

In-situ QXAFS study of CO₂ adsorption behavior on Nb and Ta mixed clusters

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Polyoxometalates (POMs) composed of Ta and Nb possess base properties that facilitate catalytic activity for Knoevenagel condensation and CO₂ fixation reactions.¹ Recently, TBA_{8-n}H_n(Ta_xNb_{6-x}O₁₉) (defined as TBA-Ta_xNb_{6-x}) with the composition of TBA-Ta₁Nb₅ efficiency promotes CO₂ fixation of styrene oxide to form styrene carbonate with high selectivity.² We proposed that single TaO₆ unit surrounded by NbO₆ units activate CO₂ and undesired styrene activation was suppressed (**Figure 1a**). Hence, this work focuses on CO₂ activation behavior of TBA-Ta₁Nb₅ through the time-resolved quick X-ray absorption fine structure (QXAFS).

TBA-Ta₁Nb₅ was synthesized by the mixture of K₈Ta₆O₁₉·nH₂O and K₈Nb₆O₁₉·nH₂O which were ionized by HCl aq. before washed and dried. The obtained powder was added into TBAOH aq. which underwent microwave irradiation.³ The synthesis was confirmed by ESI-MS, FT-IR, and CHN analysis. The CO₂ adsorption behavior was monitored through *in-situ* experimental setup at SPring-8 BL36XU as illustrated in **Figure 1b**. Accordingly, *ca.* 1 equimolar CO₂ was bound to a unit of TBA-Ta₁Nb₅, likely onto the TaO₆ unit as suggested by the DFT calculations. In **Figure 2a-b**, the decrease in pre-edge peak intensity in Ta L₁-edge XANES of TBA-Ta₁Nb₅ by the initial CO₂ exposure for 20 minutes indicates that local structure changed in the TaO₆ unit, while insignificant change was observed in the Nb K-edge XANES. Furthermore, an increase in Ta L₃-edge white-line region (**Figure 2c**) by CO₂ adsorption indicates the changes in local structure of TaO₆ unit which is consistent with the reported result.⁴ In the presentation, the geometrical parameters calculated by DFT and the obtained QXAFS data will be discussed to understand CO₂ adsorption behavior of the mixed oxide cluster.

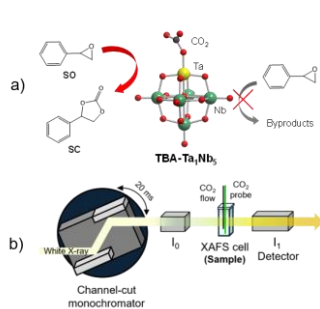


Figure 1. Schematic diagram of a) TBA-Ta₁Nb₅ catalytic activity in CO₂ fixation of styrene oxide² and b) *in-situ* QXAFS set-up.

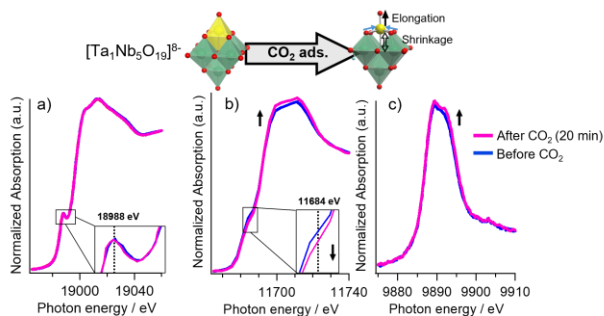


Figure 2. TBA-Ta₁Nb₅ XANES spectra before and after 20 minutes of CO₂ adsorption: a) Nb K-edge, b) Ta L₁-edge and c) Ta L₃-edge.

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