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Size-selected gold clusters on porous titania as the most “gold-efficient” heterogeneous catalysts

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Research on homogeneous and heterogeneous catalysis is indeed convergent and finds subnanometric particles to be at the heart of catalytically active species. Here, monodisperse gold clusters are deposited from the gas phase onto porous titania generating well-defined model systems and the resulting composite materials exhibit a sharp size-dependency on the number of gold atoms per cluster and exceptionally high-turnovers toward the bromination of 1,4-dimethoxybenzene are observed. This indicates that the deliberate generation of active centres is of utmost importance for the creation of the most “gold-efficient” catalysts.
were preserved on these nanoparticle-like TiO₂-clusters (diameter approx. 1 nm). Moreover, results indicate that only Au₄ and Au₇ are active for CO oxidation, creating a situation where coincidental approx. 1 nm). Moreover, results indicate that only Au₆ and Au₇ are exhibit strong metal support interaction (SMSI); and (iii) it has been discovered that Au₄/TiO₂ has been chosen for three reasons: (i) gold is very oxidation resistant and can be transferred to the gas-phase and are soft-landed (size-selected clusters) on the metal oxide support, hereby the masses can be selected on an atom-by-atom basis (cluster deposition setup is described in the experimental section). A particular system Au₄/TiO₂ has been chosen for three reasons: (i) gold is very oxidation resistant and can be transferred from ultra-high vacuum (UHV) to ambient conditions without changes in chemical integrity; (ii) gold particles on titania exhibit strong metal support interaction (SMSI); and (iii) it has been shown that Au₄/TiO₂ is a superior catalyst for homocoupling of iodobenzene compared to Au₄-PAMAM. Here it will be shown that size-selected clusters do not only act as model systems for catalysis under UHV conditions but also as very efficient catalysts for the bromination of 1,4-dimethoxybenzene in solution.

**Experimental**

Since this work contains methodology of heterogeneous catalysis in solution and cluster deposition both approaches are explained in detail in the following section.

**General experimental section**

**Analytical methods**

*XPS (X-ray photoelectron spectroscopy).* XPS spectra have been recorded using an Omicron EA 125 CHA (concentric hemispherical analyzer) with a base pressure in the main chamber of $\leq 5 \times 10^{-10}$ mbar using the Mg K$_\alpha$-line (1253.6 eV). Peak fitting was done via CASA XPS and a Gaussian–Lorentzian fit (GL30), the peak separation for Au 4f was kept at $\Delta = 3.67$ eV.

**SEM (scanning electron microscopy).** The highly porous TiO₂-layer has been characterized using a Zeiss Cross Beam 1540 XB, which is a combination of a Scanning Electron Microscope (SEM) and a Focused Ion Beam (FIB). To determine the thickness a cross-section was cut into the layer using the FIB and analyzed by SEM.

**TEM (transmission electron microscopy).** Micrographs have been obtained by dip coating TiO₂ primary particles (13.4 nm) onto copper/carbon grids, deposition of Au_{120} clusters at a cluster current of 200 pA for 2 h, and subsequent investigation within a Jeol ARM instrument.

**GC/MS (gas chromatography/mass spectrometry).** GC measurements were done using an Agilent 7890A machine equipped with a Zebron ZB-5MS column with a length of 30 m, an inner diameter of 0.25 mm and a film thickness of 0.25 μm. The temperature program for GC measurements was as follows: (i) 50 °C held for 1 min; (ii) the temperature is raised to 280 °C at a rate of 30 °C min$^{-1}$; (iii) the temperature is held at 280 °C for another 3 min. MS measurements were performed on an Agilent 5975C apparatus.

**Wet chemical methods**

*Dip coating of aerogel-like TiO₂ onto tantalum backing plates.* Arealike TiO₂ (1 mg) is suspended in 0.2 ml of ethanol (pA) and dip coated onto a 10 mm × 10 mm tantalum backing plate. The ethanol is allowed to evaporate from the sample at room temperature and then it is introduced into the deposition chamber of the cluster deposition apparatus.

**Bromination of 1,4-dimethoxybenzene.** 1,4-Dimethoxybenzene (A, 0.5 mmol, 69 mg, see Scheme 1) and N-bromosuccinimide (B, NBS, 0.5 mmol, 89 mg) are placed inside a 5 ml vial and dissolved in 2 mL dichloroethane. The catalyst (blank, AuCl₅ [5 mg], HAuCl₄ [5 mg], TiO₂ [5 mg], Au₄/TiO₂ [1 mg], Au₆/TiO₂ [1 mg], Au₇/TiO₂ [1 mg], Au₄/TiO₂ (a) [1 mg], Au₄/TiO₂ (b) [1 mg], Au₄/TiO₂ [1 mg], Au₄/TiO₂ [1 mg], Au₁₂₀/TiO₂ [1 mg]) was added, the vial sealed with a cap, and the reaction stirred for 24 h at room temperature. After that time period had elapsed the vial was reopened and dodecane (0.5 mmol, 64 μl) was added to the mixture as internal standard for GC/MS, the mixture was then filtered, and diluted in hexane prior to the actual GC/MS measurement.

In order to obtain the number of generated molecules of 1-bromo-2,5-dimethoxybenzene (C, see Scheme 1) GC calibration
with the temperature ramp mentioned above has been done. Therefore, 1 mmol of dodecane (internal standard) and 1 mmol are dissolved in hexane and the corresponding chromatogram is measured. The GC/MS method allows unambiguous identification of both substances without having to obtain chromatograms of isolated compounds first. The peak areas of C and dodecane within the chromatogram are linked by the following relationship:

$$
\frac{A_{\text{dodecane}}}{A_{\text{C}}} = \frac{n_{\text{dodecane}}}{n_{\text{C}}},
$$

where A is the area and n the number of moles of the respective substances. This procedure yields the calibration factor $f_{\text{calibration}} = \frac{A_{\text{dodecane}}}{A_{\text{C}}} = 6.43$. With this known factor the amount of C within the solution after reaction can be determined by adding a known amount of dodecane. The TONs reported in Table 2 are obtained by dividing the number of product molecules C over (i) the number of clusters in the catalyst (TON per gold cluster) or (ii) the number of gold atoms in the catalyst (TON per gold atom) given in units of number of molecules C and number of molecules C, respectively. The number of clusters/gold atoms is obtained by measuring and integrating the neutralization current during cluster deposition (see below). This number corresponds to the number of clusters/atoms within the catalyst since all materials obtained from deposition are used as reaction catalysts.

**Gas-phase methods**

**Synthesis of aerogel-like TiO₂.** The liquid precursor Ti(O18OPr)₄ is injected into the evaporation zone of the aerosol synthesis setup using a syringe pump from KD Scientific model KS200. The addition of the precursor to the evaporation zone (EZ) via the syringe pump allows us to keep an adjusted concentration of the precursor in the aerosol constant. Tube ovens from Nabertherm were used for the evaporation and the decomposition of the precursor. Exact amounts of gases (N₂ and O₂) are added using mass flow controllers from Bronkhorst (model el-flow select). Typical flow rates are $f_{\text{nitrogen}} = 1.2 \text{ L min}^{-1}$ and $f_{\text{oxygen}} = 0.3 \text{ L min}^{-1}$. The precursor concentration is given by the evaporation rate and the volume of the added gases. Typically an evaporation temperature of 90 °C was selected and the concentration of the precursor could be adjusted in the range of $10^{-5} - 10^{-4} \mu\text{g m}^{-3}$. Formation of titania takes place in the decomposition zone of the set-up, which is heated to 800 °C. Separation of the TiO₂ materials from the aerosol is achieved using a thermophoresis unit. The powder X-ray diffraction pattern of the corresponding material is shown in Fig. 2.

**Deposition of mass-selected Auₙ⁻.** Aerogel-like TiO₂ dip-coated (see above) on tantalum plates has been introduced into the deposition chamber of the cluster setup. The chamber was pumped down to \( \approx 1 \times 10^{-8} \text{ mbar} \) and Auₙ⁻ was deposited onto dip-coated tantalum plates while the neutralization current was measured and integrated to obtain the total number of clusters since they carry a single negative charge. Average deposition currents for the different clusters were 20–100 pA yielding deposition times of several hours. After deposition the samples were removed from the deposition chamber and introduced into another UHV system for XPS analysis.

**Cluster deposition setup.** The deposition of Auₙ⁻ cluster ions onto TiO₂ dip-coated on tantalum plates will be described in detail here to familiarize the reader with size-selected cluster ion deposition. A gold metal target (gold coin) is vaporized in the cluster ion source (namely: magnetron sputter source, see Fig. 1) via spattering with argon ions (see the sputter head and the cluster ion source). The vaporized gold atoms are cooled down by helium carrier gas in the aggregation tube in front of the magnetron sputter head, in turn positive, negative, and neutral clusters are formed and moved in the direction of the differential pumping stages. The sputter- and carrier gas is removed from the cluster (ion) beam via four powerful differential pumping stages. Thereafter negative clusters are accelerated by a guiding voltage of +1.5 kV to extract negative clusters from the beam. Subsequently, the beam is focused and steered by various ion optics (lenses and “steerers”) into a chamber, placed between the pole pieces of a large bending magnet, where, depending on their masses, clusters are deflected by different angles. The neutral clusters are not influenced by the magnetic field and thus are separated from the cluster ion beam. Afterwards the cluster beam should in principle contain only one Auₙ⁻ species which passes through a cooling trap in order to freeze out any hydrocarbon and hydro-silicon species arising from the operation of diffusion pumps along the cluster beamline. This beam is again focused by ion optics and soft-landed (deposition energies below 1 eV per atom) onto the sample containing dip-coated aerogel-like TiO₂ (sample holder). During deposition the negatively charged gold species are neutralized and the resulting current can be measured, an integration of this current yields the charge which in turn can be used to evaluate the number of deposited clusters since clusters typically carry a single negative charge. The mass spectrum of the corresponding Auₙ⁻ species has been
Results and discussion

Aerogel-like TiO$_2$ with a primary particle size of 13.4 nm has been used as a support material for size-selected gold clusters. The particle size of titania crystallites is determined from the analysis of peak-broadening of the signals obtained by powder X-ray diffraction (PXRD, see Fig. 2) using the Scherrer-method. In addition, TEM micrographs were checked and showed that the size of the TiO$_2$ nanocrystals is in the same region. However, it should be noted that the value obtained from PXRD provides an average size, whereas there is of course a certain polydispersity in the sample.

An innovative approach which permits complementation of real-space techniques for thin-film characterization from reciprocal space is discussed by Perlich et al.\textsuperscript{29} It involves grazing-incidence small-angle X-ray scattering (GISAXS) data and their evaluation. Unfortunately, we do not have any access to SAXS equipment capable of GI-measurements. Therefore, we could only investigate the porosity of the sample by SEM and TEM (which gives only a qualitative impression) and N$_2$ physisorption analysis, which at least gives quantitative figures for internal surface area, pore volume and pore-size distribution.

However, giving a precise value for the porosity ($V_{\text{pore}}/V_{\text{total}}$) is not possible at the moment. However, it is believed that this is also not critical information for the current contribution, since it is undoubtedly correct that the used, aerogel-like porous TiO$_2$ materials possess high porosity, low density and lots of open pore-space.

The described material has been suspended in ethanol and dip-coated onto tantalum backing plates to facilitate gold cluster deposition. An SEM investigation of the as-prepared plates shows a thickness of 16 µm and conserved porosity of the support material (Fig. 4). Furthermore the number of TiO$_2$ particle monolayers can be determined to be about 1200. The film has also been investigated by XPS, however, due to considerable film thicknesses charging effects occur. In order to account for charging Ti($^\text{+4}$) 2p$_{3/2}$, which is to be found at 259.0 eV, has been used as a reference.\textsuperscript{27} TiO$_2$/Ta plates have been inserted into a UHV deposition chamber and size-selected gold clusters have been deposited. The mass spectrum of these gold species in the gas phase is presented in Fig. 3A and B. It basically shows monodisperse clusters for small species. Deposition currents for gold clusters varied between 20 and 100 pA yielding deposition times of several hours.

Fig. 3 (A) Mass-spectrum of gold cluster anions in the gas phase as obtained by the magnetic sector field, optimized for small clusters. (B) Mass-spectrum of gold cluster anions in the gas phase without optimization to a specific mass range. (C) XPS region scan of the Au 4f signals of the composite material Au$_{120}$/TiO$_2$.

A close packed monolayer of gold, e.g., Au(111), contains about $1.5 \times 10^{15}$ atoms per cm$^2$ which in the observed deposition spot (circular with 3 mm in diameter, $7 \times 10^{-2}$ cm$^2$) translates into $\approx 1 \times 10^{14}$ atoms within the spot per monolayer. The lower limit for detection of surface species by XPS is about 1% of a monolayer corresponding to $\approx 1 \times 10^{12}$ atoms on the top monolayer of the TiO$_2$ film. For small clusters, especially Au$_4$, this cannot be achieved since these small clusters are able to penetrate deep into the porous film structure ($\approx 1200$ ML). The huge number of monolayers in addition to the small amount of gold clusters deposited makes observation of an XPS signal very unlikely, except for the largest clusters, Au$_{120}$, which is exactly what is found. In the Au$_{4\text{p}}$/TiO$_2$ composite the number of gold...
atoms is about one order of magnitude higher in comparison (see Table 1). On top of that these large clusters might have problems penetrating into the network of TiO₂ and unlike the other clusters accumulate on the top TiO₂ layer making detection via XPS possible (Fig. 3C). The binding energy after charge correction yields a value around 0.4 ng gold was deposited, 3 ng for Au₇, 5 ng for Au₈, 3 ng for Au₉, and 60 ng for Au₁₂₀ respectively. Fig. 3B presents a mass spectrum over the complete range of the respective magnetron sputter source which unequivocally shows that larger clusters are much easier to make than smaller ones. So an attempt was made to deposit large clusters in order to achieve enough material to make detection possible by EDX, however, the corresponding TEM micrograph of the sample in Fig. 5 demonstrates massive coagulation of these clusters which should not be the case if it was possible for this size to penetrate deeply into the TiO₂ network. On the other hand it was not possible to find any evidence for smaller clusters within TEM micrographs due to their very low mass and deposition currents. We believe these measurements tentatively show the low penetration depths of large Au₁₂₀ clusters into the titania framework.

The same cross-section SEM technique should in principle be useful to determine the penetration depths of the clusters into the TiO₂ layer. The problem with this approach is EDX sensitivity with a lower value of 0.5 to 1 mass%. For samples provided here 1 mg of TiO₂ was used which means that 10 μg would be needed to be deposited per sample if the cluster ion beam is focused down maybe 1 μg or less. On the Au₄ sample 0.4 ng gold was deposited, 3 ng for Au₇, 5 ng for Au₉, 3 ng for Au₁₀, and 60 ng for Au₁₂₀, respectively. Fig. 3B presents a mass spectrum over the complete range of the respective magnetron sputter source which unequivocally shows that larger clusters are much easier to make than smaller ones. So an attempt was made to deposit large clusters in order to achieve enough material to meet EDX sensitivity criteria. Au₁₂₀ was deposited for 2 h onto 1 mg of TiO₂ suspended in ethanol on a TEM grid which yielded a total amount of approximately 300 ng which was still too low to be detected by EDX, however, the corresponding TEM micrograph of the sample in Fig. 5 demonstrates massive coagulation of these clusters which should not be the case if it was possible for this size to penetrate deeply into the TiO₂ network. On the other hand it was not possible to find any evidence for smaller clusters within TEM micrographs due to their very low mass and deposition currents. We believe these measurements tentatively show the low penetration depths of large Au₁₂₀ clusters into the titania framework.

Composite materials presented in Table 1 have been used as catalysts for the bromination of 1,4-dimethoxybenzene (1) using NBS (2). The Au₉/TiO₂ materials were removed from the tantalum backing plate and transferred directly into reaction vessels containing 1 and 2 dissolved in dichloroethane which have been stirred for 24 h at room temperature (see the Experimental section). The conversion of the reaction has been checked via gas chromatography. The results are found in Table 2. Compared to previous results¹,¹³,²⁰ achieved TONs with size-selected gold clusters on titania are extremely high, while a TON of 10² is described in the literature TONs as high as 10⁶ are found for Au/TiO₂ (Table 2, entry 6, Fig. 6). This gap in TON should be ascribed to the “naked” nature of the clusters obtained by “soft-landing” in UHV compared to size-selected clusters created by dendrimer templates. Clusters formed within a dendrimer become encapsulated in the template which acts as a large ligand with multiple binding sites¹²,¹³ preventing leaching into solution but also decreasing exposure to reactants. A closer look shows that composite materials Au₇/TiO₂ (n = 4, 7, 9) exhibit similar TONs based on the number of gold atoms (Table 2, entries 5, 6, 9 and Fig. 6) which might be indicative of dissolution of clusters into the reactant solution facilitating behavior as described by J. Oliver-Meseguer et al..¹⁴ Due to its d¹⁰s¹ valence electron configuration gold is considered a “simple” metal and can be treated by the Jellium model,¹¹ according to which Au₄, Au₇,

Table 1
Overview of composite materials of type Auₙ/TiO₂ which have been prepared by size-selected gold cluster deposition onto TiO₂ covered tantalum backing plates

| Entry | Composite material | Number of Au clusters | Number of Au atoms |
|-------|--------------------|-----------------------|-------------------|
| 1     | Au₅/TiO₂           | 2.7 × 10¹⁵            | 1.1 × 10¹²         |
| 2     | Au₇/TiO₂           | 1.3 × 10¹⁵            | 9.3 × 10¹²         |
| 3     | Au₇/TiO₂ (a)       | 1.9 × 10¹⁵            | 1.5 × 10¹³         |
| 4     | Au₉/TiO₂ (b)       | 8.1 × 10¹⁴            | 6.5 × 10¹³         |
| 5     | Au₁₀/TiO₂          | 1.1 × 10¹⁴            | 1.0 × 10¹³         |
| 6     | Au₁₂₀/TiO₂         | 1.6 × 10¹⁴            | 1.9 × 10¹⁴         |

Fig. 4  SEM image of aerogel-like TiO₂ dip-coated onto a tantalum backing plate. The thickness has been determined by cross-section and is shown as green bars in the image.

Fig. 5  TEM micrograph of coagulated Au₁₂₀ clusters on TiO₂ (162.5 nm × 162.5 nm) obtained at the boundaries of the TiO₂ spot. Massive coagulation is observed which should be prevented in case of the penetration into the titania network. The predicted size of clusters from the gas phase is approximately 2 nm but sizes from 5 to 30 nm are observed here.
entities from the gas-phase onto the sample contrary to soft-landing of size-selected particles. It has to be admitted that sputter deposition is much easier to be conducted and much faster than the latter method. Moreover, the ingenious method of GISAXS is able to characterize film growth under sputter conditions in real-time, results obtained by Schwartzkopf et al.\textsuperscript{12} show four-stage growth and the corresponding thresholds with submonolayer resolution. This knowledge allows tremendous control over film properties and cluster size in the nanometer range. Work conducted by Valden et al.\textsuperscript{23} shows that gold catalysts on titania for CO oxidation at exposure times of 10 Torr CO:O\textsubscript{2} (2:1) for 120 min (7.2 $\times$ 10\textsuperscript{10} L) show best reaction rates for islands with a diameter between 2.5 and 3.5 nm. These islands show a thickness of only two layers and their activity is blamed on the high aspect ratio and related quantum size effects introducing a band-gap into these islands. Employing the GISAXS method should facilitate exceptionally simple preparation of CO oxidation catalysts in this pressure regime. However, if the reactant exposure is lowered down to 0.2–600 L only clusters Au\textsubscript{6} and Au\textsubscript{7} show catalytic activity on TiO\textsubscript{2} which was presented in a recent contribution (see above),\textsuperscript{16} i.e., indeed every atom counts. Larger and smaller clusters would be a waste of gold under such conditions. Similar results were found by J. Oliver-Meseguer et al. for the bromination of aromatics using gold clusters in solution as described above. Although sputter deposition of gold clusters is unmatched in simplicity and duration for the physical preparation of heterogeneous gold catalysts it is believed that the full potential of the non-scalable sub-nano regime can only be exploited by size-selected cluster deposition under soft-landing conditions so far.

Conclusions

Sharp size-dependencies for catalytic activities are well-known from reactions under UHV conditions with size-selected cluster catalysts,\textsuperscript{14–16,34,35} and only experiments involving size-selected deposition made it fashionable to think of the exact number of atoms in heterogeneous catalysis. Here it could be shown that the “pressure gap” can be overcome for “soft-landed” gold clusters on TiO\textsubscript{2} which act as very efficient bromination catalysts in solution under “real” catalytic conditions. Since sharp size-dependence is also observed and can be explained in terms of the Jellium model. In conclusion size-selected cluster deposition presents an invaluable tool to facilitate deliberate creation of active sites in heterogeneous catalysis which is the idea of nanocatalysis.\textsuperscript{17} As future steps deposition currents for gold clusters have to be optimized to synthesize sufficient amounts for in-depth mechanistic analysis of catalytic reactions.

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