Electronic supplementary information (ESI)

CO_2-activation by size-selected tantalum cluster cations (Ta_{1-16}^+): thermalization governing reaction selectivity

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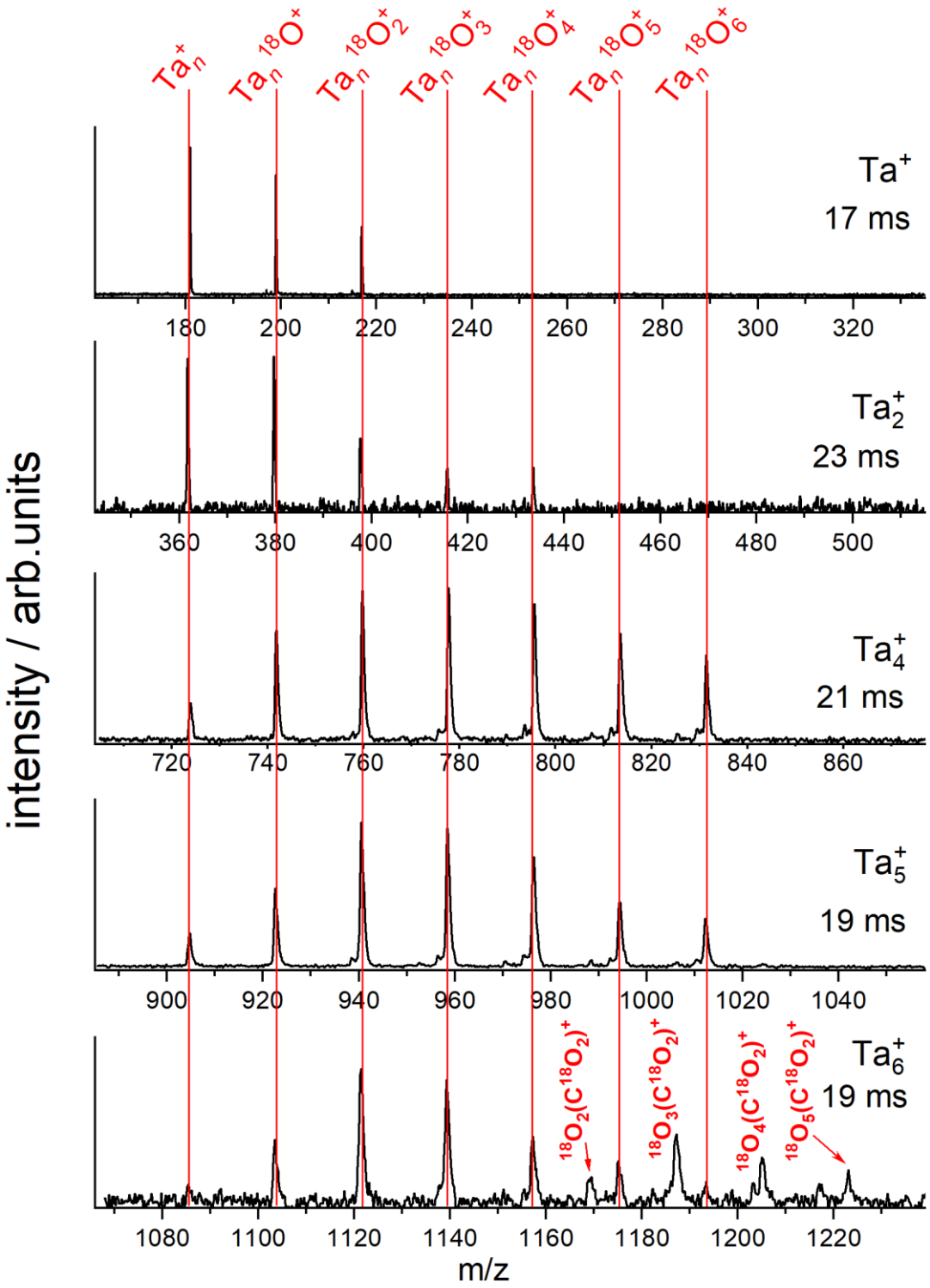

Fig. S1 Mass spectra of size-selected Ta_n^+-clusters (n = 1-6) and the corresponding products of their reaction with $C^{18}O_2$ after being stored in the ion trap for 29 ms. The total pressure in the trap amounts to 0.82 Pa, with the partial pressure of carbon dioxide being 20 ppm.

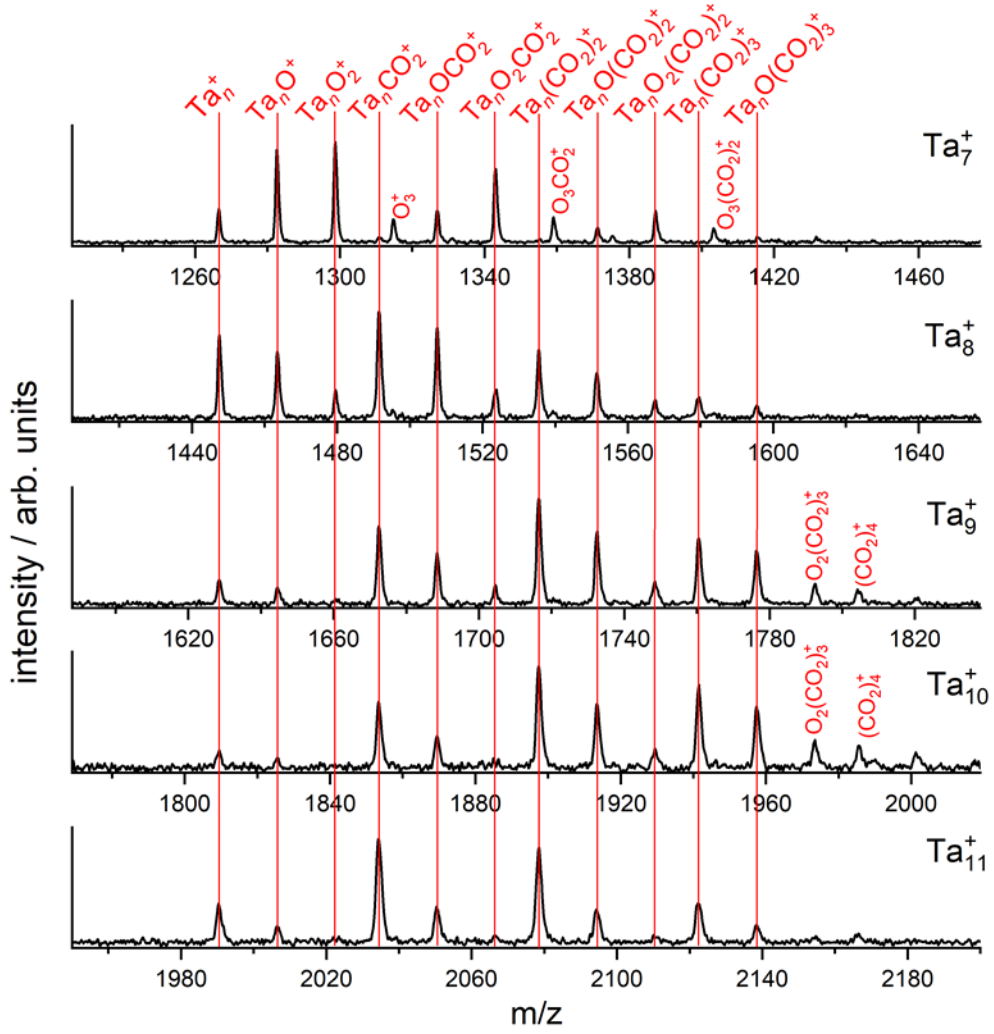

Fig. S2 Mass spectra of size-selected Ta_n^+-clusters (n = 7-11) and the corresponding products of their reaction with CO_2 after being stored in the ion trap for 29 ms (for $Ta_{7\text{-}10}^+$) and 21 ms (for Ta_{11}^+), respectively. For these cluster sizes both pathways, the oxygen atom transfer and the adsorption of an entire molecule, occur already in the reaction with the first CO_2 molecule. The total pressure in the trap amounts to 0.82 Pa, with the partial pressure of carbon dioxide being 10 ppm.

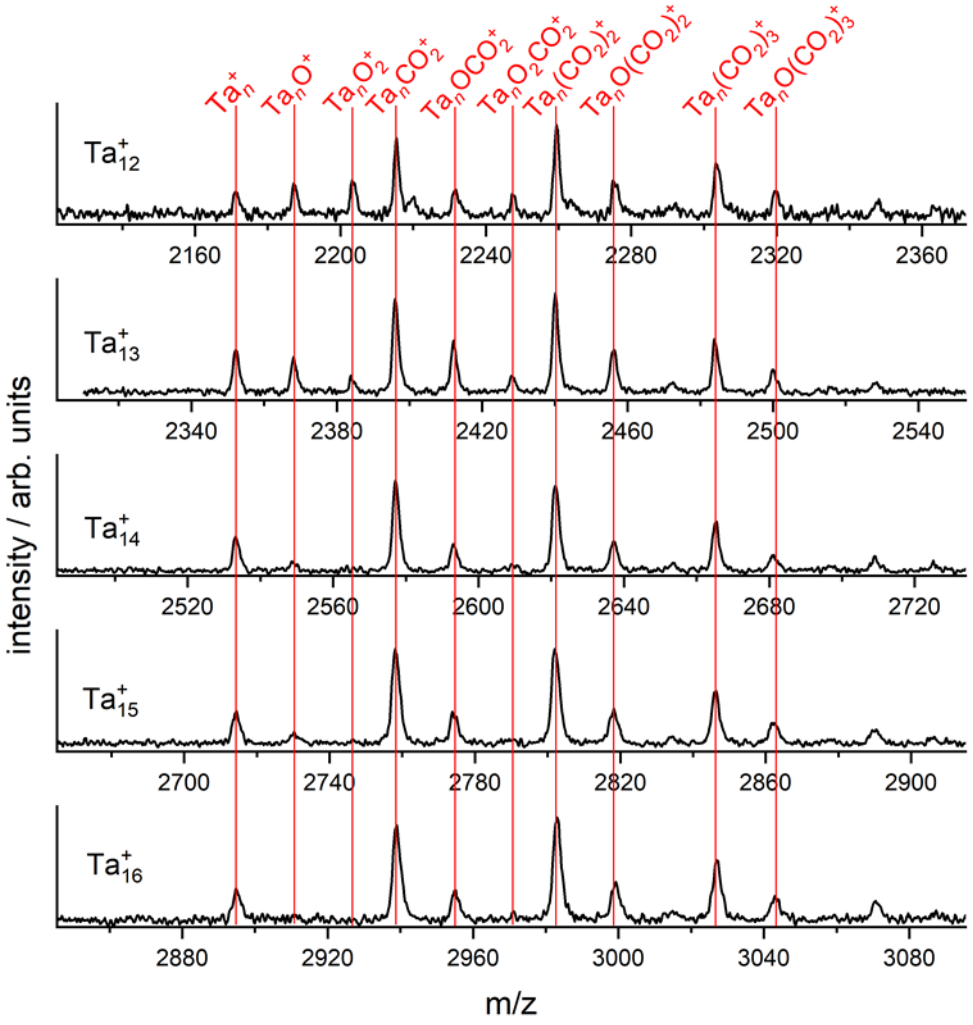

Fig. S3 Mass spectra of size-selected Ta_n^+-clusters (n = 12-16) and the corresponding products of their reaction with CO_2 after being stored in the ion trap for 21 ms (for Ta_{12}^+) and 17 ms (for $Ta_{13\text{-}16}^+$), respectively. All cluster exhibit predominantly the adsorption of an entire molecule in all reaction steps, while the oxygen atom transfer only represents a secondary reaction pathway. The total pressure in the trap amounts to 0.82 Pa, with the partial pressure of carbon dioxide being 10 ppm.

Tab. S1 Bimolecular rate coefficients $k^{(2)}$ in units of 10^{-8} cm^3 s^{-1} of the consecutive CO_2-decarbonylation and CO_2 adsorption reactions by Ta_n^+ (n = 1-6) and $Ta_6OCO_2^+$. For each reaction an average value of two or more measurements is presented with error bars reflecting corresponding statistical uncertainties. Fraction of CO_2 in buffer gas varies between 10 and 25 ppm, the total pressure in the trap is 0.82 Pa.

Product	**Ta_1^+**	**Ta_2^+**	**Ta_3^+**	**Ta_4^+**	**Ta_5^+**	**Ta_6^+**	**$Ta_6OCO_2^+$**
+O	1.1±0.1	1.6±0.2	2.7±0.1	3.3±0.3	3.7±0.4	5.4±1.3	2.2±0.1
$+O_2$	1.1±0.1	1.9±0.3	3.2±0.03	3.2±0.3	4.0±0.3	4.5±1.0	3.7±0.6
$+OCO_2$	---	---	---	---	---	<0.1	2.8±0.8
$+O_3$	---	3.2±0.3	3.5±0.2	3.8±0.4	3.6±0.2	4.0±0.8	5.1±1.4
$+O_2CO_2$	---	---	---	---	---	0.5±0.2	0.4±0.3
$+O_4$	---	3.8±0.3	3.9±0.1	4.0±0.5	4.0±0.3	3.0±0.8	3.3±0.3
$+O_3CO_2$	---	---	---	---	---	2.4±0.8	0.5
$+O_5$	---	---	4.2±0.4	3.6±0.5	4.0±0.3	3.4±2.2	0.5±0.2
$+O_4CO_2$	---	---	---	---	---	3.6±1.5	---
$+O_6$	---	---	3.3±0.6	3.2±0.5	3.8±0.5	3.8±2.1	---
$+O_5CO_2$	---	---	---	---	---	1.4±1.0	---
$+O_7$	---	---	---	---	0.08±0.05	4.1±0.7	---
$+O_6CO_2$	---	---	---	---	<0.1	---	---
$+O_8$	---	---	---	---	---	2.6±0.3	---
$+O_9$	---	---	---	---	---	3.2±0.6	---

Tab. S2 Bimolecular rate coefficients $k^{(2)}$ in units of 10^{-8} cm^3 s^{-1} of the majority of consecutive CO_2-decarbonylation and CO_2 adsorption reactions by Ta_n^+ (n = 7,8). For each reaction an average value of two or more measurements is presented with error bars reflecting corresponding statistical uncertainties. Fraction of CO_2 in buffer gas varies between 10 and 25 ppm, the total pressure in the trap is 0.82 Pa.

Product	Ta_7^+	$Ta_7CO_2^+$	$Ta_7(CO_2)_2^+$	Ta_8^+	$Ta_8CO_2^+$	$Ta_8(CO_2)_2^+$
+O	5.2±3.3	6.2±3.9	---	1.4±0.9	2.6±0.8	0.9±0.6
$+CO_2$	0.8±0.7	2.9±0.9	---	3.5±2.5	3.0±1.2	3.5±1.1
$+O_2$	4.4±1.6	---	---	2.2±0.3	2.3±1.4	2.2±0.6
$+OCO_2$	1.7±0.7	3.9±1.7	5.0±1.5	3.7±1.5	3.7±0.7	2.0±0.6
$+O_3$	1.7±0.5	1.3±0.9	0.8±0.2	---	3.3±2.1	1.8±0.7
$+O_2CO_2$	4.0±2.2	3.5±1.1	1.5±0.7	6.4±2.7	4.5±0.6	3.6±0.3
$+O_4$	---	2.9±1.8	0.6±0.4	---	---	1.9±0.3
$+O_3CO_2$	8.2±4.5	5.0±1.5	3.2±2.5	---	13.1±3.8	---
$+O_5$	---	5.4±0.1	1.5±1.3	---	---	---
$+O_4CO_2$	---	6.8±3.7	2.0±0.8	---	---	---
$+O_5CO_2$	---	3.4±0.6	---	---	---	---

Tab. S3 Bimolecular rate coefficients $k^{(2)}$ in units of 10^{-8} cm^3 s^{-1} of the first couple of consecutive CO_2-decarbonylation and CO_2 adsorption reactions by Ta_n^+ (n = 9,10). For each reaction an average value of two or more measurements is presented with error bars reflecting corresponding statistical uncertainties. Fraction of CO_2 in buffer gas varies between 10 and 25 ppm, the total pressure in the trap is 0.82 Pa.

Product	Ta_9^+	$Ta_9CO_2^+$	$Ta_9(CO_2)_2^+$	Ta_{10}^+	$Ta_{10}CO_2^+$	$Ta_{10}(CO_2)_2^+$
+O	0.5±0.4	1.1±0.1	1.0±0.1	0.6±0.4	2.1±0.4	1.1±0.5
$+CO_2$	5.9±3.1	3.1±0.1	2.6±0.01	7.3±2.7	5.1±0.8	3.2±0.4
$+O_2$	---	1.7±0.5	0.5±0.4	---	---	3.0±0.1
$+OCO_2$	5.2±1.7	3.8±0.7	2.7±0.1	9.7±3.1	11.5±1.8	3.1±1.2
$+O_2CO_2$	---	9.0±4.1	5.4±0.2	---	---	10.3±5.1

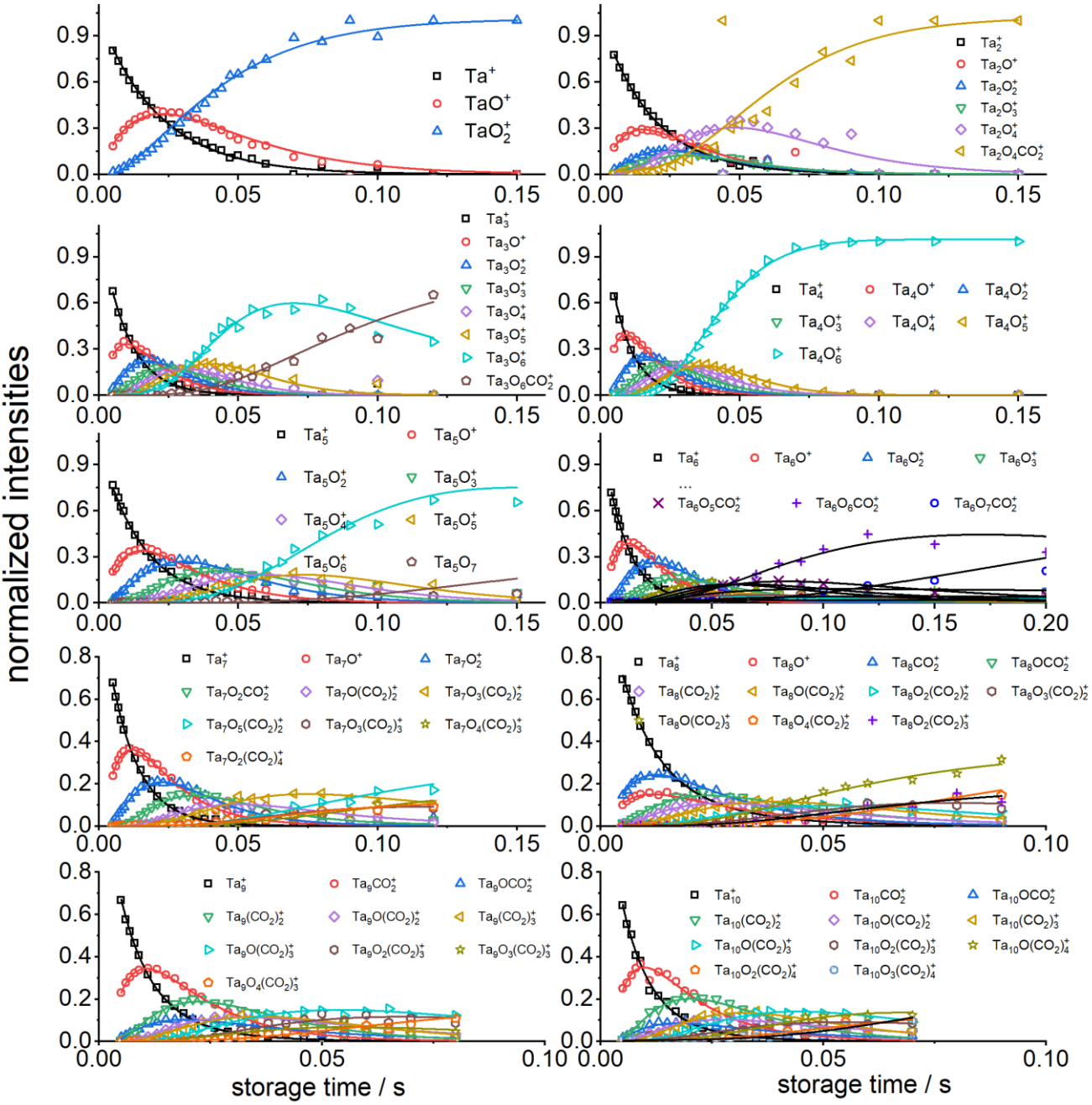

Fig. S4 Kinetic modeling of the reactions between $Ta_{1\text{-}10}^+$ and CO_2. For the reactions of $Ta_{6\text{-}10}^+$, only the most abundant species are displayed.

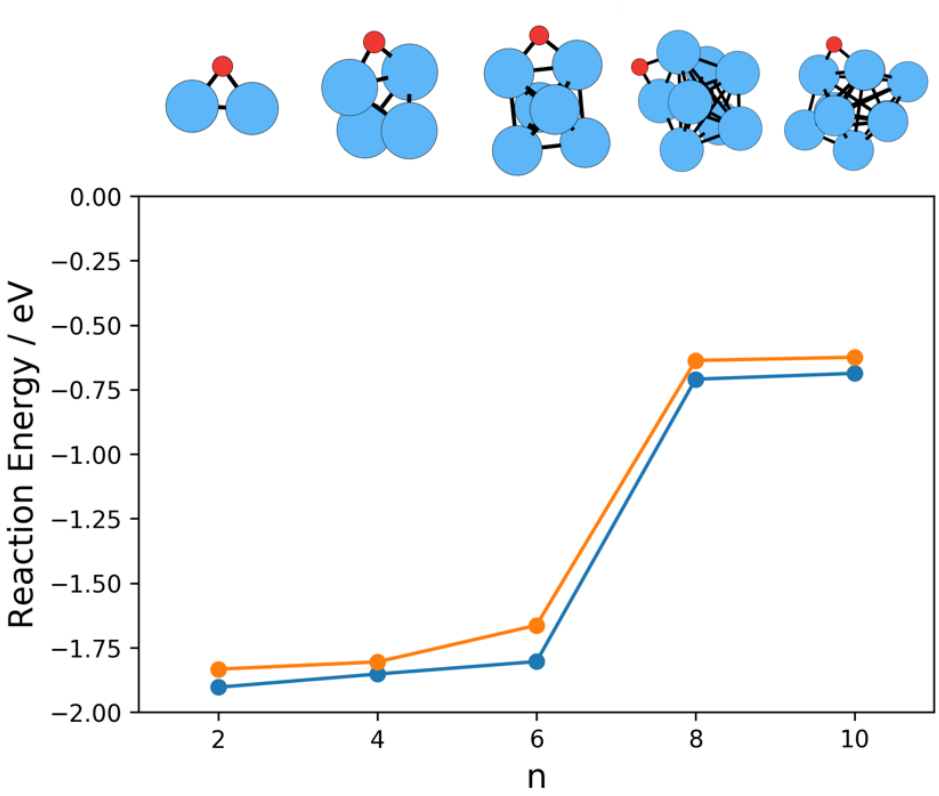

Fig. S5 Calculated reaction energies for the oxygen atom transfer from CO_2 to Ta_n^+-clusters (with n = 2,4,6,8,10) including (blue) and excluding (orange) the zero-point vibrational energy. The corresponding optimized geometries of Ta_nO^+ are also shown.

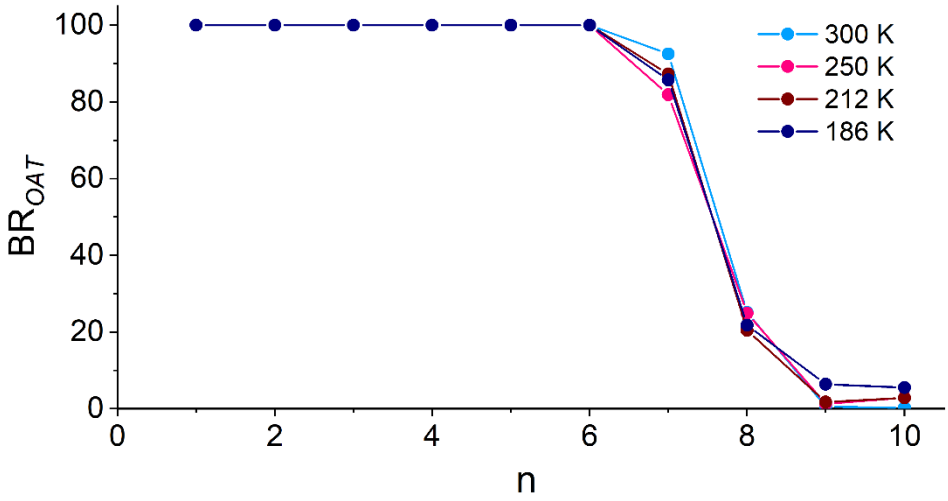

Fig. S6 Branching ration toward the oxygen atom transfer (BR_{OAT}) for Ta_n^+ (n = 1-10) in the reaction with the first CO_2 molecule. As the exothermicity of the reaction is significantly higher than the changes in energy caused by variations of the temperature, the BR_{OAT} remain constant within the error of the measurement for all temperatures. All measurements were performed at a total pressure in the trap of 0.82 Pa, with the partial pressure of carbon dioxide being 10 ppm.