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Activation of a Au/CeO_2 catalyst for the CO oxidation reaction by surface oxygen removal/oxygen vacancy formation

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Abstract

Applying quantitative temporal analysis of products (TAP) techniques, we demonstrate that after calcination, a Au/CeO_2 catalyst is only slightly active for CO oxidation. The activity is significantly increased on removal of about 7% of the surface oxygen, whereas overreduction leads to initially lower activity. Reductive activation can occur either during reaction, in the (oxidative) reaction gas, or by controlled prereduction. This is the first experimental verification of a CO oxidation rate enhancement by oxygen surface vacancies on a realistic oxide-supported Au catalyst. Consequences for the reaction mechanism are discussed.

Keywords: Au/CeO_2; CO oxidation; Activation; Oxygen vacancy

1. Introduction

CeO_2 is well known for its oxygen storage capacity [1] and thus is often used as support material for noble metal-based catalysts in oxidation reactions. In recent years, Au/CeO_2 catalysts have been proposed and investigated as promising candidates for applications in fuel gas processing for the removal of CO from H_2-rich feed gases for fuel cells by, for example, the water-gas shift reaction [2–5] or the preferential oxidation of CO [6–8]. The performance and activity of these catalysts likely depend sensitively on the oxygen content of the near-surface regions of the catalyst [2,9,10]. This is particularly true for oxidation reactions on supported Au catalysts, where the activation of oxygen is considered the limiting step [11–14]. More detailed information on this topic, which would be highly relevant to the mechanistic understanding of these catalysts and the respective reactions, is scarce, and little is known about the optimum surface composition, that is, the surface composition of the catalyst in its active state.

This is the topic of the present communication, where we report the first results of a study of the dynamics of the CO oxidation reaction on a Au/CeO_2 catalyst by applying a temporal analysis of products (TAP) technique. By titrating the consumption of the individual reactants and the formation of product CO_2 during simultaneous CO/O_2 pulses until steady-state conditions are reached, these measurements allow a very sensitive determination of the steady-state surface oxygen content of the catalyst surface relative to the initial surface and correlation of this with the catalyst activity for CO oxidation. We first followed the evolution of the CO oxidation activity of a Au/CeO_2 catalyst that had been pretreated by calcination in a 10% O_2/N_2 mixture by monitoring the CO and O_2 consumption and CO_2 formation during a sequence of simultaneous CO and O_2 pulses. To get further information on the origin and nature of the activation process (particularly in terms of whether the optimum O content of the active surface is independent of the pretreatment procedure), we performed similar measurements on Au/CeO_2 catalysts treated in different ways after the initial calcination process by (i) initial reduction through reaction with a sequence of CO pulses and subsequent reoxidation via O_2 pulsing or (ii) controlled initial reduction using a limited number of CO pulses only. Here we discuss the consequences of these measurements on the mechanistic understanding of the CO oxidation reaction. Along with their mechanistic implications, the data demonstrate the potential of quantitative TAP measurements in mechanistic studies.

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2. Experimental

The experiments were performed in a home-built TAP reactor that we describe in detail later. The reactor is of comparable design to one by Gleaves et al. (TAP-2) [15], with modifications allowing easier operation and highly reproducible pulse sequences. It consists of a gas mixing unit, two piezoelectric-driven pulse valves, and a tubular quartz glass microreactor connected to an ultra-high-vacuum (UHV) system (analysis chamber). After the gases pass through the reactor, they are analyzed by a quadrupole mass spectrometer (QMG 700, Pfeiffer) located in the analysis chamber. For in situ conditioning of the catalyst at atmospheric pressures, the reactor can be separated from the UHV system by a differentially pumped gate valve and connected directly to an adjustable roughing pump.

CO and O_2 were pulsed independently, with each pulse containing about 10^{16} molecules including 10% Ar as an internal standard for data evaluation. (Procedures for the absolute calibration of the pulses will be published later.) The pulse width was around 3 s after passing through the catalyst bed without reaction, as determined from Ar pulses (opening time of the pulse valve, 300 µs). For experimental reasons, the first pulse in a sequence was typically lower in intensity; exact numbers can be obtained by comparison with the internal Ar standard. The consumption of CO and O_2 in the respective pulses was calculated from the missing mass spectrometric intensity in these pulses compared with the intensity after saturation. The formation of CO_2 could be determined directly from the CO_2 pulse intensity.

The catalyst was prepared by a deposition-precipitation procedure that is described in detail elsewhere [16]. In the experiments described here, 1.5 mg of the catalyst (2.4 wt% Au/CeO_2; surface area, 24.2 $m^2\ g^{-1}$; mean Au particle size about 4 nm) was diluted 1:10 with quartz powder (Gebaflot 010; Dorfner GmbH, grain size 100–200 µm), which is inactive for CO oxidation in the temperature range investigated. The diluted catalyst was packed between two layers of quartz particles and fixed in the center of the tubular microreactor (90 mm long, 4.0 mm i.d.) by metal sieves. This three-zone catalyst bed [17], with an inert zone before (35 mg SiO_2) and after (100 mg SiO_2) the catalyst zone, was found to give the narrowest CO_2 signal (pulse width about 40 s) in combination with high conversion in the temperature range investigated. The catalyst temperature was 120 °C for all measurements. The reaction gases (CO 3.7, O_2 5.0, and Ar 6.0, all from Westphalen) were used as delivered.

3. Results and discussion

Exposing the freshly conditioned catalyst to simultaneous pulses of CO and O_2 (CO: 10^{16} molecules $pulse^{-1}$; O_2: 8×10^{15} molecules $pulse^{-1}$) resulted in the pulse sequences shown in Fig. 1a. After an initial period of about 30 pulses, the pulse intensities of the CO-, O_2-, and CO_2-related signals reached a constant value (Fig. 1b). Under steady-state conditions, the pulse intensities showed a stoichiometric consumption of the two reactants and a corresponding amount of CO_2 formation; that is, the consumed CO and O_2 were quantitatively transformed into CO_2, and the formation of side products was below the sensitivity of these measurements (side product formation, <5% of the total CO_2 formation). The total conversion of the two reactants was about 80% for CO (and 50% for O_2, due to excess O_2 in the gas supply).

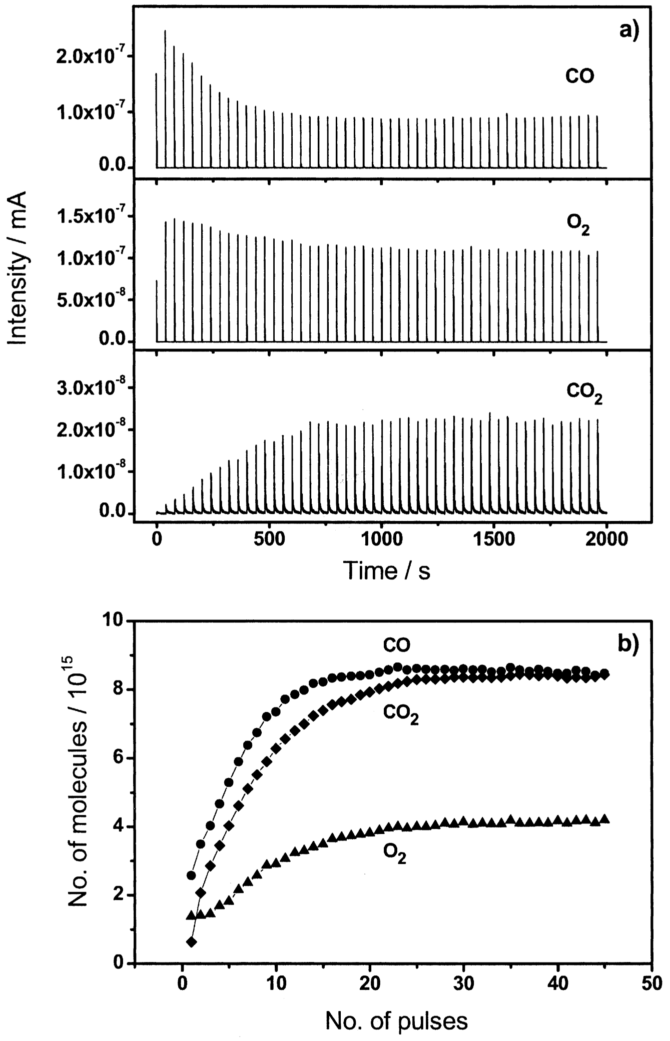

Fig. 1. (a) Sequence of simultaneous CO and O_2 pulses dosed on a Au/CeO_2 catalyst pretreated by calcination in 10% O_2/N_2 at 400 °C (30 min); (b) CO uptake (●), oxygen uptake (▲), and CO_2 formation (◆) during these pulses.

The situation was different in the initial period of the reaction, during the first 30 pulses. Initially, both CO_2 formation and reactant consumption were very low. Both reactant consumption and product formation increased steadily with time. Based on these observations, we conclude that the initial increase in educt consumption/product formation was not related to the consumption of CO_2 product species by some other reaction, such as carbonate formation [18], but actually reflects activation of the catalyst.

However, CO_2 consumption did also occur, and can be quantified based on the difference between observed CO_2 formation and CO consumption, particularly from the later increase in CO_2 formation compared with CO and O_2 consumption. The total deficit in desorbing CO_2 during the initial phase, which is ascribed to instantaneous carbonate formation [18], can be calculated as approx. 2.7×10^{16} CO_2

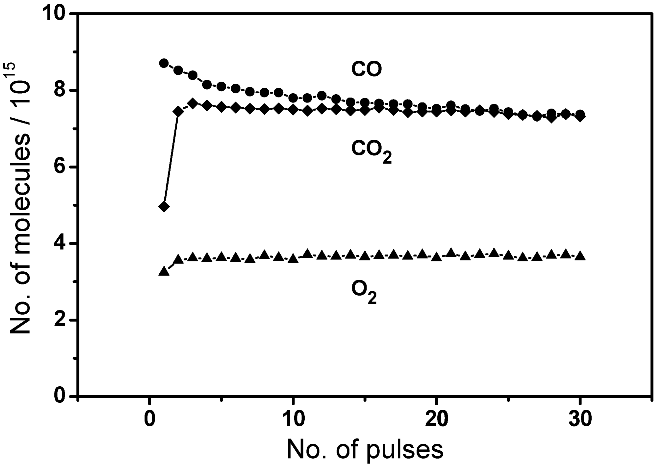

Fig. 2. CO uptake (●), oxygen uptake (▲), and CO_2 formation (◆) during simultaneous CO and O_2 pulses dosed on a Au/CeO_2 catalyst pretreated by calcination in 10% O_2/N_2 at 400 °C (30 min), subsequent reduction by exposure to 100 CO pulses and reoxidation by 50 O_2 pulses.

molecules (1.8×10^{19} molecules g_{cat}^{-1}). This is equivalent to a buildup of 0.06 monolayers (MLs) of surface carbonate (relative to the density of surface O atoms, using a density of O atoms of 1.3×10^{15} atoms cm^{-2} [19]). Furthermore, there also was a difference between the consumption of the two reactants CO and O_2. During the activation period, the consumption of CO was higher than that of O_2, implying that CO reacted not only with oxygen adsorbed from the gas phase, but also with surface oxygen of the catalyst support. Integrated over the initial 30 pulses, the additional consumption of CO amounted to about 3.4×10^{16} molecules (2.3×10^{19} molecules g_{cat}^{-1}), which is equivalent to a loss of oxygen surface coverage of 0.07 ML. Based on this observation, we tentatively attribute activation of the catalyst to a slight reduction in the initial catalyst surface after calcination. With ongoing reductive activation, the difference in CO and O_2 consumption decreased (see Fig. 1) and decayed to zero when it reached steady-state conditions.

To gain further insight into the nature and origin of the activation process, we performed a similar series of pulse measurements on a Au/CeO_2 catalyst that was also pretreated by calcination but then repeatedly reduced and reoxidized by exposure to sequences of 100 CO pulses and 50 O_2 pulses and subsequently exposed to a sequence of simultaneous CO and O_2 pulses similar to those in the previous experiment. The resulting reaction behavior (Fig. 2) was distinctly different from that obtained on the calcined catalyst discussed above. In this case, the maximum reactivity was reached instantaneously, as evidenced by the high consumption of CO in the first set of CO and O_2 pulses. During the subsequent CO/O_2 pulses, the CO consumption decayed slightly in intensity, indicative of a slight decay in activity. The pronounced difference between CO consumption and CO_2 formation in the first and (less pronounced) second pulse can be explained by an increased initial consumption of CO_2 by carbonate formation after the surface had been partly depleted of surface carbonates by the preceding O_2 pulsing (i.e., oxygen-assisted carbonate decomposition). The deficit in gaseous CO_2 desorption was equivalent to a carbonate buildup of 1.1×10^{16} molecules (7.3×10^{18} molecules g_{cat}^{-1}); the O_2-induced decomposition of carbonate during the preceding sequence of O_2 pulses amounted to 2.1×10^{16} molecules, leaving about 1.7×10^{16} molecules on the surface. Thus, the preceding loss of carbonate was not fully compensated for under steady-state conditions. Moreover, the O consumption (which remained about constant, in contrast to the slight decay in CO consumption described above) was slightly lower than the CO consumption, indicative of additional surface oxygen consumption during the reaction. However, the total (additional) surface oxygen consumption (about 1.4×10^{16} oxygen atoms) was much lower than in the previous experiment. At the end of the sequence, the signals were about constant and steady-state conditions were reached. At that point, CO and O_2 consumption were (within the experimental limits of these measurements) stoichiometric, and the two reactants were completely converted into desorbing CO_2.

This general behavior was reproducibly observed already after the first reduction–reoxidation sequence and remained stable independent of the number of reduction–reoxidation cycles applied. Using the picture of the activation process described above, this means that the reoxidation by O_2 pulsing did not lead to the less active state arrived at after calcination, but resulted directly in a state close to the (most) active state. Thus, after reduction of the catalyst by CO pulsing, subsequent O_2 pulsing at 120 °C (over limited times) was less efficient for oxidation of the catalyst than calcination at 400 °C.

In a final set of experiments, we investigated the reaction behavior of catalysts that were reduced before the reaction sequence, opposite to the final O_2 treatment in the first two experiments. Controlled reduction of the initially calcined Au/CeO_2 catalysts was obtained by exposing this to a limited number of CO pulses before starting the reaction with simultaneous CO/O_2 pulses. Because in the previous reduction–reoxidation experiments, most of the reactive oxygen was removed by CO after about 10 pulses (not shown here), we used 3, 10, and 30 CO pulses to prepare differently prereduced catalyst surfaces. Subsequently, the catalyst was exposed to simultaneous CO/O_2 pulses, as in the previous experiments (Figs. 1 and 2).

After prereduction by three CO pulses, the slight increase of CO consumption during the first 10 pulses indicated that some activation remained (Fig. 3a). However, this was significantly less pronounced compared with that on the Au/CeO_2 catalyst directly after calcination (Fig. 1b). From the higher consumption of CO compared with O_2 consumption during the simultaneous CO/O_2 pulses (excess: 2.0×10^{16} CO molecules) and the additional reactive removal of 1.1×10^{16} O atoms during the three preceding CO pulses, the active steady-state conditions are characterized by a loss of 3.1×10^{16} O surface atoms (2.1×10^{19} O atoms g_{cat}^{-1}), which is equivalent to an O loss of about 0.07 ML relative to the calcined catalyst. This is very close to the total O loss calculated in the preceding experiments for the active state. In the same way, we calculated, based on the difference between CO consumption and CO_2 formation, that 2.7×10^{16} carbonate molecules (0.06 ML) were formed during prereduction (three CO pulses) and the subsequent simultane-

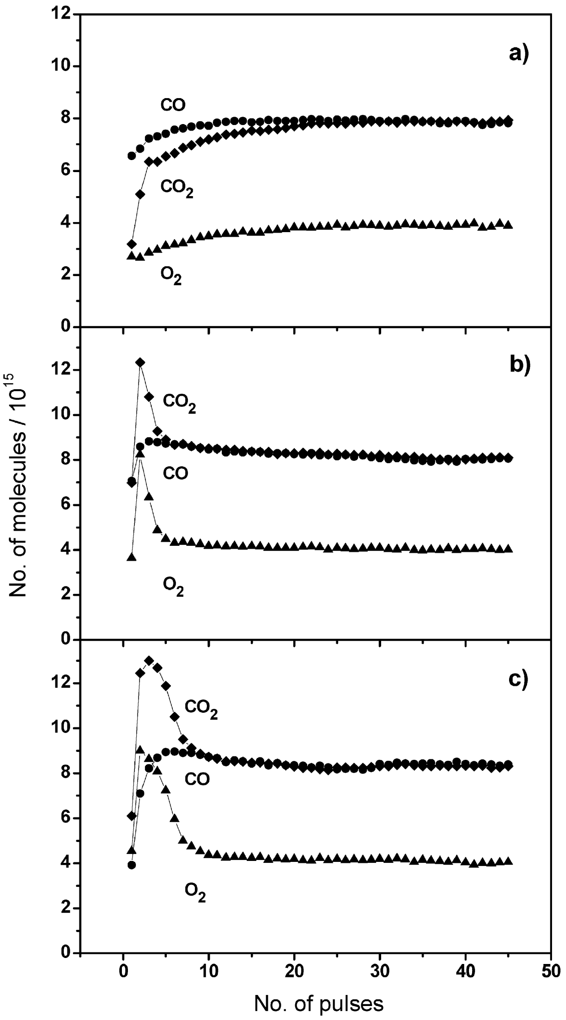

Fig. 3. CO uptake (●), oxygen uptake (▲), and CO_2 formation (◆) during simultaneous CO and O_2 pulses dosed on a Au/CeO_2 catalyst pretreated by calcination in 10% O_2/N_2 at 400 °C (30 min) and subsequent reduction by exposure to (a) 3 CO pulses, (b) 10 CO pulses, and (c) 30 CO pulses.

ous CO/O_2 pulses. These findings are comparable to those of the previous experiments.

In further experiments, we extended the number of CO pulses to 10 and 30 to prepare catalysts near their most reactive state (after 10 CO pulses) and in a more reduced state (after 30 CO pulses). The reactant consumption and product formation during simultaneous pulses of CO and O_2 after these pretreatments are illustrated in Figs. 3b and 3c. After prereduction by 10 CO pulses, we again found an initial activation, as indicated by the lower CO consumption in the first two pulses. After passing through a maximum at the third and fourth pulses, the CO consumption decayed slightly and then reached steady-state conditions. Similar to previous observations, the reaction was stoichiometric under these conditions, and gaseous CO_2 formation was essentially identical to CO consumption; that is, side product (carbonate) formation was negligible. The pronounced additional uptake of oxygen during the first few pulses demonstrates that after prereduction by 10 CO pulses, the surface was already overreduced compared with that under steady-state conditions, and that part of the initial oxygen supply during the first 5 pulses was used to increase the surface oxygen content. In contrast, the CO_2 desorption detected during this initial phase is significantly higher than the CO consumption. This can be explained by an oxygen-assisted decomposition of surface carbonates that had accumulated on the catalyst during the 10 CO pulses. Based on the total consumption of surface oxygen during CO/O_2 pulsing and the removal of surface oxygen during the preceding 10 CO pulses, the active state has a deficit of 2.9×10^{16} O atoms, or 0.06 ML, compared with the calcined sample, which again is close to the values derived in the previous experiments. In the same way, the buildup of surface carbonate from the calcined sample until steady-state conditions are reached was calculated as 2.4×10^{16} molecules (0.05 ML).

All together, these data indicate that after 10 CO pulses, the catalyst was not in its most active state but rather was already in a slightly overreduced state compared with the active steady state. This is opposite to the behavior observed after prereduction by three or fewer CO pulses, indicating that the most active state was reached after prereduction by between 3 and 10 CO pulses.

After prereduction by 30 CO pulses, the general behavior resembled that observed after pretreatment by 10 CO pulses, but the effects were much more pronounced. Even after correction for the lower intensity of the first O_2 pulse, the initial activity measured by the CO consumption was significantly lower than the steady-state value. In contrast, the initial O_2 consumption was much higher than the steady-state value, and O_2-mediated decomposition of surface carbonates built up during the preceding 30 CO pulses resulted in a distinct excess of gaseous CO_2 formation during the initial pulses. After this distinctive initial phase, the CO consumption and gaseous CO_2 formation remained constant, indicating that steady-state conditions were reached. Combining pretreatment and reaction, the total loss of surface oxygen between the calcined catalyst and the steady-state situation during CO/O_2 pulses was around 3.3×10^{16} O atoms (7.7×10^{16} molecules consumed during pretreatment and 4.4×10^{16} molecules for reoxidation during the subsequent reaction), and the buildup of surface carbonates amounted to 2.9×10^{16} molecules (5.0×10^{16} during pretreatment and -2.1×10^{16} during the subsequent reaction). In total, after prereduction by 30 CO pulses, the changes in the reaction behavior were qualitatively identical to those after 10 CO pulses, but more pronounced. Overreduction of the catalyst compared with steady-state conditions is connected to a significantly lower CO oxidation activity.

The data presented above clearly demonstrate that (i) small amounts of reactive oxygen can be rapidly and reversibly deposited and reacted away on/from Au/CeO_2 catalysts by exposure to CO or O_2 pulses; (ii) after calcination, the catalyst is significantly less active for CO oxidation, and small amounts of surface oxygen must be removed before the catalyst reaches its more active steady-state surface composition; and (iii) neither the final activity nor the surface oxygen content under steady-state conditions during simultaneous CO/O_2 pulses depends on the method of oxygen removal, whether by in situ activation during the reaction, by preceding reduction and oxidation, or by controlled reduction with few CO pulses. Furthermore, the measurements also show that at 120 °C, surface carbonates could be (partly) decomposed by O_2 exposure (oxygen-assisted decomposition).

Reactive oxygen removal from CeO_2 is a well-known reaction [1], and transient CO_2 formation also was observed in the absence of O_2 in the reaction gas [2,20]. However, these observations differ from our present findings by the much longer time scale of the oxygen deposition/depletion processes. Therefore, we assign the rapid uptake and removal of oxygen in the present TAP measurements to an essentially pure surface reaction, that can be accompanied by or (on a longer time scale) followed by slow exchange of oxygen or oxygen vacancies with the bulk of the ceria particles, depending on the deposition/reaction conditions. In that sense, the present measurements put a limit on the order of magnitude of surface oxygen that can be easily and reversibly removed by reaction with CO. The Au particles play an important role in the rapid removal and deposition of surface oxygen. Comparative TAP measurements on Au-free ceria particles showed negligible activity for these processes. This agrees well with the proposed activation of ceria for oxygen removal by Au nanoparticles under ambient conditions [2,9,10,21]. Finally, it is important to note that the amount of surface oxygen removed was below the detection limit of standard spectroscopic measurements, which do not discriminate between surface oxygen and oxygen in near-surface regions. For small ceria nanoparticles, the latter essentially includes the entire particle bulk.

The much higher activity seen after removal of 0.07 ML of surface oxygen from the calcined catalysts underscores the role of oxygen vacancies in the CO oxidation reaction on Au/CeO_2 catalysts under current reaction conditions. The participation of oxygen vacancies on reducible supports in CO oxidation on supported Au catalysts was proposed by various groups [11–14,22,23], with the catalysts ranging from size-selected Au clusters with a few Au atoms deposited on single-crystal oxide substrates to realistic, highly dispersed catalysts and the reaction conditions ranging from UHV conditions to atmospheric pressure. For $Au_n/MgO(001)$ ($n = 8$) model catalysts, it was shown that the high reactivity resulted from the negative charge on the Au_n clusters deposited on oxygen vacancies [22]. The present work provides the first clear and direct experimental evidence that oxygen vacancies not only can be formed on the support under reaction conditions (at least temporarily), but also have an effect on the CO oxidation activity of a realistic, highly dispersed oxide-supported Au catalyst.

For CO oxidation on Au/TiO_2 different mechanisms and active sites have been proposed, ranging from low-coordination sites on Au nanoparticles to sites at the interface between Au particles and the oxide substrate [24]. Recently, Shapovalov et al. proposed a mechanism for CO oxidation on Au-doped $CeO_2(111)$ that involves formation of an oxygen vacancy by reaction with CO (most favorably adjacent to the metal dopant), O_2 adsorption on the oxygen vacancy, further reaction with CO to form a carbonate species, and finally its decomposition to CO_2, with the remaining oxygen atom filling the oxygen vacancy [25]. In this case, the Au dopant reduces the barrier for the creation of an oxygen vacancy adjacent to the Au dopant atom. Although currently speculative, a similar mechanism also may be anticipated for Au/CeO_2 catalysts with Au nanoparticles as used in the present study, for example, at the interface between Au particles and CeO_2 ("adlineation sites"). Based on the Au loading and the mean particle size, the number of oxygen atoms removed was more than twice the number of O or Au atoms at these adlineation sites. Due to the high mobility of oxygen vacancies on the surface [1], however, we would not expect all oxygen vacancies to be located at the interface. Therefore, this result does not contradict the suggestion that adlineation sites act as active sites for vacancy formation.

4. Conclusion

In conclusion, we have shown by transient pulse titration measurements in a TAP reactor that a freshly calcined Au/CeO_2 catalyst becomes significantly more active for CO oxidation on removal of about 7% of the surface oxygen content. Neither this value nor the steady-state activity of the catalyst in simultaneous CO/O_2 pulses depends on the procedure followed for surface oxygen removal during reaction (i.e., by reaction with CO in the CO/O_2 reaction gas, by initial reduction with CO and subsequent mild reoxidation, or by controlled reduction). The data clearly demonstrate the role of surface vacancies in activating the CO oxidation reaction on ceria-supported Au catalysts.

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