Structure and SO₃ Decomposition Activity of CeVO₄/SiO₂ Catalysts for Solar Thermochemical Water Splitting Cycles

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ABSTRACT

Ce–V oxide catalysts supported on bimodal mesoporous SiO₂ were prepared by a wet impregnation method to study their catalytic activity for SO₃ decomposition, which is a key step in thermochemical water splitting cycles based on the sulfur-iodine process. As-prepared Ce–V/SiO₂ catalysts exhibited more than 50-fold higher turnover frequency at 600 °C compared to unsupported CeVO₄. This is in accordance with the smaller size (13 nm) of CeVO₄ particles highly dispersed in SiO₂ mesopores, compared to approximately 600 nm for unsupported CeVO₄ particles. The Ce–V/SiO₂ catalysts exhibited a higher activity than supported V₂O₅ or CeO₂ catalysts, which coexisted depending on the Ce/V ratio. Among the studied catalysts with different Ce/V molar ratios, the highest activity was achieved at Ce/V = 0.9, at which the greatest specific surface area of CeVO₄ was attained. The catalyst demonstrated SO₃ decomposition rates comparable to those of Pt/Al₂O₃ in a wide range of WHSV (3.6–110 g-H₂SO₄ g^{−1} h^{−1}) and no indication of noticeable deactivation during 40 h of the catalytic reaction at 650 °C.

KEYWORDS

Cerium vanadate, mesoporous silica, SO₃ decomposition, thermochemical water splitting, Sulfur-Iodine cycle

INTRODUCTION

A new sustainable energy strategy based on riskless technology is urgent world-wide attention. It is prompted to develop the large-scale and cost-effective alternative renewable energy. Considering the natural availability of solar radiation extraordinary larger than any other renewable energy sources, solar hydrogen production from water is of great importance [1, 2]. Thermochemical water splitting cycles using concentrated solar radiation as an unrestrictedly available source of heat are especially promising. The sulfur-iodine process is known as a cycle system consisting of the following three reactions [3-7].

Among these reactions, (1) requires the highest temperatures ($\sim 900^\circ\text{C}$), because the final step for decomposition of SO_3 into $\text{SO}_2 + 1/2\text{O}_2$ cannot proceed at moderate temperatures. Therefore, it is strongly requested to develop active catalysts that have stability under corrosive environments containing high-concentration sulfuric acid vapors, which severely damage and destroy most conventional catalytic materials [8-10]. Precious metals such as Pt are known to be the most active catalysts [10-17]. Although a number of other catalytic materials have been investigated, development of economically viable catalysts remains a challenge [18-32].

We have recently reported that a series of copper vanadate catalysts demonstrated the efficient catalytic SO_3 decomposition at moderated reaction temperatures ($\sim 650^\circ\text{C}$), because of the combination of vanadate framework having resistance to sulfate formation

and copper as a redox center [33-38]. Among four binary compounds, CuV_2O_6 , $\text{Cu}_2\text{V}_2\text{O}_7$, $\text{Cu}_3\text{V}_2\text{O}_8$ and $\text{Cu}_5\text{V}_2\text{O}_{10}$, in the $\text{CuO}-\text{V}_2\text{O}_5$ system, the highest catalytic activity was achieved for CuV_2O_6 , which corresponds to the phase with the lowest melting point (630 °C) [36, 38]. The activity could further be enhanced by the use of support materials consisting of 3-D mesoporous silica [34]. 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-precipitation mechanism. The resulting macroporous cavity with the surface coated by thin layers of active Cu–V oxide shows an efficient activity for SO_3 decomposition.

Although a wide variety of other metal vanadates also exhibit the catalytic activity for SO_3 decomposition [33], they have not been investigated in detail. In this paper, we report the preparation and SO_3 decomposition activity of silica-supported CeVO_4 . Considering the melting point higher than 1000 °C, the CeVO_4 phase should preserve a solid state under the reaction condition and thus exhibit different catalytic behaviors. We synthesized highly dispersed CeVO_4 nanocrystals using a bimodal mesoporous SiO_2 support materials and evaluated their catalytic activity. We also characterized the catalyst structure by transmission electron microscopy (TEM), Raman spectroscopy, X-ray diffraction (XRD), and X-ray absorption near edge structure (XANES) to correlate between the structure and the catalytic performance.

2. EXPERIMENTAL

2.1 Preparation and characterization

The bimodal mesoporous SiO₂ was prepared by a template synthesis technique [39]. A cationic surfactant (cetyltrimethylammonium chloride, Tokyo Chemical Industry) was dissolved in distilled water (0.5 mol L⁻¹) and mixed by stirring for 2 h, followed by addition of tetraethylorthosilicate (Si(OC₂H₅)₄, Wako, 98%) and aqueous ammonia until pH reached to 9.5 under stirring at 35 °C. After stirring the resulting mixture for 30 h at room temperature and subsequent addition of nitric acid until pH = 7, the product was kept for 60 min under a static condition. The solid product thus obtained was filtered without washing and dried at 100 °C, followed by calcination at 800 °C for 2 h. Using as-calcined SiO₂ products, supported Ce–V oxide catalysts (Ce–V/SiO₂) with the molar ratio of Ce+V : Si = 1 : 10 with varying Ce/V ratios (0.5–1.0) were prepared by impregnating aqueous solutions of Ce(NO₃)₂ (Wako, 99%) and NH₄VO₃ (Wako, 99%), subsequent calcination at 350 °C for 1 h and at 800 °C for 5 h. Unsupported vanadates containing various metals were prepared by calcining powder mixtures of corresponding metal oxides and V₂O₅ at 600 °C for 5 h [33]. A reference catalyst, 0.5 wt% Pt/γ-Al₂O₃ (*S*_{BET} = 134 m² g⁻¹), was prepared by impregnation using aqueous solutions of Pt(NH₃)₂(NO₂)₂ and subsequent calcination at 600 °C for 3 h in air.

2.2 Characterization

Powder XRD measurement was performed using monochromated Cu *K*_α radiation (30 kV, 20 mA, Rigaku Multiflex). Raman spectra were obtained on a Jasco NRS-3100 spectrometer using a 532.1 nm laser as an excitation source. Brunauer–Emmett–Teller (BET) surface area (*S*_{BET}) and pore size distribution were calculated from N₂ adsorption-

desorption isotherms at 77 K (Bel Japan Belsorp). The pore size was analyzed with the adsorption branch using the DH algorithm. A FEI TECNAI F20 transmission electron microscope (TEM) operating at 200 kV was used to obtain bright field images and high-angle annular dark-field (HAADF) images in a scanning electron microscopy (STEM) mode. XANES measurements on Ce L_{III}-edge and V K-edge were performed at the BL33XU beamline of SPring-8 using an Si(111) crystal monochromator at room temperature. The catalyst powders (10 mg) were pressed into a disc (7 mm diameter) for this measurement. The obtained data were processed using the Athena program [40].

2.3 Catalytic reactions

The catalytic reaction was carried out in a quartz tubular flow reactor. Sulfuric acid (47% or 95%) was pumped and vaporized at 450 °C in a flow of N₂ and thermally decomposed into SO₃ and H₂O at 500 °C. The resulting gas mixture consisting of 4.6% or 13.7% SO₃ was then supplied to a catalyst bed (≥ 600 °C). A granule catalyst (10–20 mesh) mixed with SiC granules (10–20 mesh) was fixed in a quartz tube (inner diameter: 8 mm) by quartz wool at both ends of a catalyst bed. The catalytic activity at various weight hourly space velocities (WHSV) in the range of 3.6–110 g-H₂SO₄ g⁻¹ h⁻¹, which were changed by varying the mass of catalysts from 0.05 to 0.50 g with keeping the catalyst bed volume constant by diluting with inert SiC granules. The gas effluent from the catalyst bed was bubbled into an aqueous solution of NaOH to remove SO₃ and was dried by a dryice-ethanol trap. The gas was finally introduced into a gas analyzing unit, where O₂ concentration was measured using a magnetopneumatic oxygen analyzer (Horiba MPA3000) and a gas chromatograph

(TCD, He carrier, an MS-5A column, Shimadzu GC8A). The steady-state conversion of SO_3 to SO_2 was calculated from concentrations of O_2 as a function of temperature at the inlet of the catalyst bed (600–800 °C). The obtained value was consistent with the SO_2 concentration in the effluent gas, which was determined using iodimetric titration.

3. RESULTS AND DISCUSSION

3.1 Catalytic activity of various vanadate catalysts

Catalytic SO_3 decomposition over metal oxides is considered to proceed via a reaction intermediate in a form of metal sulfate as was first proposed by Tagawa and his coworker [10].

Assuming this model, we attempted to correlate the catalytic activity of metal oxides with their thermodynamic parameters in terms of the decomposition temperatures (T_d) of sulfates (MSO_4), which are estimated from the standard Gibbs energy change of the decomposition, $\Delta G_d^\circ = -RT \ln p_{\text{SO}_3}$, where p_{SO_3} is the decomposition SO_3 pressure over sulfates [33]. The T_d value is defined as the temperature where p_{SO_3} corresponds to the concentration of SO_3 in the gas feed in the catalytic test (4.6%). Fig.1 shows correlations between SO_3 conversion and T_d for various M–V oxides at different reaction temperatures. At the reaction temperature of 600 °C, volcano-shaped plots were obtained in accordance with the reactions in (4) and (5). The M–V oxides on the left side of the plot interact so weakly with SO_3 and thus the formation of sulfates (4) should be slow. Conversely, the M–V oxides on

the right side produce stable sulfates and thus their decomposition (5) should be slow. The peak of the volcano plot corresponds to Cu, demonstrating Cu–V as a promising candidate catalyst. On the other hand, the SO₃ decomposition activity was negligible when M–V oxides with higher T_d values were used, because these compounds including basic metals were immediately deactivated by their sulfate formation at 600 °C. Nevertheless, it should be noted that the activity appeared even for these basic metals when the reaction temperature was higher than 600 °C. At 700 °C, for instance, Ce–V attained the SO₃ conversion of 37%, compared to 53% for Cu–V. Another noteworthy feature of the Cu–V is the proximity of the melting point to the SO₃ decomposition temperatures [36, 38]. Although the molten phase of Cu–V exhibited a higher catalytic activity than the solid phase, the potential deactivation by a vaporization loss may limit the use above 700 °C. By contrast, the higher melting point of an orthovanadate CeVO₄ phase (>1000 °C) is expected to ensure the stability of the catalyst during the reaction. Although the highest SO₃ conversion at 700 °C in Fig.1 is attained for M = Zr, the melting point of the ZrV₂O₇ phase in the sample is also as low as 750 °C, which is similar to those of Cu–V oxides. These considerations imply that the Ce–V oxide is another promising candidate as a solid catalyst for SO₃ decomposition at ≥ 700 °C. The following investigation in this study was therefore focused on the Ce–V system to enhance the SO₃ decomposition activity by preparing highly dispersed catalysts supported on bimodal mesoporous SiO₂.

3.2 Structure of Ce–V/SiO₂ catalysts

The XRD patterns of as-synthesized mesoporous SiO₂ support ($S_{\text{BET}} = 280 \text{ m}^2 \text{ g}^{-1}$) showed no sharp reflection peaks even at low diffraction angles ($\leq 1^\circ$). This is indicative of disordered pore arrangements of as-prepared catalysts. Fig.2 exhibits TEM micrographs of as-prepared SiO₂ and supported Ce–V/ SiO₂ catalysts. In a bright field image of SiO₂ (a), disordered bicontinuous mesopores with the size more than 10 nm were formed, while much smaller mesopores (2–3 nm) inside the SiO₂ frameworks were also observed as bright dots. The presence of these two types of pores are in accordance with the bimodal pore size distribution centered at the pore radius of approximately 1–2 nm and 10–20 nm as shown in Fig.3. The creation of such large mesopores is especially considered as an effective approach to diminish mass transfer resistance of reactants and products in the presence of abundant vapors under the present catalytic condition. The distribution of Ce–V oxide in bimodal mesoporous SiO₂ was studied by means of HAADF-STEM (Fig.2b), which is a powerful technique suited for *Z*-contrast images (*Z*: the atomic number), because the intensity of scattered electrons in the mode is proportional to Z^2 [41, 42]. Therefore, Ce and/or V oxide should appear as brighter contrasts on the dark matrix SiO₂ support. A HAADF-STEM image gave an overview of mesoporous SiO₂ with smooth cavity walls and spherical Ce–V particles of 10–30 nm in size were well dispersed inside the larger pores (20–100 nm) of SiO₂ as shown by white arrows. The observed particle size was close to CeVO₄ crystallite sizes obtained by X-ray diffraction line broadening analysis as discussed below (Fig.4b). It should be noted that the size of these Ce–V particles was much less than that of unsupported CeVO₄ particles, 597 nm, which was calculated from

the S_{BET} value ($2.1 \text{ m}^2 \text{ g}^{-1}$) assuming a spherical shape. The highly dispersed fine particles of CeVO_4 could be prepared successfully by using the bimodal mesoporous SiO_2 support.

Fig.4a compares the XRD patterns of Ce-V/SiO_2 with different Ce/V ratios together with unsupported CeVO_4 . Although strong diffraction peaks assignable to CeVO_4 were observed for $\text{Ce/V} = 0.50$, they became less intense with simultaneous increase of CeO_2 peaks at higher Ce/V ratios. The diffraction peaks of CeVO_4 was much broader than those of unsupported CeVO_4 (shown at the bottom of Fig.4a), indicative of smaller particle sizes. Furthermore, the peaks for Ce-V/SiO_2 tend to be broader with an increase of the Ce/V ratio. The CeVO_4 crystallite size was calculated by the line-broadening analysis using the Scherrer equation as shown in Fig.4b. With increasing the Ce/V ratio, the size decreased to approximately 13 nm at $0.67 \leq \text{Ce/V} \leq 0.9$ but increased by further increase of Ce/V . The calculated greatest specific surface area ($94 \text{ m}^2 \text{ g}^{-1}$) was nearly 45-fold greater than that of unsupported CeVO_4 ($2.1 \text{ m}^2 \text{ g}^{-1}$). This is effective for the enhancement of the catalytic SO_3 decomposition performance as described below.

Fig.5 shows Raman spectra of Ce-V/SiO_2 with different Ce/V ratios. For $\text{Ce/V} = 0.5$, the bands at 853 , 790 , and 778 cm^{-1} are characteristic of CeVO_4 , whereas those at 988 , 690 , 518 , and 397 cm^{-1} are assigned to V_2O_5 , suggesting the deposition of amorphous V_2O_5 , which was invisible in XRD (Fig.4a). With increasing the Ce/V ratio, the bands due to amorphous V_2O_5 disappeared but a new band at 460 cm^{-1} due to crystalline CeO_2 appeared and increased the intensity. Considering the low melting point of V_2O_5 (675°C), the sample at $\text{Ce/V} = 0.5$ forms a molten V_2O_5 phase during calcination at 800°C , which will penetrate into pore structure of the SiO_2 support. In such a situation, particle growth of

CeVO₄ may be significantly accelerated by wetting and/or corrosion effects of the liquid phase [33, 43]. This is a possible reason of the highly crystallized CeVO₄ for Ce/V = 0.5 as shown in XRD (Fig.5). The precipitation of CeO₂ and V₂O₅ is a clear indication of incomplete solid state reactions on SiO₂ support during calcination at 800 °C. The Raman spectra presented in Fig.5 show no evidence of the interactions between CeO₂ and SiO₂, or between V₂O₅ and SiO₂. All the spectra show an unknown broad peak at 1030 cm⁻¹, which is possibly due to the V=O stretch for pseudo-tetrahedral vanadate species. According to the previous research [44-46], this would be assigned to isolated vanadate species formed on the surface of SiO₂ or CeO₂.

Fig.6 shows Ce L_{III}-edge and V K-edge XANES spectra of Ce–V/SiO₂ with different Ce/V ratios acquired at ambient temperature. The Ce L_{III}-edge spectra for CeO₂ and Ce(CH₃COO)₃ are also shown as references for Ce⁴⁺ and Ce³⁺, respectively. As evident from these two references spectra, the line shapes of Ce³⁺ and Ce⁴⁺ are very different [47] and thus can be used to differentiate between CeVO₄ and CeO₂. The white line at approximately 5726 eV was very intense for Ce³⁺, whereas Ce⁴⁺ showed less intense peaks at higher energies >5730 eV, which split into at least two components. The white line intensity for Ce–V/SiO₂ catalyst steeply decreased with increasing the Ce/V ratio, suggesting an increased CeO₂ precipitation. The result was consistent with XRD and Raman spectra as shown in Figs.4 and 5. Conversely, V K-edge XANES showed no detectable change because V⁵⁺ was a dominant species regardless of the fraction of CeVO₄ and V₂O₅.

3.3 SO₃ decomposition activity of Ce–V/SiO₂ catalysts.

Fig.7 shows temperature dependences of steady-state SO₃ conversion over Ce–V/SiO₂ and unsupported oxides (CeVO₄, CeO₂ and V₂O₅). Among the unsupported oxides, CeO₂ is mostly inactive in a measured temperature range, where the reaction between CeO₂ and SO₃ to form Ce sulfates is thermodynamically favorable. Compared to CeO₂, CeVO₄ and V₂O₅ showed higher SO₃ conversions, while V₂O₅ catalyst could only be used below the melting point (675 °C). The SO₃ conversion over CeVO₄ tended to level off at $T > 700$ °C probably due to a mass transfer limitation caused by the low S_{BET} value (2.1 m² g^{−1}). By contrast, the Ce–V/SiO₂ catalyst (Ce/V = 0.9) achieved much higher conversions close to equilibrium values at 600–800 °C. The turnover frequency (TOF), which was calculated using the SO₃ decomposition rate at 600 °C and the apparent Ce–V loading, was more than 50-fold higher than that of unsupported CeVO₄. This is nearly consistent with the 45-fold greater specific surface area of CeVO₄ in Ce–V/SiO₂ as mentioned above. Highly dispersed CeVO₄ in the Ce–V/SiO₂ catalyst is thus very effective in enhancing the catalytic performance.

The SO₃ conversion at 650 °C is plotted versus the Ce/V ratio in Fig.8. The conversion initially increased with an increase of the Ce/V ratio and showed the maximum at approximately Ce/V = 0.9, whereas further increase of Ce/V led to steep drop in the catalytic activity. Because the similar dependence is observed for the crystallite size of CeVO₄ (Fig.4b), the activity increasing at $0.5 \leq \text{Ce/V} \leq 0.9$ is closely associated with enhanced surface area of the active CeVO₄ phase. Another possible reason for the lower activity at lower Ce/V ratios is the formation of the molten V₂O₅ phase, the corrosion effect

of which deteriorated the catalyst microstructure. On the other hand, the activity decreased beyond $\text{Ce}/\text{V} \geq 0.9$ due to the higher content of CeO_2 , which was converted into inactive Ce sulfate during the catalytic SO_3 reactions. The formation $\text{Ce}(\text{SO}_4)_2$ and $\text{Ce}_2(\text{SO}_4)_3$ was detected by XRD of the $\text{Ce}-\text{V}/\text{SiO}_2$ catalyst after the catalytic testing. Because the formation of these inert sulfates is a well-known deactivation route for the catalytic SO_3 decomposition [33], the Ce/V ratio more than 0.9 is inadequate for the present catalyst system.

Fig.9 plots the SO_3 conversion for $\text{Ce}-\text{V}/\text{SiO}_2$ ($\text{Ce}/\text{V} = 0.9$) and 0.5 wt% $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ at 650 °C versus WHSV. The activity of $\text{Ce}-\text{V}/\text{SiO}_2$ was comparable to that of $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ in a range of $3.6 \text{ g-H}_2\text{SO}_4 \text{ g}^{-1} \text{ h}^{-1} \leq \text{WHSV} \leq 110 \text{ g-H}_2\text{SO}_4 \text{ g}^{-1} \text{ h}^{-1}$, although $\text{Cu}-\text{V}/\text{SiO}_2$ in our previous reports was superior to these catalysts. As evident from Fig.7, the SO_3 conversion at 650 °C was close to the equilibrium at $\text{WHSV} \leq 3.6 \text{ g-H}_2\text{SO}_4 \text{ g}^{-1} \text{ h}^{-1}$. The stability of the $\text{Ce}-\text{V}/\text{SiO}_2$ was therefore tested at a higher WHSV of $11 \text{ g-H}_2\text{SO}_4 \text{ g}^{-1} \text{ h}^{-1}$ to observe the deactivation behavior. Nevertheless, no indication of noticeable deactivation was observed during 40 h of reaction at 650 °C (Fig.10). These results clearly suggested that the highly dispersed $\text{Ce}-\text{V}$ oxide catalyst supported on bimodal mesoporous SiO_2 is a promising catalyst material for efficient SO_3 decomposition. Although its catalytic activity is less than that of $\text{Cu}-\text{V}/\text{SiO}_2$ catalyst in our previous reports [34, 36], the higher melting point of CeVO_4 compared with $\text{Cu}-\text{V}$ oxides is expected to extend the reaction temperature range, which is beneficial for a wide variety of practical applications of solar thermochemical hydrogen production. Further studies on the catalyst stability at higher reaction temperatures are now in progress.

4. CONCLUSION

The Ce–V oxide supported on the novel bimodal mesoporous SiO₂ material has emerged as an attractive alternative to Pt catalyst for SO₃ decomposition, which is a key step of solar thermochemical hydrogen production. By the use of the SiO₂ support, highly dispersed CeVO₄ particles with the size of 13 nm could be prepared, which exhibited more than 50-fold higher turnover frequency at 600 °C compared to unsupported CeVO₄ with the particle size of 600 nm. Because the high specific surface area of CeVO₄ is an important factor for the catalytic performance, the use of the bimodal mesoporous SiO₂ support opens new perspectives in attaining highly efficient, durable and cost-effective vanadate catalysts.

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Figure captions

Fig.1 Catalytic SO_3 conversion of various M–V oxides at 600 °C, 650 °C and 700 °C versus decomposition temperature of sulfate of M.

Fig.2 (a) A TEM image of bimodal mesoporous SiO_2 and (b) an STEM-HAADF image of Ce–V/ SiO_2 catalyst (Ce/V = 0.9). Black contrast dots with size of 2–3 nm in (a) are Au nanoparticles added as markers.

Fig.3 Pore volume distribution of bimodal mesoporous SiO_2 (Ce/V = 0.9).

Fig.4 (a) XRD patterns of Ce–V/ SiO_2 catalysts with different Ce/V ratios and unsupported CeVO_4 . (b) Crystallite size of CeVO_4 in Ce–V/ SiO_2 catalysts as a function Ce/V ratio.

Fig.5 Raman spectra of Ce–V/ SiO_2 catalysts with different Ce/V ratios.

Fig.6 (a) Ce L_{III} -edge and (b) V K-edge XANES of Ce–V/ SiO_2 catalysts with different Ce/V ratios.

Fig.7 Temperature dependence of SO_3 conversion over Ce–V/ SiO_2 (Ce/V = 0.9) and unsupported CeVO_4 , CeO_2 and V_2O_5 . 4.6% SO_3 , 32.9% H_2O and N_2 balance, WHSV = 3.6 $\text{g-H}_2\text{SO}_4 \text{ g-cat}^{-1} \text{ h}^{-1}$.

Fig.8 SO_3 conversion at 650 °C for Ce–V/ SiO_2 catalysts with different Ce/V ratios. 4.6% SO_3 , 32.9% H_2O and N_2 balance, WHSV = 3.6 $\text{g-H}_2\text{SO}_4 \text{ g-cat}^{-1} \text{ h}^{-1}$.

Fig.9 SO_3 conversion at 650 °C for Ce–V/ SiO_2 (Ce/V = 0.9) and $\text{Pt/Al}_2\text{O}_3$ as a function of WHSV.

Fig.10 Catalyst stability of Ce–V/ SiO_2 (Ce/V = 0.9) at 650 °C. 14% SO_3 , 17% H_2O and N_2 balance, WHSV = 11 $\text{g-H}_2\text{SO}_4 \text{ g-cat}^{-1} \text{ h}^{-1}$.

Fig.1 Catalytic SO₃ conversion of various M–V oxides at 600 °C, 650 °C and 700 °C versus decomposition temperature of sulfate of M.

Fig.2 (a) A TEM image of bimodal mesoporous SiO₂ and (b) an STEM-HAADF image of Ce-V/SiO₂ catalyst (Ce/V = 0.9). Black contrast dots with size of 2–3 nm in (a) are Au nanoparticles added as markers.

Fig.3 Pore volume distribution of bimodal mesoporous SiO₂ (Ce/V = 0.9).

Fig.4 (a) XRD patterns of Ce–V/SiO₂ catalysts with different Ce/V ratios and unsupported CeVO₄. (b) Crystallite size of CeVO₄ in Ce–V/SiO₂ catalysts as a function Ce/V ratio.

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Fig.8 SO₃ conversion at 650 °C for Ce–V/SiO₂ catalysts with different Ce/V ratios. 4.6%

SO₃, 32.9% H₂O and N₂ balance, WHSV = 3.6 g-H₂SO₄ g-cat⁻¹ h⁻¹.

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