Molten copper hexaoxodivanadate as SO$_3$ 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 two step reactions. In the reaction (2), sulfuric acid dissociates nearly completely into H$_2$O and SO$_3$ in the gas phase at above 350 °C, but the subsequent decomposition of SO$_3$ into SO$_2$O$_2$ 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 SO$_3$ decomposition down to ≤650 °C.

Materials and Methods

Bulk oxides (CuV$_2$O$_5$) and supported catalysts (Cu-V/SiO$_2$) were prepared as described in our preceding paper [1,2]. Molar ratios of Cu:V=1:2:20 (denoted as CuV$_5$/SiO$_2$) and/or 1:1:20 (CuV$/SiO_2$) were employed to deposit monophasic CuV$_2$O$_5$ and CuV$_2$O$_5$, respectively. Catalytic reaction was carried out in a flow reactor (14% SO$_3$, 18% H$_2$O and N$_2$ balance, WHSV=55.2 g·H$_2$SO$_4$·g·cat$^{-1}$·h$^{-1}$).

Results and Discussion

Fig. 1 exhibits the evolution of SO$_3$ 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/SiO$_2$ at 650 °C (b), CuV$_5$/SiO$_2$ was found to increase the conversion with time-on-stream at 650 °C, achieving twenty times higher conversion than CuV/SiO$_2$. Higher SO$_3$ conversions of CuV$_5$/SiO$_2$ than CuV/SiO$_2$ suggest a higher intrinsic activity of CuV$_2$O$_5$ compared to CuV$_2$O$_5$. Nevertheless, it should be noted that the catalytic activity was accelerated when the reaction temperature reached the melting point of CuV$_2$O$_5$ (~630 °C). This is not the case for CuV$_2$O$_5$, 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 SO$_3$ decomposition, its thermal behavior should be a clue to elucidate the reason for the accelerated SO$_3$ decomposition at the melting point. Thermal behavior of a physical mixture of CuSO$_4$/CuV$_2$O$_5$ was next studied by TG-DTA-MS (Fig.2). When CuSO$_4$ alone was heated, sulfate decomposition started at around 550 °C (a). In the MS spectra, SO$_3$ and O$_2$ were detected, whereas SO$_3$ was negligible, suggesting the occurrence of a stoichiometric reaction; CuSO$_4$→CuO + SO$_3$ + 1/2 O$_2$. As shown in Fig. 2b, a mixture of CuSO$_4$/CuV$_2$O$_5$ also started the decomposition at around 550 °C, but a very steep increase of SO$_3$ and O$_2$ accompanied by a rapid weight loss occurred at 630 °C, where melting of CuV$_2$O$_5$ yielded a sharp endothermic peak. The maximum rate of decomposition is more than six times higher than that of CuSO$_4$ alone. These results suggest that the decomposition of CuSO$_4$ to evolve SO$_3$O$_2$ is significantly accelerated in contact with molten CuV$_2$O$_5$.

From these results, a possible mechanism for the accelerated catalytic SO$_3$ decomposition over molten copper vanadate is discussed. On the surface of molten vanadate, SO$_3$ adsorption to Cu oxide species yields Cu-SO$_4$ species, which are readily dissolved into molten vanadate consisting of tetrahedral VO$_4$ and Cu$^{2+}$/Cu$^{3+}$ redox couples, which immediately convert SO$_3$ to SO$_2$O$_2$. Free copper oxide species thus formed diffuse back to the liquid surface, where the reaction with SO$_3$ reforms Cu-SO$_4$ species. In this way, the molten copper vanadate enables such fast cycles of SO$_3$ capture and decomposition to SO$_2$O$_2$.

Significance

Molten CuV$_2$O$_5$ was identified as an active catalyst for SO$_3$ decomposition, which is an oxygen generation step in solar thermochemical water splitting cycles, at moderate temperatures.

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References