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Formation and removal of active oxygen species for the non-catalytic CO oxidation on Au/TiO₂ catalysts

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ABSTRACT

Applying quantitative temporal analysis of products reactor measurements, we studied the reactive removal of active oxygen present on Au/TiO₂ catalysts after calcination at elevated temperatures (400 °C) by CO pulses and its replenishment by O₂ pulses at 80 °C, focusing on the nature of the active oxygen species. In contrast to previous studies, which mainly focused on and clarified the nature of the active oxygen species for the catalytic CO oxidation, which is reversibly formed and replenished under typical reaction conditions, this study demonstrates that directly after calcination an additional oxygen species is present. This species is also active for the CO oxidation, but it is not or only very little formed under typical reaction conditions. Implications of these results on the mechanistic understanding of the CO oxidation on Au/TiO₂, in particular on the role of different active oxygen species, will be discussed.

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1. Introduction

Highly dispersed Au in form of nanoparticles (NPs), which are deposited on a metal oxide support, exhibits very high activities for several oxidation and reduction reactions [1]. The most prominent and by far most often investigated reaction over supported Au catalysts is the CO oxidation reaction, which is catalyzed already at very low temperatures [2–6]. Regarding the underlying reaction mechanism of the CO oxidation reaction over supported Au catalysts, there has been general agreement for a long time that mainly CO adsorbed on the surface of the Au particles is oxidized to CO₂ under typical reaction conditions, above room temperature [7–9]. At room temperature and below, CO is increasingly adsorbed also on Ti⁴⁺ sites of the support, and both CO_{ad} species are likely to contribute to the reaction. Finally, for very low temperatures (≤ 130 K), CO species adsorbed on the Au nanoparticles are hindered to reach

the active perimeter sites due to slow surface diffusion, and the reaction is dominated by CO_{ad} adsorbed on the TiO₂ support, which is still sufficiently mobile to reach these sites [10,11]. In contrast to the CO adsorption, the adsorption and activation of molecular oxygen, which was often proposed to represent the rate limiting step in the CO oxidation [7,12–14], and the nature of the active site for this have long been discussed controversially. Here it was proposed that the catalytically active oxygen species for CO oxidation may be either (1) oxygen adsorbed on Au (atomic or molecular) [15–18], (2) oxygen adsorbed on the support, most probably located at perimeter sites at the interface between gold particles and support [19–21], or (3) lattice oxygen of the metal oxide support, which is possible for reducible metal oxides only [22–24]. The latter indicates a Mars-van Krevelen mechanism for CO oxidation, as it had been proposed also by Grisel et al. [25] and Gluhoi et al. [26] earlier. Note that this classification is valid for CO oxidation under strictly dry

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reaction conditions only, in the absence of water in the system. In the presence of water traces, one additionally has to consider effects of adsorbed water and hydroxyl groups, which may lead to fundamental other reaction pathways, involving adsorbed water/hydroxyl groups as the active oxygen species for CO oxidation or as a co-catalyst for oxygen activation [6,27].

Under typical reaction conditions (temperatures of 80 °C and higher), and in the absence of water, we recently demonstrated by multi-pulse temporal analysis of products (TAP) reactor measurements that the CO oxidation on Au/TiO₂ catalysts proceeds via the reactive removal of TiO₂ surface lattice oxygen (O_{act}) by CO at the perimeter of the interface between Au nanoparticles (NPs) and the oxide support, which accordingly represent the active sites [23,28]. This results in the formation of the product CO₂ and surface lattice oxygen vacancies (V_{latt}) at these perimeter sites, which are subsequently replenished by reaction with O₂ from the gas phase:

It was further concluded that (1) the activated removal of these active oxygen species represents the rate limiting step in the CO oxidation reaction, and that (2) this mechanism, which was introduced as Au-assisted Mars-van Krevelen mechanism, likely dominates the CO oxidation reaction also on other Au catalysts supported by reducible oxides such as ZnO, ZrO₂, or CeO₂ [22,28]. In the meantime this was confirmed by numerous experimental studies as well as by theory on different reducible metal oxide supported Au catalysts [24,29–32].

Moreover, we additionally demonstrated in our previous studies that (1) the active oxygen species for continuous CO oxidation (also called ‘reversible oxygen’, O_{act}) is stable towards desorption up to at least 400 °C, and that (2) during calcination of the catalyst at 400 °C in 10% O₂/balance N₂ another type of oxygen is formed (so-called ‘irreversible oxygen’, denoted as O_{irr}), which is also reactive towards CO, but which is not regenerated by O₂ pulses subsequent to its reactive removal by CO pulsing, neither at 80 °C nor at 400 °C [22,23]. Here we want to note that the term ‘irreversible’ is related to the reaction conditions. In the present case the ‘irreversible’ consumption of oxygen directly after O400 simply means that this species cannot be replenished by subsequent O₂/Ar pulses, in contrast to the active oxygen (O_{act}) species mentioned above. Correspondingly, a new treatment of the catalyst at elevated temperatures and atmospheric pressure (O400) is likely to result in the regeneration also of the O_{irr} species. Considering that this O_{irr} species is active for the CO₂ formation upon exposure to CO, but cannot be replenished by O₂ under reaction conditions, its removal represents a non-catalytic CO oxidation process, which does not contribute to the continuous CO₂ formation as detected in kinetic measurements under typical reaction conditions. Such kind of irreversible oxygen removal is also comparable to results from Soares et al. [33,34], who reported the observation of a non-catalytic oxygen removal/CO₂ production upon exposure of freshly calcined Au/TiO₂ catalysts to CO [33], and equally also for Au₂O₃ and Au(OH)₃ [34].

The thermal stability of the active oxygen species for continuous CO oxidation (O_{act}) as well as the nature of the irreversibly removed oxygen species, however, remained open. Moreover, also the physical reason for the formation of the latter species is still unresolved. Since it is only formed during O400 (10% O₂/N₂ at atmospheric pressure), but not during O₂/Ar pulses at 400 °C, it is specifically interesting to test whether its formation during calcination is simply due to the larger exposure during calcination as compared to O₂ pulsing, or whether it is caused by the higher O₂ partial pressure. These questions are addressed in the present study by quantitative TAP reactor and temperature programmed desorption (TPD) measurements, which focus on the formation of ‘irreversible oxygen’ on Au/TiO₂ by multi-pulse experiments and its thermal stability, respectively. Additionally, we also determined and compared the formation and removal of both oxygen species by alternate exposure to multiple CO/Ar and O₂/Ar pulses, respectively, which enable us to identify their relative contributions for the CO₂ formation under typical reaction conditions. Based on these results the nature of the active oxygen species present under CO oxidation reaction conditions on Au/TiO₂ will be discussed.

2. Experimental

2.1. Catalyst preparation and characterization

The Au/TiO₂ catalyst was prepared via a deposition-precipitation method, using commercial, non-porous TiO₂ as support material (P25 from Degussa, surface area 56 m²/g) [35,36]. To exclude subsequent modifications of the catalysts with time, the samples were stored in the dark in a refrigerator [37,38]. *In-situ* pre-treatment of this catalyst prior to all temporal analysis of products (TAP) reactor measurements included drying of the sample at 100 °C for 15 h, either in a flow of Ar or under vacuum conditions, and subsequent calcination in 10% O₂/N₂ at 400 °C for 30 min (O400). This procedure resulted in well defined, fully oxidized catalysts [23]. Note that the catalytic activity of a very similar Au/TiO₂ catalyst for the CO oxidation at atmospheric pressure and its deactivation behavior have been described in detail previously [39].

The Au loading of the resulting catalyst was 2.6 wt% with a mean Au particle size of 3.0 ± 0.7 nm, measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) and transmission electron microscopy (TEM), respectively. Representative TEM images and the corresponding particle size distributions of the Au/TiO₂ catalyst directly after calcination as well as after calcination and subsequent performance of multi-pulse experiments at 400 °C (the highest temperature used in this study) are shown in Fig. 1. Quantitative evaluation of the particle size after reaction revealed that the particle size as well as the particle size distribution stays essentially unchanged, being 3.0 ± 0.8 nm after the multi-pulse experiments. Hence, the Au particles are stable under the present reaction conditions, and up to temperatures of 400 °C no Au particle sintering is observed.

Fig. 1. Representative TEM images and corresponding Au particle size distributions of the Au/TiO₂ catalyst. (a) On a freshly prepared sample, directly after calcination in 10% O₂/N₂ at 400 °C for 30 min (O400); (b) after O400 and subsequent multi-pulse experiments performed at a reaction temperature of 400 °C.

2.2. Temporal analysis of products (TAP)

Pulse experiments as well as TPD measurements have been performed in a home-built TAP reactor [40]. In general, this consists of a gas mixing unit, two piezo-electrically driven pulse valves and a tubular quartz glass micro reactor connected to an ultrahigh vacuum system (analysis chamber). Additionally, the reactor can also be separated from the analysis chamber by a home-developed differentially pumped gate valve. This enables us to connect it directly to an adjustable roughing pump for *in situ* conditioning of the catalyst under continuous flow conditions at atmospheric pressure as described above (O400). After this *in situ* calcination at 400 °C the catalyst was cooled to the reaction temperature in a stream of Ar (80 °C for all measurements described here). Once the desired reaction temperature was reached, the reactor was evacuated and directly connected to the analysis chamber via the differentially pumped gate valve. Further details are described in Ref. [40].

In all experiments described here, about 10.0 mg of the Au/TiO₂ catalyst were used. This was diluted 1:1 with quartz powder ('gebaflot 010' from Dorfner GmbH, grain size 100–200 μm), which is inactive for CO oxidation in the temperature range investigated, and packed between two layers of quartz particles. The resulting three-zone catalyst bed was fixed in the center of the tubular micro reactor by metal sieves.

2.2.1. Pulse experiments

Using piezo-electric pulse valves, gas pulses of typically 1×10^{16} molecules per pulse were generated and directed into the quartz tube micro reactor (90 mm long, 4.0 mm inner diameter), which contains the fixed catalyst bed. After passing through the catalyst bed and the differentially pumped gate valve, the effluent gases are analyzed by a quadrupole mass spectrometer (Pfeiffer Vacuum, QMG 700) located inside the analysis chamber (base pressure of $< 1 \times 10^{-9}$ mbar).

To reactively remove or replenish active oxygen species from the catalyst surface, the Au/TiO₂ powder catalyst was

alternately exposed to sequences of multiple CO/Ar and O₂/Ar pulses, respectively, with a time distance of 5 s between individual pulses. Note that for quantification on an absolute scale each pulse contained 50% Ar as an internal standard, which enables the evaluation of the overall number of molecules for every single pulse. During these alternate pulse sequences it was also ensured for every single sequence that there was no more CO consumption/CO₂ formation or O₂ consumption before changing from CO/Ar to O₂/Ar pulses or the other way around, respectively. Hence, using this approach we can calculate the maximum amount of oxygen that can be removed (upon interaction with CO) or replenished (upon the subsequent exposure to O₂) from the sum of CO or O₂ consumption within each pulse of a sequence. The latter was calculated by comparing the intensity measured by the mass spectrometer during the initial pulses, during which the catalyst state is altered, to that measured during the last pulses of a sequence and, hence, after saturation. The formation of the product CO₂, in contrast, can be detected directly. To distinguish between irreversible and reversible removal of oxygen by CO, this procedure was repeated at least three times on all samples.

2.2.2. TPD

The thermal stability of adspecies present on the Au/TiO₂ catalyst surface after different treatments, in particular oxygen, was investigated by TPD measurements under vacuum conditions, which were also performed in the TAP reactor. For all these measurements we increased the temperature of the catalyst bed with a heating rate of 25 °C/min without an additional carrier gas. The effluent gases arising from decomposition and/or desorption of the surface species were detected directly by the mass spectrometer located in the analysis chamber.

3. Results and discussion

In Fig. 2 we present typical responses recorded by the mass spectrometer during alternate exposure of the Au/TiO₂ catalyst to several sequences of CO/Ar and O₂/Ar pulses directly after calcination by O400. The usual reaction behavior during these measurements, which has already been described several times in previous studies on Au/TiO₂ [22,23,41], can be summarized as follows.

- (1) The consumption of CO and O₂ is always highest in the beginning of the corresponding sequence, during the first pulses, and decreases with ongoing pulse number until it is below the detection limit after about 200 CO/Ar and 100 O₂/Ar pulses, respectively. At this point, all of the available oxygen is removed or replenished. Note that for clarity only the first 50 pulses of each sequence are shown in Fig. 2.
- (2) CO₂ formation is observed only during CO pulses, but not during O₂ pulses. Considering that there is no gas phase oxygen present during CO/Ar pulses, this demonstrates that CO oxidation can occur via reaction of oxygen species already present on the catalyst after calcination, namely TiO₂ surface lattice oxygen located at the perimeter of the Au-TiO₂ interface. Furthermore, we can also conclude from

Fig. 2. Signals measured by the mass spectrometer during the first two cycles with alternate reduction (upper panels: CO and CO₂) and re-oxidation (lower panels: O₂) of the Au/TiO₂ catalyst at 80 °C by 200 CO/Ar pulses and by 100 O₂/Ar pulses, respectively, directly after calcination (O400).

this finding that CO is not stable adsorbed on Au/TiO₂ under present reaction conditions (80 °C), and desorbs instantaneously after the CO pulse.

- (3) The absolute amount of CO consumed/CO₂ formed during the first pulse sequence directly after calcination is higher than that in the following cycles, where it is essentially constant. Here one should note that in all sequences the amount of CO₂ formed equals the amount of CO consumed. Hence, there is no measurable accumulation of carbon containing species on the catalyst surface under present reaction conditions.
- (4) The oxygen consumption, in contrast, is essentially identical during all O₂/Ar pulse sequences.

The total (accumulated) amounts of CO and O₂ consumption during the first three cycles of CO/Ar and O₂/Ar on a freshly calcined Au/TiO₂ catalyst are displayed in Fig. 3. During the first sequence of CO/Ar pulses, 11.3×10^{16} molecules CO are consumed, resulting in the formation of an equal amount of CO₂ molecules. This corresponds to an oxygen removal from the freshly calcined catalyst surface of 11.3×10^{18} O atoms·g_{cat}⁻¹. This is significantly higher than the CO consumption / active oxygen removal in the second and subsequent CO/Ar pulse sequence, which amounts to 4.6×10^{18} O atoms·g_{cat}⁻¹. The oxygen consumption during all O₂/Ar pulse sequences is accord-

ingly 2.3×10^{16} O₂ molecules, corresponding to 4.6×10^{18} O atoms·g_{cat}⁻¹. Hence, the absolute amount of active oxygen that can be formed and removed reversibly under present reaction conditions is 4.6×10^{18} O atoms·g_{cat}⁻¹ (Table 1). This is defined as the catalysts oxygen storage capacity (OSC). As discussed in

Fig. 3. Absolute, accumulated amounts of CO and O₂ consumed during three cycles with alternate reduction and re-oxidation of the Au/TiO₂ catalyst by 200 CO/Ar pulses and by 100 O₂/Ar pulses, respectively, at 80 °C directly after calcination (O400).

Table 1

Absolute amounts of catalytic (O_{act}) and non-catalytic (O_{irr}) active oxygen species present on Au/TiO₂ at 80 °C after different treatments.

Catalyst treatment	Absolute amount (10^{18} O atoms·g _{cat} ⁻¹)	
	O_{act}	O_{irr}
Calcination (O400)	4.6	6.7
100 O ₂ /Ar pulses at 80 °C (subsequent to CO pulses at 80 °C)	4.6	<0.1
TPD (up to 600 °C) after O400	1.2	<0.1
6000 O ₂ /Ar pulses at 400 °C (subsequent to CO pulses at 80 °C)	2.3	2.5

previous studies on the nature of this so-called ‘reversible oxygen’, this is assigned to TiO₂ surface lattice oxygen located at the perimeter at the Au–TiO₂ interface, which was proposed to represent also the active oxygen species for the continuous CO oxidation, in the simultaneous presence of CO and O₂ in the gas phase [22,23,28].

Directly after calcination, however, there is a higher amount of active oxygen present on the catalyst. Based on the difference between CO consumption/CO₂ formation in the first and in the following CO/Ar pulse sequences, this amounts to 6.7×10^{18} O atoms·g_{cat}⁻¹ (Table 1). Since this species is not replenished during subsequent exposure to O₂/Ar pulses (O_{irr}), it has to be different in nature from the reversibly removed O_{act} species. From previous studies it is also known that its amount is largely independent of the temperature at which it is removed by CO: Multi-pulse experiments between 80 and 400 °C revealed that the amount of irreversible oxygen removal after calcination at 400 °C was always about $(7.8 \pm 1.1) \times 10^{18}$ O atoms·g_{cat}⁻¹, although the amount of O_{act} increases by a factor of about 4 in that temperature range [23].

To gain insight into the thermal stability of the oxygen species on Au/TiO₂ directly after calcination, where both O_{act} and O_{irr} are present on the surface, and thus to get a first idea about the nature of the O_{irr} species, we performed a TPD measurement. Here the catalyst was first pre-treated in oxygen at atmospheric pressure (O400), afterwards cooled down to 80 °C in a stream of Ar, and subsequently evacuated. The O₂ desorption signal recorded by the mass spectrometer during the following TPD run (25 °C/min, up to 600 °C) is shown in Fig. 4. Obviously, there is evolution of molecular O₂ in a temperature range from 400 to 550 °C, with a maximum for O₂ desorption at about 470 °C (note that there was no atomic oxygen detected in the gas phase). This O₂ species may arise either from desorption of molecularly adsorbed oxygen or from recombinative desorption of atomically adsorbed oxygen species. The latter was also detected for Au single crystal surfaces by Sault et al. [42] during TPD measurements after adsorption of atomic oxygen, which was deposited by a hot filament technique on a Au(110) surface. Depending on the oxygen coverage (0.06–0.95 monolayers of atomic oxygen), they detected recombinative oxygen desorption peaks at about 300–320 °C. Additionally, Bondzie et al. [43] could detect the desorption of molecular O₂

Fig. 4. Signals of oxygen (a) and water (b) during TPD measurements from 80 to 600 °C directly after O400 (red) and after O400 and subsequent multi-pulse experiments (reduction by CO pulses and re-oxidation by O₂ pulses; green) at 80 °C.

from Au particles supported on TiO₂(110) at temperatures between 270 and 470 °C, depending on the Au island thickness, also after adsorption of atomic oxygen species by applying hot filament techniques. The higher desorption temperature of oxygen from Au nanoparticles (in Au/TiO₂) compared to desorption from Au single crystal surfaces directly reflects a stronger adsorption of oxygen adatoms on small Au nanoparticles [44].

Another possibility for the origin of oxygen desorption that has to be considered is the reaction of hydroxyl groups to form gaseous water and atomically adsorbed oxygen during the TPD, where the latter may subsequently recombine and desorb. This reaction was previously demonstrated to occur on extended Au surfaces (Au(997)) at temperatures as low as 105 K [45]. To check for this possibility, we also recorded the O₂ signal during a TPD measurement performed after performing multi-pulse experiments at 80 °C, which is also shown in Fig. 4. Here the catalyst was also first pre-treated by calcination (O400), but additionally exposed to alternate sequences of CO/Ar and O₂/Ar pulses at 80 °C before starting the TPD. Although O₂ was pulsed last and, hence, directly prior to the TPD measurement, there is obviously no O₂ desorption at all up to 600 °C. This clearly demonstrates that the oxygen species detected in the previous TPD measurement directly after O400 treatment has been reactively removed by CO/Ar pulses during the multi-pulse experiments and could not be replenished by O₂ pulsing. There is, however, still desorption of significant amounts of water (Fig. 4(b)). For this reason we consider the formation of atomically adsorbed oxygen atoms and their subsequent desorption in form of molecular oxygen (after recombination) due to the reaction of hydroxyl groups to be unlikely in the present case. Moreover, the absence of a desorption peak in the

temperature range up to 600 °C indicates that the reversible oxygen species (O_{act}) is thermally stable against desorption at least up to that temperature. Based on the oxygen titration TAP measurements, the amount of the latter species should be at least equivalent to that of the irreversible oxygen species and, hence, should result in a desorption peak of comparable intensity. Additionally, this also shows that the O_{irr} species is formed only during O400, and not during the re-oxidation of the Au/TiO₂ catalyst by O₂/Ar pulses at 80 °C. The reason for this difference may be related either to the higher amount of O₂ to which the catalyst was exposed during pre-treatment at atmospheric pressure and/or to the higher temperature during pre-treatment (80 vs. 400 °C).

Before dealing with this question, which will be discussed in detail below, we first want to present and discuss the results of multi-pulse experiments performed at 80 °C directly after heating the freshly calcined catalyst to 600 °C and, hence, after thermal removal of the O_{irr} species (Fig. 4). The resulting oxygen and CO consumptions during three multi-pulse sequences after cooling the catalyst down to 80 °C in vacuum after the TPD measurement are plotted in Fig. 5. Similar to the freshly calcined catalyst (Figs. 2 and 3), we again started with a sequence of CO/Ar pulses, followed by re-oxidation of the catalyst with O₂/Ar pulses. Compared to the results obtained in multi-pulse experiments directly after O400 there are several distinct differences: (1) The amount of CO consumed during the first sequence CO/Ar pulses, and accordingly also the amount of CO₂ produced, is not higher than that consumed in subsequent sequences, as it was detected in the measurements directly after O400, but lower than in the following sequences. (2) The amount of oxygen consumed within each sequence is not the same every time, but distinctly higher during the first sequence of O₂/Ar pulses as compared to the following ones. Remarkably, the initial oxygen consumption during the first sequence even exceeds that of the (equivalent) CO consumption in all (previous and following) sequences. (3) After the first sequences of CO/Ar and O₂/Ar pulses, there is again stoichio-

Fig. 5. Absolute, accumulated amounts of CO and O₂ consumed during three cycles with alternate reduction and re-oxidation of the Au/TiO₂ catalyst by 200 CO/Ar pulses and by 100 O₂/Ar pulses, respectively, at 80 °C after O400 and subsequent heating of the catalyst up to 600 °C during the TPD measurement illustrated in Fig. 4.

metric CO and O₂ consumption in two consecutive sequences, but the overall oxygen storage capacity at 80 °C is almost a factor of four lower after the TPD measurement compared to the OSC at 80 °C measured directly after O400 calcination (1.2×10^{18} O atoms·g_{cat}⁻¹ compared to 4.6×10^{18} O atoms·g_{cat}⁻¹, respectively, see Table 1). Considering that the OSC increases about linearly with decreasing Au-TiO₂ interface perimeter length and, hence, with increasing Au particle size [46,47], we suggest that the lower OSC originates from Au particle sintering due to the treatment of the Au/TiO₂ catalyst at higher temperatures during the previous TPD measurement (up to 600 °C). This, however, is not the only reason for the decreased OSC compared to that measured directly after the O400 calcination of the catalyst. In addition, this results from water desorption during the TPD measurement, which was detected over almost the entire temperature range from 120–600 °C, with a maximum at around 230 °C (Fig. 4), and thus lowers the water content on the catalysts surface during subsequent multi-pulse experiments. Recent results in our laboratory clearly showed a distinct influence of the amount of adsorbed water and/or OH_{ad} species present on the surface of a Au/TiO₂ catalyst on the OSC, with an increasing OSC with increasing amount of adsorbed water/OH_{ad} species [47,48]. The exact origin of the increased OSC is, however, still unresolved and topic of ongoing investigations.

Moreover, water desorption during the TPD run is proposed to be responsible also for the higher oxygen uptake during the first sequence of O₂/Ar pulses after the TPD run. Here we assume that water desorption results in the formation of oxygen vacancies [49] which remain on the catalyst surface after the TPD measurement and are subsequently replenished by oxygen from the gas phase during the first sequence of O₂/Ar pulses. Considering that water may desorb from the entire TiO₂ surface during the TPD run and not just from sites which are active for the CO oxidation, this process does not necessarily result in the formation of active oxygen species only (at the perimeter of the Au-TiO₂ interface). This also explains why the oxygen consumption during the first sequence after the TPD is remarkably higher than the removal of active oxygen in the previous and following sequences by CO/Ar pulses.

Regarding the nature of the irreversible deposited oxygen species during O400, the most remarkable result is the lower CO consumption in the first sequence of CO/Ar pulses after heating the catalyst to 600 °C as compared to the following sequences. This is in clear contrast to the results obtained in multi-pulse experiments directly after O400 (Fig. 3), and clearly indicates that after the first TPD run there is no longer irreversible oxygen on the catalyst surface. Accordingly, there is no longer a non-catalytic CO₂ formation. Hence, one can directly conclude that the O₂ signal detected during a TPD measurement directly after calcination (O400) originates indeed from the O_{irr} species formed during the initial O400 calcination. It should be noted that during a blank experiment on the pure TiO₂ support, which was pre-treated in the same way as the catalyst sample (O400), no desorption of oxygen was detected in a TPD measurement over the whole temperature range up to 600 °C. The finding that the presence of Au nanoparticles on the

catalyst surface is indeed mandatory for the formation of the O_{irr} species during calcination clearly demonstrates that this species is formed on the surface of the Au NPs. From the high thermal stability of this species, with a desorption temperature of above 400 °C, we further conclude that this is also an atomic oxygen species, similar to the reversible oxygen species. A participation of hydroxyl groups, however, can be excluded from these results, since these are not stable adsorbed on Au at such elevated temperatures [45]. Most likely it corresponds to atomically adsorbed oxygen on the Au nanoparticles or traces of gold surface oxide formed during the pre-treatment process. The presence of small amounts of stable adsorbed oxygen on Au or of oxidic gold species after annealing of highly dispersed, oxide supported Au catalysts in oxygen atmosphere at high temperatures was also shown by Fu et al. [50], Venkov et al. [51,52], and Miller et al. [53]. Fu et al. [50] presented SIMS spectra of supported Au/ Al_2O_3 and Au/ TiO_2 catalysts after calcination at 350 °C, which directly indicated the existence of chemisorbed oxygen on gold NPs or a partially oxidized Au surface, although in XPS measurements only metallic Au was detected. This discrepancy was explained by the very low amount of the chemisorbed oxygen on Au/partial oxidized Au and the higher detection sensitivity of TOF-SIMS. Venkov et al. [51] detected absorption bands at about 2170 and 2140 cm^{-1} in DRIFTS measurements during CO adsorption on Au/ Al_2O_3 at 100 K after activation of the sample at 400 °C in 13.3 kPa O_2 , which they assigned to CO adsorbed on positively charged Au species (Au^+-CO). This assignment was based on the observation that such bands were not observed upon CO adsorption (at 100 K) on a catalyst which was activated in vacuum rather than in O_2 at 400 °C. Accordingly, they concluded that the Au surface was (partly) oxidized by O_2 at 400 °C [51]. Similar observations they also made after exposing a Au/ TiO_2 catalyst to a $NO + O_2$ mixture at $T \geq 300$ °C. Here it was additionally demonstrated that cationic Au species are easily reduced to metallic Au upon interaction with CO even at room temperature [52]. Moreover, Miller et al. [53] demonstrated by EXAFS spectroscopy the formation of Au surface oxides on metallic Au NPs upon oxidation in air at 225 °C, up to 10%–15% of the metallic Au for Au NPs smaller than 3 nm. A high activity of gold oxide [34] or of atomic oxygen adsorbed on either extended gold surfaces [54] or on TiO_2 supported Au nanoparticles [43,55–57] for the CO oxidation reaction has been demonstrated by several groups. Soares et al. [34] detected non-catalytic CO_2 formation directly over Au_2O_3 and over $Au(OH)_3$ upon exposure to CO, while Bondzie et al. [43] and Kim et al. [55,56] demonstrated a high activity of pre-adsorbed oxygen adatoms on supported Au/ TiO_2 model catalysts towards CO oxidation (to produce CO_2) already at temperatures as low as 35 K. From all these findings it is obvious that (1) oxidic Au species are present after annealing of highly dispersed Au/ TiO_2 catalysts in oxygen at elevated temperatures and that (2) these represent highly active species for the CO oxidation, which are no longer present after exposure to CO/during the CO oxidation reaction. Hence, the removal of oxidic Au species clearly goes along with the removal of the O_{irr} species, providing clear evidence that this is indeed the O_{irr} species.

While the results presented above allow us to identify the nature of the O_{irr} species present on the catalyst surface, it is still not clear why it is formed only during calcination in a continuous flow of 10% O_2/N_2 at 400 °C, and not by O_2/Ar pulses at temperatures between 80 and 400 °C [23]. As already mentioned above, the most important difference between these two treatments is the amount of oxygen to which the catalyst is exposed. While it is exposed to about 5×10^{17} O_2 molecules during the multi-pulse experiments (100 pulses O_2/Ar , each containing about 5×10^{15} O_2 molecules), this amounts to 1.8×10^{21} O_2 molecules during O400 treatment (30 min in 20 $NmL \cdot min^{-1}$ 10% O_2/N_2). Hence, it is more than a factor of 3000 higher in the latter case. Assuming that the dissociative adsorption of oxygen on Au and/or the surface oxidation of Au is rather slow even at 400 °C, very high exposures to gas phase O_2 are necessary in order to form sufficient amounts of these oxygen species to be detected in subsequent TAP reactor measurements. To check whether the differences in the total amount of O_{irr} species present after O400 and after O_2/Ar pulses at 400 °C are indeed only due to the difference in the number of O_2 molecules dosed to the catalyst, we extended the number of oxygen pulses for replenishment of active oxygen at 400 °C. After first measuring the OSC at 80 °C, we exposed this to additional 6000 O_2/Ar pulses with a time delay of 1 s between single pulses at 400 °C, and afterwards measured again the OSC at 80 °C. This way, the catalyst was exposed to about 3×10^{20} O_2 molecules during the pulse sequence at 400 °C. Accordingly, the total amount of O_2 offered was just a factor of six less compared to the O400 treatment. The resulting uptakes of CO and oxygen during the first three reduction/re-oxidation cycles at 80 °C after this oxidation step are shown in Fig. 6. Note that the overall oxygen storage capacity at 80 °C measured during this measurement is again considerably lower than the value obtained directly after O400 treatment (2.3×10^{18} O atoms $\cdot g_{cat}^{-1}$ compared to 4.6×10^{18} O atoms $\cdot g_{cat}^{-1}$ directly after O400, see Table 1). As described above, this results from heating the catalyst to elevated temperature during the extended O_2/Ar puls-

Fig. 6. Absolute, accumulated amounts of CO and O_2 consumed during three cycles with alternate reduction and re-oxidation of the Au/ TiO_2 catalyst by 200 CO/ Ar pulses and by 100 O_2/Ar pulses, respectively, at 80 °C after measuring the OSC at 80 °C followed by 6000 O_2/Ar pulses performed at 400 °C.

ing at 400 °C and, hence, from water desorption from the catalyst surface. Au NPs sintering during that sequence, in contrast, can be excluded considering that TEM imaging directly after O400 and after multi-pulse experiments at 400 °C revealed almost identical Au particle sizes (Fig. 1).

Most important, however, is again the result for CO consumption during the first sequence of CO/Ar pulses, which is higher than in the following sequences. As described above for the multi-pulse experiments directly after calcination, this goes along with an irreversible consumption of surface oxygen and, hence, a non-catalytic CO₂ formation. Note that the total amount of O_{irr} species formed during 6000 O₂/Ar pulses is still considerably lower than that detected directly after calcination at atmospheric pressure (2.5×10^{18} O atoms·g_{cat}⁻¹ after 6000 O₂ pulses vs. 6.7×10^{18} O atoms·g_{cat}⁻¹ after O400, see Table 1). This difference can, however, easily be explained by the about six fold lower amount of O₂ molecules dosed during O₂/Ar pulses (see above). The fact that 6000 O₂/Ar pulses are needed in order to form 2.5×10^{18} O_{irr} atoms·g_{cat}⁻¹ clearly shows that the O_{irr} species is formed with a relatively low probability compared to the replenishment of active oxygen, for which it takes well below 100 pulses in order to saturate the catalyst surface even at 80 °C (up to 4.6×10^{18} O_{act} atoms·g_{cat}⁻¹). From this comparison we can also estimate the probability for the formation of O_{irr} species during O₂/Ar pulses. Even at a much higher temperature of 400 °C it is at least a factor of 100 lower compared to the formation of O_{act} species at the perimeter of the Au-TiO₂ interface by O₂ pulses at 80 °C. This finding is also in agreement with results published by Sault et al. [42] obtained on a Au single crystal and by Wang et al. [58] on a nanoporous Au catalyst. While Sault et al. stated that there is no dissociative adsorption of molecular oxygen at temperatures between 27–237 °C and pressures up to 1400 Torr on Au (110), Wang et al. [58] could show that the formation of adsorbed oxygen on nanoporous gold (NPG), with Au ligaments in the range of a few nanometers, was possible at 30 °C, but occurs with a very low probability and to a significant extent only during prolonged exposure of the NPG samples to O₂ at atmospheric pressure. Hence, the observed differences in the oxygen content after oxidation of the Au/TiO₂ catalyst at 400 °C in a flow of O₂/N₂ at atmospheric pressure and by only 100 O₂/Ar pulses (Fig. 3) originate indeed from the differences in the total amount of O₂ molecules to which the catalyst was exposed. From the results presented above, we conclude that the O_{irr} species represents either oxygen adsorbed on Au nanoparticles or a Au surface oxide species, which is therefore clearly different in nature from the reversible O_{act} species (identified as surface lattice oxygen at the perimeter of the Au/TiO₂ interface [28]). Moreover, it is formed only during prolonged exposure to O₂ at higher temperatures and, even at 400 °C, not by the low amount of O₂/Ar pulses used in ‘normal’ multi-pulse experiments. Hence, once it is removed during the first sequence of CO/Ar pulses or during the initial period of the CO oxidation reaction, it is no longer present on the Au/TiO₂ catalyst surface under present reaction conditions.

Finally, we would like to comment on the relevance of the O_{irr} species for the ongoing CO oxidation reaction under dry

reaction conditions. Considering that the probability for the formation of O_{act} species is at least a factor of 100 higher compared to that for O_{irr} formation, the Au assisted Mars-van Krevelen mechanism proceeding via the formation and reaction of the O_{act} species defined before must be indeed the dominating reaction pathway for CO oxidation on Au/TiO₂ under typical reaction conditions. A reaction mechanism involving the O_{irr} species can compete with that and contribute significantly or even dominate the reaction only on catalysts where the reactive removal of the O_{act} species is unlikely and hence very slow, e.g., on Au catalysts supported on non-reducible oxides. This would be equivalent to a Au-only mechanism, via the formation and reaction of atomically adsorbed, active oxygen species directly on the surface of the Au nanoparticles (O_{irr}), in a Langmuir-Hinshelwood type reaction mechanism. For Au catalysts based on reducible metal oxides, such as Au/TiO₂, the contribution of the latter reaction pathway is negligible under present reaction conditions (80–400 °C). This also explains the well-known higher activity of Au catalysts based on reducible oxides compared to Au catalysts based on non-reducible metal oxides [19,22]. As noted earlier, these conclusions on the dominant reaction pathway are, however, only valid under dry reaction conditions. In the presence of water and/or hydrogen in the reaction gas feed the situation, in particular support effects in the Au catalyzed CO oxidation, may be very different [27,59–61]. A possible explanation therefore is a different dominant reaction pathway in the presence or absence of water in the reaction atmosphere and, hence, on the catalyst surface. Saavedra et al. [27] recently provided direct evidence for a water-mediated reaction mechanism on Au/TiO₂ at room temperature with rather low energy barriers for O₂ activation in the presence of (weakly) adsorbed water and CO_{ad}. The optimum water content, which gives the highest activity for CO oxidation, was 1.5 monolayers water on TiO₂ [27]. Accordingly, it may be envisioned that there is a change in the dominant reaction pathway when going from strictly dry to wet reaction conditions. Under realistic conditions, in the presence of undefined, small amounts of water vapor in the feed gas, however, both mechanisms are expected to contribute to the overall rate, where the exact contributions are expected to depend on the exact reaction conditions. Further studies are planned, where we want to unravel these contributions and, if possible, a critical water content up to which the Au-assisted Mars-van Krevelen mechanism is still dominant. Interestingly, this situation is just opposite for Pt catalysts: For the CO oxidation at the Pt-FeO interface (FeO(111) islands on Pt(111)) it was recently demonstrated that FeO surface lattice oxygen is activated in the presence of water, resulting in the formation of active hydroxyl groups, but does not participate in the CO oxidation under dry reaction conditions [62].

4. Conclusions

We have shown that during calcination of Au/TiO₂ catalysts in 10% O₂/balance N₂ at 400 °C a second oxygen species is formed (irreversible oxygen species – O_{irr}), which can also react with CO, but is formed at least 2 orders of magnitude slower

than the reversible active oxygen species dominating the reaction in the absence of water and/or H₂. The former species is most likely atomically adsorbed oxygen on the Au nanoparticles or a Au surface oxide, which desorbs in the temperature range between 400 and 550 °C. The latter species, in contrast, is associated with TiO₂ surface lattice oxygen at the perimeter of the Au–TiO₂ interface, which is stable at least up to 600 °C. Considering its slow formation, the irreversible oxygen species is hardly formed under normal reaction conditions and does not contribute significantly to the ongoing CO oxidation reaction on Au/TiO₂ catalysts under typical reaction conditions (dry reaction gases, $T \geq 80$ °C). After its formation, e.g., by calcination in O₂, it is reacted off in a stoichiometric, non-catalytic CO oxidation reaction. Accordingly, the continuous CO oxidation on Au/TiO₂ catalysts, under typical reaction conditions, is dominated by formation and reactive removal of the reversible active oxygen species. We propose that this conclusion is of general validity for Au catalysts supported on reducible oxides, and that only for Au catalysts supported on ‘inert’ (non-reducible) oxides a reaction pathway proceeding via dissociative adsorption of oxygen on the Au nanoparticles (O_{irr} species) and subsequent reaction with CO_{ad}, in a Langmuir–Hinshelwood or ‘Au-only’ mechanism, can compete and even dominate the reaction under typical reaction conditions.

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Graphical Abstract

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Formation and removal of active oxygen species for the non-catalytic CO oxidation on Au/TiO₂ catalysts

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During calcination of Au/TiO₂ atomically adsorbed oxygen on Au or a Au surface oxide (O_{irr}) is formed, that is reacted off in a stoichiometric, non-catalytic CO oxidation reaction and thus doesn't contribute significantly to the continuous CO oxidation.

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Au/TiO₂催化剂上非催化CO氧化反应中活性氧物种的生成和消除

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摘要: 在定量的瞬时产物分析(TAP)反应器中, 于80 °C下采用CO脉冲和O₂脉冲补充等方法, 研究了高温(400 °C)焙烧的Au/TiO₂催化剂上活性氧物种的移除反应活性, 特别是活性氧物种的性质。以往的研究大多关注的是CO催化氧化反应中活性氧物种及其性质, 在典型的反应条件下该物种的形成和消除是可逆的; 而研究表明, 催化剂直接焙烧后就存在额外的氧物种; 该物种对CO氧化反应也具有活性, 但其在典型的反应条件下不生成或生成很少。基于此, 讨论了Au/TiO₂催化剂上CO氧化反应的机理, 特别是不同活性氧物种的作用。

关键词: 二氧化钛; 金催化; 一氧化碳氧化; 反应机理; 活性氧; 瞬时产物分析

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