Supporting Information

Depressed transition temperature of $W_xV_{1-x}O_2$: mechanistic insights from the X-ray absorption fine structure (XAFS) spectroscopy

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V K-edge XANES spectra of the standard samples

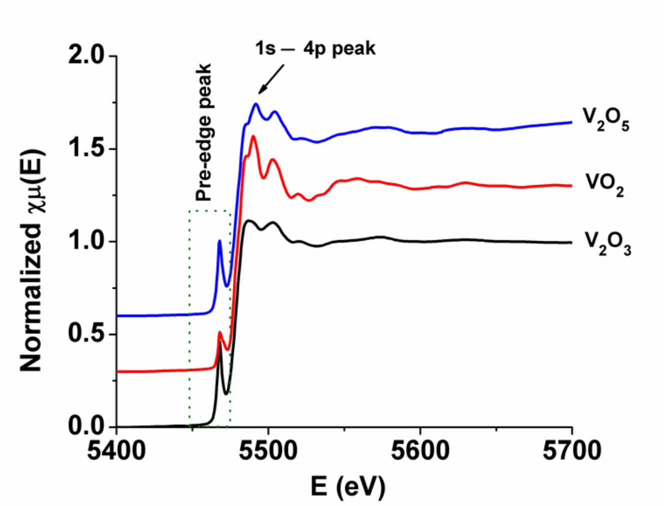

Fig. S1. V K–edge XANES spectra of the standard samples (V_2O_3, VO_2 and V_2O_5). All of these samples were used in construction of the 1s→4p peak position plot and to derive a calibration curve, as shown in Fig. 4b. V_2O_3 powder was prepared by the hydrothermal method followed with the Ar annealing treatment.

Generally, the threshold, the pre-edge peak, absorption-edge, and 1s→4p transitions exhibit a monotonic dependence of their peak positions with respect to the oxidation state according to Kunzl's law. [44] The energy required to excite a core electron is increased with increasing vanadium formal oxidation state. We also measured V K–edge XANES spectra of V_2O_3, VO_2, and V_2O_5 standard samples, as shown in Fig. S1. The energy positions of the 1s→4p peak and pre-edge peak were identified from the derivative spectra. For vanadium oxides, the energy position of the pre-edge peak or 1s→4p peak has a linear relationship with the oxidation state.[44] Therefore, the relative energy positions of 1s→4p peaks to the pre–edge peaks ($E_{1s\rightarrow 4p\ peak} - E_{pre\text{-}edge\ peak}$) also has a linear relationship with the oxidation state. In our study, the energy positions of the 1s→4p peaks can not be compared because the two standard samples (V_2O_3 and V_2O_5) and $W_xV_{1-x}O_2$ samples were not measured at the same XAFS experiment. Thus we choose the relative energy positions of 1s→4p peaks to the pre–edge peaks, in order to make the comparability between the $W_xV_{1-x}O_2$ samples and the standard samples. Then we plotted the relative energy positions of 1s→4p peaks to the pre–edge peaks as a function of the formal vanadium oxidation state to derive an approximate calibration curve, as shown in Fig. 4b, showing a linear relationship between the relative energy positions of 1s→4p peaks to the pre–edge peaks and the oxidation states. The $W_xV_{1-x}O_2$ samples were indicated on this calibration curve. This provides a good method to obtain insight into the oxidation state of V atoms.