

Supplementary information
for

Selective CO₂ fixation to styrene oxide by Ta-substitution of Lindqvist-type [(Ta,Nb)₆O₁₉]⁸⁻ clusters

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Table S1. Composition of the synthesized TBA-Ta_xNb_{6-x}.

	C ^a (%)	H ^a (%)	N ^a (%)	TBA amount	H amount	Ta ^b (%)	Nb ^b (%)	Ta/Nb ratio
TBA-Nb ₆	45.29	9.42	3.43	6.0	2.0	—	27	—
TBA-Ta ₁ Nb ₅	39.19	8.62	2.98	5.0	3.0	9.4	24	1.0/5.0
TBA-Ta ₂ Nb ₄	39.86	8.90	3.01	5.3	2.7	17	17	2.0/4.0
TBA-Ta ₃ Nb ₃	44.38	9.10	3.44	6.1	1.9	20	11	2.9/3.1
TBA-Ta ₄ Nb ₂	37.24	8.50	2.83	5.3	2.7	31	7.9	4.0/2.0
TBA-Ta ₅ Nb ₁	38.81	8.26	2.91	5.7	2.3	35	3.2	5.1/0.9
TBA-Ta ₆	37.05	7.75	2.70	5.7	2.3	41	—	—

^aDetermined by elemental analysis.

^bEstimated by Ta L₃- and Nb K-edges X-ray absorption.

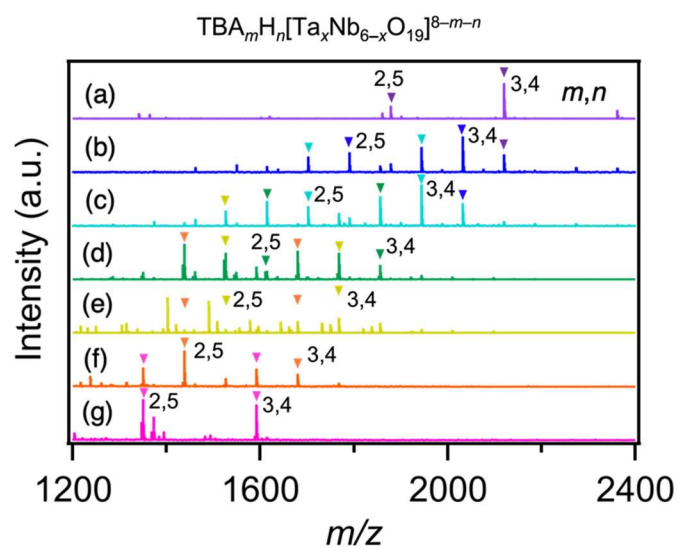


Figure S1. ESI-MS (negative ion mode) spectra of (a) $\text{TBA}_m\text{H}_n[\text{Ta}_6\text{O}_{19}]^{8-m-n}$, (b) $\text{TBA}_m\text{H}_n[\text{Ta}_5\text{Nb}_1\text{O}_{19}]^{8-m-n}$, (c) $\text{TBA}_m\text{H}_n[\text{Ta}_4\text{Nb}_2\text{O}_{19}]^{8-m-n}$, (d) $\text{TBA}_m\text{H}_n[\text{Ta}_3\text{Nb}_3\text{O}_{19}]^{8-m-n}$, (e) $\text{TBA}_m\text{H}_n[\text{Ta}_2\text{Nb}_4\text{O}_{19}]^{8-m-n}$, (f) $\text{TBA}_m\text{H}_n[\text{Ta}_1\text{Nb}_5\text{O}_{19}]^{8-m-n}$, and (g) $\text{TBA}_m\text{H}_n[\text{Nb}_6\text{O}_{19}]^{8-m-n}$ measured in aqueous solutions.

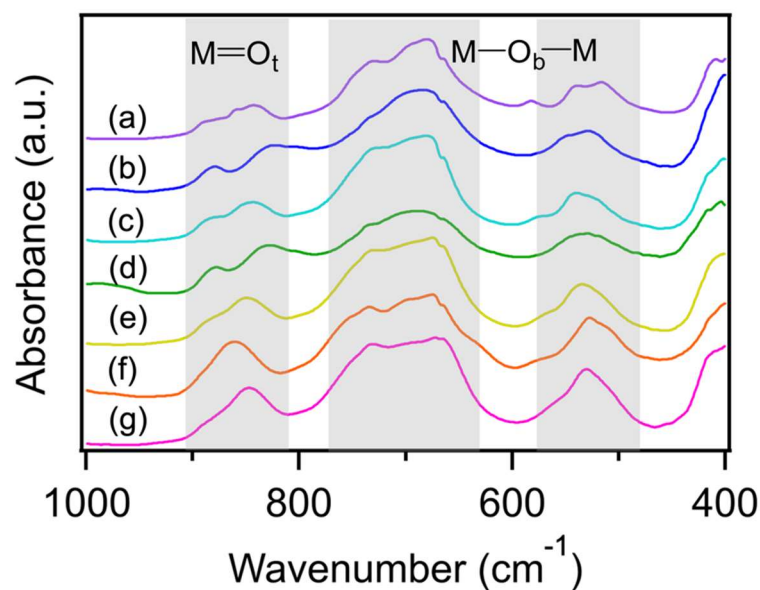


Figure S2. FT-IR spectra (ATR mode) of (a) TBA-Ta₆, (b) TBA-Ta₅Nb₁, (c) TBA-Ta₄Nb₂, (d) TBA-Ta₃Nb₃, (e) TBA-Ta₂Nb₄, (f) TBA-Ta₁Nb₅, and (g) TBA-Nb₆.

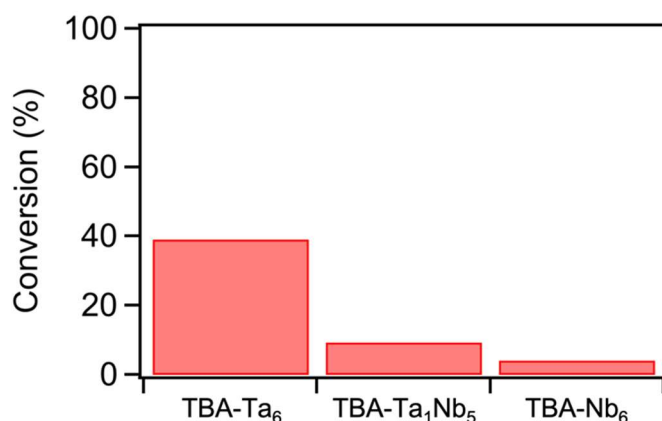


Figure S3. CO₂ fixation into **SO** promoted by TBA-Ta_xNb_{6-x} under N₂ atmosphere. Bars represent conversion of **SO**. Reaction condition: catalyst loading = 5 μmol, styrene oxide = 0.6 mL (ca. 5 mmol), N₂ = 0.1 MPa, temperature = 100 °C, reaction time = 6 h. Yield of **SC** was not detected in all cases.

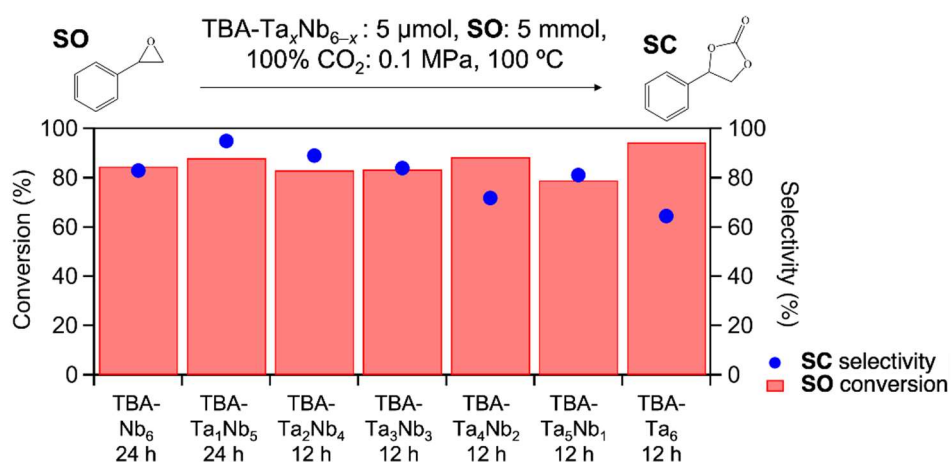


Figure S4. Results of CO₂ fixation to **SO** over TBA-Ta_xNb_{6-x}. Bars represent conversion of **SO**, blue dots represent selectivity of **SC**. Reaction condition: catalyst loading = 5 μmol, **SO** = 0.6 mL (ca. 5 mmol), 100% CO₂ = 0.1 MPa, temperature = 100 °C. The reaction time was optimized to achieve >80% conversion.

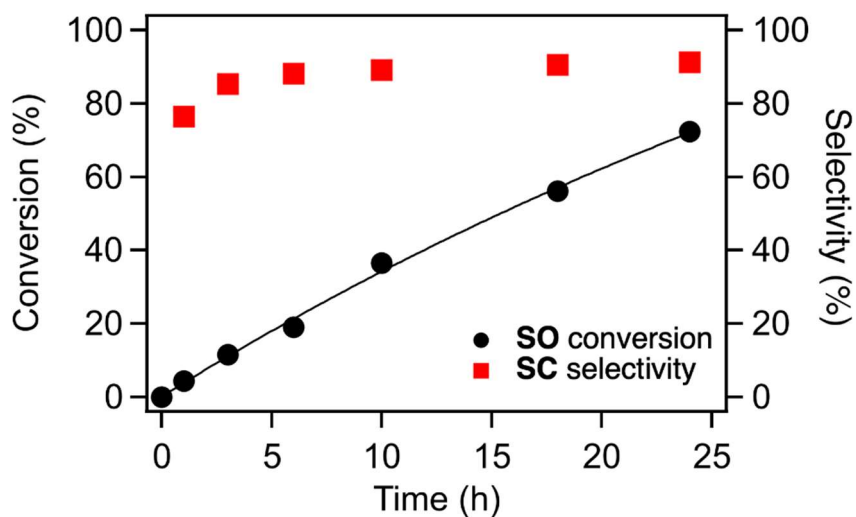


Figure S5. Time course of CO₂ fixation reaction to **SO** and selectivity of **SC** over TBA-Nb₆. Reaction condition: TBA-Nb₆ = 10 μmol, **SO** = 1.2 mL (ca. 10 mmol), 100% CO₂ = 0.1 MPa, temperature = 100 °C.

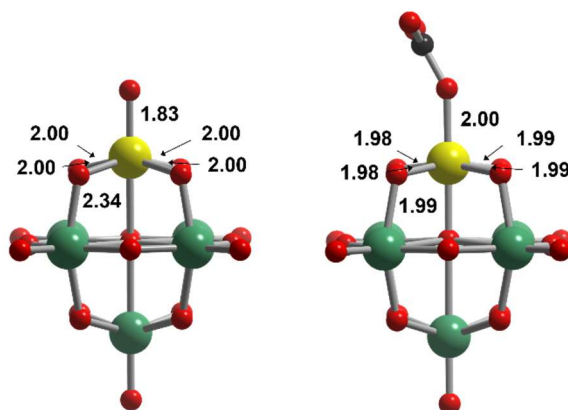


Figure S6. Optimized structure of [Ta₁Nb₅O₁₉]⁸⁻ and CO₂-adsorbed [Ta₁Nb₅O₁₉]⁸⁻. Color codes: yellow atom, Ta; green atom, Nb; blue line, Ta-coordinated O atoms; green line, Nb-coordinated O atoms; red, total O atoms.

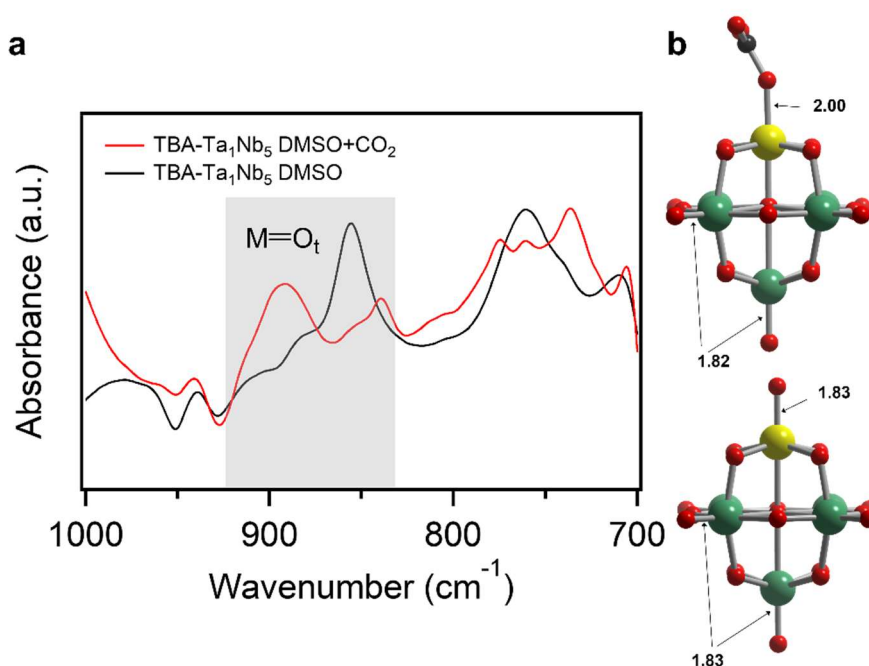


Figure S7. (a) *In-situ* FT-IR spectra (ATR mode) of TBA-Ta₁Nb₅ in DMSO before (black line) and after CO₂ adsorption (red line). (b) Optimized structure of [Ta₁Nb₅O₁₉]⁸⁻ and CO₂-adsorbed [Ta₁Nb₅O₁₉]⁸⁻.

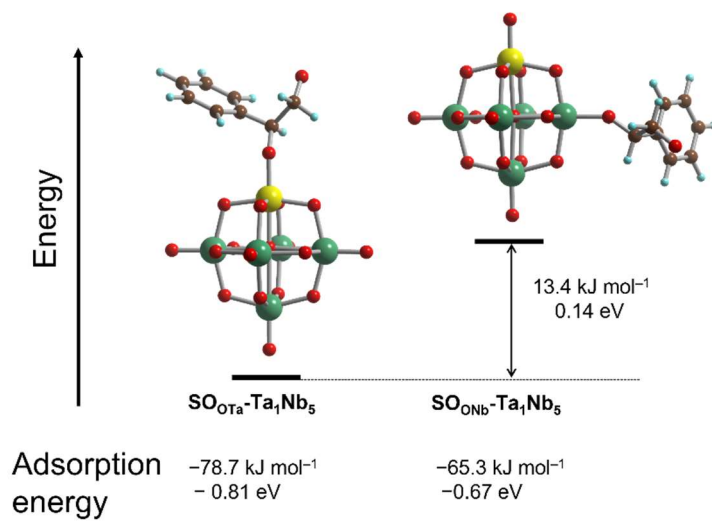


Figure S8. Total energy of SO-adsorbed [Ta₁Nb₅O₁₉]⁸⁻ at different base sites.

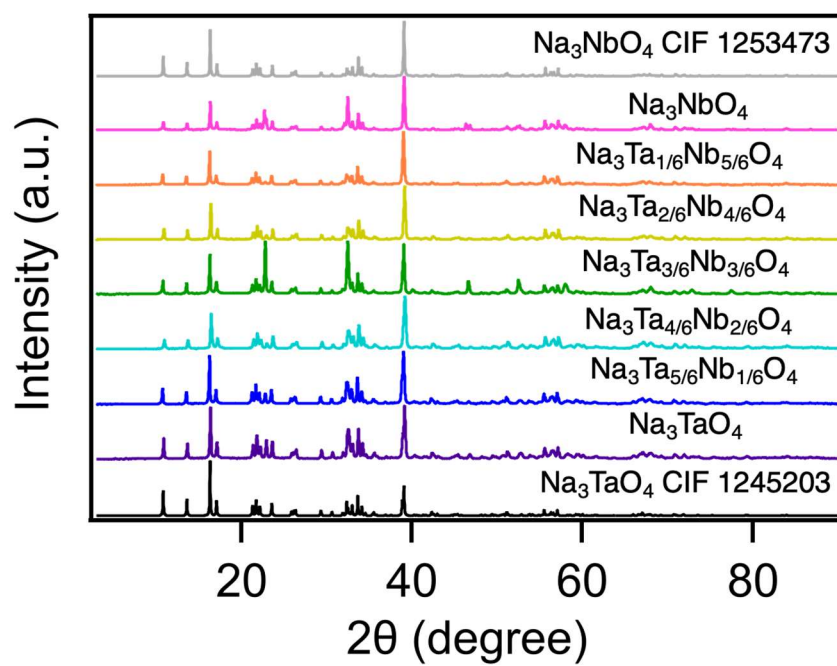


Figure S9. XRD patterns of $\text{Na}_3\text{Ta}_{(6-x)/6}\text{Nb}_{x/6}\text{O}_4$.