catalysts

Article

Competition of CO and H_2 for Active Oxygen Species during the Preferential CO Oxidation (PROX) on Au/TiO_2 Catalysts

Yeusy Hartadi, R. Jürgen Behm and Daniel Widmann *

Institute of Surface Chemistry and Catalysis, Ulm University, Albert-Einstein-Allee 47, D-89081 Ulm, Germany; yeusy.hartadi@uni-ulm.de (Y.H.); juergen.behm@uni-ulm.de (R.J.B.)
* Correspondence: daniel.widmann@uni-ulm.de; Tel.: +49-731-502-5445

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Abstract: Aiming at an improved mechanistic understanding of the preferential oxidation of CO on supported Au catalysts, we have investigated the competition between CO and H_2 for stable, active oxygen (O_{act}) species on a Au/TiO_2 catalyst during the simultaneous exposure to CO and H_2 with various CO/H_2 ratios at 80 °C and 400 °C by quantitative temporal analysis of products (TAP) reactor measurements. It is demonstrated that, at both higher and lower temperature, the maximum amount of active oxygen removal is (i) independent of the CO/H_2 ratio and (ii) identical to the amount of active oxygen removal by CO or H_2 alone. Hence, under preferential CO oxidation (PROX) reaction conditions, in the simultaneous presence of CO and H_2, CO and H_2 compete for the same active oxygen species. In addition, also the dependency of the selectivity towards CO oxidation on the CO/H_2 ratio was evaluated from these measurements. Consequences of these findings on the mechanistic understanding of the PROX reaction on Au/TiO_2 will be discussed.

Keywords: active oxygen; CO oxidation; H_2 oxidation; preferential CO oxidation (PROX); Au catalysis; Au/TiO_2; temporal analysis of products (TAP)

1. Introduction

Gold nanoparticles supported on a variety of metal oxides are well known for their exceptional high activity and selectivity for various oxidation and reduction reactions already at very low temperatures [1–4]. One of the most prominent examples is the CO oxidation reaction on supported Au catalysts, e.g., on Au/TiO_2, since it also serves as a test reaction for gas phase oxidation catalysis in heterogeneous Au catalysis in general [5]. Practical applications of monometallic supported Au catalysts are rare, so far, but they are claimed to be promising candidates for the selective removal of CO from H_2-rich reformates to values below 10 ppm [6–8] for use in low temperature Polymer Electrolyte Membrane (PEM) fuel cells [6,9]. The ultra-purification of H_2-rich fuels via the selective CO oxidation (or preferential CO oxidation—PROX) reaction requires catalysts that are highly active for the CO oxidation (Equation (1)). At the same time, the catalysts should have a very low activity for the continuous oxidation of H_2 to water (Equation (2)), although H_2 reaches concentrations up to 75% (depending on the process of H_2 generation) and is, hence, present in large excess compared to CO in the reaction gas [6,9–11]. One should note, however, that an oxidation of H_2 to adsorbed hydroperoxy-like species, which have previously been proposed to represent reaction intermediates in the preferential CO oxidation in the presence of H_2, may even be beneficial for the PROX activity of supported Au catalysts [10,12].

$$CO + ½O_2 \rightarrow CO_2 \quad (1)$$

$$H_2 + ½O_2 \rightarrow H_2O \quad (2)$$

In previous studies it has been demonstrated that metal oxide-supported Au nanoparticles (NPs) are highly selective for CO oxidation in the presence of hydrogen [9–11,13–15], where the selectivity is defined by the ratio between the oxygen consumption for CO oxidation, which equals half of the CO consumption according to the reaction stoichiometry (Equation (1)), and the overall oxygen consumption (for CO and H_2 oxidation), or the ratio between CO_2 formation and the sum of CO_2 and H_2O formation (Equation (3)):

$$S = \frac{CO\ \ consumption}{2 \times O_2\ \ consumption} = \frac{CO_2}{CO_2 + H_2O} \tag{3}$$

Despite the large excess of H_2, typically about 1% CO and up to 75% H_2 in previous studies, the selectivity of metal oxide supported Au catalysts towards CO oxidation is considerably higher than 50% under typical reaction conditions, at a reaction temperature of 80 °C [13–15], but decreases with decreasing CO content in the reaction gas atmosphere [10,13]. Considering the very low CO concentrations that can be tolerated in PEM fuel cells (<10 ppm), further improvements of existing catalysts, in particular their selectivity, is still mandatory.

Most crucial in the CO oxidation reaction on supported Au catalysts, and also most controversially debated, is the activation of molecular oxygen, which includes issues such as the active site for oxygen activation and the resulting active oxygen species for the oxidation of adsorbed CO [16]. For reaction in a CO/H_2 mixture as in the PROX reaction, this also includes the question whether CO and H_2 compete for the same adsorption sites and/or the same active oxygen species. These questions are topic of the present work, where we investigated the selective oxidation of CO in CO/H_2 mixtures on a Au/TiO_2 catalyst by quantitative temporal analysis of products (TAP) reactor measurements.

Before presenting the results of the present study, we will briefly summarize previous findings relevant for the present work. It is well known that CO mainly adsorbs on the surface of the Au nanoparticles under relevant reaction conditions, at room temperature and above [17–19], and also dissociatively adsorbed hydrogen is assumed to be located on these sites [20,21] or at Au atoms located at the perimeter of the Au-TiO_2 interface [22,23], resulting in the formation of a highly active, atomically-adsorbed hydrogen species [20,22–24]. Furthermore, there seems to be increasing agreement that CO adsorbed on the Au NPs mainly reacts with active oxygen species located at the perimeter sites of the Au-M_xO_y interface in the dominant reaction pathway for CO oxidation [19,25,26], and that for Au catalysts supported on reducible metal oxides, e.g., for Au/TiO_2, and for reaction temperatures above room temperature, surface lattice oxygen of the support represents the active oxygen species [27–33]. Based on TAP reactor measurements, we recently proposed a Au-assisted Mars-van Krevelen mechanism as the dominant reaction pathway for the CO oxidation at $T \geqslant 80$ °C on Au/TiO_2, where TiO_2 surface lattice oxygen located at the interface between Au nanoparticles and TiO_2 support represents the active oxygen species for CO oxidation, and is continuously removed and replenished during the reaction [27,31]. At lower temperatures, (below −120 °C), the dominant reaction pathway is expected to change and molecularly adsorbed oxygen is proposed to represent the active oxygen species [19,34]. Furthermore CO adsorption on the TiO_2 support becomes increasingly important for the overall reaction [19,34]. Based on similar type TAP reactor measurements, specifically from the identical amount of active oxygen species for the CO oxidation and the H_2 oxidation, and from their almost identical dependency on the Au particle size, we recently proposed that hydrogen oxidation at 80 °C and higher also proceeds via a Au-assisted Mars-van Krevelen mechanism, identical to CO oxidation, with surface lattice oxygen located at the perimeter of the Au-TiO_2 interface acting as active oxygen species [35]. This conclusion was supported recently by density functional theory (DFT) based calculations, where the lowest H_2 dissociation barrier was obtained for H_2 interacting with O^{2-} surface lattice oxygen species in TiO_2 close to the Au/TiO_2 perimeter [36]. We had speculated already from those TAP results that CO and H_2 compete for this O_{act} species when present simultaneously, and that this competition is a crucial factor for the catalysts selectivity towards CO oxidation [35]. Experimental proof for this mechanism, in the simultaneous presence of CO and H_2, is still lacking. Here one has to consider that under PROX reaction conditions the formation of hydroxyl groups and adsorbed water on the catalysts surface upon interaction with H_2 may significantly influence its CO oxidation activity [14,37–40].

In the following we report results of TAP reactor measurements, where the absolute amount of active oxygen removal by CO and H_2 and its replenishment by O_2 was evaluated upon exposure of a Au/TiO_2 catalyst to alternate sequences of CO/H_2/Ar and O_2/Ar pulses, using different CO/H_2 mixtures. From these data we will derive whether CO and H_2 compete for the same active oxygen species also in the simultaneous presence of CO and H_2. Moreover, the selectivity for CO oxidation during mixed CO/H_2 pulses can be determined. Finally we will discuss the consequences of the present finding for the mechanism of the PROX reaction on Au/TiO_2 catalysts.

2. Results and Discussions

2.1. Active Oxygen Removal by CO and H_2

Before focusing on the reaction with mixed CO/H_2/Ar pulses, we determined the removal of stable, active oxygen from the Au/TiO_2 catalyst surface by CO/Ar and H_2/Ar pulses only for calibration. The absolute amounts of active oxygen determined in these measurements will then be used as references for the active oxygen removal in the simultaneous presence of CO and H_2. Similar to our previous study [35], the catalyst was alternately exposed to several sequences of (i) CO/Ar and O_2/Ar or (ii) H_2/Ar and O_2/Ar, respectively, in order to reactively remove and replenish the available active oxygen from the catalyst surface. These measurements were performed after *in situ* calcination (O400) of the Au/TiO_2 catalyst and subsequent saturation of its surface by adsorbed water by exposure to 5000 H_2/Ar pulses at 80 °C. Additional experiments including the exposure of the catalyst to various amounts of H_2/Ar pulses and subsequent temperature programmed desorption (TPD) measurements revealed that (i) there is formation of stable adsorbed water upon exposure to H_2/Ar pulses at 80 °C and (ii) treatment with 5000 H_2/Ar pulses results in a surface saturation and, hence, equal surface concentrations of adsorbed water during all subsequent experiments. Note that, at 400 °C, in contrast, water formed during the H_2 oxidation readily desorbs, and does not need to be considered in the following measurements.

The multi-pulse experiments following this treatment (O400 and H_2 pulses) revealed an oxygen consumption of the fully-reduced catalyst during O_2/Ar pulses at 80 °C of 3.3×10^{18} O atoms$\cdot g_{cat}{}^{-1}$. This is almost identical to the CO consumption/CO_2 formation in the subsequent sequence of CO/Ar pulses (3.4×10^{18} molecules$\cdot g_{cat}{}^{-1}$), as well as to the oxygen consumption during subsequent O_2/Ar pulses (after 250 CO/Ar pulses). Hence, this (partial) reduction and re-oxidation of the catalyst surface is fully reversible under present conditions. Furthermore, in agreement with previous findings, the amount of CO_2 formation in each CO/Ar sequence always equals the amount of CO consumed, indicating that there is no significant build-up of stable adsorbed, carbon containing surface species (surface carbonates, *etc.*) under present reaction conditions [25,41]. Finally, all CO_2 is formed during CO pulses (and not during O_2 pulses), as expected for CO weakly adsorbed on the Au NPs at 80 °C, and completely desorbed before O_2 is introduced [31].

The oxygen storage capacity (OSC) at 80 °C is slightly lower in the present study (3.3×10^{18} O atoms$\cdot g_{cat}{}^{-1}$) than determined previously for a comparable Au/TiO_2 catalyst, which was also saturated with adsorbed water by H_2 pulses prior to the pulse experiments (4.6×10^{18} O atoms$\cdot g_{cat}{}^{-1}$) [35], but of a similar order of magnitude. More important for the present study, however, is the comparison between the absolute amounts of active oxygen on (fully oxidized) Au/TiO_2 for the CO oxidation and the H_2 oxidation. From the oxygen uptake during O_2/Ar pulses after 1500 H_2/Ar pulses on the Au/TiO_2 catalyst at 80 °C we obtained a value of 3.3×10^{18} O atoms$\cdot g_{cat}{}^{-1}$ for the total amount of stable oxygen which is active for the H_2 oxidation (see Table 1). Note that compared to CO/Ar a significantly higher number of H_2/Ar pulses is necessary to completely remove the active surface oxygen. While for a complete removal of all availabe O_{act}

species via the CO oxidation about 200 CO/Ar pulses were needed, almost 1500 H_2/Ar pulses are necessary for its removal via the H_2 oxidation. This reflects the much lower efficiency of hydrogen for active oxygen removal compared to CO, as was already demonstrated previously [31]. The total amounts of active oxygen for CO and H_2 oxidation, however, are almost identical also for the present Au/TiO_2 catalyst [31].

Table 1. Absolute amounts of active stable oxygen (O_{act}) removal and CO_2 formation during CO, H_2, and CO/H_2 pulses with different CO/H_2 ratios on the fully oxidized Au/TiO_2 catalyst at 80 °C, and corresponding selectivities for CO oxidation.

Ratio CO/H_2	H_2/(CO + H_2)/%	O_{act} Removal */ 10^{18} O atoms$\cdot g_{cat}^{-1}$	CO_2 Formation */ 10^{18} molecules$\cdot g_{cat}^{-1}$	Selectivity/%
CO only	0	3.3 ± 0.2	3.4 ± 0.2	100
1/0.5	33	2.9 ± 0.2	2.6 ± 0.2	92
1/1	50	2.6 ± 0.2	2.3 ± 0.2	90
1/2	67	3.1 ± 0.2	2.2 ± 0.1	71
1/4	80	3.3 ± 0.2	2.0 ± 0.1	60
1/8	89	3.1 ± 0.2	1.5 ± 0.1	49
H_2 only	100	3.3 ± 0.2	0	0

* Error estimations are based on the repeated reproduction of individual pulse sequences.

Additionally, for reaction at 400 °C, the total amounts of active oxygen for CO oxidation and for H_2 oxidation are also almost identical (12.7 × 10^{18} O atoms$\cdot g_{cat}^{-1}$ and 12.6 × 10^{18} O atoms$\cdot g_{cat}^{-1}$, respectively; see Table 2). The higher amount of O_{act} species available and, accordingly, a higher amount of TiO_2 surface lattice oxygen removal at 400 °C is in agreement with findings in previous studies, where this was explained by the migration of TiO_2 surface lattice oxygen to Au-TiO_2 perimeter sites at elevated temperatures [27]. This enables the removal also of O_{act} species which were originally located further away from the Au-TiO_2 interface perimeter. At 80 °C, in contrast, the mobility of surface lattice oxygen is negligible, and only surface lattice oxygen species located directly at Au-TiO_2 interface perimeter sites can be removed by reaction with CO_{ad} or H_{ad} [25,35]. Considering the Au loading and the Au particle size distribution (from TEM imaging), and assuming hemispherical Au nanoparticles, the total amount of these species can be estimated to be 6.2 × 10^{18} O atoms$\cdot g_{cat}^{-1}$.

Hence, the data are in full agreement with our previous proposal that CO and hydrogen are both oxidized by the same active oxygen species at both 80 °C and 400 °C, by TiO_2 surface lattice oxygen close to Au-TiO_2 perimeter sites [27]. For more details see Ref. [35].

Table 2. Absolute amounts of active stable oxygen (O_{act}) removal and CO_2 formation during CO, H_2, and CO/H_2 pulses with different CO/H_2 ratios on the fully oxidized Au/TiO_2 catalyst at 400 °C.

Ratio CO/H_2	H_2/(CO+H_2)/%	O_{act} Removal */ 10^{18} O atoms$\cdot g_{cat}^{-1}$	CO_2 Formation */ 10^{18} molecules$\cdot g_{cat}^{-1}$
CO only	0	12.7 ± 0.6	10.0 ± 0.5
1/0.5	33	11.5 ± 0.6	9.3 ± 0.5
1/1	50	11.5 ± 0.6	8.8 ± 0.4
1/2	67	12.9 ± 0.6	8.7 ± 0.4
1/4	80	12.9 ± 0.6	7.7 ± 0.3
1/8	89	11.8 ± 0.6	6.1 ± 0.3
H_2 only	100	12.6 ± 0.6	0

* Error estimations are based on the repeated reproduction of individual pulse sequences.

2.2. Active Oxygen Removal by CO/H_2 Mixtures

Similar multi-pulse experiments were performed with alternate sequences of O_2/Ar and CO/H_2/Ar pulses with various CO/H_2 ratios. At both temperatures (80 °C and 400 °C) five different

CO/H_2 mixtures were investigated, with CO/H_2 ratios ranging from 1/0.5 to 1/8 (see also Tables 1 and 2). The trends in the pulse signals of CO, CO_2, H_2, H_2O, and O_2 during reduction and re-oxidation with $CO/H_2/Ar$ pulses (CO/H_2 = 1/2) and subsequent O_2/Ar pulses, respectively, are illustrated in Figure 1 for reaction at 80 °C on Au/TiO_2. Only the first 50 pulses of each sequence are shown, where differences in the measured intensities due to consumption of educts (CO, H_2, and O_2)/formation of products (CO_2, H_2O) are visible in the raw data, while the actual number of pulses per sequence are significantly higher (see Section 3.2). For $CO/H_2/Ar$ and O_2/Ar at 80 °C the number of pulses in each sequence was 250 and 150, respectively.

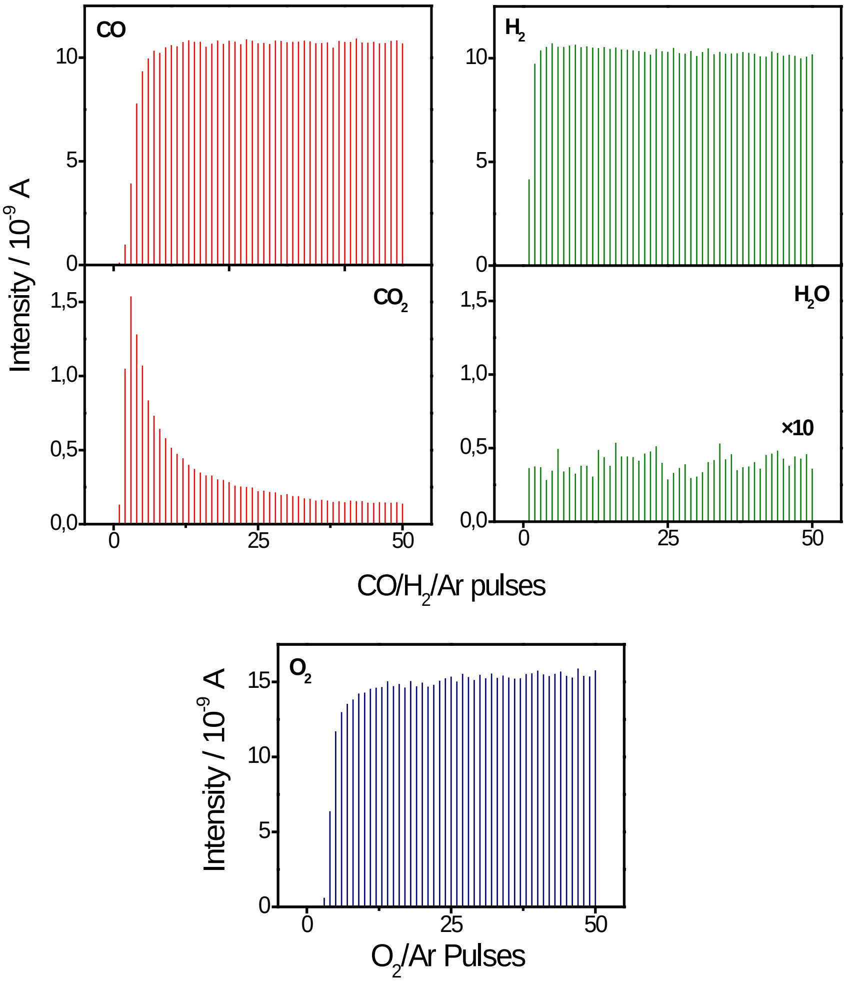

Figure 1. Mass spectrometer signals of CO, CO_2, H_2, and H_2O measured during a sequence of $CO/H_2/Ar$ pulses (CO/H_2 ratio = 1/2) on Au/TiO_2 at 80 °C after oxidation by O_2/Ar pulses, as well as the O_2 signal measured during subsequent O_2/Ar pulses at 80 °C.

During the first 10 $CO/H_2/Ar$ pulses on the fully oxidized Au/TiO_2 catalyst there is a significant consumption of CO, indicated by the much lower CO intensity compared to that after about 50 or more pulses, and in parallel the formation of CO_2 (Figure 1). Hence, also under these conditions CO oxidation proceeds by reaction with stable surface oxygen of the catalyst. With increasing number of pulses the CO consumption/CO_2 formation during each pulse decreases, until there is no visible discrepancy to the steady-state situation after about 10 pulses. The absolute amount of CO consumed/CO_2 formed during the 250 $CO/H_2/Ar$ pulses in this sequence at 80 °C was 2.2×10^{18} molecules$\cdot$ $g_{cat}{}^{-1}$. The significantly lower amount of CO_2 formation during the exposure of the fully oxidized Au/TiO_2 catalyst to CO/H_2 pulses as compared to CO pulsing (3.3×10^{18} molecules$\cdot$ $g_{cat}{}^{-1}$, see above) indicates already that stable adsorbed active oxygen is not only consumed by reaction with CO, but also by reaction with hydrogen. From the H_2 signal shown in Figure 1, however, no (or only very little) H_2 consumption can be detected, in contrast to the CO signal. A somewhat lower H_2 signal is observed only during the first 1–2 pulses, with the lower intensity measured during the first pulse originating from a generally lower overall pulse size for the first pulse in every sequence (an artifact of our TAP reactor system). Hence, from the raw data there is no indication for reduction of Au/TiO_2 by H_2 during these pulses, and also the quantitative evaluation of all $CO/H_2/Ar$ pulses could not resolve significant H_2 consumption. From previous TAP reactor studies on Au/TiO_2 as well as on Au/CeO_2 it is already known that the efficiency of H_2 for active oxygen removal is considerably lower compared to CO [35,42]. The H_2 consumption during a single pulse is, accordingly, too low to be resolved in these measurements, and the same is true for the formation of water during exposure to H_2 or CO/H_2 pulses at 80 °C [35]. As described in Section 3.2 (see below), the consumption of active oxygen by H_2 can, nevertheless, be calculated from the total oxygen uptake during subsequent O_2/Ar pulses, from the more than stoichiometric consumption of O_2 compared to the preceding CO_2 formation during two consecutive runs at 80 °C.

The O_2 signal measured during re-oxidation of Au/TiO_2 by O_2/Ar pulses, after reduction of the catalyst by CO and H_2, is also shown in Figure 1 (lower panel). Similar to CO consumption during $CO/H_2/Ar$ pulses, O_2 consumption during the first 10–15 O_2/Ar pulses is obvious already from the raw data by the lower intensity compared to that after saturation. Quantitative evaluation of the O_2 consumption during the whole sequence (150 O_2/Ar pulses) revealed that 3.1×10^{18} O atoms$\cdot g_{cat}{}^{-1}$ are needed to fully re-oxidize the catalyst at 80 °C (see also Table 1). This value is almost identical to the one determined after reduction by CO or H_2 only (3.3×10^{18} O atoms$\cdot g_{cat}{}^{-1}$ in both cases), but significantly higher than the CO_2 formation during the preceding $CO/H_2/Ar$ pulses (2.2×10^{18} molecules$\cdot g_{cat}{}^{-1}$). Accordingly, the amount of active oxygen removed by reaction with hydrogen amounts to 0.9×10^{18} O atoms$\cdot g_{cat}{}^{-1}$. These results clearly demonstrate that under present reaction conditions, with CO and hydrogen being simultaneously present on the surface, these species compete for the same active oxygen species. The higher amount of active oxygen removal by CO, in spite of the considerable excess of H_2 during the $CO/H_2/Ar$ pulses (CO/H_2 ratio of 1/2) illustrates the high selectivity of Au/TiO_2 for the CO oxidation (71% in this case) under present reaction conditions.

The results of additional measurements with different CO/H_2 ratios during the $CO/H_2/Ar$ pulses, where the amount of CO molecules per pulse was kept constant at 3×10^{15} molecules CO per pulse, while the amount of H_2 was varied between 1.5×10^{15} and 24×10^{15} molecules H_2 per pulse, are plotted in Figure 2a and listed in Table 1, together with the absolute amounts of active oxygen consumption/replenishment for CO only (0% H_2) and H_2 only (100% H_2).

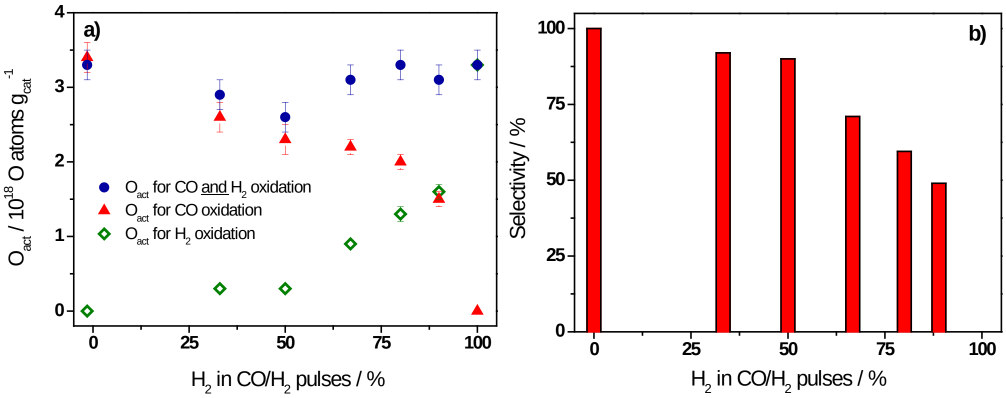

Figure 2. (**a**) Absolute amounts of active oxygen (O_{act}) removal from a fully oxidized Au/TiO_2 catalyst (after O_2/Ar pulses) by CO and/or H_2 during CO, H_2, and CO/H_2 pulses with varying ratios of H_2 (33%–89% H_2) at 80 °C, and (**b**) corresponding selectivities for CO oxidation/CO_2 formation during the $CO/H_2/Ar$ pulses at 80 °C.

These data clearly demonstrate that the total amount of oxygen that can be removed by CO/H_2 is almost identical for all mixtures and, moreover, also for "CO only" and "H_2 only" experiments. Obviously, under present reaction conditions, in the simultaneous presence of CO and H_2, these reactants are oxidized by the same active oxygen species as we have already concluded for the individual reactants before (see Section 2.1 and [35]). The existence of other active oxygen species, which may be active only for H_2 oxidation when CO and H_2 are present simultaneously, can be ruled out, since this would result in a higher amount of active oxygen species for the simultaneous CO and H_2 oxidation as compared to the CO oxidation only.

On a first glance these findings seem to contradict recent conclusions from Saavedra *et al.*, who studied, in detail, the role of water in the catalytic CO oxidation on Au/TiO_2 [40]. Based on experimental results and DFT calculations they concluded (i) that weakly adsorbed water on TiO_2 determines the catalysts activity at room temperature by changing the effective number of active sites; and (ii) that O_2 activation in the dominant reaction pathway under these conditions requires the presence of both water and CO [40]. Considering that our experiments were performed at 80 °C and under vacuum conditions (not during pulses, but between individual pulses and pulse sequences), the presence of weakly-adsorbed water on the catalyst surface can be excluded. Temperature programmed desorption (TPD) measurements performed after saturation of the catalyst with water by 1500 H_2/Ar pulses had shown that stable adsorbed water is formed upon H_2 pulsing, which desorbs with a maximum in the TPD spectra at about 230 °C. This is the only water species present during O_2 pulsing at 80 °C. Hence, our results clearly demonstrate that as long as only stable adsorbed water is present on the catalyst surface, coexisting adsorbed CO and hydrogen both are oxidized by TiO_2 surface lattice oxygen and compete for this O_{act} species. Weakly-adsorbed water species, whose presence during continuous PROX reaction cannot be ruled out from our data, may also enable another oxygen activation mechanism as described in the recent study by Saavedra *et al.* [40]. In that case, however, the dominant reaction mechanisms of CO and H_2 oxidation under PROX reaction conditions are expected to sensitively depend on the reaction temperature, due to the facile desorption of these species at higher temperatures. Similar kinds of temperature effects have been proposed earlier for the CO oxidation reaction under dry reaction conditions [31]. Another possibility that has to be considered under continuous PROX conditions, in the simultaneous presence of CO, O_2, and H_2 in the catalyst bed, is the H-assisted O_2 activation. Rousset and coworkers previously demonstrated that the presence of H_2 promotes the CO oxidation activity over various Au catalysts supported on different (reducible and non-reducible) metal oxides [10,12]. According to them, this beneficial effect of H_2 results most probably from the reaction of adsorbed hydrogen atoms with molecular oxygen to active hydroperoxy-like species that represent additional reaction intermediates in the CO oxidation. In the present approach there is an inherent difficulty in studying this effect, since CO/H_2 and O_2 are never present simultaneously in the catalyst bed during the alternate pulse sequences. Here, further work is planned to more closely investigate the influence of H_2 on the O_2 activation in pulse experiments, in particular by exposing the catalyst to mixed $CO/H_2/O_2/Ar$ pulses. In that approach it will also be highly interesting to compare the oxygen activation in the presence of H_2 on different Au catalysts supported on reducible and non-reducible metal oxides (Au/TiO_2, Au/ZnO, Au/Al_2O_3, and Au/SiO_2, for example). Numerous previous studies have demonstrated that the activity for CO oxidation largely depends on the reducibility of the metal oxide support, with Au catalysts supported on reducible oxides being much more active [43,44]. Applying TAP reactor pulse experiments we could even demonstrate a quantitative relation between the catalysts reducibility (measured by its oxygen storage capacity) and its activity for CO oxidation [41]. In the presence of H_2, however, the activity of Au catalysts supported on reducible and non-reducible metal oxides becomes very similar [10,12], reflecting a more pronounced promotional effect of H_2 on the CO oxidation activity (see above) for non-reducible than for reducible metal oxide supports.

In addition to the absolute amount of active oxygen on Au/TiO_2 we also calculated the selectivity for active oxygen removal by CO at 80 °C for different CO/H_2 ratios, where the selectivity was given by the ratio between the absolute amount of CO_2 formation and the overall oxygen removal during $CO/H_2/Ar$ pulses (see Section 3.2). Figure 2a illustrates already that the amount of CO consumption/CO_2 formation continuously decreases with increasing H_2 content in the CO/H_2 pulses at 80 °C, despite the almost constant amount of O_{act} removal (for combined CO and hydrogen oxidation). This results in a decrease of the selectivity for CO_2 formation from 92% in the presence of 33% H_2 to slightly below 50% in the presence of 89% H_2 (see Figure 2b and Table 1). A similar trend of a decreasing selectivity with decreasing CO/H_2 ratio was also observed in kinetic measurements of the PROX reaction on a Au/TiO_2 catalyst under continuous flow, but otherwise similar reaction conditions (80 °C) [14,45]. The high selectivities fully agree with the much lower efficiency for O_{act} removal by H_2 (including H_2 adsorption, dissociation, and reaction with O_{act}) compared to reaction with CO. This was already demonstrated by the much higher number of H_2 pulses needed for the complete removal of the available active oxygen species compared to reaction with CO in multi-pulse TAP reactor experiments (see Section 2.1 and Refs. [35,42]). Considering the selectivity of about 50% in the presence of 89% H_2 (CO/H_2 ratio of 1/8), this difference in the efficiency for O_{act} removal can be estimated to be about 8. This value is also in close agreement to the approximately eight times higher amount of H_2 molecules compared to CO molecules that are needed for a complete removal of all available O_{act} species (see Section 2.1). One has to keep in mind, however, that the latter averages over the entire pulse sequence, and does not necessarily reflect the difference in efficiency of a single CO or H_2 molecule. The selectivity largely originates from the competition between adsorbed CO and hydrogen for the same active oxygen species when simultaneously present on the catalyst surface. Additional effects arising, e.g., from the competition of the two adsorbing species (CO, H_2) for adsorption sites and from (de-)stabilizing interaction between the coadsorbed species, which had been suggested previously [13,14], can neither be excluded nor supported from our TAP reactor experiments measurements. It should be noted, however, that the steady-state coverages under typical reaction conditions ($\leqslant$0.5% CO, 60%–70% H_2, 80 °C, atmospheric pressure) are well below saturation. Accordingly, such effects are expected to be small, and similar conclusions were put forward also in the above studies [13,14].

Finally, we performed similar multi-pulse experiments with alternate sequences of O_2/Ar pulses and $CO/H_2/Ar$ pulses at 400 °C, using the same reaction gas mixtures for O_{act} removal from Au/TiO_2 as described above (CO, H_2, and $CO/H_2 = 1/0.5 - CO/H_2 = 1/8$). The main characteristics during reduction and re-oxidation were identical to those obtained in the experiments at 80 °C: For all measurements, CO_2 and H_2O are only formed during CO and/or H_2 pulses, respectively, and the processes of catalyst reduction and re-oxidation are fully reversible, as evidenced by at least three cycles of reduction and re-oxidation with identical absolute amounts of O_{act} removal/replenishment for each gas mixture. The absolute amounts of active oxygen removal upon exposure to CO only, H_2 only, and CO/H_2 mixtures are presented in Figure 3 and listed in Table 2.

Similar to the results at 80 °C also in this case the absolute amount of active oxygen (12×10^{18} O atoms$\cdot$ ${g_{cat}}^{-1}$) is essentially independent of the composition of the reaction gas pulses used for reduction. Hence, also at 400 °C CO and H_2 seem to compete for TiO_2 surface lattice oxygen close to the Au nanoparticles when present simultaneously. The only difference to the measurements at lower reaction temperature is that at 400 °C the increasing thermal mobility of surface lattice oxygen and surface oxygen vacancies enables the migration and, therefore, the removal and replenishment of oxygen and oxygen vacancies which were originally located further away from the perimeter sites. At 80 °C, in contrast, only oxygen species directly adjacent to the Au nanoparticles participate in the oxidation reactions [27]. Nevertheless, also at 400 °C removal of O_{act} species upon reaction with CO or H_2 is expected to occur only at Au-TiO_2 interface perimeter sites.

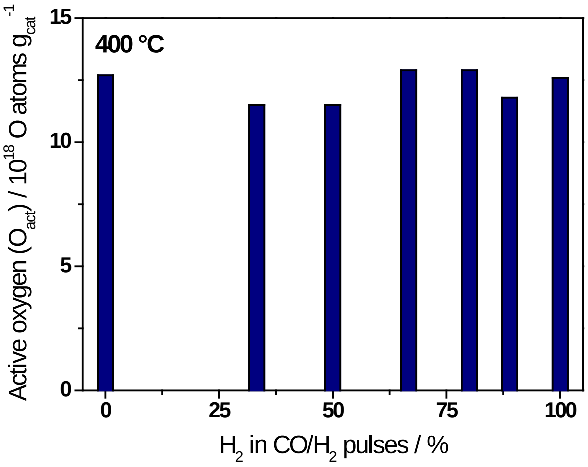

Figure 3. Absolute amounts of active oxygen (O_{act}) removal from a fully oxidized Au/TiO_2 catalyst (after O_2/Ar pulses) by CO and/or H_2 during CO, H_2, and CO/H_2 pulses with varying ratios of H_2 (33%–89% H_2) at 400 °C.

As described below (Section 3.3) it is not possible to calculate the selectivity for reaction at 400 °C, since even in the absence of H_2 there is no stoichiometric consumption of O_2 and CO (with respect to the CO oxidation). Hence, the differences between O_2 consumption and CO consumption in consecutive sequences of O_2/Ar and CO/H_2/Ar pulses cannot be assigned to active oxygen removal via the H_2 oxidation only. Nevertheless, from the continuously-decreasing amount of CO_2 formation with increasing H_2 ratio in CO/H_2/Ar pulses, from 9.3×10^{18} CO_2 molecules$\cdot g_{cat}{}^{-1}$ to 6.1×10^{18} CO_2 molecules$\cdot g_{cat}{}^{-1}$ at CO/H_2 = 1/0.5 and CO/H_2 = 1/8 (see Table 2), it is evident that also at 400 °C the reaction is dominated by the same trend of decreasing selectivity towards CO_2 formation with increasing H_2 content. Moreover, considering that even for the highest amount of H_2 during CO/H_2 pulses (CO/H_2 = 1/8) and, hence, in an eight-fold excess of H_2 compared to CO, still 6.1×10^{18} CO_2 molecules$\cdot g_{cat}{}^{-1}$ are formed, which is about 60% of the amount of CO_2 formed upon reduction by CO only (see Table 2), it can be concluded that also at 400 °C the catalyst still selectively catalyses the CO oxidation under present reaction conditions.

In total, these results, obtained at different temperatures as well as for reaction in different atmospheres, point to a competition of CO and H_2 for the same active oxygen species when present simultaneously and, hence, under PROX reaction conditions. This competition will mainly determine the catalyst selectivity towards CO oxidation, and strategies for even more selective Au catalysts under these conditions (80 °C and higher) should accordingly focus on the efficiency of H_2 and CO for active oxygen removal, which may be achieved by a systematic modification of the support material and/or the Au-support interface perimeter sites, which both significantly influence the activity for CO and H_2 oxidation via a Au-assisted Mars-van Krevelen mechanism [31,41].

3. Materials and Methods

3.1. Preparation and Characterization of Au/TiO_2

For all measurements we used a home-made Au/TiO_2 catalyst with a Au loading of 2.2 wt. %, which was prepared via a deposition-precipitation method using commercial, non-porous TiO_2 as support material (P5, surface area 56 $m^2\cdot g^{-1}$). Prior to all measurements the catalyst was pre-treated *in situ* by calcination at 400 °C in a continuous flow of 10% O_2/N_2 (20 Nml$\cdot$ min^{-1}) at atmospheric pressure for 30 min (hereafter denoted as O400), resulting in a surface-volume mean diameter of 2.4 ± 0.5 nm. The mean Au particle size was determined by transmission electron microscopy (TEM), evaluating the diameter of more than 500 Au nanoparticles after pre-treatment (O400).

3.2. TAP Reactor Measurements

Pulse experiments were performed in a TAP reactor system, which was built in our laboratory and which is described in detail in Ref. [46]. This system consists of a gas mixing unit, two piezo-electrically driven pulse valves, and a quartz glass micro-reactor (length: 90 mm, inner diameter: 4 mm), which is connected to an analysis chamber (under ultrahigh vacuum conditions), which houses the mass spectrometer for gas phase analysis. For *in situ* catalyst pre-treatment at atmospheric pressure, the micro-reactor with the catalyst inside can be separated from the analysis chamber via a differentially-pumped gate valve. This latter gate valve enables fast transitions from vacuum to ambient conditions in the micro-reactor and *vice versa* [46].

Gas pulses containing between 8×10^{15} and 3×10^{16} molecules per pulse were generated by the piezo-electrically driven pulse valves and directed to the micro-reactor. At the centre of this reactor the catalyst bed was fixed by stainless steel sieves. For all measurements the catalyst bed consisted of two outer layers of SiO_2 powder (inert under present reaction conditions) and a central catalyst zone with 10 mg of the Au/TiO_2 catalyst diluted with 10 mg SiO_2 (dilution 1:1) in between the SiO_2 layers.

Multi-pulse experiments were performed with a separation time of 5 s between two consecutive pulses. During these measurements the catalyst was alternately exposed to sequences of (i) CO/Ar; (ii) H_2/Ar; or (iii) CO/H_2/Ar and O_2/Ar pulses for removal and replenishment of stable, active oxygen species. The number of pulses in each sequence was chosen such that there is no measurable reactive removal or oxygen uptake at the end of each sequence, *i.e.*, at the end of CO/Ar, H_2/Ar, and CO/H_2/Ar pulse sequences or after the O_2/Ar pulse sequences. The exact numbers of pulses in each sequence are stated together with the results obtained (see Sections 2.1 and 2.2). Moreover, these cycles with alternate reduction and re-oxidation of the catalyst surface were always repeated at least three times in order to demonstrate the reversibility of the observed processes and, hence, to exclude permanent changes of the catalysts state during pulse experiments. The absolute amount of reversible oxygen removal and replenishment is defined as the catalysts oxygen storage capacity (OSC). Note that in each pulse Ar was included in order to enable the quantitative evaluation of the amount of CO, H_2, or O_2 consumed during every single pulse on an absolute scale. This is based on the comparison of the ratio of the intensities of the respective species and Ar during reaction (uptake/consumption of CO, H_2 and O_2) to that after saturation, where no more consumption of the corresponding species was detected. CO/Ar and O_2/Ar pulses always consisted of 50% CO or 50% O_2 and 50% Ar at a pulse size of 8×10^{15} molecules per pulse. Hence, the catalyst was exposed to about 4×10^{15} molecules CO or O_2 during each of the pulses. For pulses with a CO/H_2/Ar mixture, in contrast, the overall pulse size was between 1.2×10^{16} and 3.0×10^{16} molecules per pulse. Here we kept the amount of CO constant at 3×10^{15} molecules CO per pulse, while varying the amount of H_2 between 1.5×10^{15} and 24×10^{15} molecules H_2 per pulse. This way, CO/H_2 ratios between 1/0.5 and 1/8 were realized for the CO/H_2/Ar pulses. Note that in the discussions the H_2 ratio during CO/H_2/Ar pulses is always stated with respect to CO and H_2 only (not considering Ar), which are accordingly between 33% H_2 (CO/H_2 = 1/0.5) and 89% H_2 (CO/H_2 = 1/8).

In order to avoid complications in the direct comparison of active oxygen removal by CO and H_2 at 80 °C due to adsorption of water, which is always formed on the catalyst surface during H_2 oxidation and has a distinct impact on the CO oxidation activity (see above), we saturated the Au/TiO_2 catalyst surface with adsorbed water by exposing it to 5000 H_2/Ar pulses before starting the measurements. Note that this treatment additionally resulted in a complete removal of stable reactive oxygen (O_{act}) species for H_2 oxidation. The starting point of subsequent measurements is, hence, a fully reduced Au/TiO_2 catalyst.

3.3. Calculation of the Selectivity

Usually the selectivity for CO oxidation in CO/H_2 mixtures is defined by the ratio between the CO_2 formation rate and the overall oxygen consumption rate (for CO oxidation and H_2 oxidation, see also Equation (3)), which are determined in kinetic measurements. This is not possible in the present study, where we focused on the absolute amounts of oxygen removal and replenishment during alternate sequences of $CO/H_2/Ar$ and O_2/Ar pulses rather than on their kinetics. In this case we calculated the selectivity for CO oxidation at 80 °C by the ratio between the absolute amount of CO consumption/CO_2 formation (N_{CO} during a sequence of $CO/H_2/Ar$ pulses) and the absolute amount of atomic oxygen consumption ($2 \cdot N_{O2}$) during a subsequent sequence of O_2/Ar pulses (Equation (4)). Note that it was not possible to determine the absolute amount of H_2O formation during $CO/H_2/Ar$ pulses at 80°C, since water desorption is too slow to be resolved.

$$S = \frac{N_{CO}}{2 \cdot N_{O_2}} \tag{4}$$

For reaction at 400 °C it was not possible to calculate the selectivity in that way. From previous studies it is known that at this temperature, even in the absence of H_2, the O_2 uptake is always slightly higher than the oxygen consumption during subsequent exposure to CO during alternate sequences of O_2/Ar and CO/Ar pulses [27,35]. Therefore, the difference between CO consumption/CO_2 formation during exposure to $CO/H_2/Ar$ pulses to that of O_2 consumption during subsequent exposure to O_2/Ar pulses is not solely due to active oxygen consumption by H_2 oxidation/H_2O formation, and can not be used for determination of the selectivity. For this reason we can only provide values for O_{act} removal and CO_2 formation at 400 °C.

4. Conclusions

From the comparison of the active oxygen removal from a Au/TiO_2 catalyst by CO, H_2, and CO/H_2 pulses with varying CO/H_2 ratios in quantitative temporal analysis of products (TAP) reactor measurements at 80 °C and 400 °C, we arrived at the following conclusions on the PROX reaction mechanism:

(1) CO and hydrogen are oxidized by the same stable active oxygen species under present reaction conditions, also in the simultaneous presence of CO and H_2 in the reaction atmosphere, as evidenced by the similar amounts of active oxygen removal from a O_2/Ar pulse oxidized Au/TiO_2 catalyst upon exposure to multi-pulse sequences of CO, H_2, and CO/H_2 mixtures. This is independent of the CO/H_2 ratio. Hence, also under PROX reaction conditions CO and H_2 compete for TiO_2 surface lattice oxygen close to the Au nanoparticles/at the perimeter of the Au-TiO_2 interface as active oxygen species.

(2) The selectivity of Au/TiO_2 catalysts for CO oxidation in CO/H_2 containing gas mixtures observed in kinetic measurements is proposed to mainly result from the much higher efficiency of CO for active oxygen removal compared to hydrogen under present reaction conditions, in the simultaneous presence of H_2 and CO in the reaction atmosphere. The latter is illustrated also by the much higher amount of H_2 pulses required for complete removal of active oxygen from the catalyst compared to CO pulsing.

(3) Since we can rule out the presence of weakly-bound adsorbed water under present reaction conditions, in multi-pulse sequences, the much higher efficiency of CO for reaction with active oxygen species or the preference for this reaction pathway cannot result from effects caused by weakly-bound water species. On the other hand, stable adsorbed (strongly bound) water species, which are known to be present on the surface upon H_2 pulsing, leave the dominant reaction pathway for CO oxidation under present reaction conditions, namely reaction of CO_{ad} with surface lattice oxygen at the perimeter of the Au NP-support interface, unchanged, although the reaction rate may change.

Since the selectivity of pure Au/TiO_2 catalysts originates mainly from the intrinsic difference in the reactivity of TiO_2 surface lattice oxygen located at Au-TiO_2 perimeter sites for CO oxidation and H_2 oxidation under present reaction conditions, further improvements in the selectivity of TiO_2-based

Au catalysts should include a modification of these perimeter sites, for example by doping of the TiO_2 support.

We cannot rule out from the present data, however, that other reaction pathways contribute as well at lower reaction temperature and/or during reaction under continuous flow conditions at atmospheric pressure. Under those conditions, weakly-adsorbed water, as well as adsorbed H_{ad}, are present and may also be involved in the reaction, as recently proposed by Saavedra *et al.* [40] and Rousset *et al.* [12].

Overall, the present findings confirm previous ideas on the CO oxidation mechanism and the physical origin of the high selectivity for CO oxidation in the PROX reaction on supported Au catalysts, specifically on Au/TiO_2 catalysts, which were based on plausibility arguments extending mechanistic insights from CO oxidation and H_2 oxidation to the present case of reaction in CO/H_2 mixtures.

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Abbreviations

The following abbreviations are used in this manuscript:

O_{act}	Active Oxygen
PROX	Preferential CO Oxidation
TAP	Temporal Analysis of Products
PEM	Polymer Electrolyte Membrane
TEM	Transmission Electron Microscopy
TPD	Temperature Programmed Desorption

References

1. Hashmi, A.S.K.; Hutchings, G.J. Gold Catalysis. *Angew. Chem. Int. Ed.* **2006**, *45*, 7896–7936. [CrossRef] [PubMed]
2. Min, B.K.; Friend, C.M. Heterogeneous Gold-Based Catalysis for Green Chemistry: Low-Temperature CO Oxidation and Propene Oxidation. *Chem. Rev.* **2007**, *107*, 2709–2724. [CrossRef] [PubMed]
3. Freakley, S.J.; He, Q.; Kiely, C.J.; Hutchings, G.J. Gold Catalysis: A Reflection on Where We are Now. *Catal. Lett.* **2015**, *145*, 71–79. [CrossRef]
4. Haruta, M. Role of perimeter interfaces in catalysis by gold nanoparticles. *Faraday Discuss.* **2011**, *152*, 11–32. [CrossRef] [PubMed]
5. Freund, H.J.; Meijer, G.; Scheffler, M.; Schlögl, R.; Wolf, M. CO Oxidation as a Prototypical Reaction for Heterogeneous Processes. *Angew. Chem. Int. Ed.* **2011**, *50*, 10064–10094. [CrossRef] [PubMed]
6. Trimm, D.L.; Önsan, Z.I. On-board fuel conversion for hydrogen-fuel-cell-driven vehicles. *Catal. Rev.* **2001**, *43*, 31–84. [CrossRef]
7. Ghenciu, A.F. Review of fuel processing catalysts for hydrogen production in PEM fuel cell systems. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 389–399. [CrossRef]
8. Corti, C.W.; Holliday, R.J.; Thompson, D.T. Progress towards the commercial application of gold catalysts. *Top. Catal.* **2007**, *44*, 331–343. [CrossRef]
9. Park, E.D.; Lee, D.; Lee, H.C. Recent progress in selective CO removal in a H_2-rich stream. *Catal. Today* **2009**, *139*, 280–290. [CrossRef]
10. Rossignol, C.; Arrii, S.; Morfin, F.; Piccolo, L.; Caps, V.; Rousset, J.-L. Selective oxidation of CO over model gold-based catalysts in the presence of H_2. *J. Catal.* **2005**, *230*, 476–483. [CrossRef]

11. Bion, N.; Epron, F.; Moreno, M.; Marino, F.; Duprez, D. Preferential Oxidation of Carbon Monoxide in the Presence of Hydrogen (PROX) over Noble Metals and Transition Metal Oxides: Advantages and Drawbacks. *Top. Catal.* **2008**, *51*, 76–88. [CrossRef]
12. Quinet, E.; Piccolo, L.; Morfin, F.; Avenier, P.; Diehl, F.; Caps, V.; Rousset, J.L. On the mechanism of hydrogen-promoted gold-catalyzed CO oxidation. *J. Catal.* **2009**, *268*, 384–389. [CrossRef]
13. Kahlich, M.J.; Gasteiger, H.A.; Behm, R.J. Kinetics of the Selective Low-Temperature Oxidation of CO in H_2-rich Gas over Au/Fe_2O_3. *J. Catal.* **1999**, *182*, 430–440. [CrossRef]
14. Schumacher, B.; Denkwitz, Y.; Plzak, V.; Kinne, M.; Behm, R.J. Kinetics, mechanism and the influence of H_2 on the CO oxidation reaction on a Au/TiO_2 catalyst. *J. Catal.* **2004**, *224*, 449–462. [CrossRef]
15. Denkwitz, Y.; Schumacher, B.; Kucèrová, G.; Behm, R.J. Activity, stability and deactivation behavior of supported Au/TiO_2 catalysts in the CO oxidation and preferential CO oxidation reaction at elevated temperatures. *J. Catal.* **2009**, *267*, 78–88. [CrossRef]
16. Grzybowska, B. Nano-Au/oxide support catalysts in oxidation reactions: Provenance of active oxygen species. *Catal. Today* **2006**, *112*, 3–7. [CrossRef]
17. Bollinger, M.A.; Vannice, M.A. A kinetic and DRIFTS study of low-temperature carbon monoxide oxidation over Au-TiO_2 catalysts. *Appl. Catal. B* **1996**, *8*, 417–443. [CrossRef]
18. Boccuzzi, F.; Chiorino, A. FTIR study on Au/TiO_2 at 90K and room temperature. An insight into the nature of the reaction centers. *J. Phys. Chem. B* **2000**, *104*, 5414–5416. [CrossRef]
19. Green, I.X.; Tang, W.; Neurock, M.; Yates, J.T. Spectroscopic Observation of Dual Catalytic Sites During Oxidation of CO on a Au/TiO_2 Catalyst. *Science* **2011**, *333*, 736–739. [CrossRef] [PubMed]
20. Boronat, M.; Francesc, I.; Corma, A. Active Sites for H_2 Adsorption and Activation in Au/TiO_2 and the Role of the Support. *J. Phys. Chem. A* **2009**, *113*, 3750–3757. [CrossRef] [PubMed]
21. Panayotov, D.A.; Burrows, V.A.; Yates, J.T., Jr.; Morris, L. Mechanistic Studies of Hydrogen Dissociation and Spillover on Au/TiO_2: IR Spectroscopy of Coadsorbed CO and H-Donated Electrons. *J. Phys. Chem. C* **2011**, *115*, 22400–22408. [CrossRef]
22. Fujitani, T.; Nakamura, I.; Akita, T.; Okumura, M.; Haruta, M. Hydrogen Dissociation by Gold Clusters. *Angew. Chem.* **2009**, *121*, 9679–9682. [CrossRef]
23. Nakamura, I.; Mantoku, H.; Furukawa, T.; Fujitani, T. Active Sites for Hydrogen Dissociation over TiO_x/Au(111) Surfaces. *J. Phys. Chem. C* **2011**, *115*, 16074–16080. [CrossRef]
24. Bus, E.; Miller, J.T.; van Bokhoven, J.A. Hydrogen Chemisorption on Al_2O_3-Supported Gold Catalysts. *J. Phys. Chem. B* **2005**, *109*, 14581–14587. [CrossRef] [PubMed]
25. Kotobuki, M.; Leppelt, R.; Hansgen, D.; Widmann, D.; Behm, R.J. Reactive oxygen on a Au/TiO_2 supported catalyst. *J. Catal.* **2009**, *264*, 67–76. [CrossRef]
26. Vilhelmsen, L.B.; Hammer, B. Indentification of the Catalytic Site at the Interface Perimeter of Au clusters on Rutile TiO_2(110). *ACS Catal.* **2014**, *4*, 1626–1631. [CrossRef]
27. Widmann, D.; Behm, R.J. Active oxygen on a Au/TiO_2 catalyst: Formation, stability and CO oxidation activity. *Angew. Chem. Int. Ed.* **2011**, *50*, 10241–10245. [CrossRef] [PubMed]
28. Maeda, Y.; Iizuka, Y.; Kohyama, M. Generation of Oxygen Vacancies at a Au/TiO_2 Perimeter Interface during CO Oxidation Detected by *in Situ* Electrical Conductance Measurement. *J. Am. Chem. Soc.* **2013**, *135*, 906–909. [CrossRef] [PubMed]
29. Li, L.; Wang, A.; Qiao, B.; Lin, J.; Huang, Y.; Wang, X.; Zhang, T. Origin of the high activity of Au/FeO_x for low-temperature CO oxidation: Direct evidence for a redox mechanism. *J. Catal.* **2013**, *299*, 90–100. [CrossRef]
30. Kim, H.Y.; Henkelman, G. CO Oxidation at the Interface of Au Nanoclusters and the Stepped-CeO_2(111) Surface by the Mars-van Krevelen Mechanism. *J. Phys. Chem. Lett.* **2013**, *4*, 216–221. [CrossRef] [PubMed]
31. Widmann, D.; Behm, R.J. Activation of Molecular Oxygen and the Nature of the Active Oxygen Species for CO Oxidation on Oxide Supported Au Catalysts. *Acc. Chem. Res.* **2014**, *47*, 740–749. [CrossRef] [PubMed]
32. Duan, Z.; Henkelman, G. CO Oxidation at the Au/TiO_2 Boundary: The Role of the Au/Ti5c Site. *ACS Catal.* **2015**, *5*, 1589–1595. [CrossRef]
33. Saqlain, M.A.; Hussain, A.; Siddiq, M.; Ferreira, A.R.; Leitao, A.A. Thermally activated surface oxygen defects at the perimeter of Au/TiO_2: A DFT + U study. *Phys. Chem. Chem. Phys.* **2015**, *17*, 25403–25410. [CrossRef] [PubMed]

34. Green, I.X.; Tang, W.; Neurock, M.; Yates, J.T. Insights into Catalytic Oxidation at the Au/TiO_2 Dual Perimeter Sites. *Acc. Chem. Res.* **2013**, *47*, 805–815. [CrossRef] [PubMed]
35. Widmann, D.; Hocking, E.; Behm, R.J. On the origin of the selectivity in the preferential CO oxidation on Au/TiO_2—Nature of the active oxygen species for H_2 oxidation. *J. Catal.* **2014**, *317*, 272–276. [CrossRef]
36. Sun, K.; Kohyama, M.; Tanaka, S.; Takeda, S. A Study on the Mechanism for H_2 Dissociation on Au/TiO_2 Catalysts. *J. Phys. Chem. C* **2014**, *118*, 1611–1617. [CrossRef]
37. Daté, M.; Haruta, M. Moisture effect on CO oxidation over Au/TiO_2 catalyst. *J. Catal.* **2001**, *201*, 221–224. [CrossRef]
38. Diemant, T.; Bansmann, J.; Behm, R.J. CO oxidation on planar Au/TiO_2 model catalysts: Deactivation and the influence of water. *Vacuum* **2009**, *84*, 193–196. [CrossRef]
39. Gao, F.; Wood, T.E.; Goodman, D.W. The Effects of Water on CO Oxidation over TiO_2 Supported Au Catalysts. *Catal. Lett.* **2010**, *134*, 9–12. [CrossRef]
40. Saavedra, J.; Doan, H.A.; Pursell, C.J.; Grabow, L.C.; Chandler, B.D. The critical role of water at the gold-titania interface in catalytic CO oxidation. *Science* **2014**, *345*, 1599–1602. [CrossRef] [PubMed]
41. 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. [CrossRef]
42. Wang, L.-C.; Widmann, D.; Behm, R.J. Reactive removal of surface oxygen by H_2, CO and CO/H_2 on a Au/CeO_2 catalyst and its relevance to the preferential CO oxidation (PROX) and reverse water gas shift (RWGS) reaction. *Catal. Sci. Technol.* **2015**, *5*, 925–941. [CrossRef]
43. Schubert, M.M.; Plzak, V.; Garche, J.; Behm, R.J. Activity, Selectivity, and Long-Term Stability of Different Metal Oxide Supported Gold Catalysts for the Preferential CO Oxidation in H_2-rich Gas. *Catal. Lett.* **2001**, *76*, 143. [CrossRef]
44. Arrii, S.; Morfin, F.; Renouprez, A.J.; Rousset, J.L. Oxidation of CO on Gold Supported Catalysts Prepared by Laser Vaporization: Direct Evidence of Support Contribution. *J. Am. Chem. Soc.* **2004**, *126*, 1199–1205. [CrossRef] [PubMed]
45. Lakshmanan, P.; Park, J.E.; Park, E.D. Recent Advances in Preferential Oxidation of CO in H_2 over Gold Catalysts. *Catal. Surv. Asia* **2014**, *18*, 75–88. [CrossRef]
46. 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*, 104103. [CrossRef] [PubMed]