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PAPER

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

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The preparation of organic ligands-free, isolated tantalum oxide atoms (Ta₁) and small clusters (Ta_{n>1}) on flat silicate supports was accomplished by ultra-high vacuum (UHV) techniques followed by oxidation in air. The resulting surface complexes were thoroughly characterized and tested as supported catalysts for the epoxidation of cycloalkenes. The observed catalytic performance highlights the potential of the applied method for the production of active catalysts and the study of well-defined, ligand-free metal oxide moieties.

Introduction

The preparation of precise and realistic model catalysts is crucial in order to gain molecular-level insight into catalytic processes and for the design of heterogeneous catalysts with predictable as well as improved activity and selectivity.¹⁻³ In this context, surface science studies allow for a deeper understanding by applying advanced diagnostic and synthetic tools such as *in situ* analysis,⁴⁻⁶ preparation of single atom catalysts⁷⁻¹¹ or ultra-high vacuum (UHV) techniques for e.g. deposition of size-selected clusters.¹² Supported metal oxides represent one main class of heterogeneous catalysts that are readily available and are applied in industry for a wide range of transformations.¹³ One of the most challenging aspects in achieving

a deeper understanding of the catalytic properties of these materials is the preparation of isolated metal oxide units on the support surface. A main approach to the synthesis of well-defined, isolated supported metal complexes is by surface organometallic chemistry (SOMC).¹⁴⁻¹⁶ Recently, this method has allowed the generation of truly isolated vanadyl units on silica surface.¹⁷ However a major drawback towards the application of solution-phase grafting or of traditional techniques such as incipient wetness impregnation is the lack of suitable precursors. The steps of impregnation and/or calcination for the removal of organic ligands generally lead to a mixture of bidimensional monomeric and polymeric oxide species, or even crystals of bulk oxide.¹⁸ This limitation does not allow to assess the role of the individual surface domains and to appreciate the benefits of site-isolation. Interestingly, the deposition of size selected clusters and atoms by means of physico-chemical techniques allows preparation of pristine single atoms and clusters with precise and independent control on both size and surface coverage. Under UHV conditions, this approach has contributed to the fundamental understanding of heterogeneous catalysts by demonstrating size¹⁹ and support effects²⁰ and providing insights into catalyst deactivation.²¹ However, with few exceptions,^{22, 23, 24} the prepared catalysts are generally noble metals applied under idealized conditions far from real case scenarios with respect to pressure, materials and complexity.^{25, 26} Tantalum is frequently applied in heterogeneous catalysis as a bulk metal oxide²⁷ or in the form of well-defined surface complexes in SOMC.²⁸ Beside studies on tantalum clusters in the gas phase,^{29, 30} investigations on supported clusters of early transition metals are extremely rare,^{31, 32} with very limited application to catalysis.^{33, 34} In this work we devised a straightforward approach to employ UHV techniques for the preparation of catalysts based on isolated metal oxide complexes, applicable in catalysis under realistic conditions. Accordingly, size-selected and ligand-free single atoms and clusters of tantalum were deposited on silicate surfaces in the UHV, allowed to become oxidized by ambient oxygen²⁹ and applied as catalysts for the epoxidation of cycloalkenes. Our target in this work is to evaluate the effect of the preparation method and, in particular, of its specific features (tantalum oxide site isolation, absence of organic

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Electronic Supplementary Information (ESI) available: [The following file (PDF) is available free of charge and includes further details on samples (i.e. size distributions and ranges, mass scans), sample characterization (STEM micrographs, XP survey spectra), NMR and raw data, values and conversions of the GC-MS measurements and the hot-filtration experiments.]. See DOI: 10.1039/x0xx00000x

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ligands and calcination steps) on the final structure of the catalyst and to validate the preparation method by testing the activity and durability of the deposited tantalum atoms and clusters in a benchmark organic transformation.

Figure 1. Graphical overview of sample preparation, characterization techniques, catalytic reaction and product analysis.

The epoxidation of cyclooctene in the presence of H_2O_2 was employed as a benchmark reaction (Figure 1). Two catalyst materials were prepared: one with tantalum atoms (Ta_1) only and one with Ta clusters ($\text{Ta}_{n>1}$) excluding single tantalum atoms. The clusters were produced in the UHV using a laser ablation cluster source¹² and were deposited under soft-landing conditions onto two different silica supports (silicon wafer or TEM grid). Both Ta_1 and $\text{Ta}_{n>1}$ catalyst samples were characterized by X-ray photoelectron spectroscopy (XPS, for both wafers and TEM grids supports) and by high-angle annular dark field scanning tunnelling microscopy (HAADF-STEM, only samples on silicon TEM grids).

1. Experimental

2.1 Preparation of cluster samples

The clusters were deposited on silicon wafers with a thermally grown oxide layer and on commercially available TEM windows using a high frequency laser ablation cluster source and a transfer chamber, described in detail elsewhere.^{12, 35} In brief, the beam of a diode pumped Nd:YAG laser (DPSS Spitlite, 100 Hz, 70 mJ at 532 nm; InnoLas, Germany) was focused onto a rotating (1 Hz) metal target disk (99.99% Ta, Goodfellow, USA). Cooling of the resulting plasma was achieved via a delayed helium (He 6.0, Westfalen, Germany) gas pulse and an adiabatic expansion of the helium/tantalum vapor through a nozzle into the vacuum. Ion lenses and an octupole subsequently guided the cluster beam along the axis of a differentially pumped vacuum chamber until a quadrupole bender unit, in which the positively charged clusters were separated from the neutral ones. The deflector was operated in such a way that the cationic clusters were focused into a QMS (quadrupole mass spectrometer, ABB Extrel Merlin, U.S.A.) with a mass limit of 16000 amu where mass selection down to a single cluster size is achieved. The QMS was operated and optimized for highest transmission while still ensuring size selection down to a single mass (see Fig S1). For Ta_1 only atoms could pass the QMS, while for $\text{Ta}_{n>1}$ using only the radio frequency (RF only mode) of the QMS, it was operated as a high-pass mass filter, and consequently, unselected clusters with a tunable minimum size (in the presented study 2 atoms and more – above 281 amu – short $\text{Ta}_{n>1}$) were generated. After size selection the beam passed through a circular

aperture ($d = 1$ cm) and was focused onto the supports (wafer or TEM window).

Table 1. Properties of the prepared Ta_1 and $\text{Ta}_{n>1}$ samples with respect to size, size distribution and coverage.

Sample property	Ta_1	$\text{Ta}_{n>1}$
Low mass cut-off (QMS setting)	141 amu	281 amu
Optimized mass (QMS)	195 amu	362 amu
Minimum number of atoms	1	2
Approximate size range (mass scan)	1	2 to $\sim 15^a$
Most abundant size	1	7^b
Coverage (as charge per surface area) ^c	0.286 e/nm^2	0.371 e/nm^2
Number of atoms or clusters ^c	2.25×10^{13}	2.91×10^{13}

^a The size range for the unselected clusters ($\text{Ta}_{n>1}$) is determined by the low mass cut-off of the QMS used as a high-pass filter (RF only mode) and the optimized mass in the QMS. The resulting size distribution is shown in Figure S1 in the form of a mass scan of the cluster beam. ^b The most abundant size of $\text{Ta}_{n>1}$ is extracted from Figure S1 and describes the major fraction of clusters being in that range. ^c Assuming a deposition area ($0.785 \times 10^{-14} \text{ nm}^2$) equivalent to the size of the circular opening of the cluster source ($d = 1$ cm) through which the beams of clusters or atoms were focused for deposition on the support.

The clusters were deposited under soft-landing conditions on the support, i.e., at deposition energies lower than 1 eV per cluster atom. The coverage of the deposited clusters (reported in Table 1 in the units of charge per surface area: e/nm^2) was determined by recording and integrating the discharge current on the support during deposition and by considering a single positive charge per impacting atom or cluster. Further details on clusters preparation, size and wafer coverage can be found in Table 1.

2.2 STEM Characterization

The used TEM grids were etched Si wafer grids (TED Pella, U.S.A.) with a silicate support of 8 nm thickness. In order to protect the delicate grid structure from possible mechanical stress during the exposure to reaction conditions, the TEM grids were fixed in a Teflon holder of in-house design in which the window of the grid was exposed to the liquid phase. The holder hereby allowed for the exact same conditions, i.e. stirring, reaction vessel, temperature etc. as the wafer. After the reaction, the grids were removed from the holder, rinsed with the solvent three times and dried in a nitrogen flow. STEM measurements were performed at the KAUST analytical core lab, using a FEI Titan 80-300 STEM, equipped with a spherical aberration corrector for the probe. The spherical aberration corrector allowed for performing the Cs-corrected HRSTEM analysis of samples. We performed the analysis by using a 300 keV energy electron beam which was focused onto the samples to a diameter of about 0.25 nm. Prior to the actual data acquisition, we aligned the corrector to reduce the C3 coefficient of Condenser-2 (C2) lens to about 1 micron. The HRSTEM images were recorded with a high-angle annular dark field (HAADF) detector by using a typical camera length of 115 mm so that Z-contrast in the images

can be enhanced even more than in usual HAADF-STEM imaging. Analysis of the TEM micrographs was performed using an algorithm of in-house design based on the IGOR Pro 6.22 Particle Analysis Tool (Wavemetrics, USA). The shown statistics for the cluster area (projection), i.e., area distribution functions (ADF) of the $Ta_{n>1}$ clusters is the result of the analysis of multiple images (five) and is based on the analysis of more than 200 particles. A representative STEM micrograph of a larger area for an unselected sample is shown in Fig S2.

2.3 XPS Characterization

XPS studies were carried out by means of a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K α x-ray source ($h\nu = 1486.6$ eV) operating at 150 W, a multi-channel plate and delay line detector under a vacuum of $1 \cdot 10^{-9}$ mbar. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 eV and 20 eV, respectively. Binding energies were referenced to the C 1s binding energy of adventitious carbon contamination, which was taken to be 284.8 eV. The data were analyzed with commercially available software, CASAXPS. The metallic peaks were fitted with an asymmetric hybrid Doniach-Sunjic function convoluted with a Gaussian/Lorentzian product while non-metallic peaks were fitted with a mixture of Gaussian (70%)–Lorentzian (30%) (GL30) function after Shirley type background subtraction.

2.4 Catalysis Experiments, product quantification and hot filtration test

The catalyst samples were added to a solution of cyclooctene (0.52 mL, 4.00 mmol, 1.0 eq.) and hydrogen peroxide (0.46 mL, 50 wt-%, 8.00 mmol, 2.0 eq.) in 4 mL acetonitrile (Fisher Scientific) in a *Schlenk*-tube. The mixture was stirred (300 rotations per minute, RPM) at 60 °C for 48 h. After cooling down, water (2 mL) was added to the solution and it was extracted with diethyl ether (3 x 5 mL). The combined organic layers were washed with brine and dried over sodium sulfate. The solvent was concentrated under reduced pressure. The catalysis results for Ta_1 and $Ta_{n>1}$ are displayed in Table S2. 1H NMR was used to identify the product. The spectra were recorded using a standard 400 MHz Bruker spectrometer at room temperature in $CDCl_3$. The chemical shifts are given in δ -values (ppm) and refer to the residual $CHCl_3$ signal in $CDCl_3$ ($\delta = 7.26$ ppm). To quantify the amount of product, GC-MS was employed. 200 μ L of product were mixed with 1300 μ L of dichloromethane before sample injection. After preselection by gas chromatography (7890 A, *Agilent Technologies*) ($T_0 = 60$ °C, $T_{end} = 320$ °C, ramp: 10 °C/min) the product was identified and quantified by mass spectrometry (5975C *inert XL MSD* with triple axis detector, *Agilent Technologies*). The RAW data for each sample consisted of three GC-MS measurements for which the peak area for product and starting material were integrated. These areas were averaged and corrected by a sensitivity factor (gained from a calibration curve for each chemical compound) for each molecule to account for the different recoveries to yield a concentration. The amount of product was normalized to the combined amount of starting material and product to calculate the yield of the reaction.

From the yield and the amount of starting material used for the reaction the total number of transformed molecules was calculated. These numbers were corrected by the corresponding average numbers for three blank samples. The blank corrected numbers of molecules were normalized to the number of clusters on the samples to yield the activity per cluster. For $Ta_{n>1}$ the average number of atoms per cluster (taken from statistics from the corresponding STEM micrographs) was multiplied to get the activity per Ta atom. Dividing both numbers by the reaction time of 48 h yields the TOF for each sample per cluster and per atom.

Hot filtration tests are often applied in heterogeneous catalysis in order to assess the contribution of homogeneous species on the catalytic performance (this is typically done by removing the heterogeneous catalyst during the reaction and allowing the reaction to proceed only with the species in the homogeneous phase that left the surface).³⁶ For this purpose, two vessels containing the reaction solvent and cyclooctene were set up, but only in one of the two vessels $Ta_{n>1}$ catalyst samples (two for a larger effect) were introduced. Both vessels were kept under the reaction conditions described above for 48 h. After 48 h, the catalyst samples were transferred from the first vessel (here defined as “homogeneous”) into the second (here defined as “heterogeneous”) vessel and H_2O_2 was added to both sides to start the reaction as regular catalysis experiment (for 48 h at 60 °C). The results of the test are displayed in Table S4.

2. Results and Discussion

3.1 Characterization of Ta_1 and $Ta_{n>1}$ HAADF-STEM, in combination with two different statistical analyses of the obtained images, was used for the local characterization of the supported clusters. The results are shown in figure 2. Micrographs of the two pristine samples (Ta_1 and $Ta_{n>1}$, figure 2a and 2b,c respectively) after exposure to ambient conditions were acquired, with two different magnifications for $Ta_{n>1}$. Homogeneously distributed particles are visible for both sample types. In figure 2a single and isolated Ta atoms are visible without signs of larger clusters. In figures 2b and 2c larger clusters are observed that are comparable with each other in size. For $Ta_{n>1}$ clusters, the software assisted analysis of the images afforded a statistical distribution of the cluster size (see ESI for details) shown in figure 2e as a histogram. The FWHM of the histogram is considerably narrow as expected for a tight size distribution; it has an average area of 0.3 nm^2 and follows a log-normal shaped function that reflects the production of the cluster source and matches the corresponding mass scan of the cluster source (figure 2d). In addition, for 50 of the $Ta_{n>1}$ clusters, the atoms in the cluster were counted using images with higher magnification (figure 2b) and the resulting distribution of the atoms per cluster is shown in figure 2f. An average size of seven atoms per cluster can be extracted from this histogram that is in line with the most abundant size during deposition (see figure 2d and ESI).

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Figure 2. Representative HAADF-STEM micrographs of soft-landed (a) Ta₁ (two magnifications) and (b,c) Ta_{n>1} clusters on Si TEM grids; (d) size distribution of the Ta⁺ clusters ions passing the QMS prior to deposition; (e) statistical evaluation of the STEM micrographs in form of area distribution function (ADF – ensemble of >200 particles, dashed line shows integration of particle distribution) for Ta_{n>1} and (f) counted number of Ta atoms per Ta_{n>1} cluster. Circles around atoms and clusters in (a,b) serve as a guide to the eye to facilitate locating the structures on the surface.

Complementary to the use of STEM as a local investigation tool, the integral technique of XPS was employed (figure 3). The spectra of pristine Ta₁ and Ta_{n>1} (figure 3a) show an excerpt of the obtained survey scans ranging from 0 to 400 eV. All spectra (Ta_{n>1}, Ta₁ and the blank) show the C 1s signal at 284.8 eV from carbon as a ubiquitous impurity and the supports signals Si 2s, Si 2p and O 2s at around 150, 100 and 30 eV, respectively. A noticeable amount of Ta in the survey spectra can be seen for Ta_{n>1} as two small peaks around 231 and 243 eV, corresponding to the Ta 4d_{5/2} and 4d_{3/2} peaks, respectively.³⁷ Figure 3b shows the detail of the spectra of the Ta 4d region for both Ta_{n>1} and Ta₁ samples. The Ta 4d peak was used for a line-shape analysis in order to extract the oxidation states of the catalyst. Typically, the 4f peaks would be used for this purpose,³⁸ however, the use of this region was hindered by the overlap with the O 2s peaks.

Figure 3. XPS spectra of the Ta₁ and Ta_{n>1} samples before reaction: (a) survey spectra including a blank sample and (b) excerpts of the Ta 4d region together with the literature values for bulk Ta₂O₅ and Ta₂O₃ (both, 4d_{5/2} and 4d_{3/2} peaks are shown) represented as dotted lines. The presence of an additional impurity around 247 eV that is partially superimposing the 4d_{3/2} peaks is considered. For better visibility, the intensity signals of the data are plotted in arbitrary units (a.u.).

As expected, the tantalum atoms and clusters were found predominantly as Ta⁵⁺, however, minor amounts of a lower oxide (possibly Ta⁴⁺)³⁸ were also found on the surface. Both spectra show the presence of an impurity from the support around 247 eV that partially overlaps the Ta 4d_{3/2} peak and that was considered in the fitting. The binding energies are slightly shifted to higher values for all samples with respect to the bulk oxide values and with slight deviations between the different samples, due to a final state effect of the clusters.²³

3.2 Catalysis tests

Figure 4a displays the catalytic activity of Ta₁ and Ta_{n>1} as the (blank corrected) average number of cyclooctene oxide molecules produced over the course of the experiment (48 h) per catalytic entity (atom or cluster). All reactions provided cyclooctene oxide selectively as determined by GC-MS and confirmed by NMR analysis of the reaction products (see the ESI, figures S5, S6). The final conversion of cyclooctene was about 10% for Ta₁ and 5% for Ta_{n>1}. Based on the number of molecules of cyclooctene converted by Ta₁ with respect to Ta_{n>1} (See also table S2) it is clear that the isolated atoms are more active than the tantalum clusters (about a factor four per catalytic entity). This result is consistent with previous observations in the literature^{34, 39-41, 42} and with a mechanism^{43, 44} in which individual tantalum centres are able to epoxidize olefins by formation of hydroperoxo,⁴⁵ peroxy and superoxo species after reaction with H₂O₂.⁴⁶ The conversion data allow to calculate a blank-corrected TOF of 1.72*10⁵ h⁻¹ for Ta₁ that is proof of the potential of the employed method for the preparation of the catalytically active isolated, ligand-free metal oxo moieties. For an overview, other tantalum-based catalysts reported in the literature for the epoxidation of cyclooctene using H₂O₂ are displayed in the ESI in Table S5 along with a description of the catalyst structure and their catalytic activity in the epoxidation of cyclooctene. These systems include isolated tantalum complexes on solid supports (generally silica) and

nanoparticles. Catalytic systems based on other metals such as W, Ti, Mo, Ga are also shown.

Figure 4. Cyclooctene oxide yields for the Ta₁ and Ta_{1n-1} catalysed epoxidation: (a) averaged total number of cyclooctene oxide molecules formed over the course of multiple experiments after blank correction and per catalytic entity, i.e. atom (Ta₁) or cluster (Ta_{1n-1}); (b) recycling experiments for Ta₁ (single consecutive runs) showing the number of molecules of cyclooctene oxide form per tantalum atom through three catalytic cycles.

To note, the high TOF value obtained for Ta₁ with respect to the literature reported catalyst might, in part, arise from the low catalytic loading employed in our case. Therefore, a direct comparison between Ta₁ and such systems based on TOF values is not possible at this stage. Initial reaction rates would represent a more reliable kinetic parameter for benchmarking catalysts, however, to the best of our knowledge, they are generally not available.³

We tested Ta₁ also for the epoxidation of cyclohexene under identical conditions as for cyclooctene. This reaction is generally affected by lower selectivity than the analogous process using cyclooctene as the substrate. Beside the direct epoxidation route to afford cyclohexene oxide (I), the formation of cyclohexyl hydroperoxide by a radical mechanism (II) can lead to 2-cyclohexen-1-ol (III), 2-cyclohexen-1-on (IV) and, as an indirect route, to additional cyclohexene oxide. Part of the epoxide formed might evolve to cyclohexane-1,2-diol (V) via tantalum-catalyzed epoxide ring-opening reaction by a water molecule (Scheme 1).^{40, 41, 47-49} The use of organic ligands to coordinate the tantalum centre has been proposed to play a role in increasing the reaction selectivity.^{40, 41, 44}

When Ta₁ was used for the epoxidation of cyclohexene, the reaction produced almost exclusively (about 90% of the C6 products) cyclohexene oxide and 1,2 cyclohexane diol (See Figure S7) in a 42:58 ratio (TON: 3×10^7 ; TOF: $6.2 \times 10^5 \text{ h}^{-1}$). The total cyclohexene conversion was 30 %.

Scheme 1. Reaction network of cyclohexene epoxidation.

These data show that the direct epoxidation route of cyclohexene is clearly favoured over the radical process; assuming that the directly produced epoxide is the sum of epoxide plus diol a selectivity of 90% for the direct epoxidation pathway is observed for Ta₁ that is comparable to that obtained by Notestein *et al.* (85%) using a calixarene-derived Nb-catalyst supported on silica.⁴¹

3.3 Recyclability studies

Few data are available on the recyclability of tantalum-based heterogeneous catalysts in epoxidation reactions. Notestein *et al.* observed the absence of leaching from silica supported Ta-calixarene complexes (Table 2, entry 2), however, the reuse of the catalyst for further catalytic cycles was not reported.³⁹ Fukuoka *et al.* reused the ordered mesoporous carbon supported tantalum catalyst (Ta@CMK-1, Table 2, entry 6) for a single recycling experiment showing a decrease (25% based on TON) in catalytic activity.⁴² Therefore, we investigated the recyclability of Ta₁ and Ta_{1n-1} by recovering the catalysts and reusing them in successive experiments. Ta₁ showed activity, albeit decreasing, through three successive experiments (figure 4b), whereas the activity of Ta_{1n-1} was not different from that of the blank experiment already in the second cycle. Indeed, according to post-run characterization of the samples by XPS, the signals relative to Ta_{1n-1} nearly completely disappeared after the first catalytic run (figure S4) compared to the pristine sample. From this observation, it is concluded that the isolated tantalum atoms in Ta₁ bind more strongly to the silica support employed than the Ta_{1n-1} clusters. This was confirmed by supplementary experiments resembling a 'hot filtration test' which were carried out for Ta_{1n-1} and showed a potential influence of leached tantalum species in determining the catalytic activity of this sample (see ESI, table S3). Likely, a slower loss of tantalum atoms for Ta₁ through the catalytic cycles might play a role in the observed decrease of catalytic activity for this catalyst. Despite the loss of activity, a blank-corrected TON value of 1.38×10^6 is still observed for Ta₁ after the third catalytic cycle.

In a recent comparable work on Pt atoms and clusters supported on silica substrates, we noticed a different degree of stability according to the nature of the silica support used.¹¹ Pt atoms placed on stoichiometric SiO₂ substrates would leach to the solution phase and aggregate. Pt atoms placed on a less-than-stoichiometric silicon oxide-based support (TEM grids) would remain stable. The observed difference in stability might be attributed to the tendency of the Pt atoms to adhere stronger to a support with a higher metallic character. This observation highlights the possibility of tuning the stability of the clusters prepared by the presented method by selecting a substrate able to provide stronger interaction with the supported species and should be exploited in further studies to produce more durable catalysts.

3. Conclusion

In conclusion, we have employed UHV techniques to produce ligand-free and isolated tantalum oxide moieties (Ta_1) and tantalum clusters ($Ta_{n>1}$) on silicate support. The bare Ta_1 atoms performed as active catalyst for the selective epoxidation of cycloalkenes significantly outperforming the $Ta_{n>1}$ clusters. This observation is in line with recent advances in catalysis and materials science showing that the application of single metal atoms might lead to a strong improvement of the catalytic performance in various reactions.^{8, 11, 50, 51} The presented approach should be generally applicable to a variety of early transition metals to investigate the catalytic potential of isolated metal oxide units in a broad range of transformations.

The applicability of UHV-synthesized catalysts in industry is currently limited by the difficulty to apply the employed preparative methodology in a large scale and to the existence of well-known material gaps between UHV conditions and the actual industrial scenarios.⁵² Nevertheless, this study suggests that the generation of truly isolated, bare metal oxo units by non-conventional techniques might lead to highly active catalytic systems. This target should be further pursued by the development of methodologies able to afford independent control on particle size, metal loading and dispersion.⁵³

Notes and references

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There are no conflicts of interest to declare.

1. C. Copéret, M. Chabanas, R. Petroff Saint-Arroman and J.-M. Basset, *Angew. Chem., Int. Ed.*, 2003, **42**, 156-181.
2. F. Gao and D. W. Goodman, *Ann. Rev. Phys. Chem.*, 2012, **63**, 265-286.
3. T. Bligaard, R. M. Bullock, C. T. Campbell, J. G. Chen, B. C. Gates, R. J. Gorte, C. W. Jones, W. D. Jones, J. R. Kitchin and S. L. Scott, *ACS Catal.*, 2016, **6**, 2590-2602.
4. G. A. Somorjai, R. L. York, D. Butcher and J. Y. Park, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3500-3513.
5. J.-D. Grunwaldt, M. Caravati and A. Baiker, *J. Phys. Chem. B*, 2006, **110**, 9916-9922.
6. A. Uzun and B. C. Gates, *Angew. Chem., Int. Ed.*, 2008, **47**, 9245-9248.
7. A. Corma, P. Concepción, M. Boronat, M. J. Sabater, J. Navas, M. J. Yacaman, E. Larios, A. Posadas, M. A. López-Quintela, D. Buceta, E. Mendoza, G. Guilera and A. Mayoral, *Nat. Chem.*, 2013, **5**, 775-781.
8. G. Kyriakou, M. B. Boucher, A. D. Jewell, E. A. Lewis, T. J. Lawton, A. E. Baber, H. L. Tierney, M. Flytzani-Stephanopoulos and E. C. H. Sykes, *Science*, 2012, **335**, 1209-1212.
9. X. Li, P. Cui, W. Zhong, J. Li, X. Wang, Z. Wang and J. Jiang, *Chem. Commun.*, 2016, **52**, 13233-13236.
10. J. Lin, B. Qiao, N. Li, L. Li, X. Sun, J. Liu, X. Wang and T. Zhang, *Chem. Commun.*, 2015, **51**, 7911-7914.
11. M. Rondelli, G. Zwaschka, M. Krause, M. D. Rötzer, M. N. Hedhili, M. P. Högerl, V. D'Elia, F. F. Schweinberger, J.-M. Basset and U. Heiz, *ACS Catal.*, 2017, **7**, 4152-4162.
12. U. Heiz, F. Vanolli, L. Trento and W. D. Schneider, *Rev. Sci. Instrum.*, 1997, **68**, 1986-1994.
13. K. Alghamdi, J. S. J. Hargreaves and S. D. Jackson, in *Metal Oxide Catalysis*, ed. S. D. Jackson and J. S. J. Hargreaves, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2008, ch. 21, pp. 819-843.
14. J. D. A. Pelletier and J.-M. Basset, *Acc. Chem. Res.*, 2016, **49**, 664-677.
15. C. Copéret, A. Comas-Vives, M. P. Conley, D. P. Estes, A. Fedorov, V. Mougel, H. Nagae, F. Núñez-Zarur and P. A. Zhizhko, *Chem. Rev.*, 2016, **116**, 323-421.
16. Z. S. Qureshi, P. B. Sarawade, I. Hussain, H. Zhu, H. Al-Johani, D. H. Anjum, M. N. Hedhili, N. Maity, V. D'Elia and J.-M. Basset, *ChemCatChem*, 2016, **8**, 1671-1678.
17. S. Barman, N. Maity, K. Bhatte, S. Ould-Chikh, O. Dachwald, C. Haeßner, Y. Saih, E. Abou-Hamad, I. Llorens, J.-L. Hazemann, K. Köhler, V. D'Elia and J.-M. Basset, *ACS Catal.*, 2016, **6**, 5908-5921.
18. M. A. Bañares and I. E. Wachs, *J. Raman Spectrosc.*, 2002, **33**, 359-380.
19. S. Kunz, F. F. Schweinberger, V. Habibpour, M. Röttgen, C. Harding, M. Arenz and U. Heiz, *J. Phys. Chem. C*, 2010, **114**, 1651-1654.
20. A. S. Crampton, M. D. Rötzer, F. F. Schweinberger, B. Yoon, U. Landman and U. Heiz, *Angew. Chem., Int. Ed.*, 2016, **55**, 8953-8957.
21. A. S. Crampton, M. D. Rötzer, F. F. Schweinberger, B. Yoon, U. Landman and U. Heiz, *J. Catal.*, 2016, **333**, 51-58.
22. K. Wettergren, F. F. Schweinberger, D. Deiana, C. J. Ridge, A. S. Crampton, M. D. Rötzer, T. W. Hansen, V. P. Zhdanov, U. Heiz and C. Langhammer, *Nano Lett.*, 2014, **14**, 5803-5809.
23. J. N. Riedel, M. D. Rötzer, M. Jørgensen, U. G. Vej-Hansen, T. Pedersen, B. Sebok, F. F. Schweinberger, P. C. K. Vesborg, O. Hansen, J. Schiøtz, U. Heiz and I. Chorkendorff, *Catal. Sci. Technol.*, 2016, **6**, 6893-6900.
24. F. F. Schweinberger, M. J. Berr, M. Döblinger, C. Wolff, K. E. Sanwald, A. S. Crampton, C. J. Ridge, F. Jäckel, J. Feldmann, M. Tschurl and U. Heiz, *J. Am. Chem. Soc.*, 2013, **135**, 13262-13265.
25. P. S. Waleska and C. Hess, *J. Phys. Chem. C*, 2016, **120**, 18510-18519.
26. R. Imbihl, R. J. Behm and R. Schlögl, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3459.
27. Y. Chen, J. L. G. Fierro, T. Tanaka and I. E. Wachs, *J. Phys. Chem. B*, 2003, **107**, 5243-5250.
28. Y. Chen, E. Callens, E. Abou-Hamad, N. Merle, A. J. P. White, M. Taoufik, C. Copéret, E. Le Roux and J.-M. Basset, *Angew. Chem., Int. Ed.*, 2012, **51**, 11886-11889.
29. J. F. Eckhard, D. Neuwirth, M. Tschurl and U. Heiz, *Phys. Chem. Chem. Phys.*, 2017, **19**, 10863-10869.
30. K. A. Zemski, R. C. Bell and A. W. Castleman, *J. Phys. Chem. A*, 2000, **104**, 5732-5741.

Journal Name

COMMUNICATION

31. S. Nemana and B. C. Gates, *J. Phys. Chem. B*, 2006, **110**, 17546-17553.
32. S. Nemana, N. L. Okamoto, N. D. Browning and B. C. Gates, *Langmuir*, 2007, **23**, 8845-8854.
33. S. Nemana and B. C. Gates, *Catal. Lett.*, 2007, **113**, 73-81.
34. J. C. Mohandas, E. Abou-Hamad, E. Callens, M. K. Samantaray, D. Gajan, A. Gurinov, T. Ma, S. Ould-Chikh, A. S. Hoffman, B. C. Gates and J.-M. Basset, *Chem. Sci.*, 2017, **8**, 5650-5661.
35. S. Kunz, K. Hartl, M. Nesselberger, F. F. Schweinberger, G. Kwon, M. Hanzlik, K. J. J. Mayrhofer, U. Heiz and M. Arenz, *Phys. Chem. Chem. Phys.*, 2010, **12**, 10288-10291.
36. H. Gruber-Woelfler, P. F. Radaschitz, P. W. Feenstra, W. Haas and J. G. Khinast, *J. Catal.*, 2012, **286**, 30-40.
37. H. Demiryont, J. R. Sites and K. Geib, *Appl. Opt.*, 1985, **24**, 490-495.
38. R. Simpson, R. G. White, J. F. Watts and M. A. Baker, *Appl. Surf. Sci.*, 2017, **405**, 79-87.
39. N. Morlanes and J. M. Notestein, *Appl. Catal. A: Gen.*, 2010, **387**, 45-54.
40. N. Morlanés and J. M. Notestein, *J. Catal.*, 2010, **275**, 191-201.
41. N. E. Thornburg, A. B. Thompson and J. M. Notestein, *ACS Catal.*, 2015, **5**, 5077-5088.
42. M.-L. Lin, K. Hara, Y. Okubo, M. Yanagi, H. Nambu and A. Fukuoka, *Catal. Commun.*, 2011, **12**, 1228-1230.
43. D. A. Ruddy and T. D. Tilley, *J. Am. Chem. Soc.*, 2008, **130**, 11088-11096.
44. P. J. Cordeiro and T. D. Tilley, *Langmuir*, 2011, **27**, 6295-6304.
45. D. Meunier, A. de Mallmann and J.-M. Basset, *Top. Catal.*, 2003, **23**, 183-189.
46. D. T. Bregante and D. W. Flaherty, *J. Am. Chem. Soc.*, 2017, **139**, 6888-6898.
47. B. P. C. Hereijgers, R. F. Parton and B. M. Weckhuysen, *Catal. Sci. Technol.*, 2012, **2**, 951-960.
48. J. M. Fraile, J. I. García, J. A. Mayoral and E. Vispe, *Appl. Catal. A: Gen.*, 2003, **245**, 363-376.
49. D. A. Ruddy and T. D. Tilley, *Chem. Commun.*, 2007, 3350-3352.
50. G. Vilé, D. Albani, M. Nachtegaal, Z. Chen, D. Dontsova, M. Antonietti, N. López and J. Pérez-Ramírez, *Angew. Chem., Int. Ed.*, 2015, **54**, 11265-11269.
51. W. Liu, L. Zhang, W. Yan, X. Liu, X. Yang, S. Miao, W. Wang, A. Wang and T. Zhang, *Chem. Sci.*, 2016, **7**, 5758-5764.
52. H. Oosterbeek, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3570-3576.
53. J. Dendooven, R. K. Ramachandran, E. Solano, M. Kurttepel, L. Geerts, G. Heremans, J. Rongé, M. M. Minjauw, T. Dobbelaere, K. Devloo-Casier, J. A. Martens, A. Vantomme, S. Bals, G. Portale, A. Coati and C. Detavernier, *Nat. Commun.*, 2017, **8**, 1074.

1. Deposition of Ta clusters or atoms in the UHV **2. Ta oxidation in air** **3. Application in epoxidation catalysis**

270x152mm (120 x 120 DPI)