

## Elucidation of molecular adsorption states of strong base metal oxide cluster by X-ray absorption spectroscopy

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Metal oxide clusters consisting of group-V transition metals such as  $[M^V_6O_{19}]^{8-}$  ( $M^V = Nb, Ta$ ) have a strong basicity that is comparable to MgO. Nevertheless, they are not deactivated by molecular adsorption and catalyze Knoevenagel condensation reactions and CO<sub>2</sub> fixation reactions.<sup>1</sup> In this study, we investigated unique molecular adsorption states on  $[M^V_6O_{19}]^{8-}$  by high-energy-resolved fluorescence detection X-ray absorption spectroscopy (HERFD-XAS) which enables direct observation of the crystal field correlated with structural change.<sup>2</sup> We have acquired XANES spectra of Nb K- and Ta L<sub>3</sub>-edges in the HERFD mode and successfully observed changes in the crystal field attributed to molecular adsorption for the first time.

Tetrabutylammonium salts of  $[M^V_6O_{19}]^{8-}$  were synthesized by a microwave-assisted hydrothermal method in reference to the literature<sup>3</sup> and characterized by infrared spectra and electrospray ionization mass spectra. Molecular adsorption states of  $[Nb_6O_{19}]^{8-}$  (Nb6) were studied by pre-edge peaks in Nb K-edge HERFD-XANES spectra (Fig.a). When 1% CO<sub>2</sub> gas with N<sub>2</sub> balance and acid-base indicators as adsorbents were added to Nb6 DMF solution, the intensity of pre-edge peaks in both XANES spectra decreased compared to the pristine Nb6. These results indicate that CO<sub>2</sub> and protons adsorbed to the same base sites with an increase in their octahedral symmetry. Ta L<sub>3</sub>-edge HERFD-XANES spectra (Fig.b) also reflected *d*-orbital splitting affected by molecular adsorption to  $[Ta_6O_{19}]^{8-}$  (Ta6). From the increasement of splitting width by CO<sub>2</sub> adsorption, we conclude that Ta6 activated CO<sub>2</sub> accompanied with the increase of the octahedral symmetry near the active site of Ta6 (Fig.c).

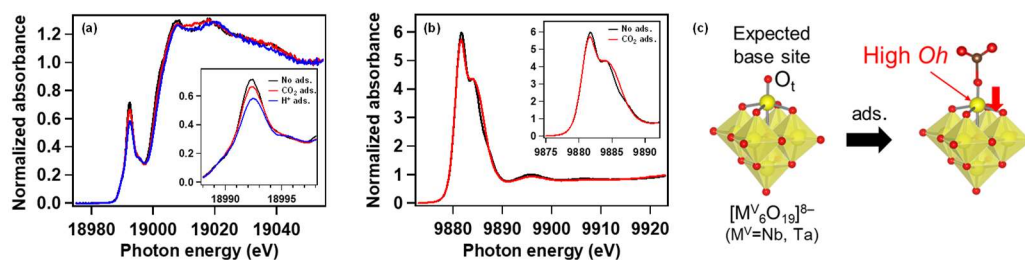


Figure (a) HERFD-XANES spectra at Nb K-edge and (b) those at Ta L<sub>3</sub>-edge. (c) Expected molecular adsorption states.

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