Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Supplementary Information

Molten Copper Hexaoxodivanadate: An Efficient Catalyst for SO_3 Decomposition in Solar Thermochemical Water Splitting Cycles

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Catalyst preparation

Figure S1 Experimental setup for catalytic SO_3 decomposition.

Figure S2 Raman spectra of CuV_2/SiO_2 and CuV/SiO_2 in comparison with each bulk copper vanadate (CuV_2O_6 and $Cu_2V_2O_7$) as references.

Figure S3 Steady-state SO_3 conversion for as-prepared CuV_2/SiO_2 and CuV/SiO_2 versus reaction temperatures.

Figure S4 Raman spectra of CuV_2/SiO_2 catalyst a) as-prepared, b) after catalytic reaction at 600 °C in a stream of 14% SO_3, 18% H_2O and N_2 balance and c) unsupported CuV_2O_6.

Figure S5 Thermogravimetry of CuV_2O_6 measured in a stream of N_2.

Catalyst preparation

Mesoporous SiO_2 with the cubic *Ia*3*d* symmetry was prepared by the method developed by Ryoo et al.[1] 6 g of a triblock copolymer, P123 ($EO_{20}PO_{70}EO_{20}$, M_W=5800, BASF) was dissolved in 217 g of distilled water and 11.8 g of 35% HCl, followed by addition of 6 g of C_4H_9OH (Wako, 98%) under stirring at 35 °C for 1 h and subsequent addition of 12.9 g of TEOS ($Si(OC_2H_5)_4$, Wako, 98%). The mixture after stirring for 24 h at 35 °C was hydrothermally treated at 100 °C for 24 h under a static condition. The solid product thus obtained was filtered without washing and dried at 100 °C. The templating agent (P123) was removed by the treatment in a C_2H_5OH/HCl mixture, followed by air-calcination at 550 °C for 5 h. Using as-calcined mesoporous SiO_2 products, supported Cu-V oxide catalysts with the molar ratios of Cu:V:Si=1:2:20 (denoted as CuV_2/SiO_2) and/or 1:1:20 (CuV/SiO_2) were prepared by stepwise impregnation using aqueous solutions of $Cu(NO_3)_2$ (Wako, 99%) and NH_4VO_3 (Wako, 99%) and subsequent calcination at 600 °C for 12 h as described in our previous paper.[2]

1. F. Kleitz, S. Hei Choi and R. Ryoo, *Chem. Commun.*, 2003, 2136-2137.
2. M. Machida, T. Kawada, S. Hebishima, S. Hinokuma and S. Takeshima, *Chem. Mater.*, 2012, **24**, 557-561.

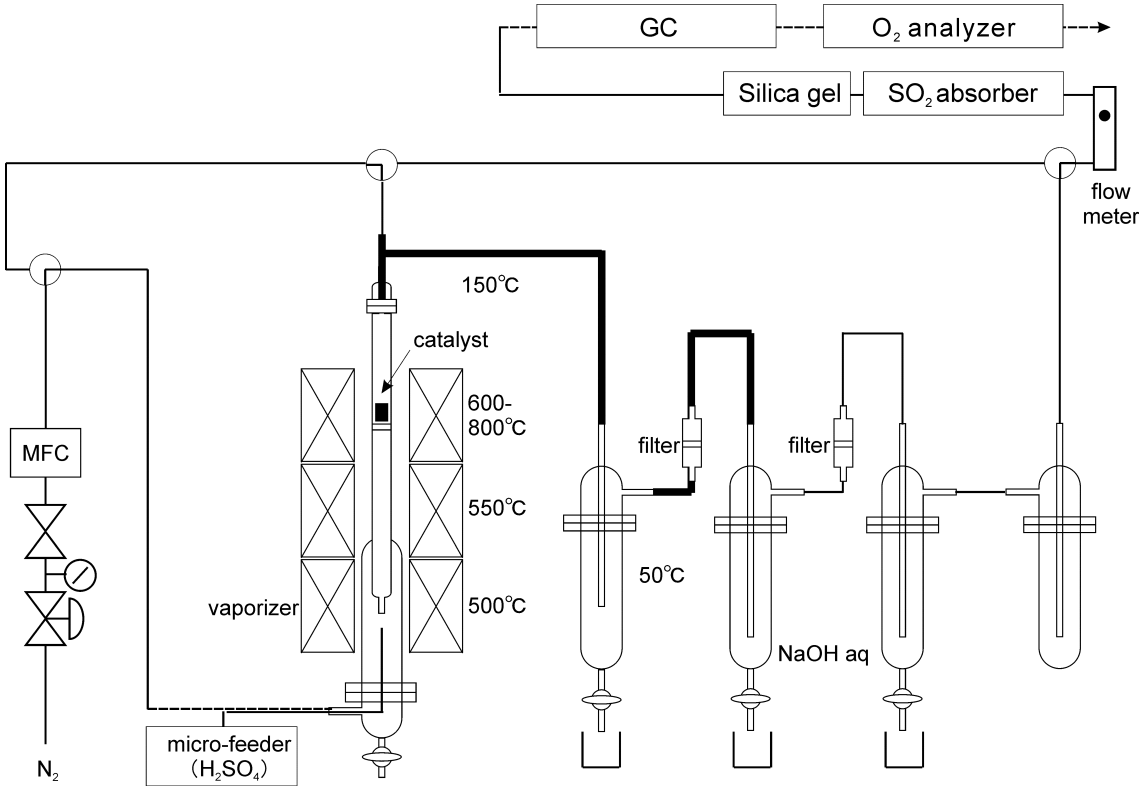

Figure S1 Experimental setup for catalytic SO_3 decomposition.

Catalytic reaction test was carried out at atmospheric pressure in a vertical tubular reactor having three heating segments; an evaporator at the bottom (500 °C), the middle (550 °C) and a catalyst bed at the top (600−800 °C). A granule catalyst (0.1 g, 10−20 mesh) mixed with SiC granules (0.4 g, 10−20 mesh) was fixed in a quartz tube (i.d. 8 mm) by quartz wool at both ends of a catalyst bed, which was placed at the top of the reactor. Concentrated sulfuric acid (95%) was pumped by a pulse-free dual-plunger pump at the rate of 50 μL min^{-1} to an evaporator unit placed at the bottom of the reactor (500 °C). The vaporized sulfuric acid mixed with a flow of N_2 supplied at 100 $cm^3 \cdot min^{-1}$ entered into the middle zone (550 °C), where decomposition of H_2SO_4 to H_2O/SO_3 took place in the gas phase. Finally, a mixing flow of 14% SO_3, 17% H_2O and N_2 balance was fed to the catalyst bed.

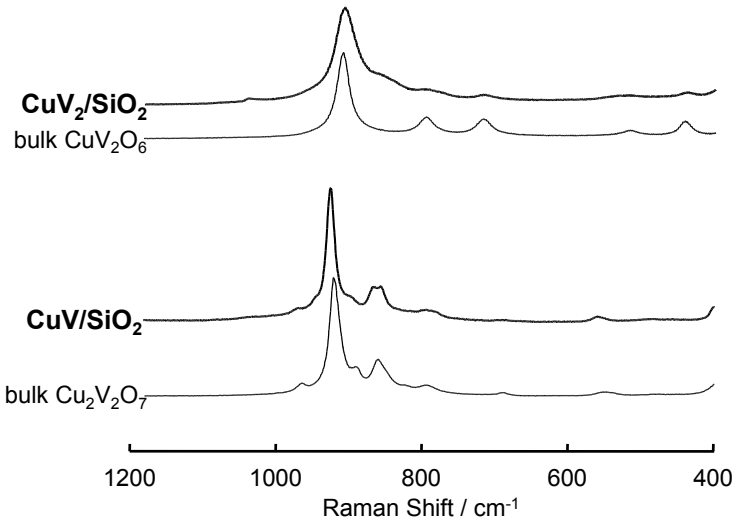

Figure S2 Raman spectra of CuV_2/SiO_2 and CuV/SiO_2 in comparison with each bulk copper vanadate (CuV_2O_6 and $Cu_2V_2O_7$) as references.

The Raman spectra suggest that CuV_2O_6 and $Cu_2V_2O_7$ were deposited on supported catalysts, CuV_2/SiO_2 and CuV/SiO_2, respectively. The difference of the spectra is associated with the crystal structure of the former consisting of distorted octahedral VO_6 in contrast to tetrahedral VO_4 in the latter.

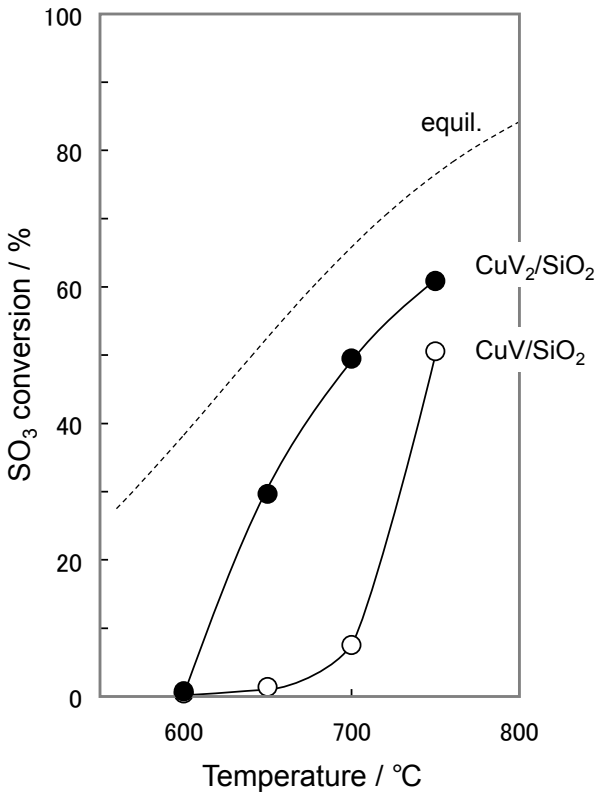

Figure S3 Steady-state SO_3 conversion for as-prepared CuV_2/SiO_2 and CuV/SiO_2 versus reaction temperatures.

This figure plots SO_3 conversion versus reaction temperatures, corresponding to the data shown in Fig. 1. CuV_2/SiO_2 exhibits much higher conversions at ≤700 °C, where CuV_2O_6 (m.p. 630 °C) is melting in contrast to the solid phase $Cu_2V_2O_7$ (m.p. 780 °C).

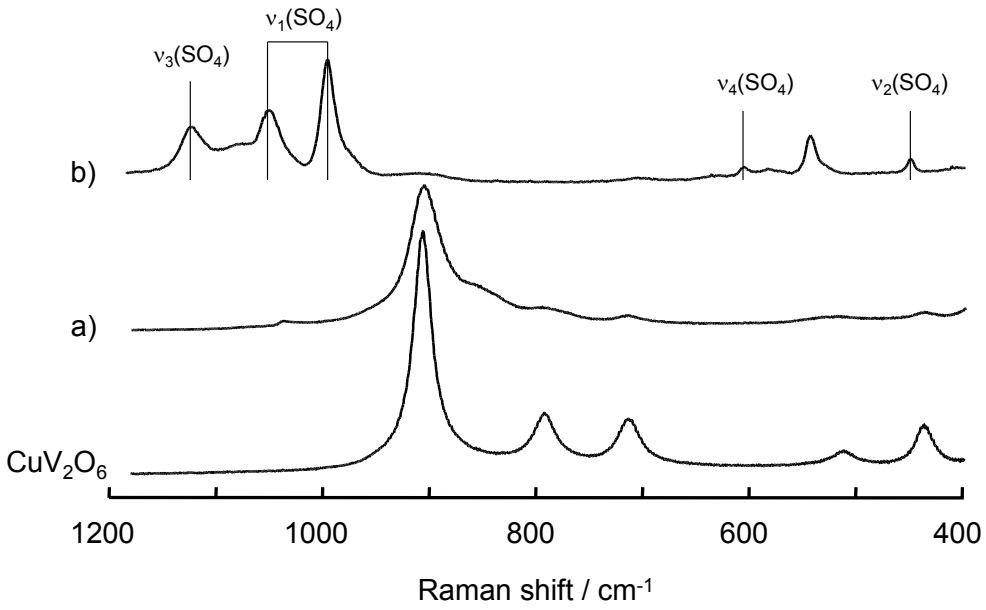

Figure S4 Raman spectra of CuV_2/SiO_2 catalyst a) as-prepared, b) after catalytic reaction at 600 °C in a stream of 14% SO_3, 18% H_2O and N_2 balance and c) unsupported CuV_2O_6.

As-prepared CuV_2/SiO_2 catalyst showed peaks assignable to CuV_2O_6, which were weakened after catalytic reaction at 600 °C. Instead, peaks assignable to symmetric and asymmetric vibration of SO_4 appeared. This suggests the formation of sulfate by the reaction between SO_3 and Cu oxide species on the catalyst surface.

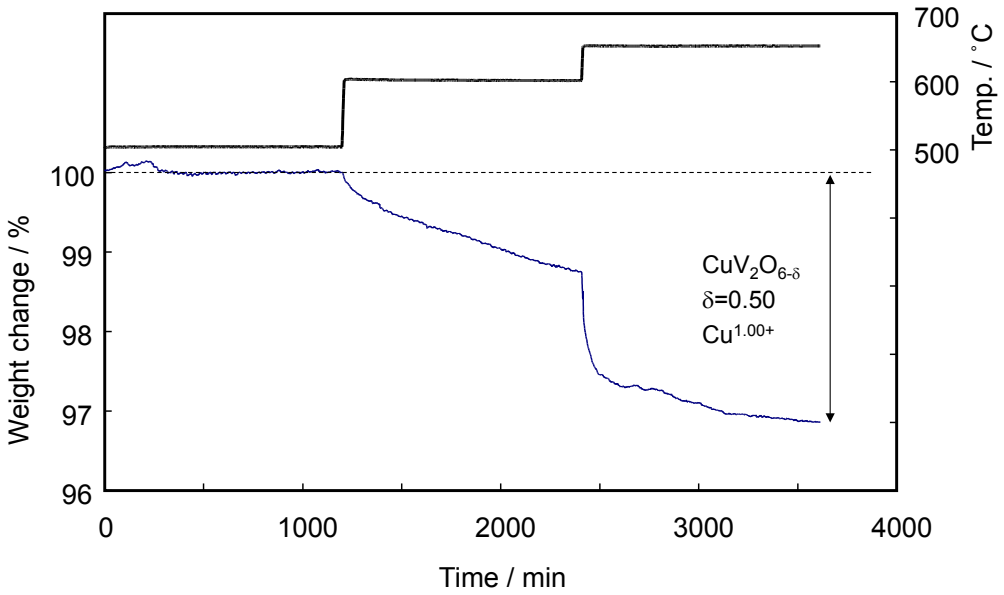

Figure S5 Thermogravimetry of CuV_2O_6 measured in a stream of N_2.

To quantify the oxygen vacancies formed as a result of oxygen desorption, thermal gravimetric analysis of CuV_2O_6 was performed at 550, 600, and 650 °C in a stream of N_2. Weight losses due to oxygen desorption occurred above 500 °C and the equilibrated weight loss was −3.0 wt% at 650 °C. This corresponds to the oxygen deficiency (δ=0.50) in the molten $CuV_2O_{6-\delta}$ and the average oxidation number of $Cu^{1.00+}$.