Chemical State Analysis for Reduction Process of Vanadium Oxide Supported on SiO_2

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Vanadium oxide can take various oxidation states and exhibits activity in a lot of catalysis reactions [1,2]. In addition, it is also promising as an active material of rechargeable battery electrode that effectively utilizes multiple electron transfer [3,4]. To improve their functionality as the catalyst and electrode material, it is important to understand the chemical state of the vanadium oxide depending on the nature of the supporting material, the loading, and the atmosphere. In this study, samples of vanadium oxide supported on SiO_2 were prepared using the impregnation method, and *in situ* XAFS analysis of the temperature-programmed reduction (TPR) process was carried out.

A mixture of an aqueous solution of vanadium oxide sulfate added to SiO_2 was dried in air at 60 °C for 24 h, and the resulting powder was subjected to calcination at 500 °C for 6 h in air. *In situ* XAFS measurements were performed for the TPR process under a H_2 gas flow diluted by He (15 vol%).

Figure 1 shows the XANES spectral change together with those of reference samples. The initial spectrum matched well with that of V_2O_5 with a pre-peak at 5.468 keV, and it changed to V_2O_3 with a white line peak at 5.485 keV at above 560 °C. Because there are isosbestic points in the spectral change, it is a two-component change from V_2O_5 to V_2O_3. The linear combination fitting (LCF) analysis was performed to clarify the composition of the vanadium species, and the results are shown in Fig. 2. Although we took into account the possibility that VO_2 was mixed, the XANES spectrum observed at 490 °C, at which the XANES spectrum was in the course of change, was sufficiently reproduced with two components of V_2O_5 and V_2O_3. Figure 2 shows the temperature change of the determined composition. The state of V_2O_5 was maintained up to 280 °C, and at 490 °C, 40% of vanadium was reduced to V_2O_3. Reduction to V_2O_3 was completed at 560 °C, and V_2O_3 was retained in the temperature range up to 700 °C. In the phase diagram of vanadium oxide, it is known that oxides with other compositions, including VO_2, exist in addition to V_2O_5 and V_2O_3 [5,6]. In this study, we provided new knowledge regarding the stability of vanadium oxides under hydrogen atmosphere.

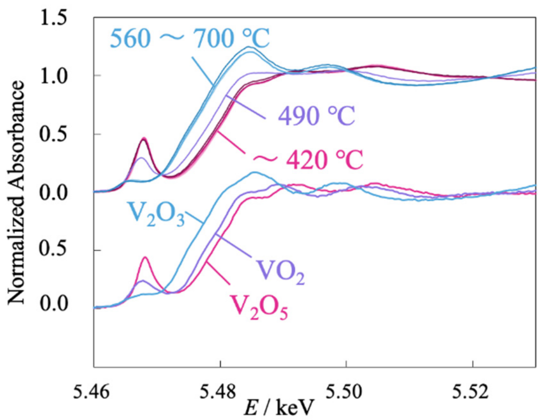

Fig. 1. XANES spectral change of V_2O_5 supported on SiO_2 during the TPR process.

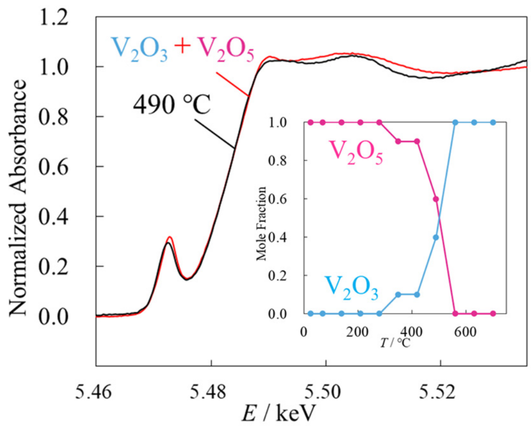

Fig. 2. Results of the LCF analysis for the XANES spectrum measured at 490 °C. The estimated composition change is given in an inset as a function of temperature.

References

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