

Molten copper hexaoxodivanadate as SO₃ decomposition catalyst for solar thermochemical water splitting cycles

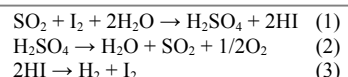
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Introduction

Thermochemical water splitting will be a promising process for hydrogen production by utilizing concentrated solar radiation as a heat source. The cost-effective production of solar hydrogen requires multi-stage processes working at lower temperatures. We are interested in so-called "IS process" as a candidate consisting of the following step reactions. In the reaction (2), sulfuric acid dissociates nearly completely into H₂O and SO₃ in the gas phase at above 350 °C, but the subsequent decomposition of SO₃ into SO₂/O₂ requires heating at ≥900 °C. Consequently, the reaction (2) is operated at the highest temperature among these three steps. The present work focused on the development of oxide catalysts that can reduce the temperature for SO₃ decomposition down to ≤650 °C.



Materials and Methods

Bulk oxides (CuV₂O₆) and supported catalysts (Cu-V/SiO₂) were prepared as was described in our preceding paper [1,2]. Molar ratios of Cu:V:Si=1:2:20 (denoted as CuV₂/SiO₂) and/or 1:1:20 (CuV/SiO₂) were employed to deposit monophasic CuV₂O₆ and Cu₂V₂O₇, respectively. Catalytic reaction was carried out in a flow reactor (14% SO₃, 18% H₂O and N₂ balance, WHSV=55.2 g-H₂SO₄ (g-cat)⁻¹h⁻¹).

Results and Discussion

Fig. 1 exhibits the evolution of SO₃ conversion over two types of supported catalysts versus time during stepwise change of reaction temperature. Although the activity of both catalysts increased with an increase of temperature, their time-on-stream behaviors were quite different. In contrast to stable but low conversion over CuV/SiO₂ at 650 °C (b), CuV₂/SiO₂ was found to increase the conversion with time-on-stream at 650 °C, achieving twenty times higher conversion than CuV/SiO₂. Higher SO₃ conversions of CuV₂/SiO₂ than CuV/SiO₂ suggest a higher intrinsic activity of CuV₂O₆ compared to Cu₂V₂O₇. Nevertheless, it should be noted that the catalytic activity was accelerated when the reaction temperature reached the melting point of CuV₂O₆ (~630 °C). This is not the case for Cu₂V₂O₇, which exhibits a higher melting points (780 °C).

XRD and Raman spectroscopy suggested that Cu sulfate was formed on the catalyst surface under the reaction condition. Considering this is an intermediate species of SO₃ decomposition, its thermal behavior should be a clue to elucidate the reason for the accelerated SO₃ decomposition at the melting point. Thermal behavior of a physical mixture of CuSO₄/CuV₂O₆ was next studied by TG-DTA-MS (Fig.2). When CuSO₄ alone was heated, sulfate decomposition started at around 550 °C (a). In the MS spectra, SO₂ and O₂ were

detected, whereas SO₃ was negligible, suggesting the occurrence of a stoichiometric reaction; CuSO₄→CuO + SO₂ + 1/2 O₂. As shown in Fig 2b, a mixture of CuSO₄/CuV₂O₆ also started the decomposition at around 550 °C, but a very steep increase of SO₂ and O₂ accompanied by a rapid weight loss occurred at 630 °C, where melting of CuV₂O₆ yielded a sharp endothermic peak. The maximum rate of decomposition is more than six times higher than that of CuSO₄ alone. These results suggest that the decomposition of CuSO₄ to evolve SO₂/O₂ is significantly accelerated in contact with molten CuV₂O₆.

From these results, a possible mechanism for the accelerated catalytic SO₃ decomposition over molten copper vanadate is discussed. On the surface of molten vanadate, SO₃ adsorption to Cu oxide species yields Cu-SO₄ species, which are readily dissolved into molten vanadate consisting of tetrahedral VO₄ and Cu²⁺/Cu⁺ redox couples, which immediately convert SO₄ to SO₂/O₂. Free copper oxide species thus formed diffuse back to the liquid surface, where the reaction with SO₃ reforms Cu-SO₄ species. In this way, the molten copper vanadate enables such fast cycles of SO₃ capture and decomposition to SO₂/O₂.

Significance

Molten CuV₂O₆ was identified as an active catalyst for SO₃ decomposition, which is an oxygen generation step in solar thermochemical water splitting cycles, at moderate temperatures.

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References

- [1] M.Machida, et al., *Chem. Commun.*, 2011, **47**, 9591; *Chem. Mater.*, 2012, **24**, 557; *J. Phys. Chem. C*, 2013, **117**, 26710.
- [2] T. Kawada, et al., *Catal. Sci. Technol.*, in press (2014).

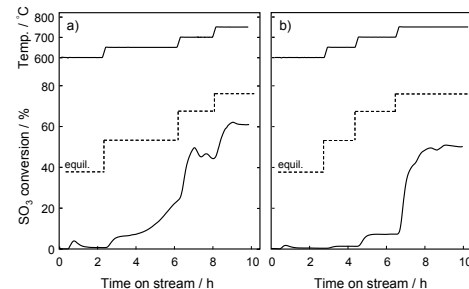


Fig. 1 Catalytic SO₃ conversion over a) CuV₂/SiO₂ and b) CuV/SiO₂ versus time-on-stream during stepwise change of reaction temperature.

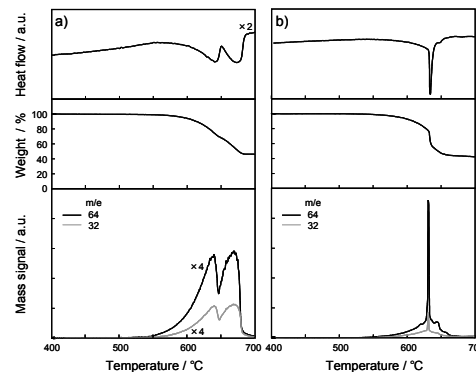


Fig. 2 TG-DTA-MS profiles for a) CuSO₄ and b) CuSO₄/CuV₂O₆ mixture measured at heating rate of 20 °C min⁻¹ in a stream of He.