Hydrothermal synthesis of CuV_2O_6 supported on mesoporous SiO_2 as SO_3 decomposition catalysts for solar thermochemical hydrogen production

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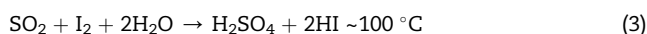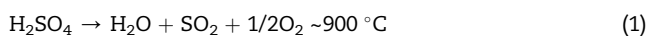
A B S T R A C T

Hydrothermal synthesis of CuV_2O_6 supported on 3-D ordered mesoporous SiO_2 (CuV/SiO_2) was studied to evaluate the catalytic activity for SO_3 decomposition, which is a key step in solar thermochemical hydrogen production. A composite oxide hydrate, $Cu_3O(V_2O_7)\cdot H_2O$, and an oxide hydroxide hydrate, $Cu_3(OH)_2V_2O_7\cdot(H_2O)_2$, were formed at lower hydrothermal temperatures ($\leq$200 °C). The oxide hydrate phase mainly yielded $Cu_2V_2O_7$ after calcination at 600 °C in air. By contrast, the hydrothermal synthesis at 250 °C (CuV/SiO_2@250) directly crystallized CuV_2O_6 from the oxide hydroxide hydrate, although its very large particle size (~5 μm) is not suitable for the catalytic application. The SO_3 decomposition activity measured at 600 °C was associated with the yield as well as the dispersion of CuV_2O_6, giving rise to the maximum for the hydrothermal synthesis at 200 °C. CuV/SiO_2@250 achieved the highest catalytic activity at the reaction temperature of 650 °C, because the melting phase of CuV_2O_6 penetrated mesoporous SiO_2 and thus improved the dispersion of the active phase.

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Introduction

Currently, energy and environment have become the most urgent problems in front of us. As one of the most efficient and clean energy carriers, hydrogen is paid more and more attention. A large-scale and cost-effective production of hydrogen by thermochemical water splitting cycles using concentrated solar radiation as a source of heat is of great significance [1–4]. Sulfur-based cycles using the decomposition of sulfuric acid as an oxygen-generating reaction become a promising candidate for such a purpose. The most famous

one is so-called sulfur—iodine (S—I) process, which is a closed cycle consisting of the following three reactions [5–7],

$$H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2 \text{ ~900 °C} \qquad (1)$$

$$2HI \rightarrow H_2 + I_2 \text{ ~400 °C} \qquad (2)$$

$$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI \text{ ~100 °C} \qquad (3)$$

In reaction (1), sulfuric acid dissociates nearly completely into mixtures of H_2O and SO_3 in the gas phase at above 350 °C,

but the subsequent decomposition of SO_3 into SO_2 and O_2 requires a temperature of about 900 °C, much higher than those in the other two reactions (2) and (3). To reduce the temperature down to around 600 °C, which will be obtained by the current large-scale solar concentration technology, economically viable catalysts for SO_3 decomposition are necessary. Although a number of catalysts have been studied for the decomposition of SO_3 [8–14], Pt was only known as an efficient catalyst working at such low reaction temperatures. Many metal oxides such as Fe_2O_3 and Cr_2O_3 have been highlighted as potential substitute catalysts, but they required much higher reaction temperatures ($\geq$800 °C) [9,11–14].

Recently, we have reported that a series of Cu–V oxides exhibit high catalytic activity for SO_3 decomposition [15–17]. Among the binary oxides with different stoichiometry, the highest catalytic activity was achieved for CuV_2O_6, which corresponds to the lowest melting point of the $CuO-V_2O_5$ system [18]. The catalytic activity could further be enhanced by the use of support materials consisting of 3-D mesoporous silica [16]. Silica is very stable in a strongly acidic vapour and against the solid-state reactions with Cu–V oxides. When the molten phase of Cu–V oxide is formed above the melting point, the liquid phase penetrates the SiO_2 support and converts mesopores to macropores via dissolution-reprecipitation mechanism [16]. The resulting macroporous cavity with the surface coated by active Cu–V oxide shows an efficient activity for SO_3 decomposition.

In order to improve the catalyst performance, the synthesis of SiO_2-supported CuV_2O_6 with a high dispersion is especially significant and necessary. Many different synthetic methods have been reported to synthesize CuV_2O_6, including solid-state method [19], hydrothermal method [20], sol–gel method [21], soft chemistry method [22] and co-precipitation method [23]. Nevertheless, their application to supported CuV_2O_6 catalysts was very limited. In the present study, we especially focused on the hydrothermal synthesis, because this method enables the direct deposition of CuV_2O_6 from liquid phase precursors onto a porous SiO_2 support at moderated temperatures. The structure, physicochemical properties and catalytic activity for SO_3 decomposition were studied as a function of hydrothermal temperature.

Experimental

Catalyst preparation

3-D Mesoporous SiO_2 was prepared by the method developed by Ryoo et al. [24]. Using the as-calcined SiO_2 product, a supported CuV_2O_6 catalyst was prepared by hydrothermal method. All of the chemical reagents were of analytical grade and used without further purification. In a typical experiment, 0.4 mmol $Cu(NO_3)_2 \cdot 3H_2O$ (Wako, 99%) was dissolved into 10 mL of deionized water at room temperature, while 0.8 mmol NH_4VO_3 (Wako, 99%) was dissolved into another 30 mL of deionized water at 80 °C. Then, as-calcined SiO_2 (after drying at 300 °C for 3 h), $Cu(NO_3)_2$ solution (0.040 mol/L) and NH_4VO_3 solution (0.027 mol/L) were mixed orderly with the molar ratio of Cu:V:Si = 1:2:15. The resulting precursor suspension was transferred into an 80 mL glass-lined autoclave

and maintained at 100~250 °C for 6 h. Upon completion of the reaction, the autoclave was opened after the whole system cooled naturally to room temperature. The solid powder in the autoclave was collected by centrifugation, washed several times with deionized water, and dried at 110 °C for 12 h. The products for each hydrothermal temperature are denoted as CuV/SiO_2@100~250. The final calcination was done at 600 °C for 3 h in air.

Characterization

X-ray diffraction (XRD) measurement was performed using monochromated Cu Kα radiation (30 kV, 20 mA, Multiflex, Rigaku). Raman spectra were obtained on a Jasco NRS-3100 spectrometer using a 532.1 nm laser as an excitation source. Specific surface area and pore size distribution were calculated from N_2 adsorption–desorption isotherms measured at 77 K (Belsorp, Bel Japan). The pore size was analysed with the adsorption branch using the DH algorithm. The scanning electron microscope (SEM) and X-ray mapping images were analysed using an electron probe microanalyzer (EPMA-1720, Shimadzu) operating at 15 keV. X-ray photoelectron spectroscopy (XPS) was performed using monochromated Al Kα radiation (12 keV, K-Alpha, Thermo).

Catalytic reaction

The catalytic reaction was carried out in a quartz tubular flow reactor as described in our previous paper [16,18]. Sulfuric acid (95%) was pumped (50 μL min^{-1}) and vaporized at 450 °C in a flow of N_2 (100 cm^3 min^{-1}) and thermally decomposed into SO_3 and H_2O at 500 °C. As-generated gas mixture of 14% SO_3, 18% H_2O and N_2 balance was supplied to a catalyst bed (WHSV = 55.2 g-H_2SO_4 (g-cat)$^{-1}$ h^{-1}). The gas feed rate corresponds to the gaseous space velocity, GHSV = 31,000 h^{-1}. The conversion of SO_3 to SO_2 was calculated from the O_2 concentration downstream of the catalyst bed with a magneto-pneumatic oxygen analyzer (MPA3000, Horiba) and a gas chromatograph (GC-8A, Shimadzu) fitted with an MS-5A column and a thermal conductivity detector. The SO_2 concentration in the effluent gas was also determined using iodometric titration.

Results and discussion

Structure of hydrothermally synthesized CuV/SiO$_2$

Fig. 1 shows XRD patterns of solid products as-synthesized at different hydrothermal temperatures before calcination. 3-D mesoporous SiO_2 exhibited no sharp diffraction peaks at $2\theta \leq 10°$, although a very intense peak due to ordered mesoporous structure was observed at around $2\theta = 1°$. When the hydrothermal temperature was 100 °C (CuV/SiO_2@100), the primary product was a composite oxide hydrate, $Cu_3O(V_2O_7) \cdot H_2O$, and a smaller amount of an oxide hydroxide hydrate, $Cu_3(OH)_2V_2O_7 \cdot (H_2O)_2$. In addition, excess vanadium was deposited in a form of $(NH_4)_2V_3O_8$ as was detected by Raman spectra. With an increase of hydrothermal temperature, $Cu_3(OH)_2V_2O_7 \cdot (H_2O)_2$ became the primary product at 200 °C.