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Active Oxygen

Active Oxygen on a Au/TiO$_2$ Catalyst: Formation, Stability, and CO Oxidation Activity**

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Dedicated to the Fritz Haber Institute on the occasion of its 100th anniversary.

Since their introduction by Haruta,[1] oxide-supported gold catalysts with gold nanoparticles (NPs) of a few nanometers in diameter have attracted enormous interest because of their high activity for various oxidation and reduction reactions,[2] most prominently the CO oxidation reaction.[2–6] Mechanistic details and hence the physical origin of their high activity, however, are still controversial. Focusing on the CO oxidation reaction, a number of different effects and active sites have been proposed as being responsible for the observed high activity,[3,7–11] both from experimental and from theoretical work, but so far agreement has not been reached.[2,4–6]

Most controversial in oxidation reactions are the activation of molecular oxygen, the active site for this reaction step, and the nature of the catalytically active oxygen species present under working conditions.[3,9–15] Stiehl et al. showed that molecularly adsorbed oxygen can be deposited on both Au(111) and Au NPs supported on TiO$_2$(110) at 77 K[16] and, moreover, that this oxygen can directly react with CO.[17] The molecular species desorbs, however, upon heating to 170 K.[17] Carretin et al. identified η^1-superoxide and peroxide species on pure and Fe-doped Au/TiO$_2$ catalysts upon interaction with O$_2$ at 253 K at atmospheric pressure, which disappeared when changing to CO/O$_2$ reaction mixtures, thus implying that these species represent the active oxygen species.[13] Stable, molecularly adsorbed oxygen species, mostly located at the perimeter of the interface between a Au cluster and TiO$_2$ support[10,11,15,18,19] or at low-coordination sites of the Au clusters,[11,20] were also identified in a number of theoretical studies and proposed as active oxygen species, which can react with coadsorbed CO with rather low activation energies via a coadsorption complex. In most cases, the dissociation of adsorbed $O_{2,ad}$ species without interaction with coadsorbed CO was found to proceed with a high activation barrier.

Recently, Kotobuki et al. demonstrated in temporal analysis of products (TAP) reactor measurements that oxygen species active for facile reaction with CO can be deposited on Au/TiO$_2$ catalysts at 80 °C by exposure to thermal O$_2$ pulses and that these species are stable against desorption at that temperature.[14] They showed that the oxygen storage capacity (OSC) and the CO oxidation activity of these catalysts during continuous CO oxidation in a microreactor both scale with the length of the perimeter of the interface between TiO$_2$ support and Au NPs. Accordingly, active oxygen species on sites along the perimeter of the interface between Au NPs and TiO$_2$ support were proposed as active species, both for reaction in the TAP reactor and during continuous reaction at atmospheric pressure in a microreactor.[14] It is important to realize that this oxygen species can hardly be identical with the molecularly adsorbed oxygen species identified in the above experimental and theoretical studies, as the calculated adsorption energies would be too low to stabilize them at 80 °C, and in the work by Stiehl et al., desorption of the molecular O$_2$ species was observed at 170 K.[16,17] Stable active oxygen species and a correlation between OSC and CO oxidation activity were reported also for other oxide-supported Au catalysts,[21] thus indicating that this species, which contrasts most proposals for the CO oxidation mechanism, is a general feature for CO oxidation on oxide-supported Au catalysts.

However, the nature of the active oxygen species could not be clarified in these studies, in particular whether it is a molecular or an atomic species.[22] Because of the very low amount of these oxygen species of about 1 % of the total amount of surface oxygen, spectroscopic identification of this species is hardly possible. Furthermore, it is also open whether these oxygen species are adsorbed at the perimeter or whether they represent surface lattice oxygen adjacent to the Au NPs, which is activated by the presence of the Au NPs.

Herein we report new results which allow us to clearly identify the nature of the active oxygen species and which provide strong evidence for their location on the catalyst surface. This study is based on multipulse measurements performed in a TAP reactor at temperatures between 80 and 400 °C. Prior to each experiment, the Au/TiO$_2$ catalyst was pretreated by in situ calcination in 10 % O$_2$/N$_2$ at 400 °C (O400) to prepare a well-defined, fully oxidized catalyst. Afterwards, the microreactor was evacuated and exposed alternately to sequences of CO/Ar pulses and O$_2$/Ar pulses (1:1, 1×10^{16} molecules per pulse each) to determine the amount of stable adsorbed oxygen that can be reversibly deposited and removed by reaction under these conditions (OSC).[14] This procedure allows us to determine even very low amounts of active oxygen stored on a catalyst's surface very precisely.

Raw data of the signals during the initial reduction and subsequent reoxidation of the Au/TiO$_2$ catalyst after O400 pretreatment (reaction temperature 80 °C) and the subse-

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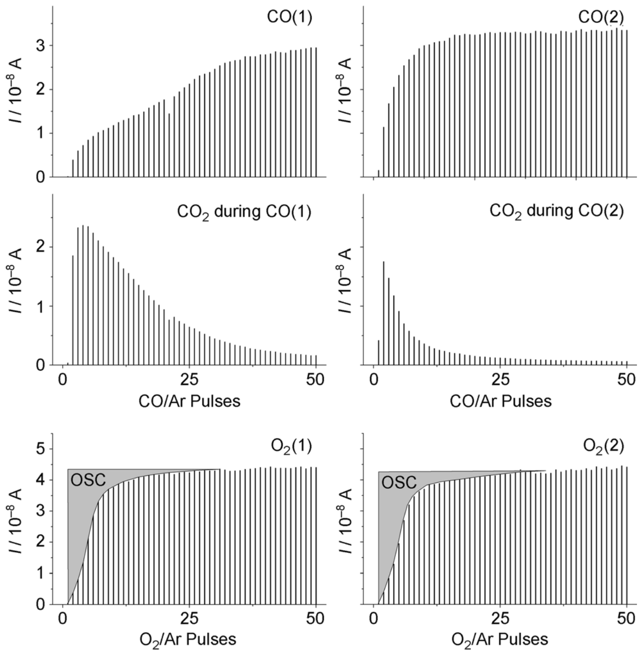

Figure 1. Upper panel: Signals for CO and CO_2 obtained during the first sequence of CO/Ar pulses (CO(1)) over the Au/TiO_2 catalyst at 80 °C directly after pretreatment (O400) and during the second sequence (CO(2)) at 80 °C after oxidation by O_2/Ar pulses. Lower panel: O_2 signal obtained during the first two sequences of O_2/Ar pulses (O_2(1), O_2(2)) at 80 °C over the Au/TiO_2 catalyst after reduction by CO/Ar pulses.

quent cycle are shown in Figure 1. In agreement with previous findings,[14,21] CO_2 is produced solely during the CO/Ar pulses over the oxidized catalyst and not during the subsequent O_2/Ar pulses, thus indicating that CO is reversibly adsorbed under these conditions and desorbs instantaneously after the CO pulse. The consumption of the educt gases, calculated from the missing mass spectrometric intensity compared to that after saturation, is highest at the beginning of each sequence and decreases with ongoing pulse number, until it reaches the zero level and the oxidation state of the catalyst surface is not changed any more. Moreover, the amount of CO consumed equals the amount of CO_2 formed. Hence, there is no measurable accumulation of carbon-containing species on the catalysts surface under these reaction conditions. This is true for all temperatures investigated. Finally, the amount of CO consumed and CO_2 produced is higher during the first sequence of CO pulses, directly after the oxidative pretreatment, than for the subsequent CO/Ar pulse sequence after oxidation by O_2/Ar pulses at 80 °C. In contrast, the amount of oxygen consumed is the same during both oxidation sequences and also in subsequent cycles. The higher consumption of CO during the first sequence was attributed to an irreversible removal of active oxygen from the freshly calcined catalyst.[14]

Quantitative results of the measurements at all temperatures investigated are presented in Figure 2, where the total amounts of CO and O_2 consumed during the first three sequences after O400 pretreatment are plotted. These plots demonstrate that irreversible consumption of oxygen, which

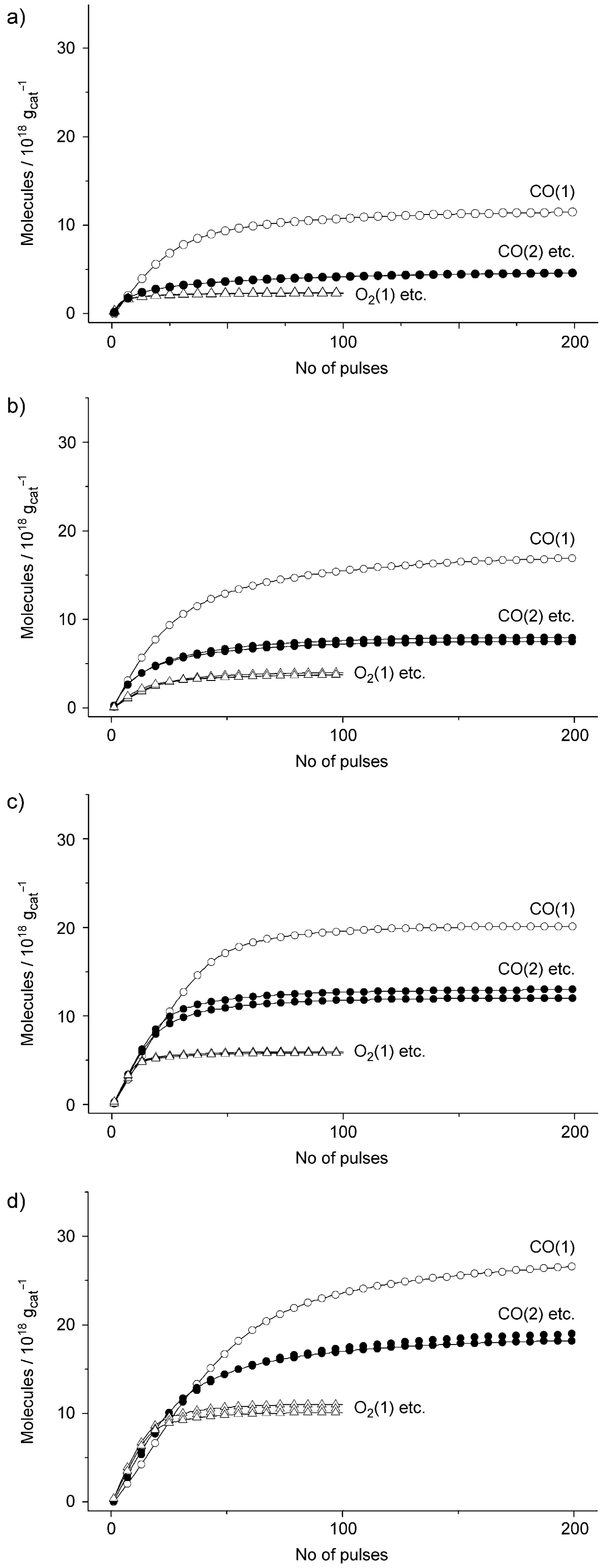

Figure 2. Absolute amount of CO and O_2 consumed during three cycles with alternating reduction and oxidation of the Au/TiO_2 catalyst by 200 CO/Ar pulses and by 100 O_2/Ar pulses, respectively, at a) 80 °C, b) 160 °C, c) 240 °C, and d) 400 °C starting with CO pulses after oxidative pretreatment (O400).

cannot be replenished by O_2/Ar pulses, occurs at all temperatures during the first sequence of CO/Ar pulses directly after O400. Afterwards, the consumption of CO and O_2 is identical, hence the amount of oxygen deposited by O_2 pulses equals the amount of oxygen reacted away during subsequent CO pulses. These processes are therefore fully reversible under present reaction conditions. Only at 400 °C is the uptake of oxygen slightly higher, which is the subject of further investigations. This finding, however, does not affect the conclusions presented herein. Most importantly, the amount of oxygen reversibly deposited and reactively removed depends strongly on the temperature and increases from 80 to 400 °C by a factor of 4.5. The corresponding values for the OSC, from 4.6×10^{18} O atoms g_{cat}^{-1} at 80 °C to 17.8×10^{18} O atoms g_{cat}^{-1} at 400 °C, are listed in Table 1. Despite this increase, the amount of removable surface oxygen is rather small, and even at 400 °C it is just 3.3 % of the entire surface oxygen content calculated from the overall surface area of the TiO_2 support. Moreover, even at 400 °C there is no measurable oxygen removal or deposition on the pure support; the Au NPs are mandatory for the removal and formation of active oxygen on the catalyst surface, as already described for Au/CeO_2[23] and Au/TiO_2.[14] Calculating the local active oxygen coverage at the interface between Au and the TiO_2 support, we obtain values of 0.89 at 80 °C, 1.95 at 160 °C, 2.46 at 240 °C, and 3.65 at 400 °C (relative to the total number of surface lattice oxygen atoms at the perimeter). The value obtained at 80 °C agrees closely with previous findings in our laboratory.[14] The increase of the OSC with higher temperature can be explained by a thermally activated increasing mobility of oxygen and oxygen vacancies at the perimeter of the Au NPs, which allows the reactive removal and replenishment of oxygen species not directly located at the perimeter sites.

Table 1: Irreversible and reversible (OSC) loss of oxygen in the reduced state of the Au/TiO_2 catalyst, after CO pulses at different temperatures, relative to the oxygen content of the fully oxidized catalyst after oxidative pretreatment (O400).

	80 °C	160 °C	240 °C	400 °C
irreversible loss of oxygen /10^{18} O atoms g_{cat}^{-1}	6.7	8.4	7.8	8.9
reversible loss of oxygen/ oxygen storage capacity (OSC) /10^{18} O atoms g_{cat}^{-1}	4.6	10.0	12.6	18.7
oxygen storage capacity (OSC)[a] /O atoms/perimeter site Au-TiO_2	0.89	1.95	2.46	3.65
oxygen storage capacity (OSC)[b] /O atoms/surface oxygen	0.008	0.018	0.023	0.033

[a] Assuming half-spherical particles.
[b] Assuming 1×10^{15} O atoms cm^{-2}.

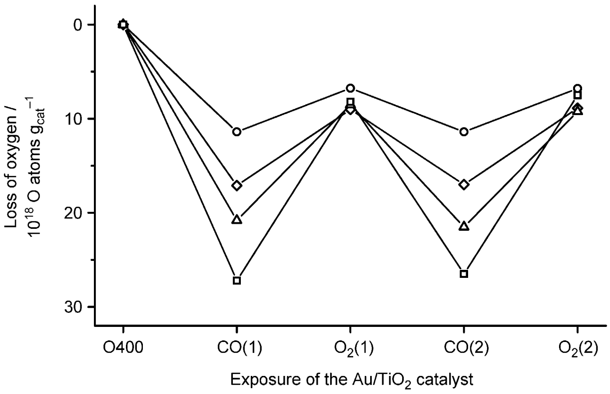

Figure 3. Loss of oxygen relative to the oxygen content after oxidative pretreatment (O400) after reduction by CO/Ar pulses (CO(1)), after reoxidation by O_2/Ar pulses (O_2(1)), and after second sequences of CO (CO(2)) and O_2 (O_2(2)) pulses at different temperatures: 80 (○), 160 (◇), 240 (△), and 400 °C (□).

Figure 3 shows the accumulated oxygen loss and oxygen redeposition during the reduction and oxidation sequences, starting with a fully oxidized surface after O400. The amount of oxygen removed from the catalysts surface in the first reduction sequence increases with higher temperature, thus indicating that the removal of oxygen is an activated process. Subsequent reoxidation of the reduced catalysts with O_2 pulses raises the oxygen content again. Interestingly, the total amount of active oxygen present on the catalyst surface after the first reduction–reoxidation cycle depends very little on the temperature, as will be discussed below. Compared to the initial state after O400 treatment, the active oxygen coverage at this point is somewhat lower, with the difference reflecting the irreversible oxygen removal. In the second and subsequent cycles, this general behavior of reduction to a temperature-dependent (but for that temperature constant) active oxygen coverage and reoxidation to a common, temperature-independent value is maintained.

The pulse-deposited oxygen species is highly stable even at temperatures as high as 400 °C: pulsing CO not directly (with a time delay of 5 s) after the O_2 pulses at 400 °C, but with a time delay of one hour between the last O_2 and the first CO pulse, we find exactly the same amount of CO consumed and CO_2 formed as during CO and O_2 pulse sequences without an additional time delay between O_2 and CO pulses at 400 °C. Hence, under these conditions there is no measurable desorption of the active oxygen species within one hour.

From the above data, we derive the following conclusions on the nature of the active oxygen species for CO oxidation on Au/TiO_2 catalysts:

1. The high stability of the active oxygen species (up to at least 400 °C) is incompatible with molecularly adsorbed oxygen. Therefore, we propose that the active oxygen species is an atomic species (O_{act}), which is formed by adsorption, activation, and dissociation of molecular oxygen on the previously formed active perimeter sites on the catalyst surface.
2. The fact that thermal activation increases the amount of O_{act} depletion during reduction, but not the absolute level of O_{act} present on the surface after reoxidation by O_2 pulses, is interpreted in terms of active oxygen removal from surface lattice sites at the perimeter of the Au NPs; the resulting vacancies can subsequently be replenished upon O_2 pulse deposition. At 80 °C, only sites directly adjacent to the perimeter of the Au NPs can be accessed,

while at higher temperatures sites slightly further away can also be depleted and replenished, indicative of activated migration of surface oxygen and oxygen vacancies to the interface sites. This step is responsible for the temperature dependency of the OSC.

3. Deposition of reversible O_{act} is fast and not or only slightly activated, pointing to facile dissociation of molecularly adsorbed O_2 precursors to O_{act} species on the active sites. In contrast, the irreversible active oxygen species is formed only during prolonged exposure at elevated temperature (O400). Its formation is therefore slow and activated and it is likely to be different in nature from the "reversible O_{act}" species identified herein; for example, it could be a gold surface oxide.[24,25] Under reaction conditions, only the reversible O_{act} is present on the surface.
4. Based on previous TAP measurements,[14,21] the active oxygen species detected in the pulse measurements is identical with the active oxygen species in reaction experiments under atmospheric pressure.
5. The formation and decomposition of stable carbon-containing surface species such as surface carbonates is negligible under present reaction conditions compared to active oxygen storage and depletion.
6. Au NPs have two roles in the CO oxidation reaction: First, they accumulate adsorbed CO, and second, they activate surface lattice oxygen at the Au-TiO_2 perimeter sites. In the absence of Au NPs, surface oxygen is not reactive under "normal" reaction conditions.

These observations result in a reaction mechanism for CO oxidation on Au/TiO_2 catalysts at $T \geq 80\,^{\circ}C$, which is illustrated schematically in Figure 4. It involves a) CO adsorption on Au NPs, b) reaction with activated surface lattice oxygen species at the perimeter of the Au-TiO_2 interface (interface sites), and c) replenishment of these sites by dissociative adsorption of O_2 at them. At higher temperatures (> 80 °C), migration of surface lattice oxygen and surface oxygen vacancies also gives access to neighboring oxygen surface lattice sites. During reaction under "normal" reaction conditions, only the perimeter sites are involved. This mechanism, which is close to a Mars–van Krevelen mechanism but involves surface lattice oxygen at or close to perimeter sites only ("Au-assisted Mars–van Krevelen mechanism"), is in contrast to most previous mechanistic predictions[9–11,13,15,18–20] in that it involves a highly stable active oxygen species and facile dissociation of the molecular $O_{2,ad}$, without assistance by coadsorbed CO_{ad} via a $CO_{ad}\cdot O_{2,ad}$ complex. At lower temperatures, however, a transition to an alternative reaction pathway proceeding via a more weakly bound, molecularly adsorbed $O_{2,ad}$ species may occur, but for reaction at "normal" conditions, the above reaction pathway is dominant. It would be interesting to test this reaction pathway in calculations, where to our knowledge it has not been included to date. A mechanism involving formation and decomposition of surface carbonates can be ruled out as the dominant reaction channel under present, strictly dry reaction conditions. This may be different in the presence of adsorbed water or larger amounts of OH groups, which were found to affect the reaction kinetics and possibly also the reaction mechanism.[26] This question is the topic of ongoing studies in our laboratory.

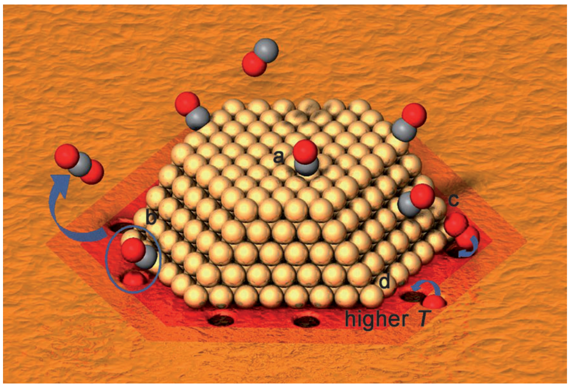

Figure 4. Schematic description of the pathway for CO oxidation on Au/TiO_2 catalysts at $T \geq 80\,^{\circ}C$, involving a) CO adsorption on Au NPs, b) reaction with activated surface lattice oxygen species at the perimeter of the Au-TiO_2 interface (interface sites), and c) replenishment of these sites by dissociative adsorption of O_2 at the perimeter sites. d) At higher temperatures (> 80 °C), migration of surface lattice oxygen and surface oxygen vacancies also gives access to neighboring surface lattice oxygen. During reaction under "normal" reaction conditions, only the perimeter sites are involved.

In summary, we have shown that the active oxygen species for CO oxidation is a highly stable atomic oxygen species, whose formation is facile and only slightly activated, in contrast to previous proposals of a weakly bound molecular oxygen species. Most likely, the active oxygen species is surface lattice oxygen at the perimeter of Au NPs, leading to a Au-assisted Mars–van Krevelen reaction mechanism.

Although demonstrated here explicitly only for Au/TiO_2, a similar reaction mechanism is also expected for other oxide-supported Au catalysts, at least for those on reducible oxides, considering the close correlation between OSC and reactivity on various Au catalysts derived recently.[21] In that sense, the present work represents an important step towards the mechanistic understanding of the CO oxidation reaction on oxide-supported Au catalysts in general.

Experimental Section

The pulse experiments were performed in a home-built TAP reactor, which has been described in reference [27]. Piezoelectric pulse valves were used to generate gas pulses of typically 1×10^{16} molecules per pulse, which were directed into the quartz tube microreactor. After passing through the catalyst bed, the effluent gases were analyzed by a quadrupole mass spectrometer located in the analysis chamber. For in situ conditioning at atmospheric pressure, the reactor can also be separated from the analysis chamber and connected directly to an adjustable roughing pump. For experimental details regarding the catalyst preparation and characterization and the TAP reactor measurements, see the Supporting Information.

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