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Very small "window of opportunity" for generating CO oxidation active Au_n on TiO₂

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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 acetylene² and the oxidation of carbon monoxide at subzero temperatures³ gold has become ubiguitous in heterogeneous^{4,5,6,7} and homogeneous⁸ 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 MqO.^{9,10,11} Only then, inspired by these findings, it has 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, the bromination of aromatics with Nbromo-succinimide¹⁴ 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 no more than 13 atoms are formed. Moreover it indicated that the ester-assisted hydration of alkynes is catalyzed by Au₃ to Au₅ while the bromination of aromatics is catalyzed significantly only by Au₇ to Au₉ clusters.¹⁴ Similar results were obtained in heterogeneous CO oxidation over Au/FeO_x catalysts. Aberrationcorrected 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 no 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 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".^{10,17,18,19} On MgO supports, namely MgO(001), CO oxidation activity is not observed for 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 TiO₂(110) show significant CO oxidation activity only for Au₆ and Au₇.^{17,18} With a combined study including results from the cluster science labs at the Technical University of Munich (TiO₂ thin film studies) and the Johns Hopkins University in Baltimore (TiO₂ cluster studies) it is aimed at showing that gold clusters on TiO₂ 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. TiO₂ thin film studies

Studies on MgO(001) thin films have shown that Au₈ clusters are only CO oxidation active due to charge transfer between support and cluster, leading to negatively charged Au_a, 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 ¹⁸O₂ and ¹³CO. 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 Au₈.^{9,10,20,21} Larger clusters, e.g., Au₁₃, Au₁₆, and Au₂₀, 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 TiO₂ 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.^{24,25,26,27,28} The stage of reduction can be monitored by 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.^{31,32,33} Removing the oxygen vacancies is as simple as producing them, the samples just need to be annealed in oxygen atmosphere.^{24,31,32,33} Reduced and oxidized TiO₂ films with a thickness of 10 monolayers (ML) were grown in situ onto Mo(100) single crystals and subsequently 6×10¹² clusters per cm² for temperature programmed desorption (TPD) were landed (soft-landing conditions) which amounts to 0.28% ML of clusters. The cluster deposition setup is described in detail elsewhere.^{34,35,36} For TPD experiments 0.5 L of reaction gases at 90 K were dosed and the desorbing reaction products were monitored by a quadrupole mass spectrometer (QMS) as a function of temperature with a heating rate of 2 K/s.²²

TPD measurements were conducted on different size-selected Au_n (n = 8, 13, 16, 20) deposited on reduced (A) and oxidized (B) films, see Figure 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 there is a small signal of CO_2 formation which is not reproducible and might originate from sample holder, heating wire, etc.



Figure 1. TPD spectra of ${}^{13}C^{18}O^{16}O$ from Au_n (0.28% ML of clusters, see above) on TiO₂ and the pristine TiO₂ thin films. The samples are exposed to 0.5 L ${}^{18}O_2$ and subsequently ${}^{13}CO$ (0.5 L) at 90 K. A depicts the measurements on reduced and B on oxidized films.²²

To investigate if the order of gas dosing is important TPD experiments were carried out on small gold clusters Au_n with $n \ge 13$. Figure 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 case of the Au/MgO system.¹⁰



Figure 2. TPD spectra of ${}^{13}C^{18}O^{16}O$ from Au_n (n \ge 13, 0.5% ML of clusters, see above) on TiO₂. A. Sample is exposed to 0.5 L ${}^{18}O_2$ and subsequently to ${}^{13}CO$ (0.5 L) at 90 K. B. Sample is exposed to 0.5 L ${}^{13}CO$ and subsequently to ${}^{18}O_2$ (0.5 L) at 90 K.²²

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*)

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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 Au₈ is active for CO oxidation. Below it will be shown that Au₈ in a series of experiments for n = 5 to 8 is not particularly active while Au₆ and Au₇ present highly active catalysts. This tentatively indicates that Au₈ and larger clusters are not active for CO oxidation on TiO₂ support materials.

B. TiO₂ 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 "supporting information".

There are considerable problems associated with gold clusters and their interaction toward dioxygen (oxygen activation) due to the very low sticking probability of O2, so that either atomic oxygen^{38,39,40,41} or alternatively a high oxygen dose of 600 L^{17,18} have been applied. It was found that low doses of oxygen lead to very low sticking probabilities to the gold clusters and that ¹⁸O₂ binds at oxygen vacancies on TiO₂.¹⁷ 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 supporting information. Taking into account the size-dependence of the catalytic activity of Au_n/TiO₂(110) towards CO oxidation as discovered by Lee et al.^{17,18} and the negative results on Au₈/TiO₂ (see above) Au₅ to Au₈ were selected for catalytic investigation. Synthesis of composite materials always involved cleaning of the HOPG via Scotch-tape method, heating to 473 K for 20 min, deposition of 30% ML of (TiO₂)₉₃ and subsequent deposition of 5% ML of Au_n. CO oxidation experiments always contained the same sequence of steps for different Aun clusters: (i) CO oxidation with oxygen dose at 400 K and CO dose at 180 K, (ii) a second CO oxidation experiment, (iii) CO (5L) adsorption at 180 K, and finally (iv) CO (50 L) adsorption at 180 K.

The first material investigated by the described procedure was Au₅/(TiO₂)₉₃/HOPG (see Figure 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 (Figure 3 A). The reaction probability for ¹³C¹⁶O is approximately 5 % as found via the integration of the ¹³C¹⁶O and the ¹³C¹⁶O¹⁸O desorption features which is as low as for unfunctionalized (TiO₂)₉₃/HOPG (see supporting information). However, CO₂ 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 Au₆ clusters after 600 L ¹⁸O₂ predosing.^{17,18} The activity is still very low (or nonexistent) as found by Lee *et al.* for Au₅/TiO₂(110).^{17,18} The second high temperature desorption feature that was found for (TiO₂)₉₃/HOPG (Figure S 6 right) after oxygen dosing is lost for the Au₅ functionalized material. The broad low temperature ¹³C¹⁶O desorption feature of (TiO₂)₉₃/HOPG (Figure S 6 right) is shifted to 280 K on Au₅/(TiO₂)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 ¹³C¹⁶O¹⁸O

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Au₅/(TiO₂)/HOPG a room temperature CO oxidation catalyst. The CO oxidation reaction on Au₅/(TiO₂)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 catalyst (see below for Au₆ and Au₇). Au₅ particles change CO adsorption behavior on (TiO₂)₉₃/HOPG considerably. Sintering of the clusters occurred after repeated heating cycles, see Figure 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 Au₁ to Au₇ on TiO₂(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 the 50 L dose, the 50 L dose shows massive desorption of ¹³C¹⁶O from the sample (almost one order of magnitude higher, see Figure 3 C and D). ¹³C¹⁶O¹⁸O formation is not observed after just CO dosing. However, the total CO desorption intensity from Au₅/(TiO₂)₉₃/HOPG is about an order of magnitude higher than for (TiO₂)₉₃/HOPG (Figure S 6).



Figure 3. A. ¹³C¹⁶O, ¹⁸O₂, and ¹³C¹⁶O¹⁸O desorption from Au₅/(TiO₂)₉₃/HOPG after adsorption of 10 L ¹⁸O₂ at 400 K and 5 L of ¹³C¹⁶O at 180 K (first run). B. ¹³C¹⁶O, ¹⁸O₂, and ¹³C¹⁶O¹⁸O desorption from Au₅/(TiO₂)₉₃/HOPG after adsorption of 10 L ¹⁸O₂ at 400 K and 5 L of ¹³C¹⁶O at 180 K (second run). C. ¹³C¹⁶O, ¹⁸O₂, and ¹³C¹⁶O¹⁸O desorption from Au₅/(TiO₂)₉₃/HOPG after adsorption of 5 L of ¹³C¹⁶O at 180 K. D. ¹³C¹⁶O, ¹⁸O₂, and ¹³C¹⁶O¹⁸O desorption from Au₅/(TiO₂)₉₃/HOPG after adsorption of 50 L of ¹³C¹⁶O at 180 K.

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Figure 4. XPS region scans of Au 4f signals of Au_n/(TiO₂)₉₃/HOPG (n = 5 to 8). The XPS signal intensity for Au 4f in Au₈/(TiO₂)₉₃/HOPG is significantly decreased compared to other Au_n/(TiO₂)₉₃/HOPG composite materials. This is blamed to less than ideal sample positioning in front of the hemispherical analyzer and therefore tainted XPS results. During deposition of Au₈ the same amount of gold has been landed according to integrated currents during the procedure.

Au₆/(TiO₂₎₉₃/HOPG has also been synthesized and subject to the series of experiments described above (Figure 5). When dosed with ¹⁸O₂ (10 L) at 400 K and subsequently with ¹³C¹⁶O (5 L) at 180 K high CO oxidation activity can be observed for Au₆/(TiO₂)₉₃/HOPG with a reaction probability of around 34%, which is expected according to the activities found by Lee et al.¹⁸ The ¹³C¹⁶O 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 case of Au₅/(TiO₂)₉₃/HOPG. Desorption of ¹³C¹⁶O¹⁸O is at 237 K and 263 K which is also associated with the onset of ¹⁸O₂ 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 Figure 5 A). ¹³C¹⁶O desorption levels from Au₆/(TiO₂)₉₃/HOPG are back to the ones observed for (TiO₂)₉₃/HOPG but unlike in the (TiO₂)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 Au₅. It is possible that activated oxygen diffuses from gold particles to the TiO₂ 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 Au₅ but a reactive surface compared to pure (TiO₂)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 for complete sintering of the particles. Sintering of the particles is supported by XPS data (Figure 4) after four consecutive TPD runs and exposure to air. A shift of the Au 4f7/2 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 catalytic activity of nanoparticles.^{47,48} However, it seems unlikely since it is usually observed after annealing above 700 K⁴⁹ 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. ¹³C¹⁶O desorption from Au₆/(TiO₂)₉₃/HOPG is almost the same at the 5 L and the 50 L $^{13}C^{16}O$ dose (Figure 5 C and D) which is neither the case for Au₅/(TiO₂)₉₃/HOPG nor (TiO₂)₉₃/HOPG. At the 50 L $^{13}C^{16}O$ dose formation of ¹³C¹⁶O¹⁸O can be recovered at 320 K at the desorption feature for ¹³C¹⁶O at 317 K (Figure 5 D). The ¹³C¹⁶O¹⁸O 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 ¹³C¹⁶O 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 ¹³C¹⁶O. This "spilt over" oxygen on titania particles/HOPG surface might also be responsible for the efficient sintering of the Au₆ particles on the surface during TPD experiments (Figure 4).



Figure 5. A. ¹³C¹⁶O, ¹⁸O₂, and ¹³C¹⁶O¹⁸O desorption from Au₆/(TiO₂)₉₃/HOPG after adsorption of 10 L ¹⁸O₂ at 400 K and 5 L of ¹³C¹⁶O at 180 K (first run). B. ¹³C¹⁶O, ¹⁸O₂, and ¹³C¹⁶O¹⁸O desorption from Au₆/(TiO₂)₉₃/HOPG after adsorption of 10 L ¹⁸O₂ at 400 K and 5 L of ¹³C¹⁶O at 180 K (second run). C. ¹³C¹⁶O, ¹⁸O₂, and ¹³C¹⁶O¹⁸O desorption from Au₆/(TiO₂)₉₃/HOPG after adsorption of 5 L of ¹³C¹⁶O at 180 K. D. ¹³C¹⁶O, ¹⁸O₂, and ¹³C¹⁶O¹⁸O desorption from Au₆/(TiO₂)₉₃/HOPG after adsorption of 50 L of ¹³C¹⁶O at 180 K.

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 (Figure 6 A). ${}^{13}C^{16}O$ desorption features are found at 217 K, 230 K, and 245 K which are the same as in 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). ¹³C¹⁶O¹⁸O desorption is clearly associated with ¹⁸O₂ desorption at the same temperature, there is, however, a second ¹⁸O₂ desorption peak at 390 K which does not show any CO oxidation activity. In the second run ¹³C¹⁶O desorption features are shifted towards higher temperatures (like in the Au₆ case) 250 K, 280 K, and 320 K and two ¹³C¹⁶O¹⁸O 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 Au₆ but the XPS region scan of Au 4f suggests sintering with a value of 84.0 eV for the $4f_{7/2}$ peak (see Figure 4). ¹³C¹⁶O desorption from Au₇/(TiO₂)₉₃/HOPG is comparable for the 5 L and the 50 L case (Figure 6 C and D) like in the case of Au₆/(TiO₂)₉₃/HOPG (Figure 5 C and D). Here even after the 5 L dose some ¹³C¹⁶O¹⁸O desorption can be detected in a broad peak between 290 K and 350 K. In the 50 L case behavior like in the first run can be recovered, only that the ¹³C¹⁶O¹⁸O desorption peak is now shifted from 230 K to 310 K. ¹³C¹⁶O and ¹⁸O₂ 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 Au₆ and Au₇ even at a dose of only 10 L of ¹⁸O₂. The slow shift of the CO₂ desorption peak on the Au₇ functionalized material from Figure 6 A 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 Au₆ and Au₇ composite materials massive desorption of oxygen is seen which is not the case for all other materials including Au₈ (see below) which is indicative for more strongly bound oxygen species from activation processes. Clear ¹⁸O₂ desorption peaks can be observed on $Au_7/(TiO_2)_{93}/HOPG$, thus for future experiments is might be rewarding to investigate peak positions in terms of different doses of oxygen to elucidate the order of the desorption process. In case of oxygen dissociation and subsequent spillover second order desorption should be observed.



Figure 6. A. ${}^{13}C^{16}O$, ${}^{18}O_2$, and ${}^{13}C^{16}O^{18}O$ desorption from Au₇/(TiO₂)₉₃/HOPG after adsorption of 10 L ${}^{18}O_2$ 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 Au₇/(TiO₂)₉₃/HOPG after adsorption of 10 L ${}^{18}O_2$ 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 Au₇/(TiO₂)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 Au₇/(TiO₂)₉₃/HOPG after adsorption of 50 L of ${}^{13}C^{16}O$ at 180 K.

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As a last example composite material $Au_8/(TiO_2)_{93}/HOPG$ has been investigated (Figure 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 Au₅/(TiO₂)₉₃/HOPG (approx. 5 %, Figure 7 A 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, Figure 4). The XPS signal for Au 4f_{7/2} is again at bulk gold binding energy after two TPD runs and pure ¹³C¹⁶O dosing (50 L). ¹³C¹⁶O desorption from Au₈/(TiO₂)₉₃/HOPG takes place in two features at 160 K and 175 K which is from the temperature comparable to desorption from sample holder, however, now two peaks are observed while only one is found for the sample holder. ¹³C¹⁶O¹⁸O desorption is observed at 175 K making this composite material a low temperature oxidation catalyst (Figure 7 A and B), again this feature is comparable to desorption from the sample holder (Figure S 4 right). Both runs show comparable CO oxidation activities which can be recovered in the 50 L CO dose (Figure 7 C) 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 absent CO oxidation activities for Au_n (n = 8, 13, 16, 20) on reduced and oxidized TiO₂ thin films as presented in section A. Compared to Au₆ and Au₇, Au₅ and Au₈ (Figure 5, Figure 6; Figure 3 and Figure 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 (TiO₂)₉₃/HOPG might be explained by some sort of CO activation by those two cluster sizes and subsequent diffusion onto 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.



Figure 7. A. ${}^{13}C^{16}O$, ${}^{18}O_2$, and ${}^{13}C^{16}O^{18}O$ desorption from Au₈/(TiO₂)₉₃/HOPG after adsorption of 10 L ${}^{18}O_2$ 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 Au₈/(TiO₂)₉₃/HOPG after adsorption of 10 L ${}^{18}O_2$ 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 Au₈/(TiO₂)₉₃/HOPG after adsorption of 50 L of ${}^{13}C^{16}O$ at 180 K.

The results of section B can be summarized as (*i*) adsorption behavior of $(TiO_2)_{93}/HOPG$ composite material is governed by deposited TiO₂ clusters (see supporting information). (*ii*) TiO₂(110) and $(TiO_2)_{93}$ in this work exhibit properties of oxidized (oxygen-vacancy free) TiO₂ since D₂O desorption at 500 K³³ is absent in both cases (see supporting information). (*iii*) The size-dependence of catalytic activity is preserved when going from single crystal experiments $(TiO_2[110])^{17,18}$ to cluster composite material $(TiO_2)_{93}/HOPG$ as catalyst support. (*iv*) Au₈ is (almost) inactive for CO oxidation on TiO₂ 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 Au₆ and Au₇ clusters show a reaction probability for CO which is significantly higher than for the pristine materials TiO₂(110) and (TiO₂)₉₃/HOPG. The overlap between thin film and cluster support allows to conclude that Au₈ is not an active CO oxidation catalyst (Figure 1 and Figure 7) and thus it is very likely that larger clusters, namely Au_{13, 16, 20}, are inactive as well (Figure 1). This supports the claim that the window of creating catalytically active species towards CO oxidation on TiO₂ materials is equally small as the window observed for gold-catalyzed ester-assisted hydration of alkynes (Au₃₋₅) and bromination of aromatics (Au₇₋ _a) 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 the rational design of high-end "metalefficient" catalysts.

More specifically composite materials of the type Au_n/(TiO₂)₉₃/HOPG are much more efficient in dioxygen activation than Au_n/TiO₂(110) materials reported previously.^{17,18} The CO reaction probability of 35% for Au₆ and Au₇ is traced back to oxygen spillover from gold clusters to the (TiO₂)₉₃/HOPG support. The particular efficiency exhibited might originate from special properties of the TiO₂/HOPG interface. From literature 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 TiO₂ 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 dose 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 TiO₂. However, FTIR studies have shown that Au clusters are stable on TiO₂ thin films up to 300 K (see above)²² and since CO₂ desorption takes place at 240 K stability might be easily achieved.

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The probability for creating CO oxidation-active species on TiO₂ is very small since only Au₆ and Au₇ are catalytically active.