In situ HERFD-XANES study on CO_2 activation on niobium oxide clusters

Metal oxide clusters consisting of several MO_6 metal oxide units (M: metal ions), called polyoxometalates, exhibit unique reactivities and physical properties owing to their electronic and geometric structures, unlike their bulk materials counterparts. We found that group 5 transition metal Nb/Ta oxide clusters, such as $[M_6O_{19}]^{8-}$ (MV = Nb, Ta) and $[Nb_{10}O_{28}]^{6-}$, possess large negative charges and have demonstrated effectiveness as base catalysts [1,2]. Notably, the $[Ta_6O_{19}]^{8-}$ (**Ta6**) cluster shows high activity for CO_2 fixation reactions with styrene oxide and amine compounds. DFT calculations predict that the terminal oxygen (Ta=O) on the surface of **Ta6** acts as a Lewis base, facilitating monodentate CO_2 coordination [2]. Understanding the structural dynamics of CO_2 adsorbed on **Ta6** is crucial to elucidating its high catalytic activity.

The recent development of a high-energy-resolved fluorescence detection (HERFD) method has garnered attention for its ability to measure XANES spectra with high-energy resolution. This method detects fluorescent X-rays with specific wavelengths, achieving an energy resolution beyond the core electron lifetime width, thereby enhancing the clarity of peaks in XANES spectra [3]. This technique has revealed small peaks that conventional methods often miss and has been applied to evaluate the symmetry of Ce_n oxide clusters (n = 2, 6, 24, 38, 40) [4]. However, HERFD-XANES studies remain relatively limited.

In this study, we measured *in situ* Ta L_3-shell HERFD-XAFS of **Ta6** in DMF during CO_2 adsorption at SPring-8 **BL36XU** beamline (Fig. 1) [5]. The HERFD-XANES measurements revealed previously undetected peaks within the white line region, that could not be observed by the conventional transmission method. In addition, we traced the CO_2 adsorption process on **Ta6** and experimentally clarified that the ligand field splitting is changed by the local structural change of Ta due to CO_2 adsorption.

The Ta L_3-edge HERFD-XANES spectrum of Ta_6 prior to CO_2 adsorption in DMF solution is shown in Fig. 2(a). Peaks (A_1 and B_1) along with a shoulder peak (C_1), which were not visible using the conventional transmission method at SPring-8 **BL01B1** with a Si(111) double crystal, were detected using the HERFD method. These peaks correspond to the electronic transition from 2*p* to 5*d* orbitals, which are expected to split due to the ligand field in the distorted octahedral **Ta6** units. These distortions approximate C_{4V} symmetry, enabling a detailed discussion of local distortions using Ta L_3-edge HERFD-XANES.

From the *in situ* HERFD-XANES spectra, we observed gradual changes in the electronic state of **Ta6** in DMF under CO_2 gas flow (Fig. 2(b)). The secondary differential spectra of Ta L_3-edge HERFD XANES showed slight shifts in peaks A_1 and B_1 to A_2 (–0.2 eV) and B_2 (+0.2 eV), respectively, while peak C_2 emerged at 9885.6 eV, replacing the vanished C_1 peak (Fig. 2(c)). Experimental data revealed that five CO_2 molecules were adsorbed onto **Ta6**, with spectral changes attributed to structural modifications around the Ta centers.

To further elucidate the structural changes, DFT calculations were employed to CO_2 adsorbed **Ta6** (**Ta6-CO$_2$**) model. The surface Ta=O bonds within the $\{TaO_6\}$ unit elongated, while the bridged Ta–O bonds

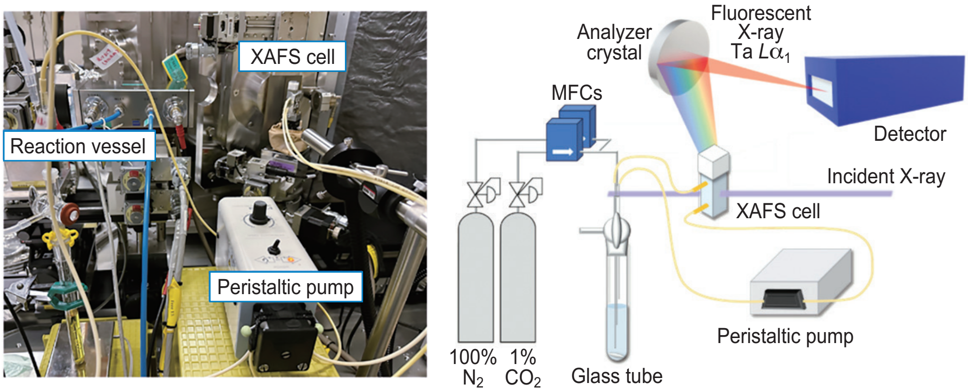

Fig. 1. Experimental setup for *in situ* HERFD-XANES measurement.

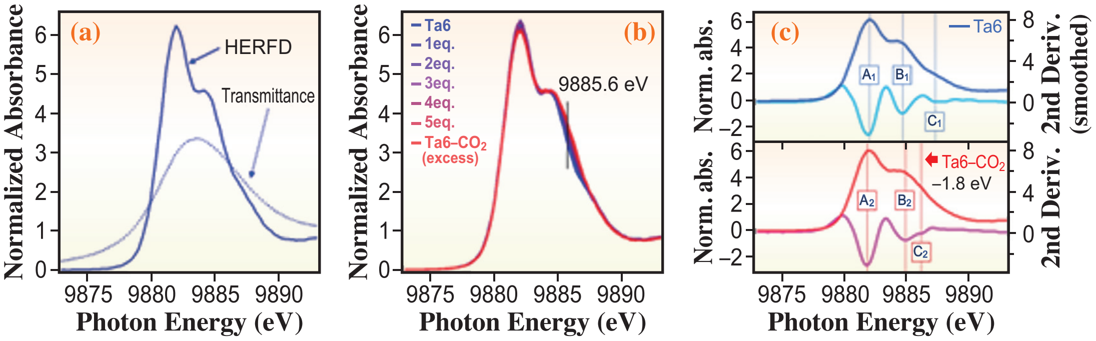

Fig. 2. **(a)** Comparison of XANES spectra of **Ta6** measured by HERFD and transmittance mode. **(b)** *In situ* HERFD-XANES spectra of **Ta6** during CO_2 adsorption. **(c)** HERFD-XANES spectra of **Ta6** and **Ta6-CO_2** along with their corresponding second derivative spectra.

shortened upon CO_2 adsorption (Fig. 3). This structural adjustment indicated a shift of the Ta atom toward the octahedral center, pushing the $\{TaO_6\}$ unit closer to O_h symmetry. Energy calculations and electronic structure analyses were performed for the $\{TaO_6\}$ and CO_2 adsorbed one ($\{TaO_6\text{-}CO_2\}$), as shown in Fig. 3. In the $\{TaO_6\}$ unit, regions A_1 (d_{xy}, d_{yx}, d_{zx}), B_1 (d_{z2}, d_{x2-y2}, $d_{z2}+\sigma_O$), and C_1 ($d_{x2-y2}+\sigma_O$) unit correlated with peaks A_1, B_1, and C_1 of **Ta6**. Upon CO_2 adsorption, these evolved into regions A_2 (d_{xy}, d_{yx}, d_{zx}), B_2 (d_{z2}, $d_{z2}+\sigma_O$), and C_2 (d_{x2-y2}), corresponding to peaks A_2, B_2, and C_2 of **Ta6-CO_2**. The disappearance of C_1 and the appearance of C_2 were linked to the destabilization of the d_{x2-y2} orbitals, including the hybrid orbital of Ta d_{x2-y2} + 2*p* orbitals and stabilization of d_{z2} orbitals caused by the structural centering effect. This is mainly due to the compression of the bridged Ta–O bonds and the elongation of the Ta=O bonds.

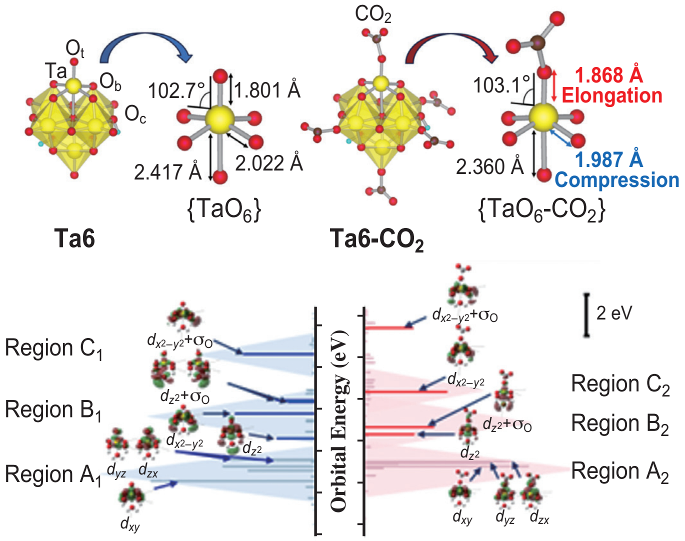

Fig. 3. Schematic illustration showing the contribution of Ta-based *d*-orbitals in TaO_6 and $TaO_6\text{-}CO_2$.

In summary, we observed a change in the ligand-field splitting of the Ta 5*d* orbitals in a **Ta6** catalyst upon CO_2 interaction, using *in situ* Ta L_3-edge HERFD-XANES. Theoretical calculations indicated that the three peaks observed before CO_2 adsorption correspond to transitions to molecular orbitals with significant contributions from the Ta 5*d* orbitals, which are split by the ligand field of the distorted O_h symmetrical $\{TaO_6\}$ units. The observed peak replacement reflects the destabilization of the d_{x2-y2} orbitals and the stabilization of the d_{z2} orbital, induced by the centering effect from the off-center arrangement of the $\{TaO_6\}$ units upon CO_2 attachment to the terminal oxygen. We demonstrate that HERFD-XANES is an effective tool for tracking subtle changes in the electronic and geometric structures of materials in their working state.

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