

## SUPPORTING INFORMATION

# Supported sub-nanometer Ta oxide clusters as model catalysts for the selective epoxidation of cyclooctene

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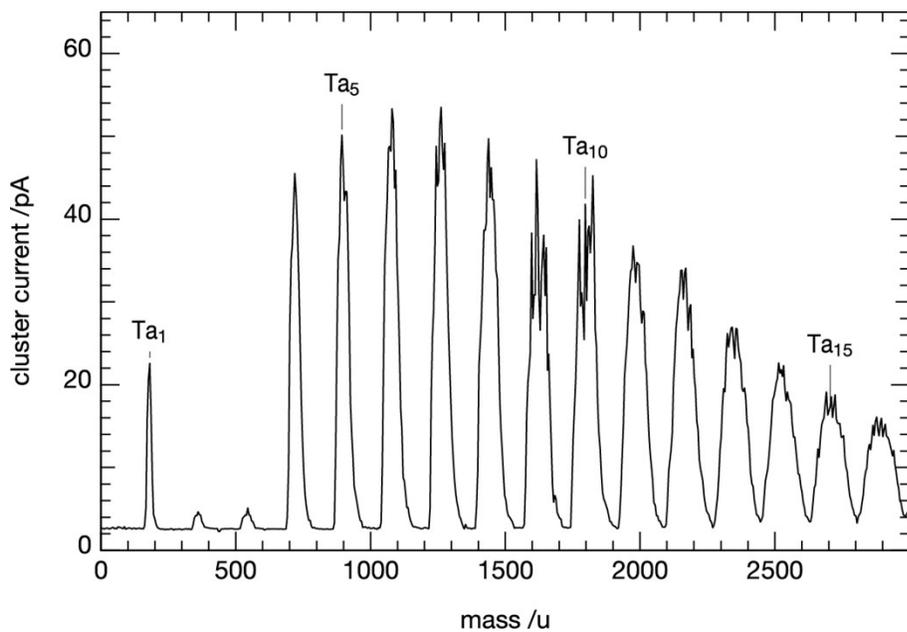
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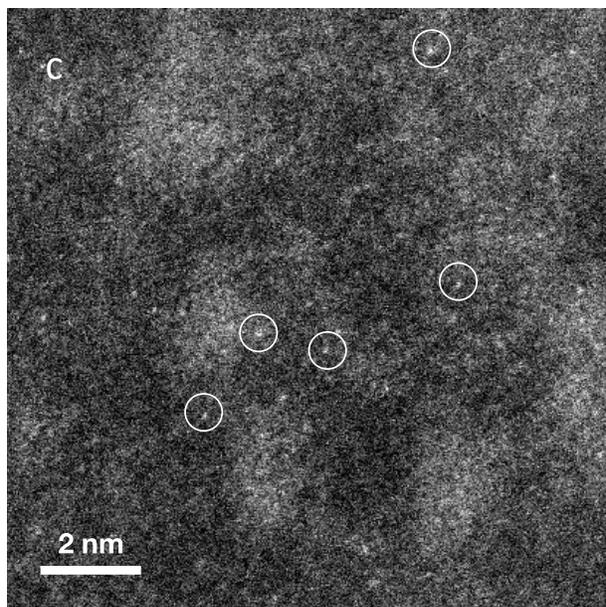
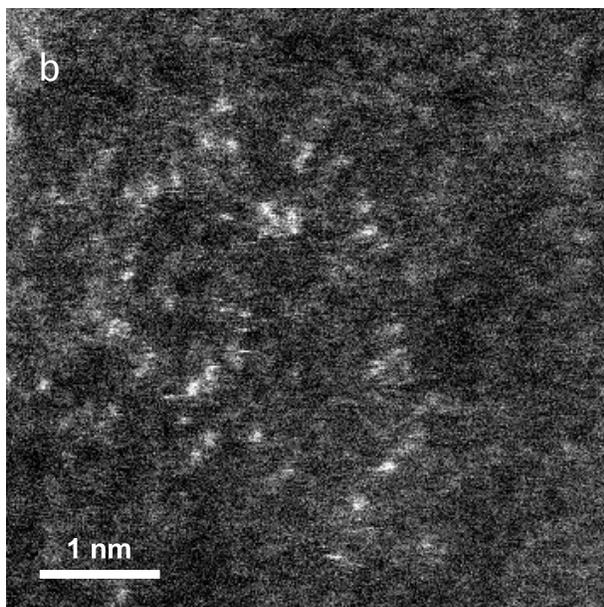
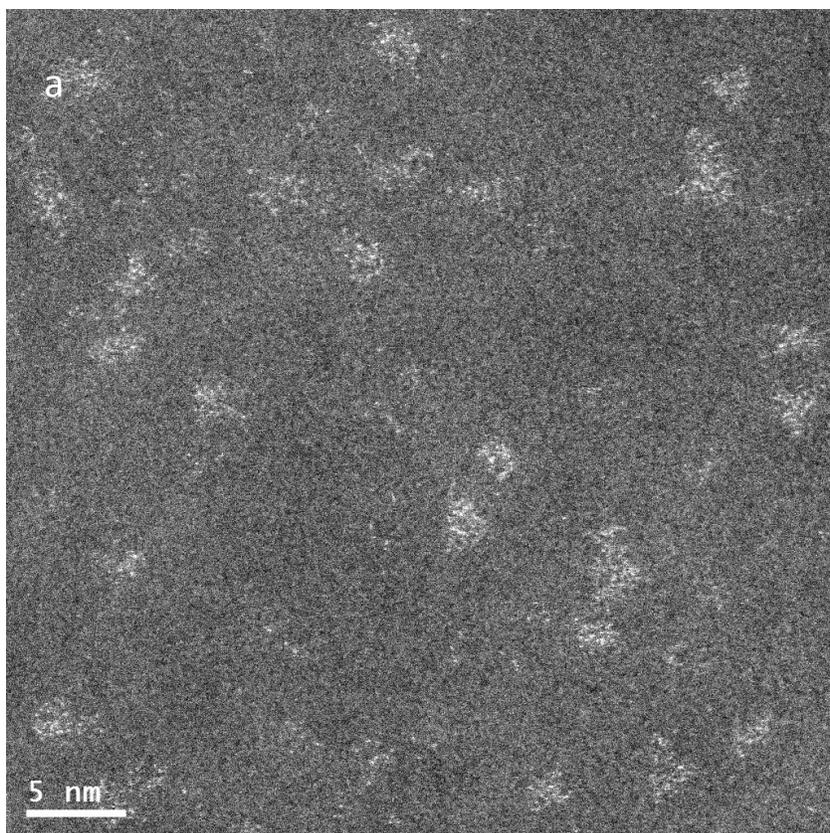
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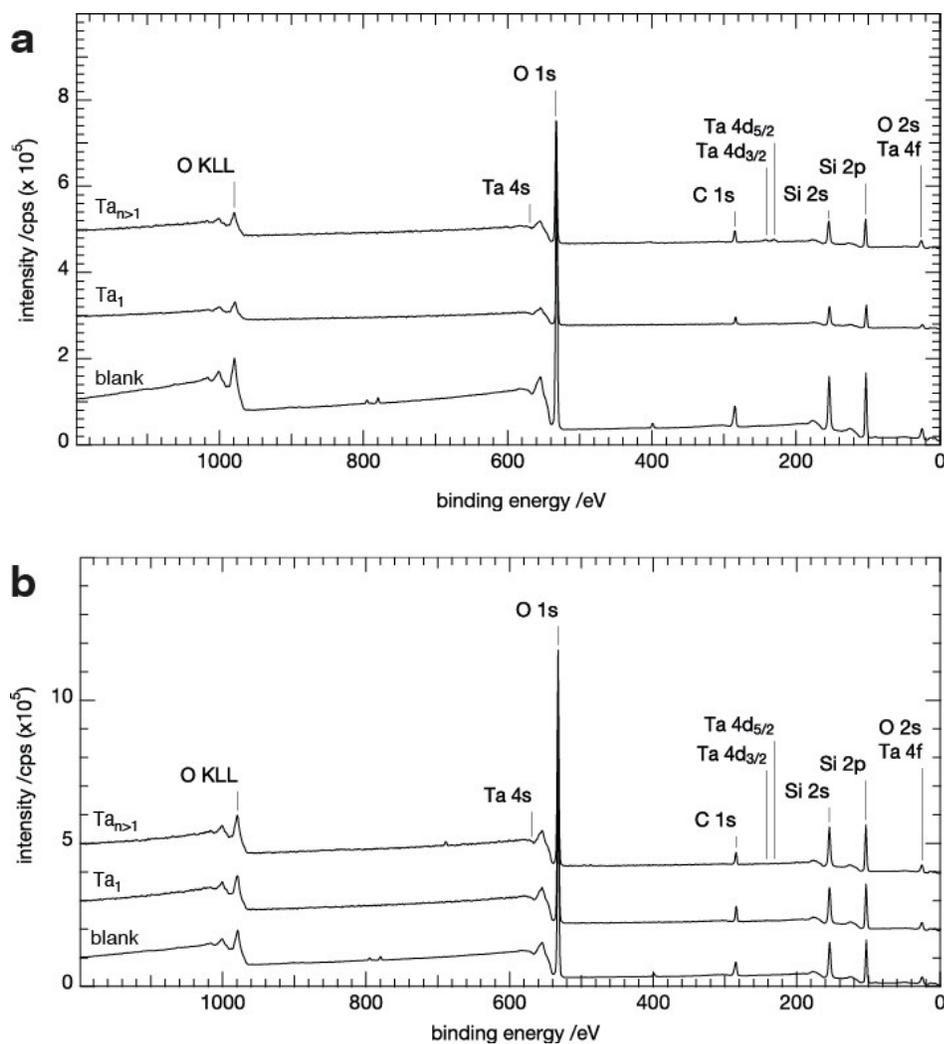
## 1. Additional Data for Sample Preparation and Characterization



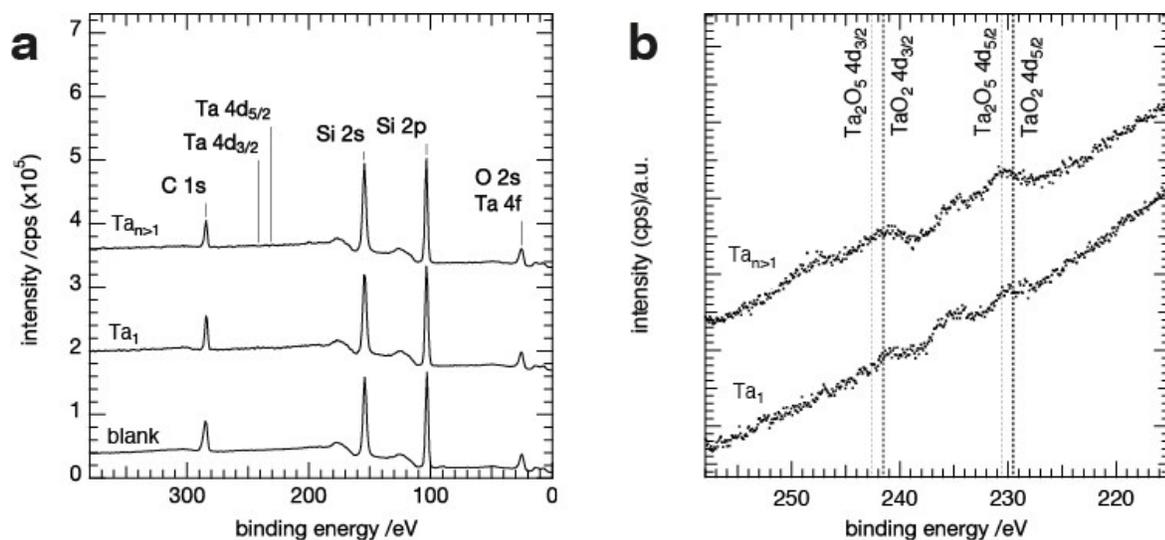
**Figure S1:** Mass scans over Ta<sub>n</sub><sup>+</sup> cluster beam as selected by the QMS. The same setting for both samples was used, the only difference being, that for the atom the QMS was used employing the RF, while turning it off for the unselected clusters. The mass scan shows Ta<sub>7</sub> as the most abundant cluster size for Ta<sub>n>1</sub>.



**Figure S2:** Representative Scanning Transmission Electron Micrograph (STEM) of a larger overview area of a  $Ta_{n>1}$  cluster sample. The cluster and atoms are evenly distributed on the surface and show in the case of the clusters a homogeneous size distribution. To achieve high magnification, a large amount of energy was introduced into the sample consequently some particle fragmentation occurred (e.g. upper left, subfigure a).



**Figure S3:** XP spectra of the samples on which differently sized Ta cluster catalysts were deposited, (a) survey spectra of  $Ta_1$ ,  $Ta_{n>1}$  and a blank sample before the reaction and (b) after the reaction. The spectra of  $Ta_1$  and  $Ta_{n>1}$  are offset for better visibility. For all samples the presence of the expected elements from the support (Si, O) and the ubiquitous impurity C is observed; Ta exhibits 4s, 4d and 4f peaks in the investigated region. The only noticeable qualitative change from (a) to (b) is the nearly complete disappearance of the Ta  $4d_{5/2}$  and  $4d_{3/2}$  peaks for  $Ta_{n>1}$ . Additionally, some peaks have changed in intensity: the O KLL Auger transition and the C  $1s$  and O  $2s$  peaks.

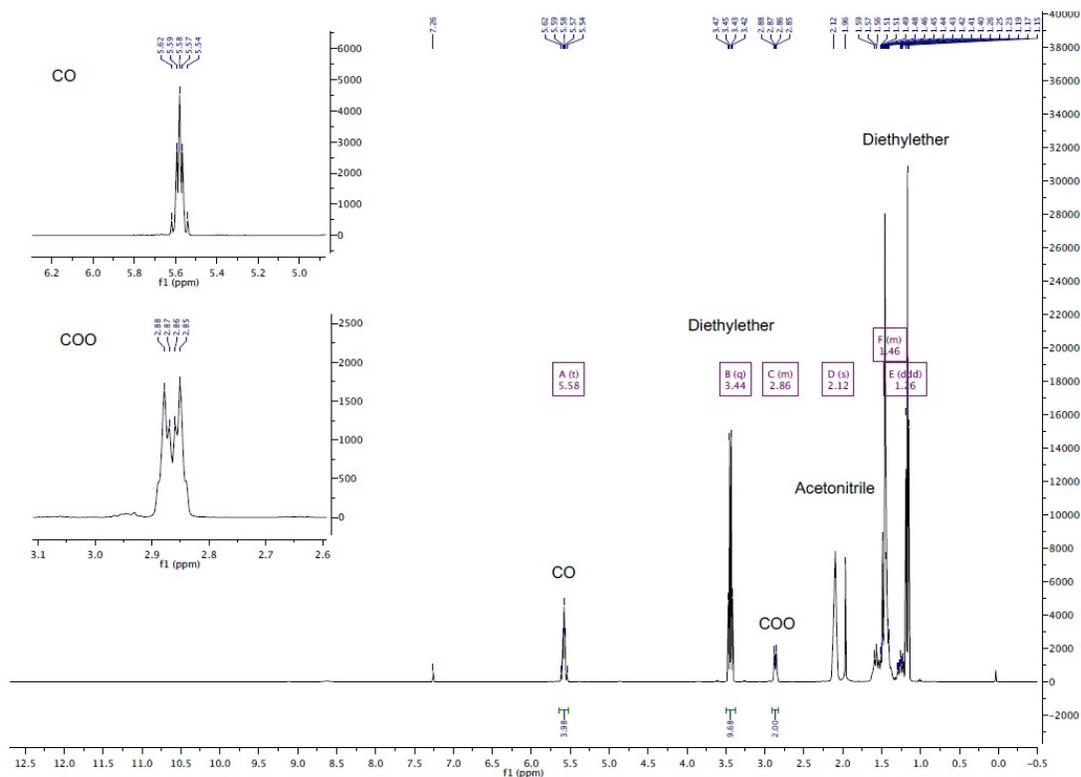


**Figure S4:** XP spectra of the samples on which differently sized Ta cluster catalysts were collected after one catalytic reaction cycle of 48 h, (a) survey spectra including a blank sample in the BE region 0-400 eV (for full spectra see fig. S3) and (b) excerpts of the Ta 4d region together with literature values for bulk TaO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> (both, 4d<sub>5/2</sub> and 4d<sub>3/2</sub> peaks) represented as dotted lines. For all samples in the survey spectra (a) the presence of the expected elements from the support (Si, O) and the ubiquitous impurity C is observed; Ta exhibits 4d and 4f peaks in the investigated region. (b) Excerpts are shown of the Ta 4d region (because the Ta 4f peaks are superimposed by the O 2s peak) and show residual tantalum oxide species. For better visibility, the intensity signals of the data are plotted in arbitrary units (a.u.).

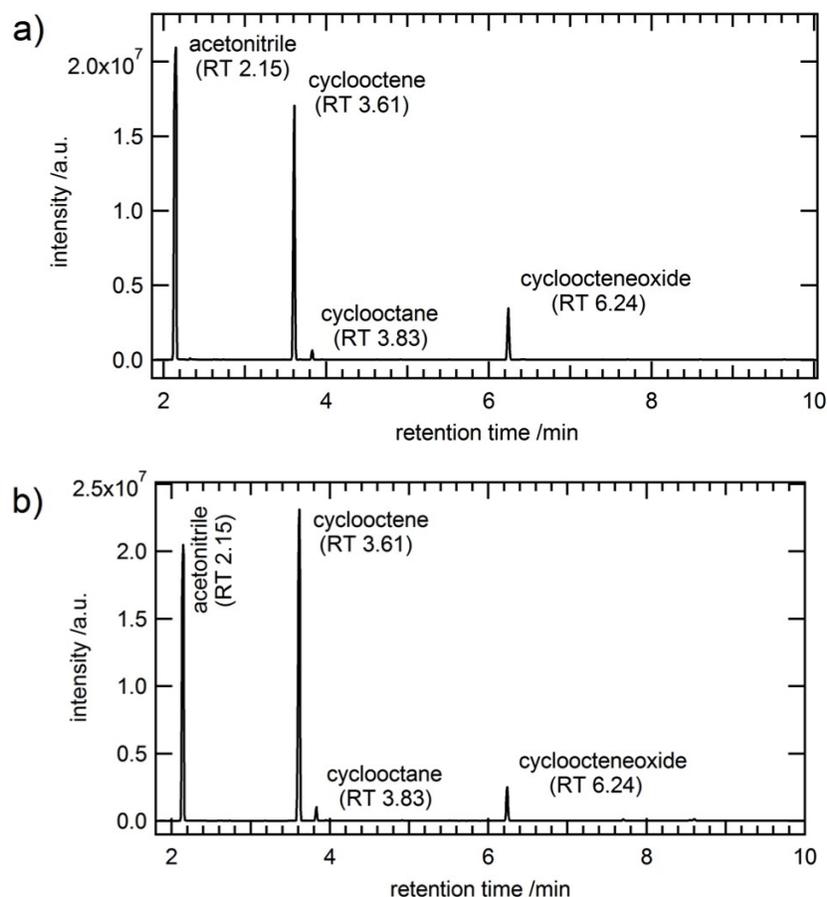
**Table S1:** Surface composition in % as determined by XPS for both catalyst samples.

Element /%	C	O	Si	Ta	Si/Ta
Ta <sub>1</sub>	12.64	52.48	34.87	0.0146	2388
Ta <sub>n&gt;1</sub>	16.18	54.22	29.09	0.515	56

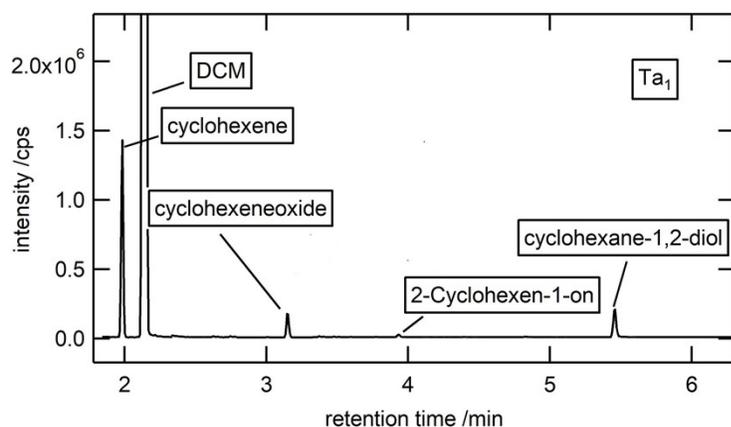
## 2. Additional Data for the Catalysis Experiments



**Figure S5:** Representative  $^1\text{H-NMR}$  spectrum – peak assignment for the starting material<sup>1</sup> and product,<sup>2</sup> as well as for acetonitrile and diethyl ether (solvent of the reaction and the work-up, respectively). The shown spectrum is the result of a successful catalysis experiment with Ta<sub>1</sub> clusters (COO stands for cycloocteneoxide and CO for cyclooctene).



**Figure S6:** Representative GC chromatograms of a)  $Ta_1$  and b)  $Ta_{n>1}$  product solutions: cycloocteneoxide (product), cyclooctene (starting material), acetonitrile (solvent) and cyclooctane (an impurity of the starting material) were detected. The measurement extends to 30 min, but no peaks appear after the product.



**Figure S7:** GC chromatogram of the reaction of cyclohexene epoxidation using  $Ta_1$  as the catalyst. (Cyclohexene: retention time: 1.98 min; Area: 4082392; Cyclohexene oxide: retention time: 3.15 min; Area: 668528; 2-Cyclohexen-1-on: retention time: 3.93 min; Area: 183828; Cyclohexane-1,2-diol: retention time: 5.46 min; Area: 934089).

**Table S2:** Raw GCMS data for the different samples based on the averaged results of multiple samples; (COO stands for cycloocteneoxide).

Sample	Raw GCMS (total number of COO molecules after 48 h)	GCMS corrected for blank performance (total number of COO molecules after 48 h)	COO molecules per atom or clusters (incl. coverage correction)	TOF (molecules per hour and cluster; averaged over 48 h) / h <sup>-1</sup>
blank (chip without clusters)	$6.13 \pm 0.63 * 10^{19}$	-	-	-
Ta <sub>1</sub>	$2.47 \pm 0.42 * 10^{20}$	$1.86 \pm 0.42 * 10^{20}$	$8.25 \pm 0.85 * 10^6$	$1.72 \pm 0.39 * 10^5$
Ta <sub>n&gt;1</sub>	$1.20 \pm 0.21 * 10^{20}$	$5.83 \pm 2.10 * 10^{19}$	$2.00 \pm 0.34 * 10^6$	$0.42 \pm 0.07 * 10^5$

**Table S3:** Raw GCMS values for recycling experiments using the same Ta<sub>1</sub> sample (errors for each run from multiple GC-MS measurement); (COO stands for cycloocteneoxide).

Sample	Raw GCMS (total number of COO molecules after 48 h)	GCMS corrected for blank performance (total number of COO molecules after 48 h)	COO molecules per atom (incl. coverage correction)	TOF (molecules per hour and cluster; averaged over 48 h) / h <sup>-1</sup>
blank (chip without clusters)	$6.13 \pm 0.63 * 10^{19}$	-	-	-
Run 1	$2.89 \pm 0.02 * 10^{20}$	$2.27 \pm 0.07 * 10^{20}$	$10.11 \pm 0.03 * 10^6$	$2.11 \pm 0.06 * 10^5$
Run 2	$1.60 \pm 0.04 * 10^{20}$	$1.00 \pm 0.07 * 10^{20}$	$4.45 \pm 0.03 * 10^6$	$0.93 \pm 0.07 * 10^5$
Run 3	$0.93 \pm 0.08 * 10^{20}$	$0.31 \pm 0.10 * 10^{20}$	$1.38 \pm 0.05 * 10^6$	$0.29 \pm 0.10 * 10^5$

**Table S4:** Raw GCMS values for the ‘hot filtration test’ for Ta<sub>n>1</sub> (COO stands for cycloocteneoxide).

Sample	Raw GCMS (total number of COO molecules after 48 h)	GCMS corrected for blank performance (total number of COO molecules after 48 h)	COO molecules per clusters (incl. coverage correction)	TOF (molecules per hour and cluster; averaged over 48 h) / h <sup>-1</sup>
blank (chip without clusters)	6.21 ±0.76 *10 <sup>19</sup>	-	-	-
‘homogeneous’	1.18 ±0.20 *10 <sup>20</sup>	5.63 ±2.14 *10 <sup>19</sup>	1.25 ±0.48 *10 <sup>6</sup>	2.61 ±0.99 *10 <sup>4</sup>
‘heterogeneous’	1.39 ±0.06 *10 <sup>20</sup>	7.70 ±0.95 *10 <sup>19</sup>	1.71 ±0.21 *10 <sup>6</sup>	3.56 ±0.44 *10 <sup>4</sup>

The results in Table S4 show that the “homogeneous” and the “heterogeneous” experiments lead to the formation of a comparable amount of molecules of cycloocteneoxide. This observation suggests that a) catalytically active species remain on the surface of Ta<sub>n>1</sub> after treatment for 48 h under the reaction conditions b) the Ta<sub>n>1</sub> is prone to leaching after prolonged exposure to the reaction conditions. The impact of the leached tantalum species on the catalytic activity of Ta<sub>n>1</sub> is likely to be overestimated with respect to a regular catalysis experiment because in the “hot filtration” test the sample was kept 48 h under the reaction conditions prior to the addition of H<sub>2</sub>O<sub>2</sub>.

**Table S5.** Comparison of catalytic performance (TON, TOF) between Ta<sub>1</sub> and literature reported catalysts for the epoxidation of cyclooctene using H<sub>2</sub>O<sub>2</sub> as oxidant (all catalysts in the table have a selectivity above 90%).

Entry	Catalyst	Conditions (T, time)	TON/TOF(h <sup>-1</sup> ), <sup>a</sup> (Yield or conversion (%))	Catalyst Description	Ref.
1	Ta <sub>1</sub>	60 °C, 48 h	8.25*10 <sup>6</sup> / 1.72 *10 <sup>5</sup> (10)	Ligand-free isolated, oxidized Ta(V) atoms	This work
2	Ta-calixarene@SiO <sub>2</sub>	60 °C, 2 h	105/57.5, (12)	Isolated Ta atoms with calixarene ligands.	3
3	TaO <sub>x</sub> clusters	60 °C, 2 h	83/41.5, (8)	Ligand-free TaO <sub>x</sub> clusters	3
4	Ta <sub>x</sub> N <sub>y</sub> /TaO <sub>x</sub> N <sub>y</sub> /SiO <sub>2</sub> (0.2 wt.% Ta)	60 °C, 18 h	1395/77.5, (24)	0.5-3 nm Ta <sub>x</sub> N <sub>y</sub> and TaO <sub>x</sub> N <sub>y</sub> NPs supported on silica	4
5	Ta <sub>x</sub> N <sub>y</sub> /TaO <sub>x</sub> N <sub>y</sub> /SiO <sub>2</sub> (3.5 wt.% Ta)	60 °C, 18 h	≈350/≈19.4, (≈100)	0.5-3 nm Ta <sub>x</sub> N <sub>y</sub> and TaO <sub>x</sub> N <sub>y</sub> NPs supported on silica	4
6	1 wt.% Ta@CMK-1 <sup>b</sup>	65 °C, 24 h	760/31.7	Ta <sub>2</sub> O <sub>5</sub> on carbon support	5
7	Ta <sub>2</sub> O <sub>5</sub> NPs	60 °C, 18 h	21.7 <sup>c</sup> /1.2, (57)	Ta <sub>2</sub> O <sub>5</sub> NPs (20-25 nm)	6
8	TaON NPs	60 °C, 18 h	34.6 <sup>d</sup> /1.9, (96)	TaON NPs (20-25 nm)	6
9	PW@HMP(3) <sup>f</sup>	60 °C, 4 h	592/148		7
10	Ti@MFI zeolite	60 °C, 2 h	54/27		8
11	WO <sub>3</sub> nanoparticles	80 °C, 4 h	560/140		9
12	MoO <sub>2</sub> @TiO <sub>2</sub>	70 °C, 6 h	3333/556		10
13	W-Zn@SnO <sub>2</sub>	80 °C, 6 h	650/108		11
14	Ga <sub>2</sub> O <sub>3</sub> -nanorods	80 °C, 4 h	266/66.5		12
15	Gd <sub>26</sub> clusters framework	68 °C, 24 h	2.94*10 <sup>4</sup> /1239 <sup>e</sup>		13
16	Mesoporous Nb silicate	50 °C, 2 h	50/25		14

<sup>a</sup> Averaged over the whole reaction time. <sup>b</sup> CMK: Ordered mesoporous carbon. <sup>c</sup> Calculated on the basis of the following published data: Use of Ta<sub>2</sub>O<sub>5</sub> (40.0 mg, 0.09 mmol; 0.18 mmol of tantalum) for the conversion of cyclooctene (0.92 mL; 6.84 mmol) with a yield of cycloocteneoxide of 57% (3.90 mmol). <sup>d</sup> Calculated on the basis of the following published data: Use of TaON (40.0 mg, 0.19 mmol; 0.19 mmol of tantalum) for the conversion of cyclooctene (0.92 mL; 6.84 mmol) with a yield of cycloocteneoxide of 96% (6.57 mmol). <sup>e</sup> Homogeneous catalyst. <sup>f</sup> Polytungstic acid supported on hierarchical meso-macroporous poly(ionic liquids). <sup>g</sup> Using <sup>t</sup>BuOOH as an oxidant.

### 3. Supporting References

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