

# Activation of Molecular Oxygen and the Nature of the Active Oxygen Species for CO Oxidation on Oxide Supported Au Catalysts

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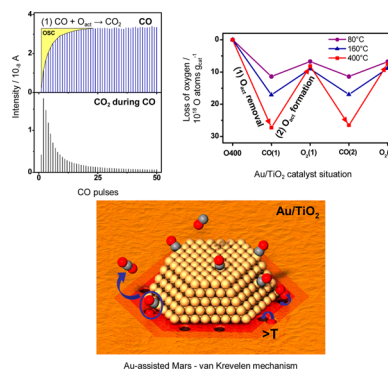
RECEIVED ON AUGUST 14, 2013

## CONSPECTUS

**A**lthough highly dispersed Au catalysts with Au nanoparticles (NPs) of a few nanometers in diameter are well-known for their high catalytic activity for several oxidation and reduction reactions already at rather low temperatures for almost 30 years, central aspects of the reaction mechanism are still unresolved. While most studies focused on the active site, the active Au species, and the effect of the support material, the most crucial step during oxidation reactions, the activation of molecular oxygen and the nature of the resulting active oxygen species ( $O_{act}$ ), received more attention just recently.

This is topic of this Account, which focuses on the formation, location, and nature of the  $O_{act}$  species present on metal oxide supported Au catalysts under typical reaction conditions, at room temperature and above. It is mainly based on quantitative temporal analysis of products (TAP) reactor measurements, which different from most spectroscopic techniques are able to detect and quantify these species even at the extremely low concentrations present under realistic reaction conditions. Different types of pulse experiments were performed, during which the highly dispersed, realistic powder catalysts are exposed to very low amounts of reactants, CO and/or  $O_2$ , in order to form and reactively remove  $O_{act}$  species and gain information on their formation, nature, and the active site for  $O_{act}$  formation.

Our investigations have shown that the active oxygen species for CO oxidation on Au/TiO<sub>2</sub> for reaction at 80 °C and higher is a highly stable atomic species, which at 80 °C is formed only at the perimeter of the Au–oxide interface and whose reactive removal by CO is activated, but not its formation. From these findings, it is concluded that surface lattice oxygen represents the  $O_{act}$  species for the CO oxidation. Accordingly, the CO oxidation proceeds via a Au-assisted Mars–van Krevelen mechanism, during which surface lattice oxygen close to the Au NPs is removed by reaction with CO, resulting in a partially reduced TiO<sub>2</sub> surface, which is subsequently reoxidized by  $O_2$ . We demonstrate that this is the dominant reaction pathway for Au catalysts based on reducible metal oxides in general, at typical reaction temperatures, while for less active Au catalysts based on nonreducible metal oxides, this reaction pathway is not possible and the remaining activity must arise from another pathway, most probably a Au-only mechanism. At lower reaction temperature, reactive removal of  $O_{act}$  becomes increasingly inhibited, leading to a change in the dominant reaction pathway.



## 1. Introduction

Gold is known as one of the most chemically inert elements. Accordingly, it has been considered to be catalytically inactive for a long time, and it was stated still a few decades ago that gold cannot act as a catalyst for oxidation or hydrogenation reactions at ambient temperatures.<sup>1</sup> The first observations contradicting these ideas were reported in 1973 by Bond and Sermon, who demonstrated that highly dispersed, supported Au particles are able to

dissociatively chemisorb  $H_2$  already at a temperature as low as 100 °C and can catalyze hydrogenation and hydrocracking reactions at ambient temperatures.<sup>2</sup> They suggested that the Au particle size may be the decisive factor for achieving highly active Au catalysts.<sup>2</sup> Nevertheless, it took another 10 years for the breakthrough of gold based catalysis research, which remained unbroken since this time and is still increasing.<sup>3</sup> This was mainly triggered by two findings: Haruta et al. reported in 1987 that metal oxide

supported Au catalysts are highly active for the CO oxidation, initiating this reaction already at temperatures as low as  $-70\text{ }^{\circ}\text{C}$ ,<sup>4</sup> and Nkosi et al. showed in 1988 that Au based catalysts are most effective for acetylene hydrochlorination.<sup>5</sup> Since then, supported Au catalysts containing Au nanoparticles (NPs) of a few nanometers in diameter have been shown to be highly active for various oxidation and reduction reactions, most prominently the CO oxidation reaction.<sup>3,4</sup> Research regarding the molecular scale mechanistic understanding of these reactions, specifically of the CO oxidation reaction, focused mainly on the active Au species,<sup>6,7</sup> on the active site for CO oxidation,<sup>8–12</sup> and on the origin of the pronounced Au particle size effect.<sup>13,14</sup> O<sub>2</sub> activation, which to our belief is the most crucial step in Au catalyzed oxidation reactions, received more attention only recently and is discussed most controversially. This includes the nature of the active site for the activation of molecular oxygen, the nature of the resulting active oxygen (O<sub>act</sub>) species, and its location on the catalyst, for example, on the Au NPs, on the support surface or at the perimeter of the interface between these two.

These latter questions are topic of this Account, where we summarize characteristic findings and insights gained in our recent efforts to tackle these aspects. We will focus on the CO oxidation reaction under typical reaction conditions, at room temperature and above. The latter is important to note, since, as discussed below, the reaction temperature is a decisive factor for the dominant reaction mechanism. Our results are based on pulse experiments performed in a temporal analysis of products (TAP) reactor, which is largely based on the TAP-2 system of Gleaves et al.<sup>15,16</sup> The relatively small number of molecules per pulse ( $\sim 10^{16}$  molecules) used enables us to detect even extremely small amounts of oxygen consumption and active oxygen formation on the catalyst surface, well below 1% of the totally available oxygen on the catalyst surface.<sup>10,17</sup>

After a short review of previous findings from theoretical and experimental studies on the nature of the O<sub>act</sub> species present on Au catalysts, we will first focus on the active site for oxygen activation and for CO oxidation and on the nature of the O<sub>act</sub> species using Au/TiO<sub>2</sub> catalysts as a model system. Next, we will concentrate on support effects and demonstrate how the nature of the support, specifically its reducibility, affects the formation of active oxygen species and the activity for CO oxidation. Third, we will elucidate the role of the reaction conditions, in particular of the reaction temperature, on the oxygen storage capacity (OSC) and the activity for CO oxidation. Finally, we will summarize the

implications of these findings on the mechanistic understanding of Au catalyzed oxidation reactions.

## 2. Mechanism of the CO Oxidation

There is general agreement that during the CO oxidation on metal oxide supported Au catalysts under “normal” reaction conditions, CO is largely adsorbed on the surface of the Au NPs.<sup>18–20</sup> Only for very low temperatures or high CO partial pressures, CO is also adsorbed directly on the support to a significant extent.<sup>19,20</sup>

The situation is much less clear for the activation of molecular oxygen, including the active site for this reaction step and the nature of the resulting O<sub>act</sub> species, which is still discussed controversially and far from being resolved.<sup>10,21–24</sup> A number of previous theoretical studies arrived at the conclusion that weakly bound molecular O<sub>2,ad</sub> species represent the active oxygen species, which are dissociated with a rather low activation barrier upon interaction with coadsorbed CO via a [CO<sub>ad</sub>·O<sub>2,ad</sub>] adsorption complex.<sup>20,22,23</sup> Mullins and co-workers showed that molecularly adsorbed oxygen can indeed be adsorbed on both Au(111) and Au NPs supported on TiO<sub>2</sub>(110) at 77 K and that this oxygen species can directly react with CO.<sup>11</sup> Green et al. demonstrated by IR spectroscopy measurements that preadsorbed CO can be reactively removed at 120 K upon exposure to O<sub>2</sub> (see section 7).<sup>20</sup> At higher temperatures, however, O<sub>2,ad</sub> is not stable and desorbs upon heating to 170 K,<sup>11</sup> in agreement with the rather low adsorption energies calculated in theoretical studies.<sup>20,22,23</sup> Due to its low stability, this species is hardly conceivable as active oxygen species at room temperature and above.

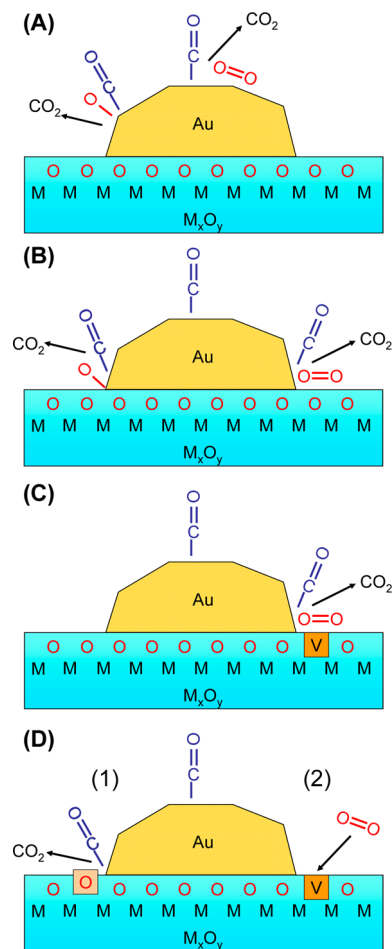
In another model, it was proposed that surface oxygen vacancies on the support represent the active sites for O<sub>2</sub> adsorption and activation.<sup>9,25</sup> Charge transfer from the support to the adsorbed O<sub>2</sub> species results in negatively charged O<sub>2</sub> species such as superoxides or peroxides, which were considered as active species for CO oxidation. At lower temperatures (less than or equal to room temperature), superoxide and peroxide species could even be directly identified by electron spin resonance (ESR) and Raman spectroscopy measurements.<sup>24–26</sup> At higher temperatures, however, similar observations have not been reported.

Overall, there seems to be ample evidence that at low temperatures molecularly adsorbed oxygen represents the active species for CO oxidation. Above room temperature, however, O<sub>2,ad</sub> is not stably adsorbed, and there is also no direct evidence for such active oxygen species from spectroscopic techniques. Hence, little is known about the nature of

the O<sub>act</sub> species and the active site for oxygen activation under normal reaction conditions. Nevertheless, there have been numerous proposals for the reaction mechanism, which are schematically illustrated in Figure 1. All of them involve CO adsorbed on the Au NPs, while the active oxygen species is either atomically or molecularly adsorbed oxygen on the Au particles (Figure 1A, “Au-only mechanism”),<sup>23</sup> atomically or molecularly adsorbed oxygen at perimeter sites (Figure 1B, “interface mechanism”),<sup>12,21,23,27</sup> oxygen molecularly adsorbed on surface vacancies, most probably located also at perimeter sites (Figure 1C, “interface mechanism”),<sup>9,24,25</sup> or surface lattice oxygen from the support itself (Figure 1D).<sup>28</sup> While the first three reaction pathways correspond to a Langmuir–Hinshelwood type mechanism, with both reactants adsorbed on the catalyst surface, the latter one represents a Mars–van Krevelen (MvK) type mechanism. Here surface lattice oxygen is removed by reaction with CO in a first step, leading to the formation of CO<sub>2</sub> and a surface oxygen vacancy (1), before in a second step gas phase oxygen reoxidizes the partly reduced catalyst surface (2).

### 3. Formation and Detection of Stable Adsorbed Active Oxygen on Au/TiO<sub>2</sub>

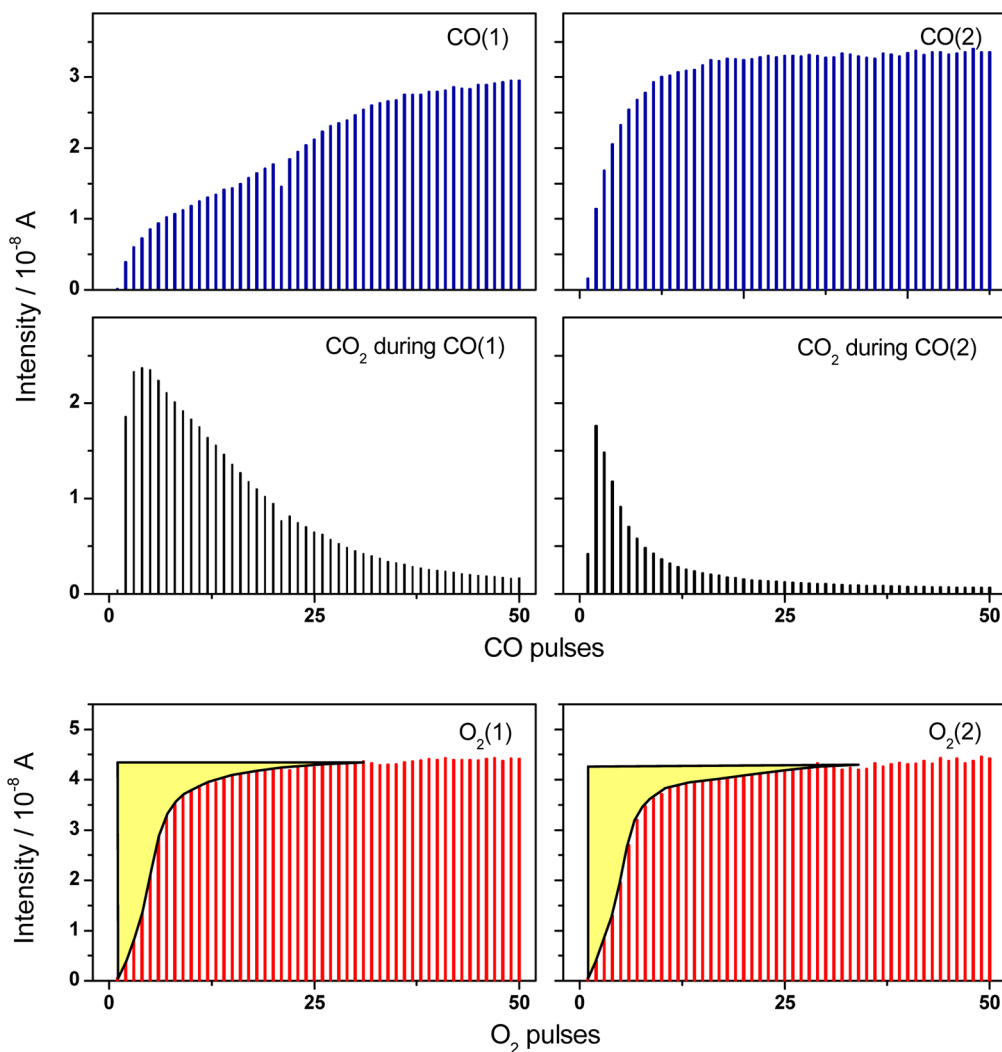
Our approach to study the nature and formation of the active oxygen species for the CO oxidation at typical reaction temperatures, above room temperature, is based on pulse experiments performed in a home-built TAP reactor.<sup>17</sup> The measurements were performed in titration mode, where active oxygen is reactively removed by reaction with multiple CO pulses and subsequently replenished in a sequence of O<sub>2</sub> pulses. Prior to the measurements, the realistic powder catalysts are pretreated *in situ* by calcination in O<sub>2</sub>/N<sub>2</sub> at elevated temperatures and atmospheric pressure, leaving the catalyst in the same state as that used for kinetic measurements. Afterward, the reactor is evacuated, and the catalyst is exposed to gas pulses of defined size. After passing through the catalyst bed, the effluent gases are analyzed by a quadrupole mass spectrometer, which enables us to calculate the absolute amounts of CO and O<sub>2</sub> consumed in the respective pulses as well as the formation of CO<sub>2</sub>.<sup>17</sup> Integration over the pulses in a multipulse sequence yields the total amounts of active oxygen reactively removed or deposited by alternating sequences of CO and O<sub>2</sub> pulses (multipulse experiment). Considering that weakly adsorbed species desorb between deposition and removal of active oxygen, this corresponds to the absolute amount of *stable* adsorbed oxygen removed or deposited under these conditions (oxygen storage



**FIGURE 1.** Schematic description of the possible reaction pathways proposed for the CO oxidation over supported Au catalysts. Description see text.

capacity, OSC).<sup>10</sup> The catalytic activity for CO oxidation can be evaluated, at least in a qualitative way, by exposing the samples to CO and O<sub>2</sub> at the same time by simultaneous CO/O<sub>2</sub> pulses (single-pulse experiments).<sup>10,29</sup> Further experimental details can be found in the Supporting Information.

A sequence of mass spectrometric signals recorded during a multipulse experiment performed on a standard Au/TiO<sub>2</sub> catalyst (Au loading 2.6 wt %, mean Au particle size  $3.0 \pm 0.7$  nm, commercial, nonporous P25 support) is illustrated in Figure 2, which shows the CO and CO<sub>2</sub> signals during the first reduction sequence directly after calcination (CO(1)), O<sub>2</sub> signals during subsequent reoxidation by O<sub>2</sub> pulses (O<sub>2</sub>(1)), and the same signals during a subsequent cycle, after the initial O<sub>2</sub> pulsing (CO(2), O<sub>2</sub>(2)) at a reaction temperature of 80 °C.<sup>30</sup> From the fact that CO<sub>2</sub> is formed during CO pulsing, it was concluded that the presence of gas phase O<sub>2</sub> is not required for the CO oxidation reaction on the Au/TiO<sub>2</sub> catalyst at 80 °C. Hence, stable



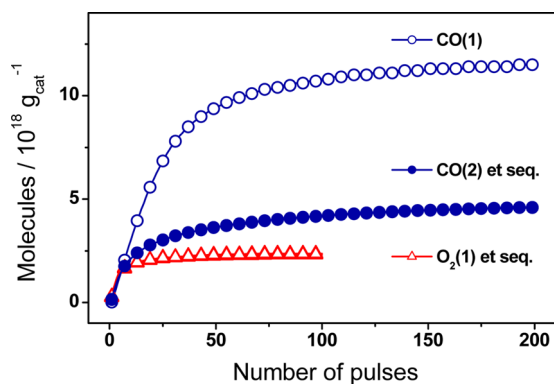
**FIGURE 2.** Signals for CO and CO<sub>2</sub> obtained during the first sequence of CO pulses over the Au/TiO<sub>2</sub> catalyst directly after oxidative pretreatment (CO(1)) and during the second sequence after oxidation by O<sub>2</sub> pulses (CO(2)) at 80 °C and O<sub>2</sub> signal obtained during the first two sequences of O<sub>2</sub> pulses at 80 °C after reduction by CO pulses (O<sub>2</sub>(1); O<sub>2</sub>(2)).

adsorbed oxygen, which must have been present on the catalyst surface already before CO pulsing, reacts with CO to form CO<sub>2</sub>. During O<sub>2</sub> pulsing, in contrast, no CO<sub>2</sub> formation is detected. Hence, CO is not stably adsorbed under these conditions and desorbs instantaneously after the CO pulse. Quantitative evaluation of these and subsequent measurements yields the total amounts of CO and O<sub>2</sub>, respectively, consumed during each of the first three sequences of CO and O<sub>2</sub> pulses after calcination (Figure 3). Note that the amount of CO<sub>2</sub> formed during a pulse sequence of CO pulses is always identical to the amount of CO consumed, indicating that for this catalyst there is no measurable accumulation of carbon containing species such as surface carbonates on the catalysts surface under present reaction conditions.<sup>29,30</sup>

A second aspect that should be noted is that the amount of CO consumed and CO<sub>2</sub> produced during the first sequence

of CO pulses, directly after the oxidative pretreatment, is higher than that in the second and following CO pulse sequences, after reoxidation by O<sub>2</sub> pulses at 80 °C, and also higher than the amount of oxygen consumed during O<sub>2</sub> pulses. The latter one, in contrast, is identical in all oxidation sequences. Hence, part of the oxygen removed during the first CO pulse sequence is not replenished by subsequent O<sub>2</sub> pulses ("irreversibly removed oxygen"), indicating that the amount of strongly adsorbed active oxygen is higher after calcination in O<sub>2</sub>/N<sub>2</sub> at atmospheric pressure than upon O<sub>2</sub> pulsing. A comparable result was obtained recently also by Zheng et al. for a Au/SiO<sub>2</sub> catalyst in similar measurements.<sup>16</sup> Since its formation is slow and highly activated, we propose the irreversibly removed oxygen species to be different in nature from the oxygen deposited during O<sub>2</sub> pulses and tentatively assign





**FIGURE 3.** Accumulated absolute amounts of CO and O<sub>2</sub> consumed during three cycles with alternating reduction and oxidation of the Au/TiO<sub>2</sub> catalyst by 200 CO pulses and by 100 O<sub>2</sub> pulses, respectively, at 80 °C, starting with CO pulses after oxidative pretreatment. The amount of CO<sub>2</sub> formation is identical to the CO consumption.

it to a gold surface oxide.<sup>7,10</sup> After this first reduction sequence, however, there is a constant and stoichiometric consumption of CO and O<sub>2</sub>. These processes are fully reversible under present reaction conditions, with the total amount of reversibly removed active oxygen being  $4.6 \times 10^{18}$  O atoms  $g_{\text{cat}}^{-1}$ . This corresponds to about 1% of the totally available TiO<sub>2</sub> surface oxygen, as calculated from the specific surface area of the catalyst. Hence, oxygen removal is possible only at specific sites on the Au/TiO<sub>2</sub> surface, and it is completely inhibited in the absence of Au NPs, on pure TiO<sub>2</sub>.<sup>10,30</sup> The small amount of active oxygen species explains also straightforwardly why this species had not been detected in titration experiments under continuous reaction conditions, where due to the high gas flow the time required to deplete or refill O<sub>act</sub> is much too short to be resolved (see ref 29) and why this had not been accessible by spectroscopic measurements.

#### 4. Active Sites for Oxygen Activation and CO Oxidation on Au/TiO<sub>2</sub> Catalysts

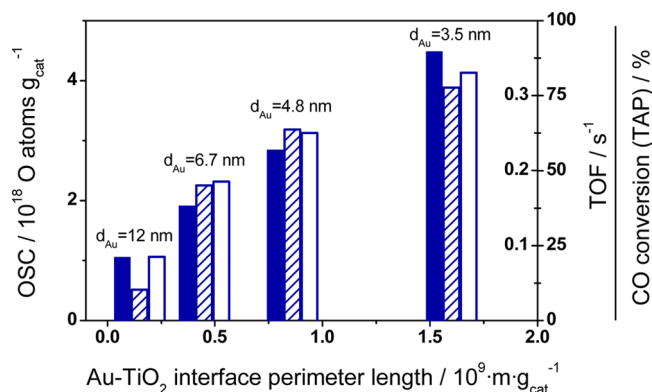
From the above data and arguments, it is clear that the active oxygen species are stable on the Au/TiO<sub>2</sub> catalyst surface for extended times at 80 °C and that their amount is very small under these conditions. The data do not, however, provide direct information on the nature of the active site or of the active oxygen species.

The first evidence for the nature of the active site comes from the absolute amount of active oxygen species, which agrees well with the number of perimeter sites at the Au–TiO<sub>2</sub> interface (Figure 3, 0.89 O atoms/perimeter site Au–TiO<sub>2</sub>). A possible correlation between the OSC and the number of perimeter sites was tested by a series of

measurements determining the OSC of four different Au/TiO<sub>2</sub> catalysts with identical Au loading but different Au particle sizes ( $d_{\text{Au}} = 3.5 \pm 0.9, 4.8 \pm 1.0, 6.7 \pm 1.5,$  and  $11.6 \pm 3.1$  nm), which were prepared from the same initial catalyst by controlled annealing.<sup>10</sup> Furthermore, the activity of the resulting catalyst was tested by exposing them to simultaneous CO/O<sub>2</sub> pulses, taking the amount of CO consumed during each pulse in steady state as measure for the catalytic activity. The resulting data, which are illustrated in Figure 4, show that both the OSC and the activity of the catalysts increase about linearly with the length of the Au–TiO<sub>2</sub> perimeter and hence with increasing number of Au perimeter sites. This correlation provides strong support for an assignment of these sites as active sites for the formation of stable but nevertheless active oxygen species. Furthermore, in the absence of other chemical differences between the catalysts, the correlation between OSC and activity indicates that the removable oxygen detected in the multipulse experiments represents also the dominant active oxygen species in the CO oxidation reaction in the presence of gas phase O<sub>2</sub>.

To verify that mechanistic assignments obtained in the TAP reactor measurements are valid also under normal reaction conditions, we determined the activities of the above Au/TiO<sub>2</sub> catalysts also in kinetic measurements at atmospheric pressure. The corresponding turnover frequencies (TOFs) at 80 °C are included in Figure 4. As expected for Au/TiO<sub>2</sub> catalysts with mean diameters above 3 nm,<sup>13</sup> the activity decreases with decreasing Au particle size, following the trend in the TAP activity measurements. Similar Au particle size effects, using Au surface area normalized TOFs, were reported previously by a number of other groups<sup>13,14,21</sup> and explained by a variety of different effects, ranging from quantum size effects<sup>13</sup> via a size-related decrease in the number of under-coordinated Au sites<sup>14</sup> to perimeter sites at the Au–TiO<sub>2</sub> interface.<sup>8,9,14</sup> Interestingly, when the TOFs are recalculated in Figure 4, normalizing them to the amount of Au perimeter atoms, this gives almost constant values for the four catalysts: 2.5, 2.6, 2.7, and 1.7 s<sup>-1</sup>, respectively, with a somewhat smaller value only for the catalyst with the highest Au particle size, supporting our proposal of the perimeter sites as active sites also under continuous reaction conditions.<sup>10</sup>

In total, the data provide strong evidence that the perimeter sites at the interface between TiO<sub>2</sub> and Au NPs are the active sites not only for the formation and adsorption of O<sub>act</sub> but also for the CO oxidation reaction both in the TAP reactor measurements and under

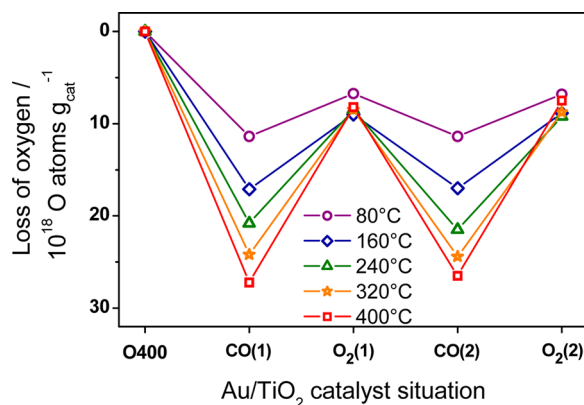


**FIGURE 4.** Oxygen storage capacity (OSC) at 80 °C (filled bars), relative conversion of CO during simultaneous CO/O<sub>2</sub> pulses at 80 °C (empty bars), and turnover frequencies (TOF, dashed bars) during CO oxidation at 80 °C (1 kPa CO, 1 kPa O<sub>2</sub>, rest N<sub>2</sub>) of Au/TiO<sub>2</sub> catalysts with identical Au loading but different Au particle sizes plotted against the length of the Au–TiO<sub>2</sub> interface perimeter.

continuous reaction conditions.<sup>10</sup> Similar conclusions were drawn by Maeda et al. from electric conductivity measurements during reaction on Au/TiO<sub>2</sub> catalysts at 200 °C.<sup>31</sup>

## 5. Nature of the Active Oxygen Species for CO Oxidation

Similar measurements were performed to gain more information on the nature of the stable adsorbed O<sub>act</sub> species, especially whether it is molecular or atomic oxygen, this time varying the reaction temperature between 80 and 400 °C in multipulse experiments identical to those described above.<sup>30</sup> TEM measurements of the Au/TiO<sub>2</sub> catalyst performed before and after such multipulse experiments at 400 °C revealed that the Au particles are essentially stable under these reaction conditions, as evidenced by the similar mean particle sizes and particle size distributions (3.0 ± 0.8 nm and 3.0 ± 0.7 nm, see Supporting Information). The variation in temperature enables us (i) to determine the thermal stability of the O<sub>act</sub> species and (ii) to unravel whether O<sub>act</sub> removal by CO or its replenishment by O<sub>2</sub> is significantly affected by thermal activation and, if so, which of them. Here one should note that experiments with labeled <sup>18</sup>O<sub>2</sub> provide only limited information on the nature of the O<sub>act</sub> species due to the rapid oxygen exchange between CO<sub>2</sub> formed during CO pulses and the TiO<sub>2</sub> support of the Au/TiO<sub>2</sub> catalyst.<sup>10</sup> Figure 5 illustrates the accumulated loss of oxygen relative to a fully oxidized surface during two subsequent reduction and oxidation sequences, starting after the initial oxidative pretreatment. First oxygen is removed from the catalyst surface by reduction with CO, lowering the oxygen content of the catalyst. From the



**FIGURE 5.** Loss of oxygen relative to the oxygen content after oxidative pretreatment (O400) after reduction by CO pulses (CO(1)), after reoxidation by O<sub>2</sub> pulses (O<sub>2</sub>(1)), and after second sequences of these pulses (CO(2); O<sub>2</sub>(2)) at different temperatures (80 to 400 °C).

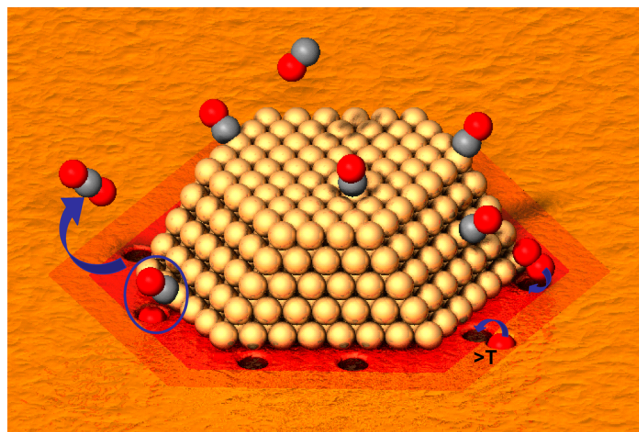
increasing total amount of CO<sub>2</sub> formed and oxygen removed in the first reduction sequence with increasing temperature, one can directly conclude that the removal of oxygen is an activated process. In the second step, during reoxidation by O<sub>2</sub> pulses, the oxygen content rises again. Interestingly, the total amount of active oxygen present on the catalyst surface after reoxidation is almost identical for all temperatures investigated. Hence, only the removal of O<sub>act</sub> is activated but not its replenishment, at least not on the sensitivity scale of these measurements. The somewhat lower oxygen content after O<sub>2</sub> pulsing compared with the initial state after oxidative pretreatment, which occurs independent of the reaction temperature, reflects the irreversible removal of oxygen, most likely surface oxide species, as discussed above. In the following cycles, there is stoichiometric consumption of CO and O<sub>2</sub>, with the difference in O<sub>act</sub> content between the catalyst in its fully reduced state (after CO pulsing) and in its fully oxidized state (after O<sub>2</sub> pulsing) representing the temperature dependent OSC of the catalyst. The latter increases with increasing temperature, from about 1% of the entire TiO<sub>2</sub> surface oxygen at 80 °C to finally 3.3% at 400 °C. Furthermore, it could be demonstrated that even at 400 °C there is no desorption induced loss of O<sub>act</sub> species with time.<sup>30</sup> These results can be understood in a simple mechanistic picture of the reaction: First of all, the high stability of the active oxygen species is incompatible with a molecularly adsorbed oxygen species, indicating that O<sub>act</sub> is an atomic species, which is formed by adsorption and dissociation of molecular oxygen at perimeter sites. At 80 °C, only oxygen species directly adjacent to the perimeter of the Au NPs can be accessed by CO. At higher temperatures, however, oxygen from sites slightly further away can also

participate in the CO oxidation. We suggest this is due to activated migration of surface oxygen to perimeter sites, where it is finally removed by reaction with CO<sub>ad</sub>. Moreover, from the fact that only the O<sub>act</sub> removal by reaction with CO<sub>ad</sub> is activated, we further conclude that surface lattice oxygen of TiO<sub>2</sub> at the perimeter sites rather than adsorbed atomic oxygen at these sites represents the active oxygen species for CO oxidation.<sup>30</sup> In combination with the fact that Au NPs are necessary for the reductive removal of O<sub>act</sub> (see above), this results in a Au-assisted MvK mechanism for the CO oxidation reaction, which is illustrated in Figure 6: CO adsorbed on the Au NPs reacts with surface lattice oxygen beside the perimeter of the Au NPs, forming CO<sub>2</sub> and a surface oxygen vacancy in the TiO<sub>2</sub> lattice, which is subsequently replenished by dissociative adsorption of oxygen. While these partial reactions proceed simultaneously in the CO oxidation reaction, considering the overall catalyst surface, they occur independently in a microscopic, local picture, resulting in a steady-state concentration of surface lattice oxygen during reaction.

The formation of surface oxygen vacancies at Au–TiO<sub>2</sub> perimeter sites during CO oxidation was recently demonstrated also by Maeda et al., applying *in situ* electrical conductance measurements.<sup>31</sup> In perfect agreement with our results, they showed that only a small fraction of the available surface oxygen (<1%) can be removed by CO at 200 °C, which is reactive for CO oxidation. Moreover, the participation of surface lattice oxygen in the CO oxidation in a Au-assisted MvK mechanism (denoted as redox mechanism in ref 32) was demonstrated recently also for Au catalysts supported on other reducible support materials, both in theoretical<sup>32</sup> and in experimental studies.<sup>33</sup>

## 6. Support Effects During the Au Catalyzed CO Oxidation

For a Au-assisted MvK mechanism, where surface lattice oxygen of the support is directly involved in the CO oxidation reaction, it is obvious that the activity of the Au catalyst should sensitively depend on the nature of the support material, foremost on its reducibility. Based on numerous studies, there is no doubt that the support has a pronounced effect on the activity.<sup>9</sup> Open and not yet resolved, however, is the origin of this effect. The support may either directly participate in the reaction, as discussed above, or affect the reaction indirectly, by influencing the shape and size of the Au nanoparticles, by support-induced strain in the Au NPs, or by chemical interaction with and charge transfer from or to the Au NPs. In order to determine the influence of the

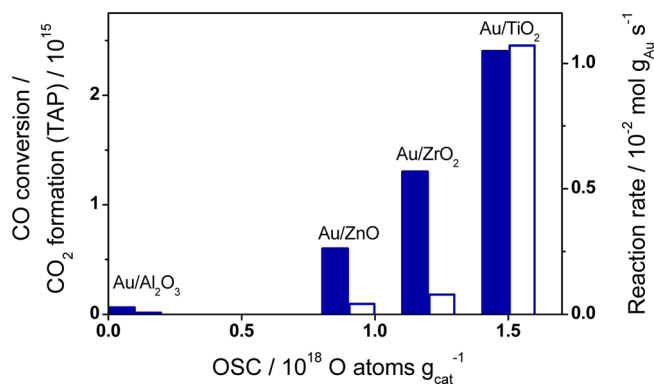


**FIGURE 6.** Schematic description of the pathway for CO oxidation on Au/TiO<sub>2</sub> catalysts at  $T \geq 80$  °C, involving (i) CO adsorption on Au NPs, (ii) reaction with activated surface lattice oxygen species at the perimeter of the Au–TiO<sub>2</sub> interface (perimeter sites), and (iii) replenishment of these sites by dissociative adsorption of O<sub>2</sub>. At higher temperatures ( $>80$  °C), migration of surface oxygen vacancies gives access also to neighboring surface lattice oxygen.

support material on the catalytic performance of Au catalysts and especially to evaluate whether it affects the activation of oxygen and the active site for oxygen activation, we determined the oxygen storage capacity (OSC) and its correlation with the CO oxidation activity of four different Au catalysts, supported on Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZnO, and ZrO<sub>2</sub>, but prepared in the same way with comparable Au loadings and Au particle sizes (Au particle size distributions are included in the Supporting Information).<sup>29</sup> Kinetic measurements over these four catalysts performed at atmospheric pressure and 80 °C (Figure 7, empty bars), revealed pronounced differences in the catalytic activity for CO oxidation, which cannot be explained by the rather small variation in Au NP sizes and Au loadings, underlining a distinct effect of the support on the activity of these different Au catalysts. The trends obtained are in good agreement with earlier results of Schubert et al., who distinguished between two major groups of support materials, reducible materials leading to “active” catalysts and nonreducible materials resulting in “inactive” catalysts.<sup>9</sup> The difference was tentatively attributed to the different ability of these materials to create oxygen vacancies on the support, close to the Au particles.<sup>9</sup> In addition, the crystalline structure and the polymorph of the supporting metal oxides may also affect the catalytic behavior, as shown for Au/TiO<sub>2</sub> by Haruta et al.<sup>34</sup> This, however, cannot explain the huge differences in catalytic activity observed for different metal oxides as described above.

This proposal from Schubert et al. was tested by comparing the steady-state activities with the OSCs and the catalytic





**FIGURE 7.** Absolute amounts of CO converted and CO<sub>2</sub> produced in steady state during simultaneous CO/O<sub>2</sub> pulses (filled bars) and reaction rates during continuous CO oxidation (empty bars; 1 kPa CO, 1 kPa O<sub>2</sub>, rest N<sub>2</sub>) at 120 °C on differently supported Au catalysts plotted against the OSC of the corresponding catalysts.

activity determined by multipulse and single-pulse TAP reactor experiments. The corresponding results are also summarized in Figure 7. The filled bars show the absolute amounts of CO converted and CO<sub>2</sub> produced in steady state during simultaneous CO/O<sub>2</sub> pulses on the different Au catalysts, plotted against their respective OSC. Also under instationary conditions, the activity strongly depends on the support material, with the same trend as in the kinetic measurements.

The similar order of the activity obtained in TAP measurements and of the reaction rates in kinetic measurements is further evidence that the mechanistic insights gained from TAP reactor studies are also valid under stationary reaction conditions at atmospheric pressure. Moreover, there is a clear correlation between OSCs and CO oxidation activities of the catalysts, demonstrating that the activity is largely controlled by the OSC of the catalyst, with the activity increasing with higher OSC. From this finding, we propose that also for the other Au catalysts supported on reducible metal oxides, the CO oxidation proceeds via a Au-assisted MvK mechanism and hence that surface lattice oxygen of the support located at the perimeter of the Au–oxide interface represents the active oxygen species. For Au/Al<sub>2</sub>O<sub>3</sub>, the OSC is hardly detectable within the precision of the experiments, indicating that in this case the participation of surface lattice oxygen in the CO oxidation is negligible, as expected for a nonreducible support. Accordingly, the dominant reaction pathway over these catalysts has to be different. Here a “Au-only mechanism” may be dominant, which should be active and of similar order of magnitude for all Au catalysts.<sup>23,29</sup>

## 7. Effect of the Reaction Conditions

It is well-known that the reaction conditions, including reaction temperature<sup>8,20</sup> and the level of humidity in the

reaction gas mixture,<sup>12,35</sup> play an important role in the CO oxidation on supported Au catalysts.

It has been reported already more than a decade ago that the measured apparent activation energy for CO oxidation depends sensitively on the temperature and that it decreases to almost zero for reaction on Au/TiO<sub>2</sub> when going to temperatures below room temperature, which was associated with a change in the dominant reaction pathway.<sup>8</sup> Preliminary results of OSC measurements on Au/TiO<sub>2</sub> catalysts in the temperature range between 400 and –25 °C yielded a pronounced deviation of the OSC below 80 °C from the trend at higher temperatures (80–400 °C), with a minimum at 25 °C and a subtle increase at lower temperature. Although further measurements are required, these results also indicate a change in the rate limiting process for oxygen storage and oxygen activation in this temperature range, similar to the findings in kinetic measurements.

The conclusion of surface lattice oxygen being the active oxygen species for CO oxidation seems to be in contrast with previous proposals that CO is oxidized by molecularly adsorbed oxygen.<sup>20</sup> This apparent discrepancy can be easily resolved, however, when the different temperatures of these studies are considered. It is likely that the activated reactive removal of surface lattice oxygen essential for the Au-assisted MvK mechanism is inhibited at the low temperatures used in those studies, whereas the weakly bound O<sub>2,ad</sub> species required for the molecular mechanism become increasingly longer living and hence more effective for the reaction.<sup>20</sup>

Finally, it is well-known that the presence of trace impurities of water in the feed strongly affects the reaction kinetics and possibly also the reaction mechanism.<sup>12,35</sup> Both questions are topics of ongoing studies in our laboratory. (Note that all measurements described before were performed under strictly dry reaction conditions.) First results indicated that the OSC increases with increasing amounts of H<sub>2</sub>O and OH groups adsorbed on the catalyst surface. Hence, also in this case both OSC and activity show clear effects induced by the presence of adsorbed H<sub>2</sub>O/OH species, indicative of a change or modification in the dominant reaction pathway.

## 8. Concluding Remarks

Our TAP reactor studies demonstrate that under common reaction conditions and on Au catalysts supported on reducible metal oxides, CO oxidation proceeds via a Au-assisted MvK mechanism, during which surface lattice oxygen at the perimeter of the Au–M<sub>x</sub>O<sub>y</sub> interface is removed by reaction



with CO and subsequently replenished by reaction with O<sub>2</sub> from the gas phase. The latter process is fast and not or very little activated, pointing to a facile dissociation of molecularly adsorbed O<sub>2</sub> precursors to O<sub>act</sub> species on oxygen vacancies formed previously at the perimeter sites. Other reaction pathways come into play and may even become dominant i) for Au catalysts based on non-reducible supports, where this reaction pathway is not possible and the residual reactivity may be explained by a "Au-only mechanism", ii) for low reaction temperatures, where removal of lattice oxygen is increasingly inhibited, or iii) in the presence of coreactants such as adsorbed H<sub>2</sub>O or OH species.

We suggest that, in addition to the CO oxidation reaction, these results and findings are important also in a more general sense, for the mechanistic understanding of oxidation reactions over oxide supported Au catalysts in general, where the same active oxygen species is expected to participate in the reaction.

The authors thank R. Leppelt, M. Kotobuki, D.A. Hansgen, G. Bräth, and T. Häring. We are indebted to F. Schüth and his group for very fruitful collaboration. The authors also acknowledge financial support from the Deutsche Forschungsgemeinschaft (DFG) via Priority Program SPP 1181.

**Supporting Information.** Experimental details of the TAP reactor and kinetic measurements and characterization of the different Au catalysts (TEM images and particle size distributions). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## BIOGRAPHICAL INFORMATION

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## FOOTNOTES

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## REFERENCES

- Bond, G. C. The Catalytic Properties of Gold. *Gold Bull.* **1972**, *5*, 11–13.
- Bond, G. C.; Sermon, P. A. Gold Catalysts for Olefin Hydrogenation. *Gold Bull.* **1973**, *6*, 102–105.
- Hashmi, A. S. K.; Hutchings, G. J. Gold Catalysis. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896–7936.
- Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. Novel Gold Catalysts for the Oxidation of Carbon Monoxide. *Chem. Lett.* **1987**, *16*, 405–408.
- Nkosi, B.; Coville, N. J.; Hutchings, G. J. Reactivation of a Supported Gold Catalyst for Acetylene Hydrochlorination. *J. Chem. Soc., Chem. Commun.* **1988**, 71–72.
- Finch, R. M.; Hodge, N. A.; Hutchings, G. J.; Meagher, A.; Pankhurst, Q.; Siddiqui, M. R. H.; Wagner, F. E.; Whyman, R. Identification of Active Phases in Au-Fe Catalysts for Low Temperature CO Oxidation. *Phys. Chem. Chem. Phys.* **1999**, *1*, 485–489.
- van Bokhoven, J. A.; Louis, C.; Miller, J. T.; Tromp, M.; Safonova, O. V.; Glatzel, P. Activation of Oxygen on Gold-Alumina Catalysts: In-Situ High Energy-Resolution Fluorescence and Time-Resolved X-Ray Spectroscopy. *Angew. Chem., Int. Ed.* **2006**, *45*, 4651–4654.
- Haruta, M.; Daté, M. Advances in the Catalysis of Au Nanoparticles. *Appl. Catal., A* **2001**, *222*, 427–437.
- Schubert, M. M.; Hackenberg, S.; van Veen, A. C.; Muhler, M.; Plzak, V.; Behm, R. J. CO Oxidation Over Supported Gold Catalysts - 'Inert' and 'Active' Support Materials and Their Role for the Oxygen Supply During Reaction. *J. Catal.* **2001**, *197*, 113.
- Kotobuki, M.; Leppelt, R.; Hansgen, D.; Widmann, D.; Behm, R. J. Reactive Oxygen on a Au/TiO<sub>2</sub> Supported Catalyst. *J. Catal.* **2009**, *264*, 67–76.
- Gong, J.; Mullins, C. B. Surface Science Investigations of Oxidative Chemistry on Gold. *Acc. Chem. Res.* **2009**, *42*, 1063–1073.
- Fujitani, T.; Nakamura, I. Mechanism and Active Sites of the Oxidation of CO Over Au/TiO<sub>2</sub>. *Angew. Chem., Int. Ed.* **2011**, *50*, 10144–10147.
- Valden, M.; Lai, X.; Goodman, D. W. Onset of Catalytic Activity of Gold Clusters on Titania With the Appearance of Nonmetallic Properties. *Science* **1998**, *281*, 1647–1650.
- Overbury, S. H.; Schwartz, V.; Mullins, D. R.; Yan, W.; Dai, S. Evaluation of the Au Size Effect: CO Oxidation Catalyzed by Au/TiO<sub>2</sub>. *J. Catal.* **2006**, *241*, 56–65.
- Gleaves, J. T.; Yablonskii, G. S.; Phanawadee, P.; Schuurman, Y. TAP-2: An Interrogative Kinetics Approach. *Appl. Catal., A* **1997**, *160*, 55–88.
- Zheng, X.; Veith, G. M.; Redekop, E.; Lo, C. S.; Yablonsky, G. S.; Gleaves, J. T. Oxygen and CO Adsorption on Au/SiO<sub>2</sub> Catalysts Prepared by Magnetron Sputtering: The Role of Oxygen Storage. *Ind. Eng. Chem. Res.* **2010**, *49*, 10428–10437.
- Leppelt, R.; Hansgen, D.; Widmann, D.; Häring, T.; Bräth, G.; Behm, R. J. Design and Characterization of a Temporal Analysis of Products Reactor. *Rev. Sci. Instrum.* **2007**, *78*, No. 104103.
- Bollinger, M. A.; Vannice, M. A. A Kinetic and DRIFTS Study of Low-Temperature Carbon Monoxide Oxidation Over Au-TiO<sub>2</sub> Catalysts. *Appl. Catal., B* **1996**, *8*, 417–443.
- Bocuzzi, F.; Chiorino, A. FTIR Study on Au/TiO<sub>2</sub> at 90K and Room Temperature. An Insight into the Nature of the Reaction Centers. *J. Phys. Chem. B* **2000**, *104*, 5414–5416.
- Green, I. X.; Tang, W.; Neurock, M.; Yates, J. T. Spectroscopic Observation of Dual Catalytic Sites During Oxidation of CO on a Au/TiO<sub>2</sub> Catalyst. *Science* **2011**, *333*, 736–739.
- Haruta, M. Size- and Support-Dependency in the Catalysis of Gold. *Catal. Today* **1997**, *36*, 153–166.
- Liu, Z.-P.; Gong, X.-Q.; Kohanoff, J.; Sanchez, C.; Hu, P. Catalytic Role of Metal Oxides in Gold-Based Catalysts: A First Principles Study of CO Oxidation on TiO<sub>2</sub> Supported Au. *Phys. Rev. Lett.* **2003**, *91*, No. 266102.
- Remediakis, I. N.; Lopez, N.; Nørskov, J. K. CO Oxidation on Rutile-Supported Au Nanoparticles. *Angew. Chem.* **2005**, *117*, 1858–1860.
- Carrettin, S.; Hao, Y.; Aguilar-Guerrero, V.; Gates, B. C.; Trasobares, S.; Calvino, J. J.; Corma, A. Increasing the Number of Oxygen Vacancies on TiO<sub>2</sub> by Doping With Iron Increases the Activity of Supported Gold for CO Oxidation. *Chem.—Eur. J.* **2007**, *13*, 7771–7779.
- Liu, H.; Kozlov, A. I.; Kozlova, A. P.; Shido, T.; Asakura, K.; Iwasawa, Y. Active Oxygen Species and Mechanism for Low-Temperature CO Oxidation Reaction on TiO<sub>2</sub>-Supported

- Au Catalyst Prepared From Au(PPh<sub>3</sub>)(NO<sub>3</sub>) and As-Precipitated Titanium Hydroxide. *J. Catal.* **1999**, *185*, 252–264.
- 26 Okumura, M.; Coronado, J. M.; Soria, J.; Haruta, M.; Conesa, J. EPR Study of CO and O<sub>2</sub> Interaction With Supported Au Catalysts. *J. Catal.* **2001**, *203*, 168–174.
- 27 Laursen, S.; Linic, S. Geometric and Electronic Characteristics of Active Sites on TiO<sub>2</sub>-Supported Au Nano-Particles: Insights From First Principles. *Phys. Chem. Chem. Phys.* **2009**, *11*, 11006–11012.
- 28 Grisel, R. J. H.; Nieuwenhuys, B. Selective CO Oxidation of CO Over Supported Au Catalysts. *J. Catal.* **2001**, *199*, 48–59.
- 29 Widmann, D.; Liu, Y.; Schüth, F.; Behm, R. J. Support Effects in the Au Catalyzed CO Oxidation - Correlation Between Activity, Oxygen Storage Capacity and Support Reducibility. *J. Catal.* **2010**, *276*, 292–305.
- 30 Widmann, D.; Behm, R. J. Active Oxygen on a Au/TiO<sub>2</sub> Catalyst - Formation, Stability and CO Oxidation Activity. *Angew. Chem., Int. Ed.* **2011**, *50*, 10241–10245.
- 31 Maeda, Y.; Iizuka, Y.; Kohyama, M. Generation of Oxygen Vacancies at a Au/TiO<sub>2</sub> Perimeter Interface During CO Oxidation Detected by in Situ Electrical Conductance Measurement. *J. Am. Chem. Soc.* **2013**, *135*, 906–909.
- 32 Kim, H. Y.; Henkelman, G. CO Oxidation at the Interface of Au Nanoclusters and the Stepped-CeO<sub>2</sub>(111) Surface by the Mars-Van Krevelen Mechanism. *J. Phys. Chem. Lett.* **2013**, *4*, 216–221.
- 33 Li, L.; Wang, A.; Qiao, B.; Lin, J.; Huang, Y.; Wang, X.; Zhang, T. Origin of the High Activity of Au/FeO<sub>x</sub> for Low-Temperature CO Oxidation: Direct Evidence for a Redox Mechanism. *J. Catal.* **2013**, *299*, 90–100.
- 34 Haruta, M.; Uphade, B. S.; Tsubota, S.; Miyamoto, A. Selective Oxidation of Propylene Over Gold Deposited on Titanium-Based Oxides. *Res. Chem. Intermed.* **1998**, *24*, 329–336.
- 35 Daté, M.; Haruta, M. Moisture Effect on CO Oxidation Over Au/TiO<sub>2</sub> Catalyst. *J. Catal.* **2001**, *201*, 221–224.