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Very small "window of opportunity" for generating CO oxidation-active Au_n on TiO_2†

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Recent research in heterogeneous catalysis, especially on size-selected model systems under UHV conditions and also in realistic catalytic environments, has proved that it is necessary to think in terms of the exact number of atoms when it comes to catalyst design. This is of utmost importance if the amount of noble metal, gold in particular, is to be reduced for practical reactions like CO oxidation. Here it is shown that on TiO_2 only Au_6 and Au_7 clusters are active for CO oxidation which holds for the single crystal, thin films, and titania clusters deposited on HOPG. Size-selected cluster deposition and TPD methods have been employed to investigate the CO oxidation activity of Au_n/TiO_2 systems which are compared to recent results reported by Lee *et al.* to form a consistent picture in which only two species can be regarded as "active". The efficiency of investigated $Au_n/(TiO_2)_{93}$/HOPG composite materials is attributed to carbon-assisted oxygen spillover from gold to support particles and across grain boundaries.

Introduction

Gold as the most noble of metals for a long time has presented very little fascination for chemists due to its inertness in the bulk state.[1] However, since the discoveries of Hutchings and Haruta that gold catalyzes the hydrochlorination of acetylene[2] and the oxidation of carbon monoxide at subzero temperatures,[3] gold has become ubiquitous in heterogeneous[4–7] and homogeneous[8] catalysis alike. The search for very small gold grains consisting of just a couple of atoms, *i.e.* small gold clusters, has been initiated by fundamental studies on size-selected gold clusters where Au_8 has been shown to be the smallest active catalyst for the oxidation of CO when adsorbed on MgO.[9–11] Only then, inspired by these findings, did it become fashionable to think in terms of the exact number of atoms when heterogeneous catalysts are considered. However, for the vast majority of homogeneously catalyzed reactions the catalytically "active site"[12] is still much better understood than for their heterogeneous counterparts. "Active sites" at present are best known for homogeneous and biological reactions owing to the well-defined nature of these "active sites".[13] Consequently, gigantic turn over numbers, approaching the efficiency of enzymes, have recently been observed for the ester-assisted hydration of alkynes, bromination of aromatics with *N*-bromo-succinimide[14] and the gold-catalyzed phenol and spiro compound synthesis.[15] In the former study matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) and UV-Vis absorption studies on solutions containing Au(+1) or Au(+3) salts showed that very small clusters of not more than 13 atoms are formed. Moreover it indicated that the ester-assisted hydration of alkynes is catalyzed by Au_3 to Au_5 while the bromination of aromatics is catalyzed significantly only by Au_7 to Au_9 clusters.[14] Similar results were obtained in heterogeneous CO oxidation over Au/FeO_x catalysts. Aberration-corrected scanning transmission electron microscopy facilitated the investigation of subnanometric gold particles on the supporting oxide for the first time. It was found that the real catalytically active species were indeed subnanometric bilayer particles of not more than ten atoms.[7]

CO oxidation is of great interest, especially at low temperatures, because it is the main reaction catalyzed by the three-way converter in internal combustion engine driven automobiles.[16] Since the noble metal content in these converters is still a major issue size-selected model catalysts have been prepared on different oxide supports and tested for their oxidation activity towards CO to identify the "active species".[10,17–19] On MgO supports, namely MgO(001), CO oxidation activity is not observed for

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gold clusters below 8 atoms and is associated with the presence of F-centers (oxygen vacancies) in the support material.[10] On the other hand size-selected gold clusters on TiO_2(110) show significant CO oxidation activity only for Au_6 and Au_7.[17,18] A combined study including results from the cluster science labs at the Technical University of Munich (TiO_2 thin film studies) and the Johns Hopkins University in Baltimore (TiO_2 cluster studies) is aimed at showing that gold clusters on TiO_2 need to have 6 or 7 atoms in order to be active catalysts for CO oxidation, *i.e.*, the window is equally small as demonstrated for selected homogeneously catalyzed reactions in solution.[14] These studies are very important for minimizing the noble metal content of CO oxidation catalysts by the application of only "active species".

Results and discussion

A. TiO_2 thin film studies

Studies on MgO(001) thin films have shown that Au_8 clusters are only CO oxidation active due to charge transfer between the support and the cluster, leading to negatively charged Au_8, which is correlated with the presence of oxygen vacancies and therefore reduced surfaces. Such a surface decorated with Au_8 is able to catalyze the reaction at temperatures as low as 140 K with gas dosing as low as 0.2 L for $^{18}O_2$ and ^{13}CO. Also the order of reactant dosing is not important for the outcome of the reaction, in contrast to most other metals. Oxidized surfaces without those vacancies do not exhibit CO oxidation activity if functionalized by Au_8.[9,10,20,21] Larger clusters, *e.g.*, Au_{13}, Au_{16}, and Au_{20}, do indeed exhibit catalytic activities on oxidized surfaces also.[22,23] In turn it is imperative to study CO oxidation on titania for reduced and oxidized films. This is feasible since TiO_2 samples can be reduced easily by annealing, resulting in n-type semiconductors due to the formation of oxygen vacancies, so-called F or color centers.[24–28] The stage of reduction can be monitored by the sample color since it changes from transparent (completely oxidized) to dark blue (reduced).[29,30] The amount of oxygen vacancies created by annealing was estimated to be about several percent of the surface.[31–33] Removing the oxygen vacancies is as simple as producing them, the samples just need to be annealed in an oxygen atmosphere.[24,31–33] Reduced and oxidized TiO_2 films with a thickness of 10 monolayers (ML) were grown *in situ* onto Mo(100) single crystals and subsequently 6×10^{12} clusters per cm^2 for temperature programmed desorption (TPD) were landed (soft-landing conditions) which amount to 0.28% ML of clusters. The cluster deposition setup is described in detail elsewhere.[34–36] For TPD experiments 0.5 L of reaction gases at 90 K were dosed and the desorbing reaction products were monitored using a quadrupole mass spectrometer (QMS) as a function of temperature at a heating rate of 2 K s^{-1}.[22]

TPD measurements were conducted on different size-selected Au_n (n = 8, 13, 16, 20) clusters deposited on reduced (a) and oxidized (b) films, see Fig. 1. None of the investigated gold clusters are active for CO oxidation independent if they are supported on reduced or oxidized films. For the pristine film

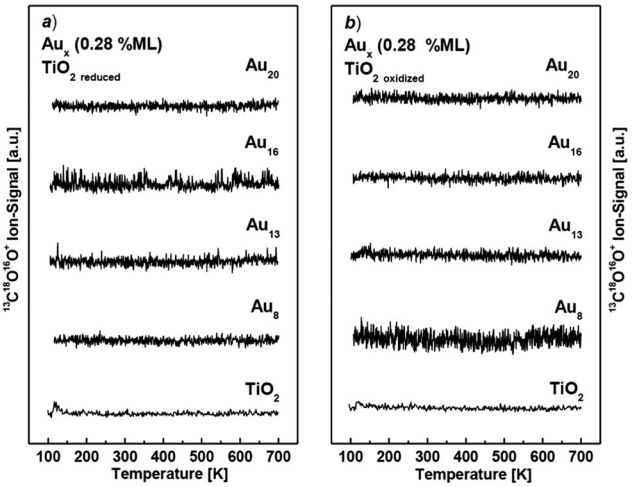

Fig. 1 TPD spectra of $^{13}C^{18}O^{16}O$ from Au_n (0.28% ML of clusters, see above) on TiO_2 and the pristine TiO_2 thin films. The samples are exposed to 0.5 L $^{18}O_2$ and subsequently ^{13}CO (0.5 L) at 90 K. (A) Measurements on reduced and (B) oxidized films.[22]

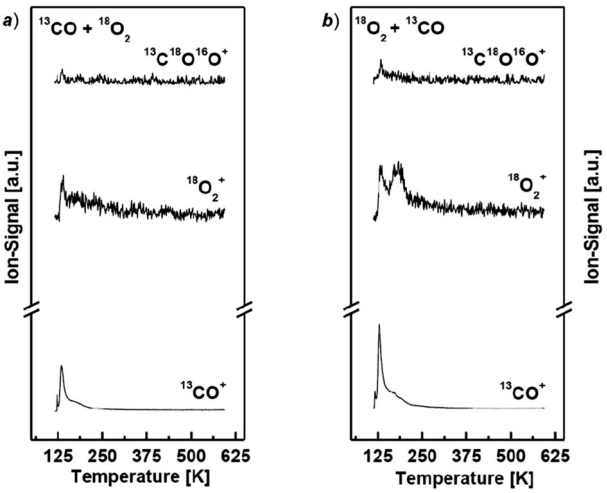

Fig. 2 TPD spectra of $^{13}C^{18}O^{16}O$ from Au_n ($n \geq 13$, 0.5% ML of clusters, see above) on TiO_2. (A) Sample is exposed to 0.5 L of $^{18}O_2$ and subsequently to ^{13}CO (0.5 L) at 90 K. (B) Sample is exposed to 0.5 L of ^{13}CO and subsequently to $^{18}O_2$ (0.5 L) at 90 K.[22]

there is a small signal of CO_2 formation which is not reproducible and might originate from the sample holder, heating wire, *etc.*

To investigate if the order of gas dosing is important TPD experiments were carried out on small gold clusters Au_n with $n \geq 13$. Fig. 2 shows experiments with first CO and then O_2 dosing (a) and *vice versa* (b). In both cases no significant amount of CO_2 is produced indicating that the order is not influential on the activity of these clusters. The only difference between the two measurements is the absence of the second $^{18}O_2$ desorption peak if ^{13}CO was dosed first. The independence from the dosing order is also observed in the case of the Au/MgO system.[10]

These observations together with Fourier transform infrared experiments (FTIR, not shown)[22] present the following picture: (i) CO is adsorbed very weakly on small gold clusters and

supporting films. No CO is left on the surface around room temperature. (ii) More than one infrared absorption band was observed indicating different adsorption sites on clusters. (iii) Clusters seem to be stable and do not agglomerate since the experiments were repeated after annealing the sample to temperatures of about 300 K and no difference in the infrared absorption was detected. (iv) TPD experiments showed no CO_2 production in all cases, which is not affected by changing the order of gas dosing. These results seem to be in contrast to the investigations conducted by Lee *et al.*,[17,18] however, they only investigated Au_n (n = 1 to 7), so the question remains if Au_8 is active for CO oxidation. Below it will be shown that Au_8 in a series of experiments for n = 5 to 8 is not particularly active while Au_6 and Au_7 present highly active catalysts. This tentatively indicates that Au_8 and larger clusters are not active for CO oxidation on TiO_2 support materials.

B. TiO_2 cluster studies

In order to shed light on more realistic catalytic support materials (nanostructured TiO_2) in combination with mass-selected clusters back-to-back deposition of $(TiO_2)_{93}$ and Au_n (n = 5 to 8) was carried out in a newly designed cluster deposition setup with TPD capability at Johns Hopkins University in Baltimore.[37] Preliminary experiments and blank tests have been carried out which are presented in the ESI.†

There are considerable problems associated with gold clusters and their interaction toward dioxygen (oxygen activation) due to the very low sticking probability of O_2, so that either atomic oxygen[38–41] or alternatively a high oxygen dose of 600 L[17,18] has been applied. It was found that low doses of oxygen lead to very low sticking probabilities to the gold clusters and that $^{18}O_2$ binds at oxygen vacancies on TiO_2.[17] However, investigations on oxidized MgO films showed that CO oxidation is possible with oxygen doses as low as 0.5 L (see above).[22,23] So an intermediate dose of 10 L was chosen corresponding to the procedure of Kaden *et al.* for $Pd_n/TiO_2(110)$[42] as described in the ESI.† Taking into account the size-dependence of the catalytic activity of $Au_n/TiO_2(110)$ towards CO oxidation as discovered by Lee *et al.*[17,18] and the negative results of Au_8/TiO_2 (see above) Au_5 to Au_8 were selected for catalytic investigation. Synthesis of composite materials always involved cleaning of the HOPG *via* a Scotch-tape method, heating to 473 K for 20 min, deposition of 30% ML of $(TiO_2)_{93}$ and subsequent deposition of 5% ML of Au_n. CO oxidation experiments always contained the same sequence of steps for different Au_n clusters: (i) CO oxidation with the oxygen dose at 400 K and the CO dose at 180 K, (ii) a second CO oxidation experiment, (iii) CO (5 L) adsorption at 180 K, and finally (iv) CO (50 L) adsorption at 180 K.

The first material investigated by the described procedure was $Au_5/(TiO_2)_{93}$/HOPG (see Fig. 3). When dosed with 10 L of oxygen at 400 K and subsequently with CO (5 L) at 180 K moderate CO oxidation activity can be found (Fig. 3A). The reaction probability for $^{13}C^{16}O$ is approximately 5% as found *via* the integration of the $^{13}C^{16}O$ and $^{13}C^{16}O^{18}O$ desorption features which is as low as for unfunctionalized $(TiO_2)_{93}$/HOPG (see ESI†). However, CO_2 desorption is shifted to higher temperatures (see below). In the work of Lee *et al.* the reaction probability is only ≈1% even in the case of very active Au_6 clusters after 600 L of $^{18}O_2$ predosing.[17,18] The activity is still very low (or non-existent) as found by Lee *et al.* for $Au_5/TiO_2(110)$.[17,18] The second high temperature desorption feature that was found for $(TiO_2)_{93}$/HOPG (Fig. S6 right, ESI†) after oxygen dosing is lost for the Au_5

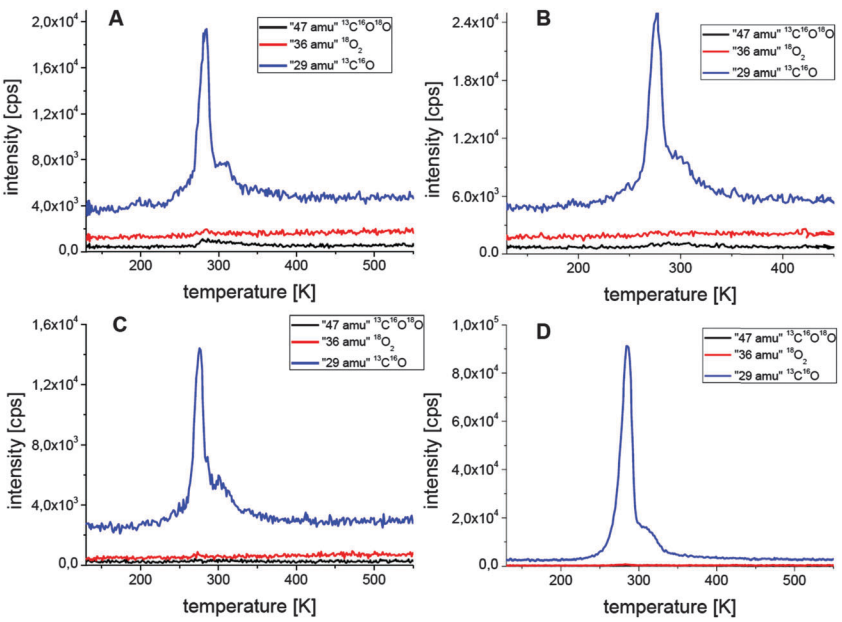

Fig. 3 (A) $^{13}C^{16}O$, $^{18}O_2$ and $^{13}C^{16}O^{18}O$ desorption from $Au_5/(TiO_2)_{93}$/HOPG after adsorption of 10 L of $^{18}O_2$ at 400 K and 5 L of $^{13}C^{16}O$ at 180 K (first run). (B) $^{13}C^{16}O$, $^{18}O_2$, and $^{13}C^{16}O^{18}O$ desorption from $Au_5/(TiO_2)_{93}$/HOPG after adsorption of 10 L of $^{18}O_2$ at 400 K and 5 L of $^{13}C^{16}O$ at 180 K (second run). (C) $^{13}C^{16}O$, $^{18}O_2$, and $^{13}C^{16}O^{18}O$ desorption from $Au_5/(TiO_2)_{93}$/HOPG after adsorption of 5 L of $^{13}C^{16}O$ at 180 K. (D) $^{13}C^{16}O$, $^{18}O_2$, and $^{13}C^{16}O^{18}O$ desorption from $Au_5/(TiO_2)_{93}$/HOPG after adsorption of 50 L of $^{13}C^{16}O$ at 180 K.

functionalized material. The broad low temperature $^{13}C^{16}O$ desorption feature of $(TiO_2)_{93}$/HOPG (Fig. S6 right, ESI†) is shifted to 280 K on $Au_5/(TiO_2)_{93}$/HOPG and higher desorption intensities are found. The desorption feature has a clear shoulder towards the high temperature side (another desorption site for CO), however, the onset of $^{13}C^{16}O^{18}O$ desorption is clearly associated with the large feature ($\approx$280 K) which makes $Au_5/(TiO_2)$/HOPG a room temperature CO oxidation catalyst. The CO oxidation reaction on $Au_5/(TiO_2)_{93}$/HOPG has been carried out twice in a row and almost the same curve is observed in both runs, which means these particles are either very stable or do not act as catalysts (see below for Au_6 and Au_7). Au_5 particles change CO adsorption behavior on $(TiO_2)_{93}$/HOPG considerably. Sintering of the clusters occurred after repeated heating cycles, see Fig. 4. An XPS region scan of the Au 4f peaks after CO oxidation and air exposure shows the main peaks at 84.0 eV for Au $4f_{7/2}$ which corresponds to the bulk gold signal. According to Lee *et al.* the binding energy for Au $4f_{7/2}$ is at 84.7 eV for Au_1 to Au_7 on $TiO_2(110)$.[18] The investigation of CO desorption after CO oxidation experiments shows that the main desorption features remain at the same position for the 5 L and 50 L doses, the 50 L dose shows massive desorption of $^{13}C^{16}O$ from the sample (almost one order of magnitude higher, see Fig. 3C and D). $^{13}C^{16}O^{18}O$ formation is not observed after just CO dosing. However, the total CO desorption intensity from $Au_5/(TiO_2)_{93}$/HOPG is about an order of magnitude higher than for $(TiO_2)_{93}$/HOPG (Fig. S6, ESI†).

$Au_6/(TiO_2)_{93}$/HOPG has also been synthesized and subject to the series of experiments described above (Fig. 5). When dosed with $^{18}O_2$ (10 L) at 400 K and subsequently with $^{13}C^{16}O$ (5 L) at 180 K high CO oxidation activity can be observed for $Au_6/(TiO_2)_{93}$/HOPG with a reaction probability of around 34%, which is expected according to the activities found by Lee *et al.*[18] The $^{13}C^{16}O$ desorption features are now shifted towards low temperatures and three desorption (adsorption) sites at 217 K, 230 K, 245 K are found as opposed to 280 K in the case of $Au_5/(TiO_2)_{93}$/HOPG. Desorption of $^{13}C^{16}O^{18}O$ is at 237 K and 263 K which is also associated with the onset of $^{18}O_2$ desorption, *i.e.*, the catalytic activity probably stems from the adsorption sites at 230 K and 245 K and the site at 217 K is probably not active for CO oxidation (*i.e.*, the catalyst works at low temperatures for CO oxidation, see Fig. 5A). $^{13}C^{16}O$ desorption levels from $Au_6/(TiO_2)_{93}$/HOPG are back to the ones observed for $(TiO_2)_{93}$/HOPG but unlike in the $(TiO_2)_{93}$/HOPG case the surface is now reactive for CO oxidation, which is probably related to oxygen activation on Au_6 which is not observed for Au_5. It is possible that activated oxygen diffuses from gold particles to the TiO_2 support and also onto the HOPG (oxygen spillover[43,44]) and changes the surface of these materials. Such a modified surface might be the reason for lower CO adsorption compared to Au_5 but a reactive surface compared to pure $(TiO_2)_{93}$/HOPG if predosed with oxygen. In the second run the CO oxidation activity of Au_6 is completely lost, see below, which is indicative of complete sintering of the particles. Sintering of the particles is supported by XPS data (Fig. 4) after four consecutive TPD runs and exposure to air. A shift of Au $4f_{7/2}$ of 84.0 eV is found which is also indicative for bulk gold. Another possibility is the encapsulation of the particles by a reduced titania layer (strong metal–support interaction),[45,46] which is known to suppress the catalytic activity of nanoparticles.[47,48] However, it seems unlikely since it is usually observed after

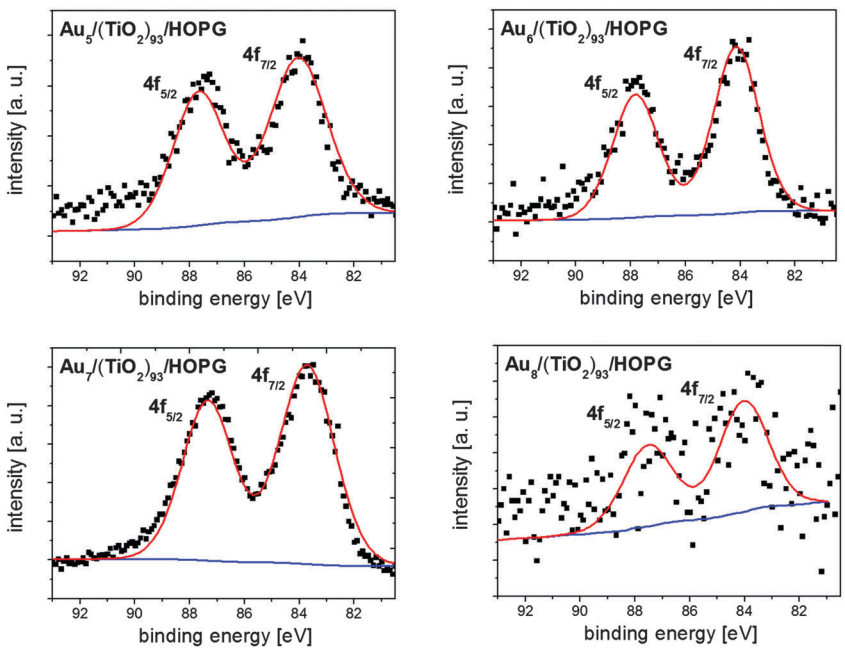

Fig. 4 XPS region scans of Au 4f signals of $Au_n/(TiO_2)_{93}$/HOPG (n = 5 to 8). The XPS signal intensity for Au 4f in $Au_8/(TiO_2)_{93}$/HOPG is significantly decreased compared to that for other $Au_n/(TiO_2)_{93}$/HOPG composite materials. This is attributed to less than ideal sample positioning in front of the hemispherical analyzer and therefore tainted XPS results. During deposition of Au_8 the same amount of gold has been deposited according to integrated currents during the procedure.

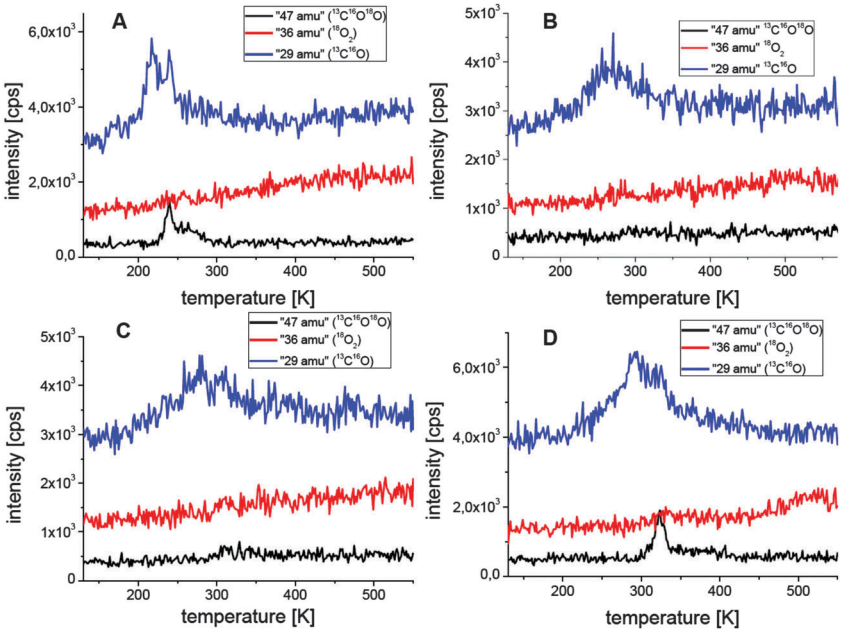

Fig. 5 (A) $^{13}C^{16}O$, $^{18}O_2$, and $^{13}C^{16}O^{18}O$ desorption from $Au_6/(TiO_2)_{93}$/HOPG after adsorption of 10 L of $^{18}O_2$ at 400 K and 5 L of $^{13}C^{16}O$ at 180 K (first run). (B) $^{13}C^{16}O$, $^{18}O_2$, and $^{13}C^{16}O^{18}O$ desorption from $Au_6/(TiO_2)_{93}$/HOPG after adsorption of 10 L of $^{18}O_2$ at 400 K and 5 L of $^{13}C^{16}O$ at 180 K (second run). (C) $^{13}C^{16}O$, $^{18}O_2$, and $^{13}C^{16}O^{18}O$ desorption from $Au_6/(TiO_2)_{93}$/HOPG after adsorption of 5 L of $^{13}C^{16}O$ at 180 K. (D) $^{13}C^{16}O$, $^{18}O_2$, and $^{13}C^{16}O^{18}O$ desorption from $Au_6/(TiO_2)_{93}$/HOPG after adsorption of 50 L of $^{13}C^{16}O$ at 180 K.

annealing above 700 K[49] which is not the case in the presented experiments. But it also cannot be completely ruled out since XP spectra of as-deposited clusters could not be obtained to be compared to the post catalysis ones. $^{13}C^{16}O$ desorption from $Au_6/(TiO_2)_{93}$/HOPG is almost the same at the 5 L and 50 L $^{13}C^{16}O$ doses (Fig. 5C and D) which is neither the case for $Au_5/(TiO_2)_{93}$/HOPG nor $(TiO_2)_{93}$/HOPG. At the 50 L $^{13}C^{16}O$ dose formation of $^{13}C^{16}O^{18}O$ can be recovered at 320 K at the desorption feature for $^{13}C^{16}O$ at 317 K (Fig. 5D). The $^{13}C^{16}O^{18}O$ desorption peak from the first run is now shifted to higher temperatures (325 K) and might result from forcing the CO molecules into adsorption sites which are already covered by activated oxygen and might not be gold catalyzed thus explaining the increased temperature. The fact that $^{13}C^{16}O$ desorption is almost the same for 5 L and 50 L indicates a surface covered with "spilt over" oxygen preventing adsorption of massive amounts of $^{13}C^{16}O$. This "spilt over" oxygen on titania particles/HOPG surface might also be responsible for the efficient sintering of the Au_6 particles on the surface during TPD experiments (Fig. 4).

CO oxidation and desorption experiments were also carried out with $Au_7/(TiO_2)_{93}$/HOPG. When dosed with $^{18}O_2$ (10 L) at 400 K and subsequently with $^{13}C^{16}O$ (5 L) at 180 K the reaction probability is also high in the case of $Au_7/(TiO_2)_{93}$/HOPG, as found by Lee *et al.* for $Au_7/TiO_2(110)$,[17,18] also 35% are observed (Fig. 6A). $^{13}C^{16}O$ desorption features are found at 217 K, 230 K, and 245 K which are the same as in the case of $Au_6/(TiO_2)_{93}$/HOPG, however, $^{13}C^{16}O^{18}O$ generation is only exhibited in significant amounts from the feature at 230 K which is depleted compared to the other ones. Only one desorption peak for $^{13}C^{16}O^{18}O$ is found at 234 K and no desorption at higher temperatures is observed (low temperature oxidation catalyst). $^{13}C^{16}O^{18}O$ desorption is clearly associated with $^{18}O_2$ desorption at the same temperature, there is, however, a second $^{18}O_2$ desorption peak at 390 K which does not show any CO oxidation activity. In the second run $^{13}C^{16}O$ desorption features are shifted towards higher temperatures (like in the Au_6 case) 250 K, 280 K, and 320 K and two $^{13}C^{16}O^{18}O$ desorption features are observed at 280 K and 295 K, while CO oxidation activity is decreased considerably. This decrease is not as drastic as in the case of Au_6 but the XPS region scan of Au 4f suggests sintering with a value of 84.0 eV for the $4f_{7/2}$ peak (see Fig. 4). $^{13}C^{16}O$ desorption from $Au_7/(TiO_2)_{93}$/HOPG is comparable for the 5 L and 50 L cases (Fig. 6C and D) like in the case of $Au_6/(TiO_2)_{93}$/HOPG (Fig. 5C and D). Here even after the 5 L dose some $^{13}C^{16}O^{18}O$ desorption can be detected in a broad peak between 290 K and 350 K. In the 50 L case behavior similar to the first run can be recovered, only that the $^{13}C^{16}O^{18}O$ desorption peak is now shifted from 230 K to 310 K. $^{13}C^{16}O$ and $^{18}O_2$ desorption peaks are also shifted towards higher temperatures by the same amount, which is comparable to the behavior of Au_6 under the same conditions. It must be concluded that oxygen activation and spillover are very efficient processes on Au_6 and Au_7 even at a dose of only 10 L of $^{18}O_2$. The slow shift of the CO_2 desorption peak on the Au_7 functionalized material from Fig. 6A to D can be accounted for by successive cluster sintering until the reaction is no more gold catalyzed but merely a reaction between activated oxygen and CO. From Au_6 and Au_7 composite materials massive desorption of oxygen is seen which is not the case for all other materials including Au_8 (see below) which is indicative of more strongly bound oxygen species from activation processes. Clear $^{18}O_2$ desorption peaks can be observed on $Au_7/(TiO_2)_{93}$/HOPG, thus for future experiments it might be rewarding to investigate peak positions in

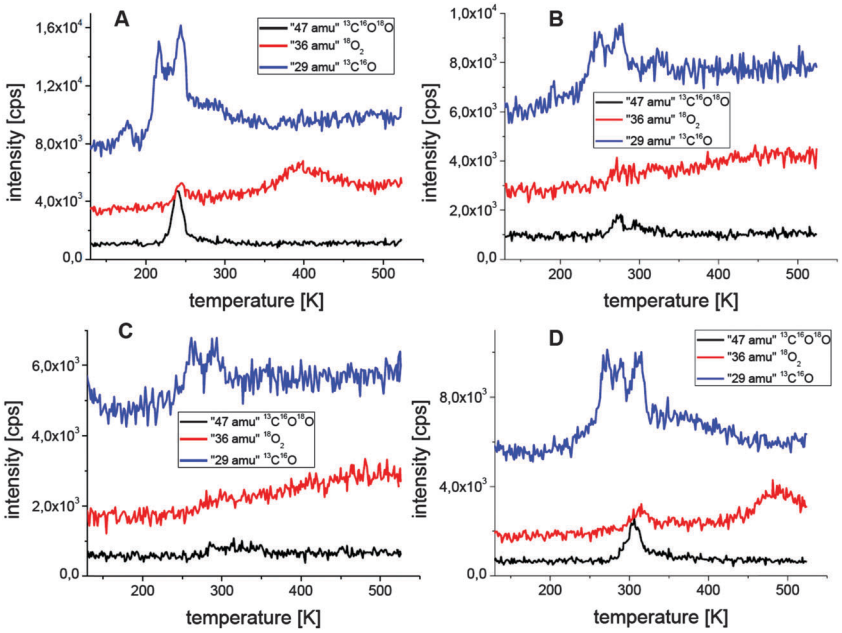

Fig. 6 (A) $^{13}C^{16}O$, $^{18}O_2$, and $^{13}C^{16}O^{18}O$ desorption from $Au_7/(TiO_2)_{93}$/HOPG after adsorption of 10 L of $^{18}O_2$ at 400 K and 5 L of $^{13}C^{16}O$ at 180 K (first run). (B) $^{13}C^{16}O$, $^{18}O_2$, and $^{13}C^{16}O^{18}O$ desorption from $Au_7/(TiO_2)_{93}$/HOPG after adsorption of 10 L of $^{18}O_2$ at 400 K and 5 L of $^{13}C^{16}O$ at 180 K (second run). (C) $^{13}C^{16}O$, $^{18}O_2$, and $^{13}C^{16}O^{18}O$ desorption from $Au_7/(TiO_2)_{93}$/HOPG after adsorption of 5 L of $^{13}C^{16}O$ at 180 K. (D) $^{13}C^{16}O$, $^{18}O_2$, and $^{13}C^{16}O^{18}O$ desorption from $Au_7/(TiO_2)_{93}$/HOPG after adsorption of 50 L of $^{13}C^{16}O$ at 180 K.

terms of different doses of oxygen to elucidate the order of the desorption process. In the case of oxygen dissociation and subsequent spillover the second order desorption should be observed.

As a last example the composite material $Au_8/(TiO_2)_{93}$/HOPG has been investigated (Fig. 7). When dosed with $^{18}O_2$ (10 L) at 400 K and subsequently with $^{13}C^{16}O$ (5 L) at 180 K the reaction probability is low and comparable to $Au_5/(TiO_2)_{93}$/HOPG (approx. 5%, Fig. 7A and B). However, less Au_8^- might have been deposited since the XPS spectrum has lower intensity (which is probably due to wrong sample positioning during data acquisition, Fig. 4). The XPS signal for Au $4f_{7/2}$ is again at bulk gold binding energy after two TPD runs and pure $^{13}C^{16}O$ dosing (50 L).

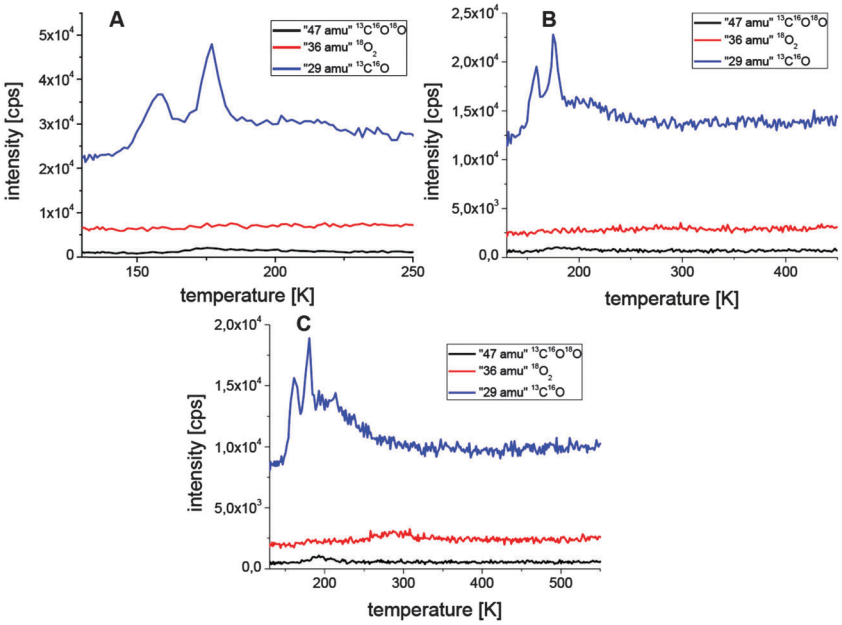

Fig. 7 (A) $^{13}C^{16}O$, $^{18}O_2$, and $^{13}C^{16}O^{18}O$ desorption from $Au_8/(TiO_2)_{93}$/HOPG after adsorption of 10 L of $^{18}O_2$ at 400 K and 5 L of $^{13}C^{16}O$ at 180 K (first run). (B) $^{13}C^{16}O$, $^{18}O_2$, and $^{13}C^{16}O^{18}O$ desorption from $Au_8/(TiO_2)_{93}$/HOPG after adsorption of 10 L of $^{18}O_2$ at 400 K and 5 L of $^{13}C^{16}O$ at 180 K (second run). (C) $^{13}C^{16}O$, $^{18}O_2$, and $^{13}C^{16}O^{18}O$ desorption from $Au_8/(TiO_2)_{93}$/HOPG after adsorption of 50 L of $^{13}C^{16}O$ at 180 K.

$^{13}C^{16}O$ desorption from $Au_8/(TiO_2)_{93}$/HOPG takes place in two features at 160 K and 175 K which is from the temperature comparable to desorption from the sample holder, however, now two peaks are observed while only one is found for the sample holder. $^{13}C^{16}O^{18}O$ desorption is observed at 175 K making this composite material a low temperature oxidation catalyst (Fig. 7A and B), again this feature is comparable to desorption from the sample holder (Fig. S4 right, ESI†). Both runs show comparable CO oxidation activities which can be recovered in the 50 L CO dose (Fig. 7C) and are close to the unfunctionalized materials. So it must be concluded that this material is a very modest CO activation catalyst at best. This finding is congruent with the absence of CO oxidation activities for Au_n (n = 8, 13, 16, 20) on reduced and oxidized TiO_2 thin films as presented in Section A. Compared to Au_6 and Au_7, Au_5 and Au_8 (Fig. 5 and 6 and Fig. 3 and 7) show almost no oxygen desorption. This explains the comparatively high CO desorption from Au_5 and Au_8 and hence their low CO oxidation activity which is triggered by oxygen activation. The high levels of CO desorption compared to $(TiO_2)_{93}$/HOPG might be explained by some sort of CO activation by those two cluster sizes and subsequent diffusion into the support materials. Unfortunately, the behavior of sole CO desorption without prior O_2 adsorption has not been investigated but will be interrogated in further studies. However, the deeper reason for the efficient oxygen activation of Au_6 and Au_7, which probably lies within their electronic structure, cannot be elucidated by our approach but needs supporting theoretical calculations.

The results of Section B can be summarized as (i) adsorption behavior of the $(TiO_2)_{93}$/HOPG composite material is governed by deposited TiO_2 clusters (see ESI†). (ii) $TiO_2(110)$ and $(TiO_2)_{93}$ in this work exhibit properties of oxidized (oxygen-vacancy free) TiO_2 since D_2O desorption at 500 K[33] is absent in both cases (see ESI†). (iii) The size-dependence of catalytic activity is preserved when going from single crystal experiments (TiO_2[110])[17,18] to the cluster composite material $(TiO_2)_{93}$/HOPG as a catalyst support. (iv) Au_8 is (almost) inactive for CO oxidation on TiO_2 thin films and $(TiO_2)_{93}$/HOPG.

Conclusions

From a general point of view it could be shown that on TiO_2 supports under UHV conditions only Au_6 and Au_7 clusters show a reaction probability for CO which is significantly higher than for the pristine materials $TiO_2(110)$ and $(TiO_2)_{93}$/HOPG. The overlap between thin film and the cluster support allows us to conclude that Au_8 is not an active CO oxidation catalyst (Fig. 1 and 7) and thus it is very likely that larger clusters, namely $Au_{13,16,20}$, are inactive as well (Fig. 1). This supports the claim that the window of creating catalytically active species towards CO oxidation on TiO_2 materials is equally small as the window observed for gold-catalyzed ester-assisted hydration of alkynes (Au_{3-5}) and bromination of aromatics (Au_{7-9}) in homogeneous solution.[14] The approach of using high-surface area supports to increase the chance of formation of the "correct" species might not be enough for the successful creation of an active catalyst if the window is as small as described herein. This in turn supports the idea of "nanocatalysis" stating that the "active species" has to be deliberately created.[50] These "active species" can be found by investigating the size-dependence of the catalytic activity towards a certain reaction on well-described single-crystal surfaces[17,18] since it could be demonstrated here that this dependency is essentially the same as on $(TiO_2)_{93}$ which acts as a model for high-surface area support materials. This makes size-selected cluster deposition an invaluable tool for the rational design of high-end "metal efficient" catalysts.

More specifically composite materials of the type $Au_n/(TiO_2)_{93}$/HOPG are much more efficient in dioxygen activation than $Au_n/TiO_2(110)$ materials reported previously.[17,18] The CO reaction probability of 35% for Au_6 and Au_7 is traced back to oxygen spillover from gold clusters to the $(TiO_2)_{93}$/HOPG support. The particular efficiency exhibited might originate from special properties of the TiO_2/HOPG interface. From studies on hydrogen storage it is well-known that secondary and tertiary spillover processes can be facilitated across grain boundaries *via* carbon bridges (spillover from the metal particle to the support particle to the carbon bridge [carbonized sucrose] to another support particle).[51] A similar mechanism might come into play for oxygen spillover in the case described here, where oxygen is efficiently transported away from the gold particle on HOPG or TiO_2 permitting the activation of more oxygen molecules. This mechanism is backed by the observation that active catalysts cover the surface with oxygen (oxygen desorption is seen) and the 5 L and 50 L CO doses show approximately the same amount of CO desorption. Results obtained by this work can only substantiate the claim that the ability to dissociate (activate) dioxygen (from TPD it is not possible to tell if dioxygen is dissociated or otherwise activated) is the key for catalytic activity.[39] The very active gold particles unfortunately are destroyed in two consecutive TPD runs and are either not very stable against sintering at higher temperatures or encapsulation by TiO_2. However, FTIR studies have shown that Au clusters are stable on TiO_2 thin films up to 300 K (see above)[22] and since CO_2 desorption takes place at 240 K stability might be easily achieved.

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