

Supporting Information

Stability of Molten-phase Cs–V–O Catalysts for SO₃ Decomposition
in Solar Thermochemical Water Splitting

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Experimental details

Preparation of mesoporous SiO₂

The precursor was prepared by dissolving 6 g a triblock copolymer P123 (BASF) in 217 g distilled water and 11.8 g 35% HCl, followed by addition of 6 g C₄H₉OH (Wako, 98%) under stirring at 35 °C for 1 h and subsequent addition of 12.9 g tetraethyl orthosilicate (Si(OC₂H₅)₄, Wako, 98%). After stirring for 24 h at 35 °C, the as-obtained mixture was hydrothermally treated at 100 °C for 24 h under static conditions. The solid product was filtered without washing and dried at 100 °C followed by treatment in C₂H₅OH/HCl solution and calcination in air at 550 °C for 5 h.

Catalytic reactions

SO₃ decomposition reactions were carried out in a flow reactor system as shown in Figure S1. Sulfuric acid (95%) was pumped and vaporized at 450 °C in a flow of N₂ and thermally decomposed into SO₃ and H₂O in the gas phase. The resulting gas mixture of 14 vol% SO₃, 18 vol% H₂O, and N₂ balance was then supplied to the catalyst bed at 500 or 600 °C. A granular catalyst (10–20 mesh and 2.0–0.8 mm in size) was fixed in a quartz tube (inner diameter: 8 mm) with quartz wool at both ends of the catalyst bed. The weight hourly space velocity (WHSV) was 11 or 110 g-H₂SO₄ g-cat⁻¹ h⁻¹, depending on the mass of the catalyst, i.e., 0.50 and 0.05 g, respectively. The gas effluent from the catalyst bed was bubbled into an aqueous solution of NaOH to remove SO₃ and dried using a dry ice/ethanol trap. The gas was finally introduced into a gas analyzing unit, where the O₂ concentration was measured using a magneto-pneumatic oxygen analyzer (MPA3000, Horiba) and a gas chromatographer (TCD, He carrier, an MS-5A column, GC8A, Shimadzu). The steady-state conversion of SO₃ to SO₂ was calculated from the concentration of O₂ in the gas effluent. The obtained value was consistent with the SO₂ concentration in the effluent gas, which was determined using iodimetric titration. Catalyst-stability tests were performed in a similar manner, but a granular catalyst (10–20 mesh, 0.15 g) was fixed in a quartz tube (inner diameter: 6 mm) with quartz wool at both ends of the 12-mm long catalyst bed. At a constant temperature of 550 or 600 °C, the reaction mixture was supplied at WHSV = 11 g-H₂SO₄ g-cat⁻¹ h⁻¹, and the deactivation behavior was recorded in terms of SO₃ conversion as a function of time-on-stream.

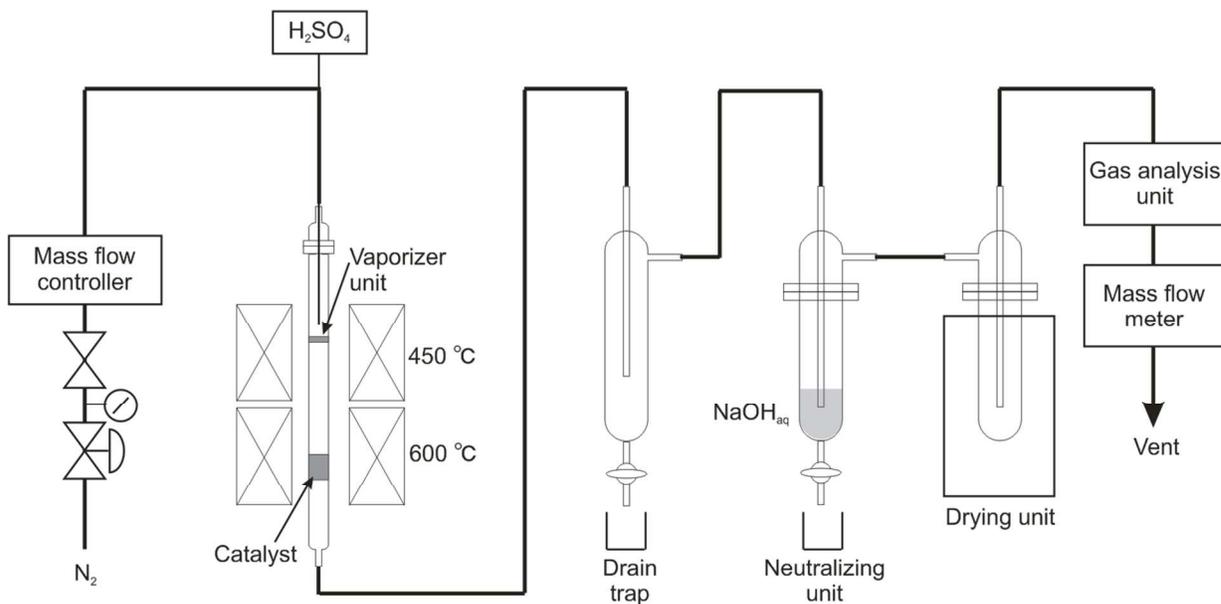


Figure S1. Schematic diagram of catalytic SO_3 decomposition test apparatus.

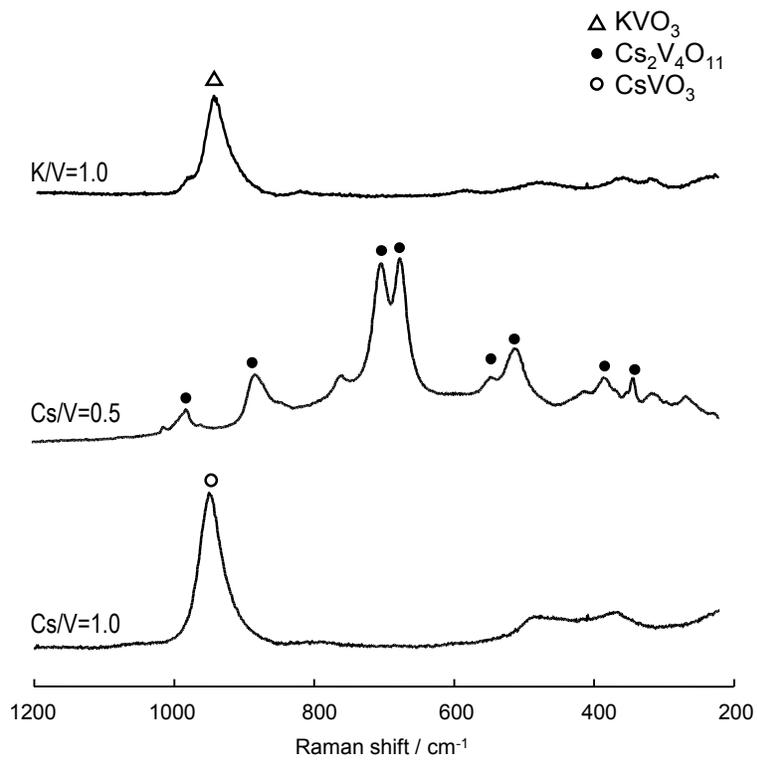


Figure S2. Raman spectra of as-prepared K–V–O/SiO₂ (K/V = 1.0) and Cs–V–O/SiO₂ (Cs/V = 0.5 and 1.0).

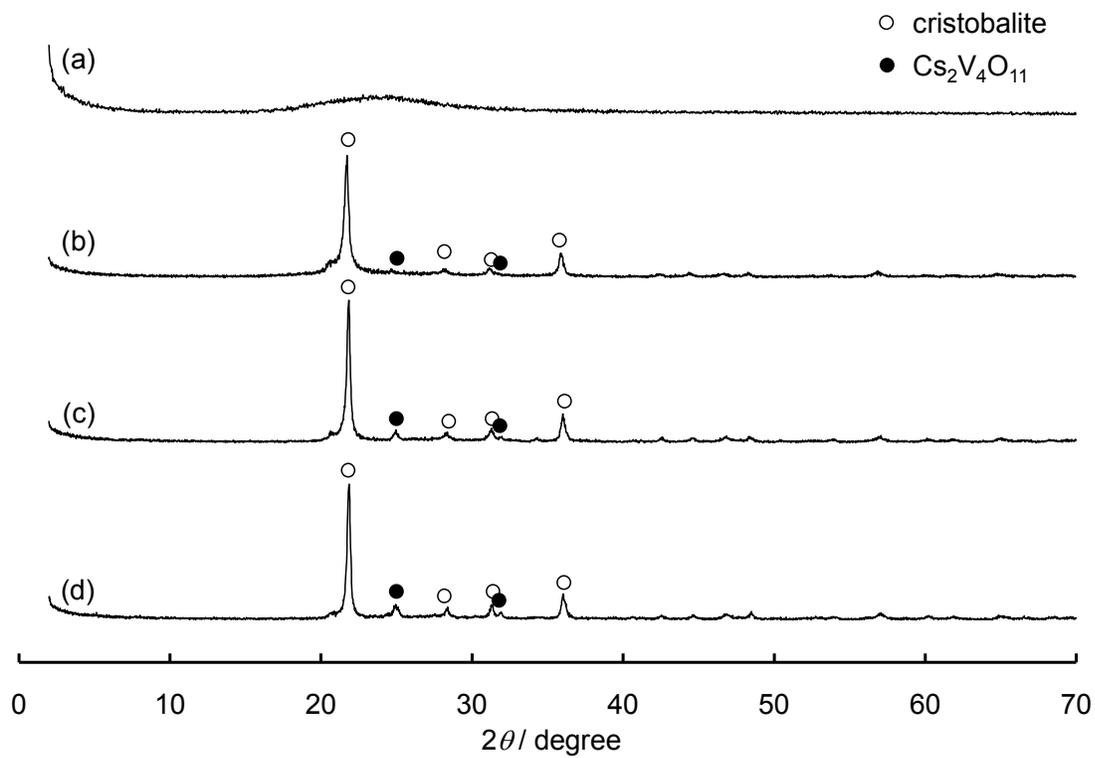


Figure S3. XRD patterns of Cs–V–O/SiO₂ (Cs/V = 1.0) (a) as-prepared and (b-d) after stability test at 600 °C for 1,000 h. (b) Upstream and (c) downstream sections of the tested catalyst bed. (d) Catalyst bed inverted every 100 h.

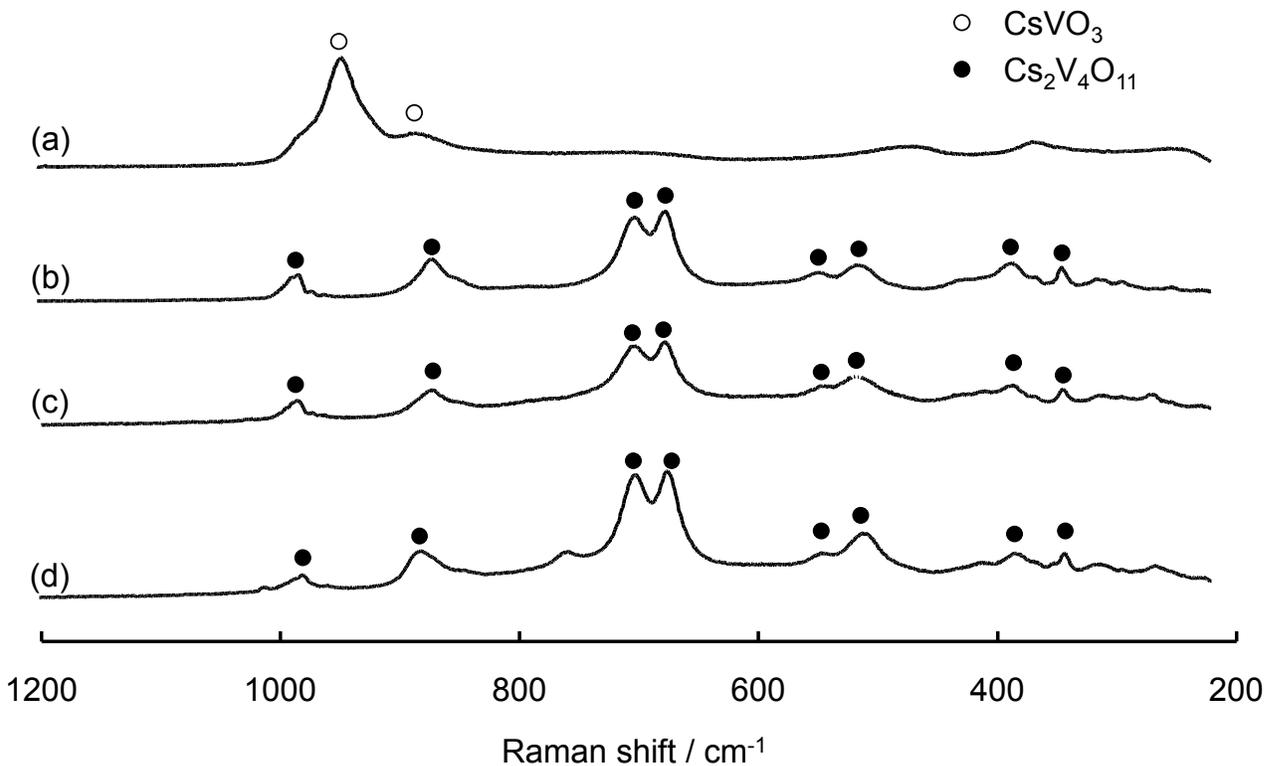


Figure S4. Raman spectra of Cs–V–O/SiO₂ (Cs/V = 1.0) (a) as-prepared and (b-d) after stability test at 600 °C for 1,000 h. (b) Upstream and (c) downstream sections of the tested catalyst bed. (d) Catalyst bed inverted every 100 h.

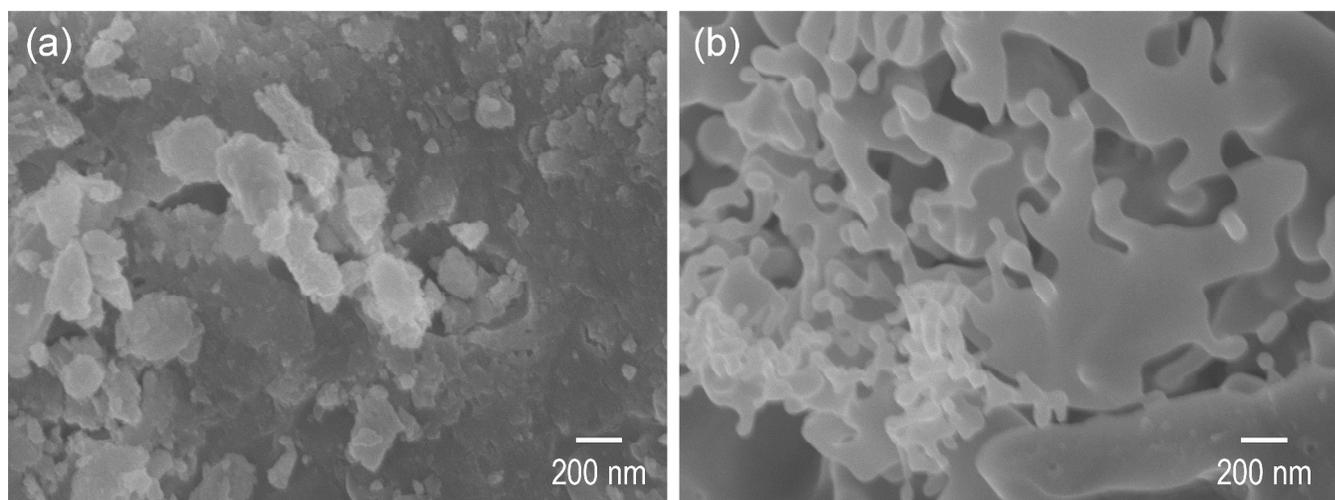


Figure S5. SEM micrographs of Cs-V-O/SiO₂ (Cs/V = 1.0) (a) as-prepared and (b) after stability test at 600 °C for 1,000 h.

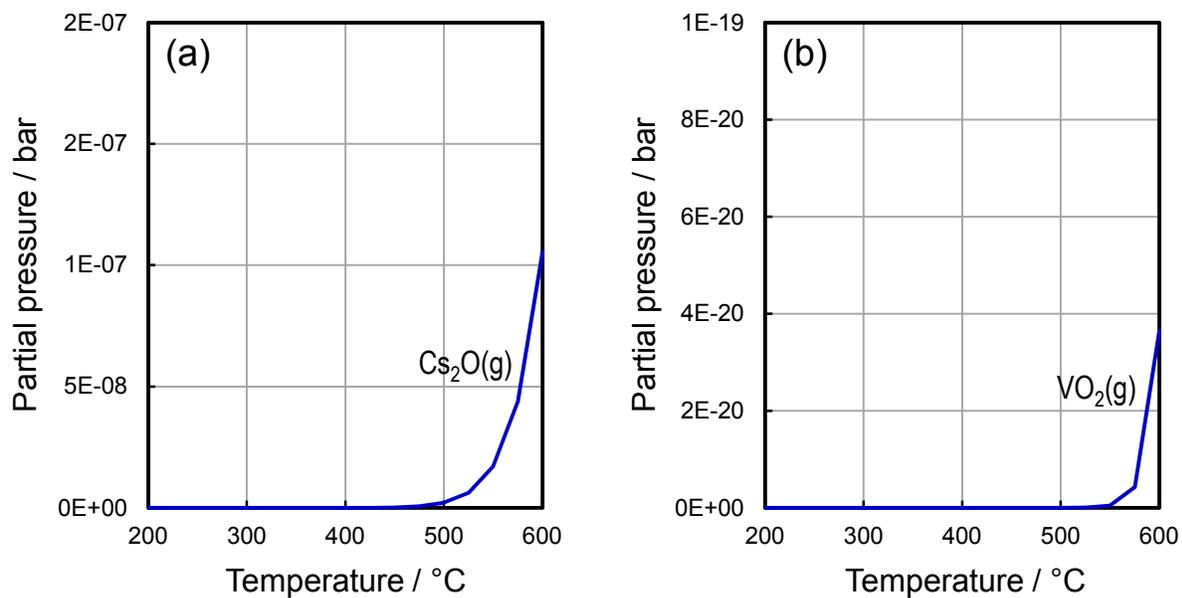


Figure S6. Calculated vapor pressures for (a) Cs_2O and (b) V_2O_5 in 5% O_2 and N_2 balance (1 bar).

The thermodynamic calculations for the equilibrium partial pressures were done using a commercially available piece of software (HSC Chemistry®, Outokumpu Research Oy).

Table S1 BET surface area of A-V-O/SiO₂ after different periods of catalytic SO₃ decomposition

		S_{BET} (m ² g ⁻¹)
A = K (K/V = 1.0)	as-prepared	299
	550 °C, 100 h	7
	550 °C, 500 h	5
A = Cs (Cs/V = 1.0)	as-prepared	225
	550 °C, 100 h	7
	550 °C, 500 h	4
	600 °C, 1,000 h	4