (blue square), 400 K (sky blue circle), 500 K (green diamond), and 600 K (orange triangle); and (b) logarithmic-scaled isotherms. Adsorption isotherms of CO₂ by the 20 nm-nanocatalysts at 300 K (black circle) is for comparison. Closed and open symbols represent adsorption and desorption, respectively.

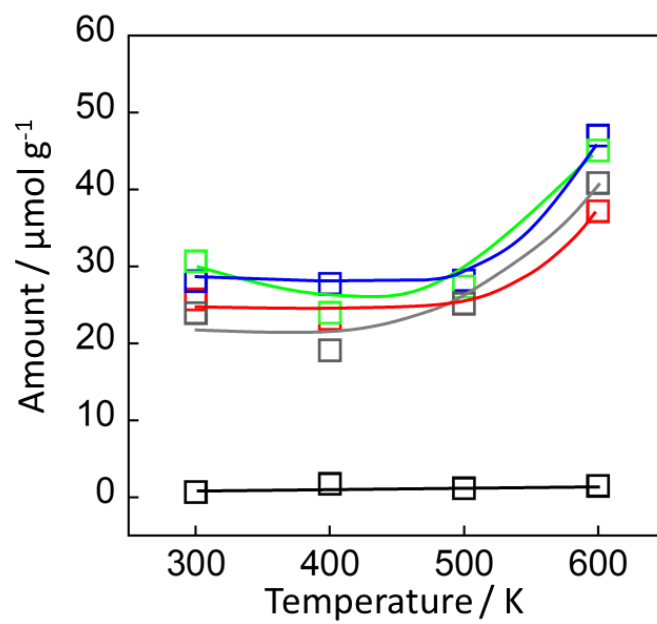


Fig. S8 Differential amount between CO₂ adsorption and desorption on the 10 nm-nanocatalysts under 0.01 (red), 0.1 (blue), 1 (green), 10 (gray), and 100 kPa (black).

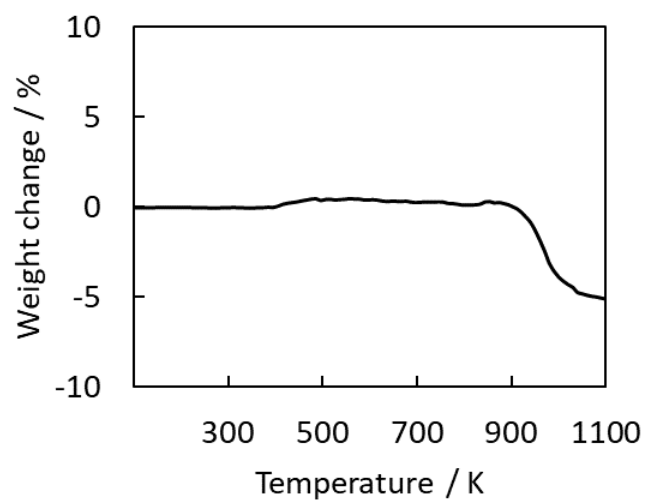


Fig. S9 Weight change of the 10 nm-nanocatalysts heated under Ar atmosphere.

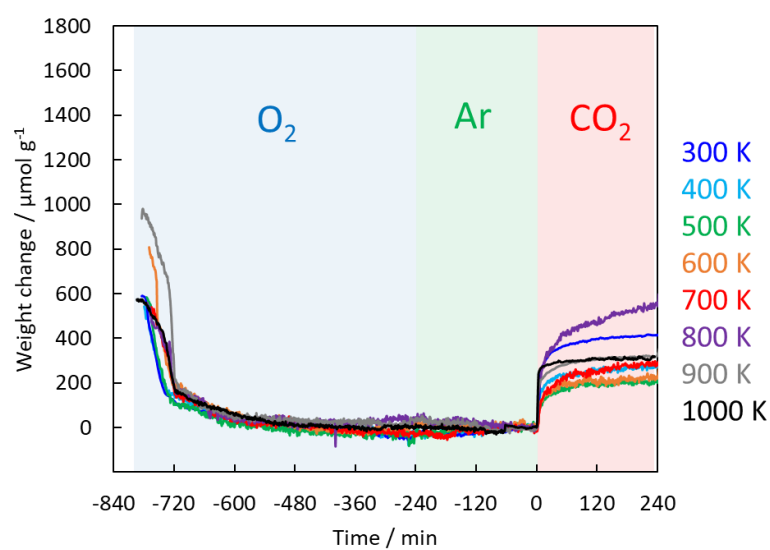


Fig. S10 Weight change of the nanocatalysts under isothermal conditions at 300–1000 K for 4 h. The weight changes were set to zero just before CO₂ flow. The samples were heated up to the target temperatures 300–1000 K at 10 K min⁻¹ and kept at the temperatures for 8 h. The atmosphere was then replaced with Ar for 4 h and the isothermal measurements were finally started in CO₂ atmosphere.

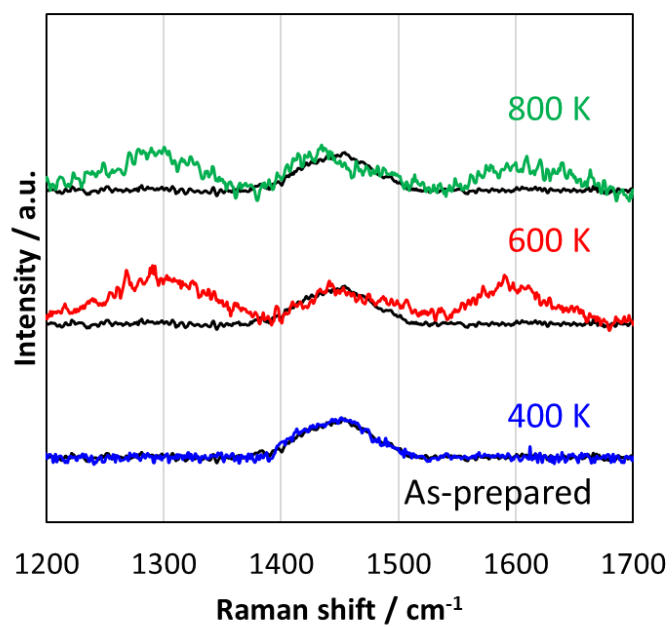


Fig. S11 Raman scattering spectroscopies on 10 nm-nanocatalysts after heating at 400, 600, and 800 K in CO₂ atmosphere for 24 h.

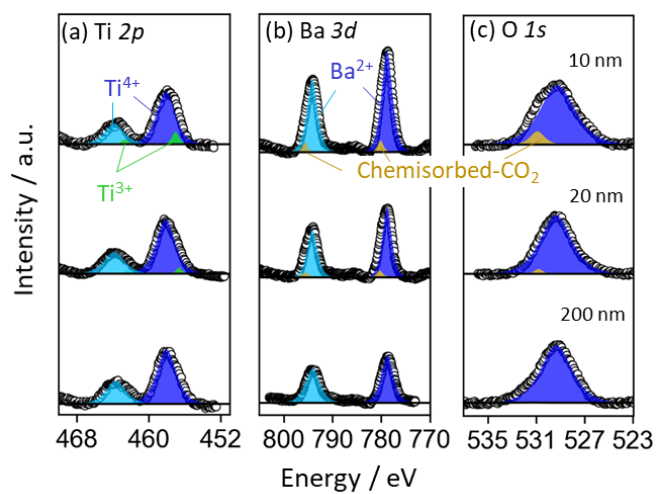


Fig. S12 XPS spectra of (a) Ti 2p, (b) Ba 3d, and (c) O 1s of the as-synthesized 10 nm- (top), 20 nm- (center), and 200 nm-nanocatalysts (bottom). The peak area was standardized by the Ti 2p area.

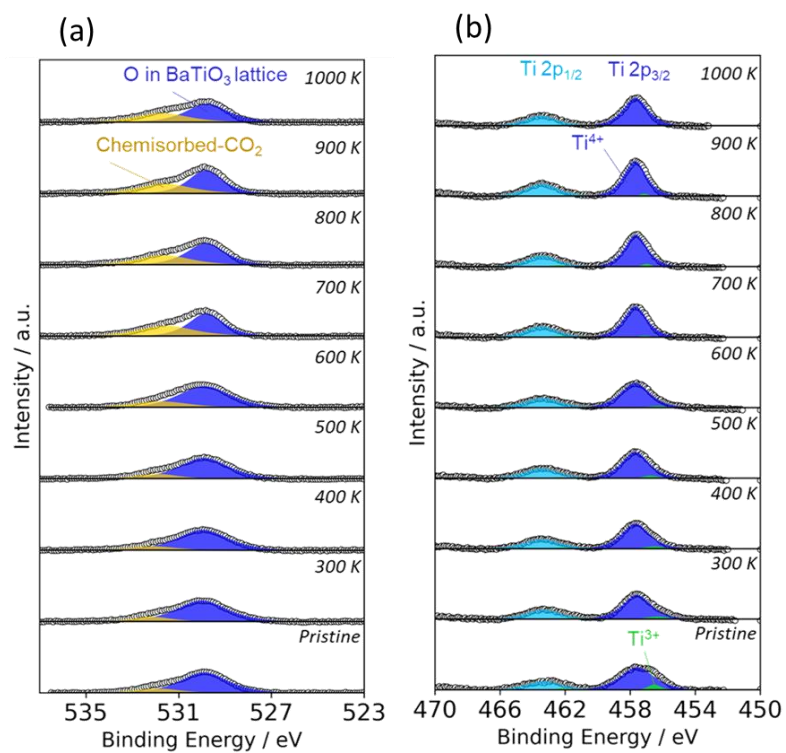


Fig. S13 (a) O 1s and (b) Ti 2p XPS spectra of the 10 nm-nanocatalysts after heating under CO₂ atmosphere.

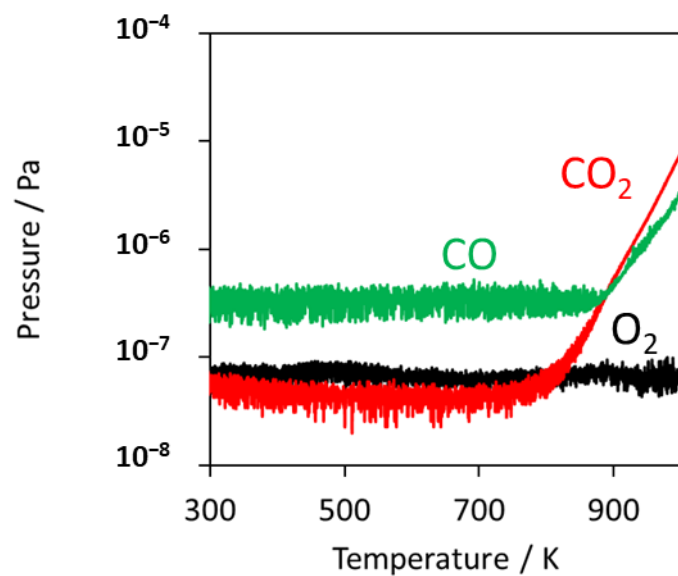


Fig. S14 Temperature-programmed desorption of the 10 nm-nanocatalysts after the isothermal catalytic reaction with CO₂ at 800 K for 24 h.

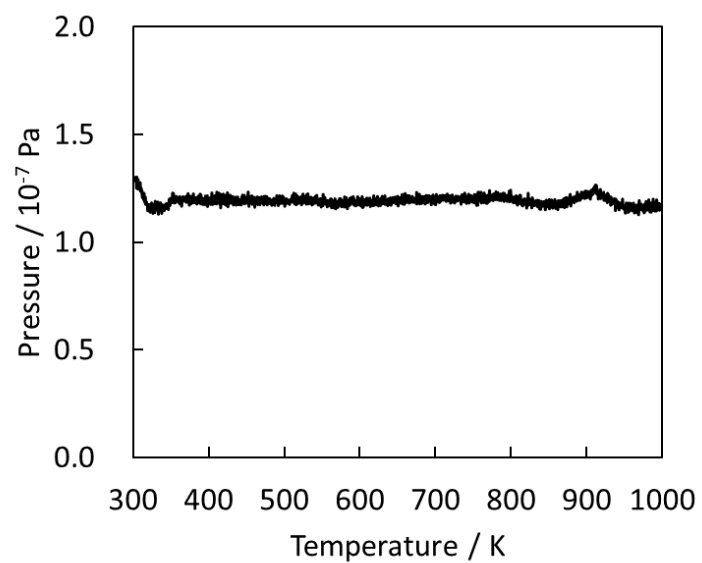


Fig. S15 Temperature programmed desorption of O₂ for the pristine 10 nm-nanocatalysts. The 10 nm-nanocatalysts was heated at 300–1000 K under vacuum.