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Activity, stability, and deactivation behavior of supported Au/TiO_2 catalysts in the CO oxidation and preferential CO oxidation reaction at elevated temperatures

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ABSTRACT

The influence of elevated reaction temperatures on the activity, long-time stability, and deactivation behavior of Au/TiO_2 catalysts for CO oxidation was studied by kinetic and in situ IR measurements in the temperature range 80–180 °C, both in an idealized, H_2-free reaction atmosphere and in a H_2-rich gas mixture. The results are discussed in a molecular picture. Most important for practical applications (PROX reaction), the selectivity for CO oxidation in H_2-rich gas mixtures decreases sharply with increasing temperature, from ~60% at 80 °C to ~15% at 180 °C. The increasing tendency for H_2 oxidation is reflected also by a distinctly lower apparent activation energy for CO oxidation in the presence of H_2 (18 ± 3 kJ mol^{-1}) compared to reaction in a H_2-free reaction mixture (30 ± 3 kJ mol^{-1}). In all cases, carbonate formation is observed and proposed to contribute to the deactivation, but with different extents depending on the reaction conditions.

1. Introduction

Highly disperse, metal oxide-supported Au (Au/MeO_x) catalysts have been found to be highly active for various oxidation and hydrogenation reactions, in particular for CO oxidation, already at low temperatures [1–5]. For instance, Au/TiO_2 catalysts were reported to be active for CO oxidation already at 90 K [6]. Nevertheless, in specific cases, higher reaction temperatures may be advantageous or even mandatory due to technical reasons. A typical example is the catalytic removal of CO from H_2-rich feed gases for Polymer Electrolyte Fuel Cells (PEFCs), which is present in feed gases generated by reforming of hydrocarbons or alcohols and which acts as catalyst poison for the fuel cell anode, by preferential oxidation of CO (PROX) [7,8]. Because of its high activity already at low temperatures, Au/MeO_x catalysts can be operated at the temperature level of the fuel cell, at around 80 °C, and essentially all studies on the PROX performance of Au/MeO_x catalysts have been performed in this temperature range [9]. Due to technical reasons, however, operation at higher temperatures, e.g., at the temperature level of a preceding water gas shift stage in a reformer system of about 200 °C, may be more attractive. Furthermore, higher reaction temperatures may be beneficial for increasing the stability of the catalysts toward deactivation, which is generally a weak point of Au catalysts [9–14]. This hypothesis is based on the assumption that also at higher reaction temperatures, up to 200 °C, the deactivation is mainly due to chemical modification of the surface, e.g., by the formation of surface carbonates (see below), rather than being caused by irreversible Au nanoparticle sintering. In that case, higher reaction temperatures may promote thermal decomposition of the reaction-hindering surface species. Therefore, we were interested in the reaction and deactivation behavior of Au/TiO_2 catalysts at these elevated temperatures.

In the present work, we investigated these properties in the temperature range between 80 and 180 °C, using Au/TiO_2 catalysts whose CO oxidation characteristics had been characterized in detail for reaction temperatures of $T \leqslant 80$ °C previously [15,16]. The catalytic activity, given in Au mass-normalized rates and turn-over frequencies, the apparent activation energy, and the stability for CO oxidation were determined both in an idealized H_2-free reaction atmosphere and in a H_2-rich atmosphere. In the latter atmosphere, the selectivity for CO oxidation was determined as well. The Au/TiO_2 catalysts were synthesized via an established modified deposition–precipitation procedure, which allows a highly reproducible preparation of the catalysts [12,15,17]. For further information on the physical origin of the deactivation process, we performed DRIFTS measurements before, during, and after the reaction, respectively, focusing on the role of side or intermediate products under reaction conditions and on possible reaction-induced modifications of the Au particle sizes. The Au particle sizes were determined by TEM before and after the reaction.

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An extensive review of the numerous previous studies on the CO oxidation reaction on Au/TiO_2 catalysts, both in the absence and in the presence of H_2, can be found in Ref. [9]. The activation energies reported for the reaction in H_2-free gas mixtures vary between ~20 and ~60 kJ mol^{-1}, although for the most active catalysts and catalysts based on commercial TiO_2 (P25, Degussa) they seem to concentrate on values around 30 kJ mol^{-1} [9,12,18,19]. Because of the high activity of the catalyst, kinetic and mechanistic studies were mostly limited to temperatures below 100 °C. For the selective CO oxidation in H_2-rich gas mixtures, data are more scarce [9]. Studies on the reaction behavior at temperatures >80 °C are, to the best of our knowledge, limited to a study on the temperature-dependent conversion of CO in a H_2-rich mixture [19]. Activation energies for CO oxidation were reported to be around 30 kJ mol^{-1} as well, but to decrease significantly for decreasing CO contents [12]. Similar values of the apparent activation energy for CO oxidation, together with a rapidly decreasing selectivity with temperature, were also reported also for reaction on Au/Fe_2O_3 catalysts [10,20–22].

The accumulation of carbonate-like surface species as a source for deactivation had been proposed by Schubert et al. [22] for the selective CO oxidation in H_2-rich gases over Au/Fe_2O_3 and by Kung et al. [23] for CO oxidation over Au/Al_2O_3, respectively. For Au/TiO_2, surface carbonate species have also been detected during CO oxidation in several studies [12,15,24–27]. Their role in the deactivation process, however, was discussed controversially; while in several studies they were not identified as source of the deactivation [24–27], we presented evidence that the accumulation of these species increasingly inhibits the CO oxidation reaction [12,15]. In two other studies, carbonates were described as 'spectator species' that do not participate in the reaction [25,26]. Reaction-induced sintering of Au particles has been studied by a number of groups, with differing results. A scanning tunneling microscopy (STM) study on planar $Au/TiO_2(110)$ and Au/TiO_2-film/Mo(110) model catalysts showed distinct modifications in the Au particle size upon treatment in a 1:5 CO/O_2 mixture (1.3 kPa total pressure, 27 °C, 2 h) [28]. In contrast, atomic force microscopy (AFM) measurements on $Au/TiO_2(110)$ model catalysts prepared by Au evaporation [29] or by deposition of micelle-stabilized Au nanoparticles and subsequent reactive removal of the polymer stabilizer [30], gave no indication of significant sintering effects upon exposure to a reaction atmosphere at 200 °C (1:4 CO/O_2 mixture, 5 kPa total pressure, 13 h). More recently, Comotti et al. studied reaction-induced changes in high surface area Au/TiO_2 catalysts, which were prepared by deposition of Au colloids on a commercial TiO_2 support (P25, Degussa), by TEM, and found no significant changes during CO oxidation in reaction cycles between −40 and 200 °C [31].

2. Experimental

2.1. Preparation of the Au/TiO_2 catalysts and characterization

The catalysts were prepared following the procedures described previously [12,15,17]. In short, TiO_2 powder (Degussa P25) was suspended in water at 60 °C. Then an aqueous solution of $HAuCl_4\cdot 3H_2O$ (99.5%, grade for analysis, Merck) was added dropwise at constant temperature under continuous stirring. The pH of the solution was kept constant at about 5.0–5.5 by adding a 0.1 M solution of Na_2CO_3. Subsequently, the mixture was stirred for additional 30 min. The precipitate was cooled to room temperature, filtered, and washed by water of 40 °C. The filtrate was dried over night at room temperature in vacuum. The resulting Au content of 3.3 wt.% was derived from inductively coupled plasma atom emission spectroscopy (ICP-AES) measurements. The BET surface area was determined to be 56 m^2. Prior to the experiments, the catalysts were dried in situ in 20 Nml min^{-1} N_2 at 100 °C for 15 h, if not mentioned otherwise, then calcined in 10% O_2/N_2 (20 Nml min^{-1}) at 400 °C for 30 min in the microreactor, and finally cooled down in N_2 (20 Nml min^{-1}) to the respective reaction temperature. At this stage, the catalyst consisted of pure TiO_2, and mainly metallic gold particles, as evidenced by the Ti^{4+}- and Au^0-dominated Ti(2p) and Au(4f) signals in X-ray photoelectron spectra [15]. The Au particle sizes were determined by transmission electron microscopy (TEM) after conditioning and after reaction, using a Philips CM 20 microscope (200 kV). For each sample, at least 300 particles were evaluated.

2.2. Activity measurements

The activity measurements were performed at atmospheric pressure in a quartz tube microreactor (i.d. 4 mm), located in a ceramic tube oven, with typically 60–70 mg diluted catalyst (catalyst bed length 5–7 mm). The catalyst samples were diluted with α-Al_2O_3, which is not active for CO oxidation under present reaction conditions, in order to obtain differential reaction conditions (conversion <15%). The measurements were carried out at a gas flow of 60 Nml min^{-1} (space velocity 57,300–36,000 h^{-1}) at elevated temperatures between 80 and 180 °C in two different atmospheres: (i) an idealized CO oxidation mixture containing 1 kPa CO, 1 kPa O_2, and balance N_2 ('H_2-free atmosphere') and (ii) a H_2-rich atmosphere containing 1 kPa CO, 1 kPa O_2, 75 kPa H_2, and balance N_2, which is typical for catalytic CO removal from H_2-rich feed gases via the preferential CO oxidation (PROX) reaction. Influent and effluent gases were analyzed by on-line gas chromatography (Dani GC 86.10HT). High purity reaction gases (CO 4.7, O_2 5.0, H_2 5.0, N_2 6.0 from Westphalen) were used, which were additionally passed through a moisture removal filter (Varian GC–MS filter CP 17973) to ensure that water concentrations are below 0.1 ppm. Evaluation of the Weisz criterion showed the absence of mass-transport-related problems [32]. For further details, in particular on the determination of activities and selectivities see [33].

2.3. Infrared investigations

In situ IR investigations were performed in a DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) configuration with a Magna 560 spectrometer from Nicolet, equipped with a MCT narrow band detector and a commercial in situ reaction cell unit from Harricks (HV-DR2). This set-up allows measurements in a continuous flow of gas mixtures, equal to those used in the kinetic studies, and at elevated temperatures. Typically, 400 scans (acquisition time 3 min) at a nominal resolution of 8 cm^{-1} were added for one spectrum. Prior to the experiments, background spectra were recorded on the freshly conditioned catalyst at the reaction temperature in a flow of pure nitrogen. The IR intensities were evaluated in Kubelka–Munk units, which are linearly related to the adsorbate concentration [34]. For possible deviations from this linear behavior see [35]. Background subtraction and normalization of the spectra were performed by subtracting the spectra recorded in a flow of N_2 at the reaction temperature directly before starting the reaction. To remove the changes in the reflectivity of the respective catalysts, the spectra were scaled to similar background intensities at 2430 cm^{-1}, which does not interfere with any other signals and where the shape of the raw spectrum shows negligible changes during the measurements. The gas phase CO signal was removed by subtracting the spectral region of gas phase CO (2040–2240 cm^{-1}) from a spectrum recorded on pure α-Al_2O_3 in CO-containing atmosphere.

Prior to reaction, the catalyst was treated in the same way as for the kinetic measurements. For the measurements, a layer of typically 15–20 mg of α-Al_2O_3-diluted catalyst (1:2 dilution) was deposited on a base of pure α-Al_2O_3 (~60 mg) powder in the DRIFTS reaction cell.

3. Results and discussion

3.1. Stability, activity, and selectivity

3.1.1. Stability in H_2-free and H_2-rich atmosphere

The temporal evolution of the CO oxidation activity for reaction in H_2-free atmosphere (empty symbols), measured at different temperatures in the range between 80 and 180 °C under differential reaction conditions over 1000 min on stream and normalized to the conversion after 10 min reaction, is presented in Fig. 1a and b. General characteristic of the activity–time curves is a steady decrease of the activity, mainly over the first 200 min on stream. After 1000 min, steady-state conditions are essentially reached. The absolute values of the initial reaction rates (10 min) are given in Table 1. For reaction at 80 °C, the initial and final reaction rates of 4.1×10^{-3} and 0.9×10^{-3} mol g_{Au}^{-1} s^{-1}, respectively, are in the range of activities of highly active Au/TiO_2 catalysts reported previously [1,15,19,36–39]. They also agree closely with results in our previous studies on similar type catalysts [15,16]. Using the mean particle size determined by TEM (see below), the rates correspond to turn-over frequencies of 2.3 and 0.6 s^{-1}. The reaction temperature has a significant influence both on the activity and on the deactivation behavior. With increasing temperature, the rate increases steadily, reaching values of 11.5×10^{-3} and 8.2×10^{-3} mol g_{Au}^{-1} s^{-1} after 10 and 1000 min reaction, respectively, at 180 °C, equivalent to TOFs of 6.6 and 4.7 s^{-1}. The deactivation over 1000 min on stream decreases with the temperature in the order 80 °C > 100 °C > 140 °C > 180 °C (see Table 1).

In addition to the measurements on the dried 3.3 wt.% Au/TiO_2 catalyst, we also performed similar measurements on a 3.1 wt.% Au/TiO_2 catalyst, which was prepared in the same way. After identical pre-treatment, the resulting activity–time curve (Fig. 1a and b, curve +) is essentially identical to that of the 80 °C curve of the 3.3 wt.% Au/TiO_2 catalyst, illustrating the excellent reproducibility of the catalyst properties. A very different initial activity and deactivation behavior was obtained, however, if the catalyst was only calcined at 400 °C for 30 min prior to the reaction, without the 15 h drying step before calcination (Fig. 1a and b, curve ×). In that case, the initial activity was lower, but after some time this was compensated by a much lower deactivation of only 23% over 1000 min on stream. The resulting final activity is higher than that obtained after drying and subsequent calcination under otherwise similar reaction conditions (curve +). Similar effects of the drying procedure were observed also on Au/TiO_2 catalysts based on mesoporous TiO_2, and attributed to higher water and hydroxyl contents on the non-dried catalysts [40].

Comparing our results with the deactivation behavior reported in the previous studies, there is no unique trend, despite the rather good agreement with several reports for reaction in H_2-free atmosphere at low temperatures ($\leqslant$80 °C). For instance, Zanella et al. reported a significant deactivation during CO oxidation at 5 °C (1% CO, 2% O_2, balance N_2) for catalysts which were prepared in a similar way, via deposition–precipitation, using Degussa P25 as support material [38]. After 5 h on stream, the activity was found to decrease to 20–75% of the initial values, depending on the initial calcination temperature (200–400 °C) [38]. For reaction at room temperature, Konova et al. observed a loss of activity of about 50% during 1000 min on stream (0.06–0.24 vol.% CO in air) on catalysts which had been calcined in air at 120 °C for 1 h (support: Anatase prepared by hydrolysis of $TiCl_4$, 3 wt.% Au) [41]. In previous studies on similar Au/TiO_2 catalysts as used here (P25, 3.1 wt.% Au), we observed a significant deactivation of 70–85% of the initial activity over 1000 min on stream at 80 °C, both for unconditioned catalysts [16] and for catalysts calcined at 400 °C prior to reaction [15]. On the other hand, Mallick et al. did not see any deactivation during 200 min in 10% CO, 10% O_2, and balance He at slightly lower reaction temperatures (30–60 °C) on a

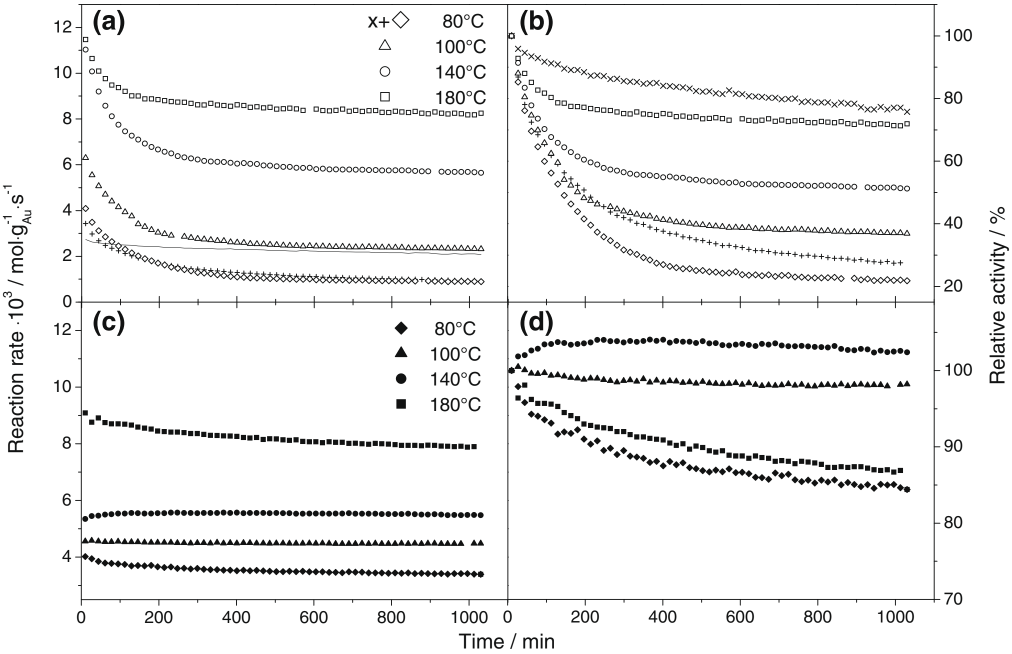

Fig. 1. Activity (left panels) and stability/deactivation (right panels) of the 3.1 wt.% (+, ×) and 3.3 wt.% (other symbols) Au/TiO_2 catalysts during reaction in different atmospheres (H_2-free (empty symbols): 1 kPa CO, 1 kPa O_2, balance N_2), (H_2-rich (filled symbols): 1 kPa CO, 1 kPa O_2, 75 kPa H_2, balance N_2) in the temperature range 80–180 °C (□, ■: 180 °C, ○, ●: 140 °C, △, ▲: 100 °C, and ◇, ◆, ×, +: 80 °C). All catalysts were dried for 15 h in N_2 at 100 °C followed by calcination at 400 °C, except (×), which was only calcined at 400 °C.

Table 1

Absolute and relative activity for CO oxidation on 3.3 wt.% Au/TiO_2 after 15 h drying plus calcination in 10% O_2/N_2 at 400 °C (30 min).

Reaction conditions	H_2-free: 1 kPa CO, 1 kPa O_2, balance N_2			H_2-rich: 1 kPa CO, 1 kPa O_2, 75 kPa H_2, balance N_2			
Temperature	Initial/final activity × 10^3 (mol g_{Au}^{-1} s^{-1})	Initial/final activity (TOF) (s^{-1})	Activity after 1000 min reaction (%)	Initial/final activity × 10^4 (mol g_{Au}^{-1} s^{-1})	Initial/final activity (TOF) (s^{-1})	Activity after 1000 min reaction (%)	Initial/final selectivity (%)
80	4.1/0.9	2.3/0.5	22	4.0/3.4	2.3/1.9	85	55/56
100	6.3/2.3	3.6/1.3	37	4.6/4.5	2.6/2.6	98	38/41
140	11.0/5.7	6.3/3.3	52	5.1/5.2	2.9/3.0	102	24/25
180	11.5/8.2	6.6/4.7	71	9.1/7.7	5.2/4.4	87	12/15

catalyst, which was also prepared via deposition–precipitation on a Degussa P25 support [42]. It should be noted, however, that in the latter study high amounts of catalyst were used, resulting in conversions of ⩾80%. Therefore it cannot be excluded that the apparent stability is an artifact of the reaction conditions, caused by the presence of 'unused' catalyst. Employing a higher reaction temperature of 160 °C, Arri et al. did not observe any deactivation of Au/TiO_2 catalysts prepared via laser vaporization over 70 h on stream (2% CO, 2% O_2, balance He) [43]. Also in that study, however, the CO conversion was very high (98%), so that artifacts arising from excess catalyst (equivalent to incomplete utilization of the catalyst) cannot be excluded. In total, a quantitative comparison of the deactivation behavior in various CO oxidation studies is not straightforward and often difficult due to the different reaction conditions used. However, in general, Au catalysts tend to deactivate significantly during CO oxidation in H_2-free atmosphere at 80 °C.

For reaction in H_2-rich atmosphere, the rate equally increases with temperature, from initial/final rates of 4.0×10^{-3} mol $g_{Au}^{-1}s^{-1}$ (TOF 2.3 s^{-1})/3.4×10^{-3} mol g_{Au}^{-1} s^{-1} (TOF 1.9 s^{-1}) at 80 °C to values of 9.1×10^{-3} mol g_{Au}^{-1} s^{-1} (TOF 5.2 s^{-1})/7.7×10^{-3} mol g_{Au}^{-1} s^{-1} (TOF 4.4 s^{-1}) at 180 °C (Table 1). The activity at 80 °C fits well to our previous results on similar type catalysts [15,16]. The deactivation of the catalyst is generally less pronounced than during reaction in H_2-free atmosphere. Deactivation over 1000 min on stream decreases with temperature in the order 80 °C (15%) > 100 °C (2%) > 140 °C (0%). At 140 °C, no deactivation was observed over the 1000 min on stream (final activity: 102% of initial activity). At the highest reaction temperature (180 °C), the deactivation slightly increased again to about 13% after 1000 min of reaction.

Studies done on the deactivation of Au/TiO_2 catalysts during the PROX reaction are scarce. Yu et al. reported negligible deactivation during reaction at room temperature over 15 h on stream ($CO:O_2:H_2:N_2$ = 1:1:50:48), using a Au/TiO_2 catalyst prepared via a deposition–precipitation procedure [44]. In our own previous studies, we observed a deactivation by 20–30% of the initial activity over 1000 min reaction at 80 °C on similar type catalysts [15], which is comparable to the present findings, and a slightly higher deactivation of ∼35% on catalysts prepared in the same way, but using a different support material (Anatase, VP9413/3, Sachtleben) [17]. Temperature-dependent deactivation studies have not been reported for this reaction so far.

For reaction at lower temperatures, up to 80 °C, the deactivation was mainly attributed to increasing surface blocking by stable surface species, in particular surface carbonates, which are built up during the reaction, although details of the deactivation process are not yet resolved [15,16,38,41]. For higher reaction temperatures, around 180 °C, irreversible Au nanoparticle sintering may also contribute to or even become the main source for deactivation. This was tested by recording TEM images before and after reaction in H_2-free and in H_2-rich atmosphere at 180 °C (1000 min). The resulting particle size distributions are depicted in Fig. 2. They clearly demonstrate that the reaction-induced increases of the particle sizes are negligible and within the error range of the measurements, independent of the reaction atmosphere, with mean Au particle diameters of 3.2 ± 0.7 nm after conditioning and 2.8 ± 0.7 nm after reaction (both atmospheres). Negligible Au particle growth for temperatures up to 200 °C was reported also by Comotti et al., who investigated the change in Au particle size distribution on a Au/TiO_2 catalyst prepared by deposition of preformed Au colloids upon catalyst storage and upon CO oxidation cycles in the temperature range between −40 and 200 °C by TEM [31]. Our own measurements on planar Au/TiO_2 model catalysts also showed no indications of Au particle growth (particle heights ∼3 nm) after exposure to CO/O_2 reaction mixtures (1:4 $CO:O_2$ mixture, 5 kPa total pressure, 13 h) at 200 °C [29,30]. On the other hand, Valden et al. reported morphology and size changes of the Au nanoparticles on TiO_2(110) and TiO_2(001)/Mo(100) already at a reaction temperature of 27 °C, with the size of the Au nanoparticles increasing from 2.6 ± 0.7 to 3.6 ± 1.4 nm after 50 min reaction, accompanied by a rapid deactivation of the model catalyst (Au/TiO_2(001)/Mo(100), $CO:O_2$ = 1:5, total pressure 5.3 kPa) [28]. In total, our present results, which showed that irreversible Au particle sintering can essentially be excluded for 3 nm particles and reaction up to at least 180 °C, agree with many of the literature data. Finally, the present results agree perfectly with our observation on Au/CeO_2 catalysts, which showed no measurable increase of the Au particle size during the water gas shift reaction at 180 °C [14], and even at 300 °C reaction temperature the increase in Au particle size was found to be small [45]. In consequence, the deactivation of the Au/TiO_2 catalyst during CO oxidation must be mainly due to (reversible) chemical modification of the catalyst surface, e.g., by reaction-induced formation of adsorbed surface species such as surface carbonates.

3.1.2. Activation energy and temperature dependence of the selectivity

The temperature dependence of the activity in the two reaction atmospheres and, for the PROX reaction, also of the selectivity, were followed at different temperatures between 80 and 180 °C. Before varying the temperature, the catalyst was first exposed to the reaction mixture over 1000 min, either at 80 °C or at 180 °C, to reach steady-state conditions of the catalyst. Subsequently, the temperature was stepwise increased or decreased, staying 90 min at each temperature.

The temperature-dependent activities (Au mass-normalized rates) resulting from three measurements in H_2-free atmosphere are plotted in the Arrhenius diagram in Fig. 3. In two of the measurements (○, □), the catalysts were deactivated at 180 °C and the measurements covered only the range between 120 and 180 °C (○: 180 °C → 120 °C, □: 120 °C → 180 °C), while for the third one (◇, 80 °C → 180 °C), the catalyst was deactivated at 80 °C and the measurement extended over the entire temperature range. In these measurements, the CO conversion was always below 15% (O_2 conversion below 8%). In all cases, the logarithmic rates show a linear increase with $1/T$, with the activities being slightly lower after initial deactivation at 180 °C (○, □) than after deactivation at 80 °C (◇). The slopes, however, are essentially identical, and cor-

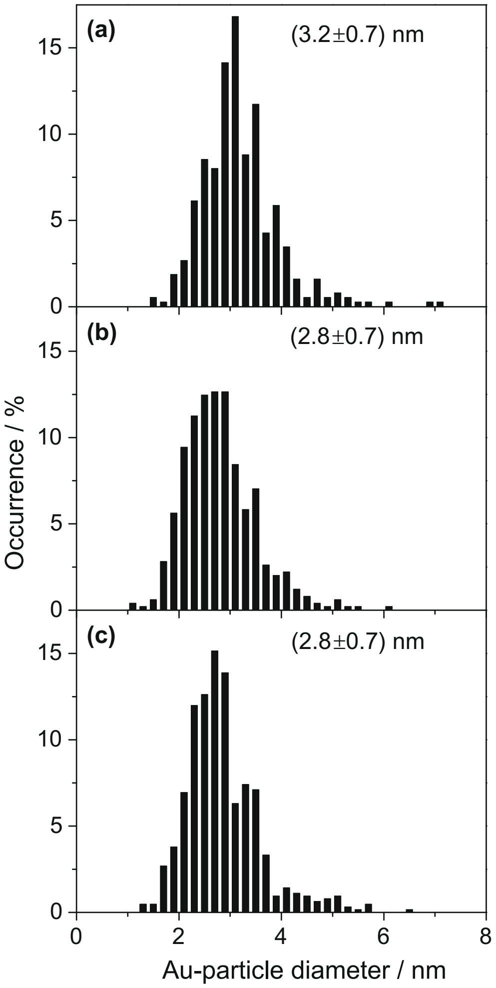

Fig. 2. Au particle size distribution of the 3.3 wt.% Au/TiO_2 catalyst after (a) conditioning, (b) conditioning and subsequent CO oxidation in a $CO/O_2/N_2$ mixture (1 kPa CO, 1 kPa O_2, 75 kPa H_2, balance N_2) at 180 °C, and (c) conditioning and subsequent preferential CO oxidation in H_2-rich atmosphere (1 kPa CO, 1 kPa O_2, 75 kPa H_2, balance N_2) at 180 °C.

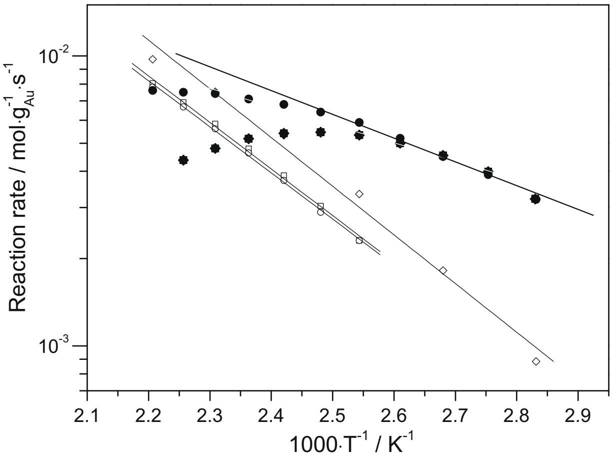

Fig. 3. Arrhenius plot of the temperature-dependent rates for CO oxidation in H_2-free atmosphere (empty symbols, 1 kPa CO, 1 kPa O_2, balance N_2) and in H_2-rich atmosphere (filled symbols, 1 kPa CO, 1 kPa O_2, 75 kPa H_2, balance N_2) in the temperature range 80–180 °C. Before changing the temperature, the catalyst was held on stream over 1000 min at 80 °C (◇) or 180 °C (□, ○, ♦, ■, ●). During the temperature change, the catalyst was held for 90 min at each temperature (◇, □, ♦: 80 °C or 120 °C → 180 °C, ○, ■, ●: 180 °C → 80 °C or 120 °C). Two different dilutions were used: (♦, □, ○, ■: dilution 1:170, ○: dilution 1:550). Note that the data points for ■ and ♦ are essentially on top of each other.

respond to apparent activation energies of 32 ± 3 kJ mol^{-1} and 30 ± 3 kJ mol^{-1} after deactivation at 80 and 180 °C, respectively. The fact that the logarithmic activities are located along a straight line in the Arrhenius plot indicates already that the rate-determining step(s) do(es) not change in this temperature range. The resulting value of the apparent activation energy agrees closely with the value obtained from a similar evaluation of the final rates in the temperature-dependent measurements shown in Fig. 1a (29 ± 3 kJ mol^{-1}). It should be noted that the initial activities shown in Fig. 1a lead to a much lower value of 15 ± 4 kJ mol^{-1}, due to the decreasing deactivation at higher reaction temperatures. Hence, measurements of the apparent activation energy, performed without proper aging of the catalyst, may result in very different values. Recently, we determined an activation energy of 33 ± 3 kJ mol^{-1} on a similar type Au/TiO_2 catalyst in the temperature range of 50–110 °C [46]. Obviously, increasing the temperature to 180 °C has no significant influence on the apparent activation energy and hence on the reaction mechanism, supporting our above conclusion of an unchanged reaction mechanism and rate-determining step(s) in this temperature range. The present result of about 30 kJ mol^{-1} agrees closely with the results of comparable previous studies, which reported apparent activation energies between 27 and 37 kJ mol^{-1} for reaction temperatures in the range between −30 and 150 °C [1,9,19,36,39,47]. Lin et al. reported values of the apparent activation energy for CO oxidation over Au/TiO_2 (P25) of about 38 and 8 kJ mol^{-1} for the temperature ranges below 87 °C and above 87 °C (pre-treatment: calcination at 400 °C). For different pre-treatment procedures, they obtained even lower values of −0.8 kJ mol^{-1} for a 2.3 wt% Au/TiO_2 catalyst after reduction at 200 °C (2 h, 100 kPa H_2) and about 6 kJ mol^{-1} for the same catalyst, but after reduction at 500 °C (2 h, 100 kPa H_2) [18]. The reason for the apparent discrepancy with other data is not yet understood, but likely related to differences in the catalyst preparation or reaction conditions [9].

The determination of the activation energy in H_2-rich atmosphere turned out to be more complicated. In Fig. 3, we present the data from a measurement performed in a similar way as those in H_2-free atmosphere (♦, ■, deactivation at 180 °C, ■: 180 °C → 80 °C, ♦: 80 °C → 180 °C). The data points deviate strongly from a straight line, and the rates even decay at temperatures ⩾130 °C. (Note that the upwards (♦) and downwards (■) measured data lie essentially on top of each other.) The origin of this behavior is clear when plotting not only the rates, but also the related conversions versus the temperature (Fig. 4a). The plots illustrate that the rates deviate increasingly from a simple Arrhenius-type behavior as soon as the O_2 conversion exceeds 10–15%. Under these conditions, the reaction leaves the range of differential reaction conditions, and the reaction rates cannot be evaluated any more by assuming constant reactant concentration throughout the reactor. Such effects are much more pronounced for reaction in H_2-rich atmosphere, where because of the high H_2 and low O_2 concentrations even relatively low H_2 conversions result in significant O_2 consumption. The strong decrease in O_2 partial pressure in turn increasingly affects the CO oxidation rate in the rear part of the reactor. For the present measurement, O_2 consumption reaches almost 70% for the reaction at 180 °C (Fig. 4a, open triangle). Similar effects of a decreasing CO oxidation activity at higher temperature in a H_2-rich reaction atmosphere were reported earlier also by Rossignol et al., who followed the temperature-dependent conversion of CO and H_2 during the selective CO oxidation in a H_2-rich atmosphere on Au/TiO_2 (2% CO, 2% O_2, 48% H_2, balance He) at temperatures up to 450 °C. They obtained a maximum CO conversion of

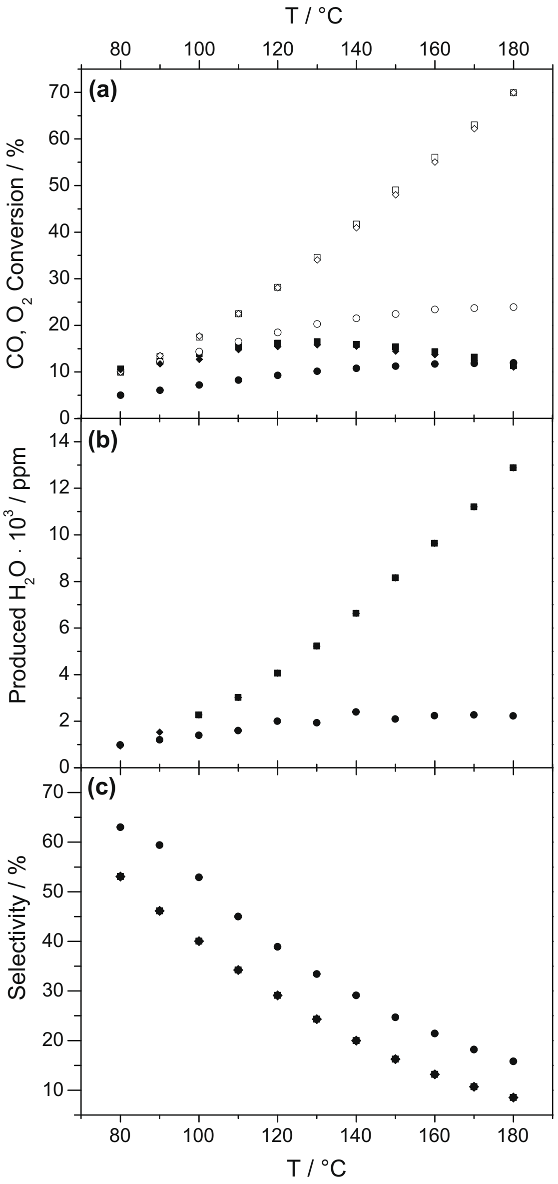

Fig. 4. (a) CO conversion (♦, ■, ∘) and O_2 conversion (♦, □, ∘) during CO oxidation in H_2-rich atmosphere (1 kPa CO, 1 kPa O_2, 75 kPa H_2, balance N_2) at different temperatures (■, □, •, ∘: 180 °C → 80 °C; ♦, ◇: 80 °C → 180 °C). Before changing the temperature, the catalyst was held on stream over 1000 min at 180 °C. Each temperature was held for 90 min. (b) Water formation during the reaction, and (c) temperature dependence of the selectivity during the above measurements (♦, ◇, ■, □: dilution 1:170, •, ∘: dilution 1:550). Note that the data points for ■/□ and ♦/◇ are essentially on top of each other.

60% at 196 °C, while at higher temperatures the CO conversion decreased, accompanied by a further increase in H_2 conversion. They explained this result by a combination of two effects, by 'a preference for hydrogen oxidation' and by the increasing O_2 consumption [19]. For reaction in H_2-free atmosphere, the latter effect is not important, since O_2 consumption occurs only by CO conversion, and the amount of CO in the reaction mixture is of similar magnitude as that of O_2.

Repeating similar measurements on a more strongly diluted catalyst (•, 1:550 dilution rather than the 1:170 dilution in the above measurement) results in the activity–temperature relation indicated by filled circles in Fig. 3. In this case, the logarithmic rates are much closer to a simple Arrhenius-type behavior, although here also we find a slight deviation at temperatures above 130 °C. The O_2 conversion is now limited to <18% at 180 °C (Fig. 4a). On the other hand, this means that the CO_2 and O_2 concentrations measured in the low temperature range are very low (80 °C: CO_2 concentration 320 ppm, O_2 consumption: 550 ppm), and therefore are less precise. The rates in the low temperature regime ($T \leqslant 110$ °C) are essentially identical to those determined on the less diluted catalyst. Neglecting the slight bend-off of the high temperature rates, we obtain an apparent activation energy of 18 ± 3 kJ mol^{-1}.

The apparent activation energy for CO oxidation in H_2-rich atmosphere is significantly lower than that in H_2-free atmosphere. Evidently, the presence of hydrogen has a considerable effect not only on the deactivation behavior and the absolute rates, but also on the reaction mechanism and/or the rate-limiting step(s). Most simply, this may be related to competitive adsorption between H_2 and CO. But other effects such as a hydrogen-induced activation of oxygen [48] may also be possible. Furthermore, it is well known that the presence of small amounts of water has significant effects on the CO oxidation activity (see also Fig. 1 and Refs. [49,50]), and this may also affect the reaction mechanism and the apparent activation energy. For the 1:170 diluted catalyst, the reaction leads to a water concentration of ~13,000 ppm at 180 °C reaction temperature (Fig. 4b). Daté et al. reported that water concentrations >3000 ppm have a negative influence on the CO oxidation activity, while lower amounts accelerate the reaction [49]. Therefore, the high water content in the 180 °C measurement using the less diluted (1:170) sample could further contribute to the decreasing activity at high temperatures (above 130 °C), in addition to the increasing lack of O_2 [19].

In a previous study on similarly prepared Au/TiO_2 catalysts based on an Anatase support (VP9413/3, Sachtleben), we estimated an apparent activation barrier of 25 ± 8 kJ mol^{-1} from the temperature dependence between 40 and 80 °C, which, however, dropped significantly, down to values around 0 kJ mol^{-1}, for CO partial pressures of 0.1 kPa and less [12]. The pronounced pressure dependence clearly indicates that the apparent activation energy does not correspond to the barrier in an elementary reaction, but reflects the effective barrier in a more complex reaction scheme. Considering also the much higher temperatures in the present study and the increasing slope in the low temperature range of the Arrhenius plot (see Fig. 3), those data seem to be consistent with the present ones. Higher activation energies around 30 kJ mol^{-1} were determined also on Au/Fe_2O_3 catalysts from the temperature-dependent reaction rates between 40 and 100 °C [10,20,22]. In the presence of H_2O (1.3 kPa), however, the apparent activation energy was found to decrease to 20 kJ mol^{-1} [22]. Hence, for that catalyst, the effect of additional H_2 in the gas phase appears to be less pronounced than for Au/TiO_2 catalysts.

3.1.3. Selectivity for the preferential CO oxidation

Fig. 4c illustrates the selectivity for the preferential CO oxidation at various temperatures, determined during the temperature-dependent measurements described above. The selectivity is defined by the amount of O_2 used for CO oxidation, divided by the total amount of O_2 consumed, and calculated from the balance between CO_2 formation and O_2 consumption [33]. It should be noted that this method of evaluation is correct only as long as the H_2O and CO_2 levels are not affected by any other reaction such as the water gas shift (WGS) reaction ($CO + H_2O \leftrightarrows CO_2 + H_2$) or the methanation reaction ($CO + 3H_2 \leftrightarrows CH_4 + H_2O$). This assumption appears justified considering previous measurements of the forward WGS reaction on a Au/TiO_2 catalyst under comparable reaction conditions [51].

The selectivity decreases strongly with increasing temperature, from about 60% at 80 °C to ~10% at 180 °C. Clearly, H_2 oxidation becomes increasingly favorable for higher temperatures. Therefore, the original idea of using Au/TiO_2 catalyst for CO removal from H_2-rich feed gases at elevated temperatures up to 180 °C must be discarded because of the low selectivity of these catalysts in this temperature range. On the other hand, high selectivities at lower temperatures were also reported previously, e.g., in Ref. [12], where a selectivity of up to 64% was measured at a reaction temperature of 40 °C on an anatase-supported catalyst, or in Ref. [44], where a selectivity of ~75% was determined at room temperature on a Au/TiO_2 catalyst (catalyst preparation: deposition–precipitation, $CO:O_2:H_2:N_2 = 1:1:50:48$). Hence, the reaction temperature is a crucial factor for the selectivity for CO oxidation. Finally, the data seem to indicate that also the conversion may have an effect on the selectivity, which in a kinetic picture would correspond to different reaction orders for O_2 in the CO oxidation and the H_2 oxidation reactions. This needs to be investigated, however, in more detail.

A rapidly decreasing selectivity with increasing temperature was observed also in conversion measurements on a P25-based Au/TiO_2 catalyst [19] and also for Au/Fe_2O_3 [22]. In a kinetic picture, it can be associated with a higher apparent activation energy for H_2 oxidation [22]. Also in this case it needs to be verified, however, whether this really corresponds to a higher barrier in the elementary reaction step for oxidation of adsorbed hydrogen. Another reason for the decreasing selectivity (Fig. 4c) at higher temperatures is probably the rapidly decreasing steady-state coverage of CO_{ad} on the Au nanoparticles, due to the weak adsorption of CO on Au, which increases the chance for adsorbed hydrogen to reach the active sites and react to water (see Section 3.2.2).

3.2. Reaction intermediates and surface species during reaction

To gain more information on the origin of the temperature dependence in the deactivation and selectivity behavior, we followed the reaction by in situ DRIFTS measurements in both H_2-free and H_2-rich atmospheres in the temperature range 80–180 °C.

3.2.1. Time-dependent changes at different reaction temperatures of 80 and 180 °C

First, we followed the CO oxidation at constant temperatures of 80 and 180 °C, respectively, in the two reaction atmospheres. Representative spectra, recorded after 1, 5, 10, 15, 30 min, 1, 4, 10, and 20 h reaction time, are presented in Figs. 5 (80 °C) and 6 (180 °C). Full spectra, without removal of the gas phase CO signal, are given in the bottom panels (Figs. 5c, f and 6c, f), while the upper panels present details of the spectral regions typical for OH groups (Figs. 5a, d and 6a, d) and for CO (Figs. 5b, e and 6b, e). In the latter spectra, the contributions from the gas phase CO signal were removed (see Section 2).

For reaction at 80 °C, linearly adsorbed CO on metallic Au is observed with peaks at 2123 and at 2108 cm^{-1} in the two reaction atmospheres (Fig. 5b and e), respectively [24,52]. Apparently, the presence of H_2 in the gas mixture leads to a weakening of the C–O bond compared to adsorption in H_2-free atmosphere. This may be caused by two different reasons: by the presence of coadsorbed hydrogen or by the onset of TiO_2 support reduction [53–55]. Considering that the difference in wave number exists from the beginning, and that TiO_2 reduction was found to be a slow process under these conditions, requiring a few minutes [53], we favor the former explanation. The characteristic signals for gaseous CO_2 appear at 2362 and 2335 cm^{-1}. Their intensity decreases measurably (10%) with time for reaction in H_2-free atmosphere (Fig. 5b), while the decrease is negligible for reaction in H_2-rich atmosphere. This behavior closely follows the findings in the activity measurements (Fig. 1), at least on a qualitative scale. (A quantitative comparison is hardly possible because of the different reaction conditions in the two measurements caused by the different catalyst dilutions, etc.) The significant deactivation in H_2-free atmosphere (Fig. 1, empty diamonds) is accompanied by a considerable decrease of the intensity of adsorbed CO_{ad} by ~30%. Also for this species, the decrease is much less (10%) in H_2-rich atmosphere. Hence, deactivation seems to be correlated with a reduction in Au surface area available for CO adsorption [12,16].

More information on the deactivation process is obtained from the signals in the spectral region between 1300 and 1600 cm^{-1} (Fig. 5c and f). For reaction in H_2-free atmosphere, pronounced carbonate peaks develop at 1574 cm^{-1} (ν(C=O) of bidentate carbonate), 1436 cm^{-1} (ν_{as}(COO) of monodentate carbonate), and 1346 cm^{-1} (ν_s(COO) of monodentate carbonate) [24,52,56]. In contrast to previous DRIFTS measurements on a similarly prepared Au/TiO_2 catalysts based on an Anatase support (VP9413/3, Sachtleben)

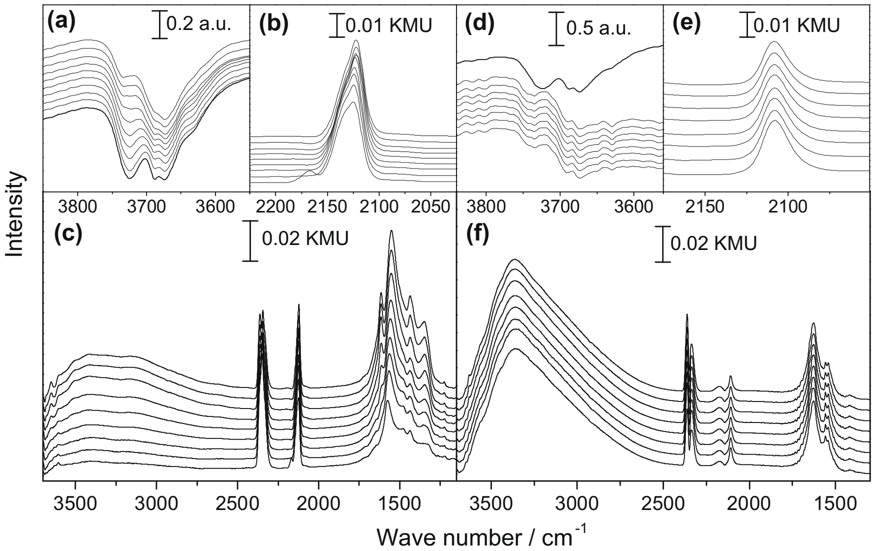

Fig. 5. Sequences of DRIFT spectra recorded during CO oxidation (a–c) in H_2-free atmosphere (1 kPa CO, 1 kPa O_2, rest N_2; left panel) and (d–f) in H_2-rich atmosphere (1 kPa CO, 1 kPa O_2, 75 kPa H_2, balance N_2; right panel) at 80 °C. The spectra were recorded (from bottom to top) after conditioning and cool-down to reaction temperature (background spectra: bold curve) and after 1, 5, 10, 15, 30 min, 1, 4, 10, and 20 h reaction time. Each panel shows the complete spectrum (c), (f) no removal of gas phase CO signal as well as details of the OH (a), (d) and CO (b), (e) gas phase CO signal removed regions. The catalyst (15–20 mg) was diluted 1:2 with α-Al_2O_3.

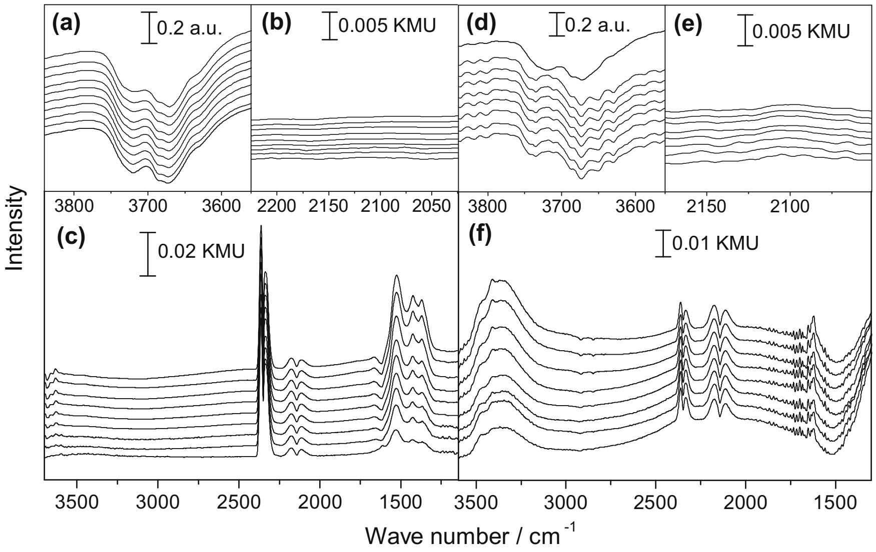

Fig. 6. Sequences of DRIFT spectra recorded during CO oxidation (a–c) in H_2-free atmosphere (1 kPa CO, 1 kPa O_2, rest N_2; left panel) and (d–f) in H_2-rich atmosphere (1 kPa CO, 1 kPa O_2, 75 kPa H_2, balance N_2; right panel) at 180 °C. The spectra were recorded (from bottom to top) after conditioning and cool-down to reaction temperature (background spectra: bold curve) and after 1, 5, 10, 15 min, 1, 4, 10, and 20 h reaction time. Each panel shows the complete spectrum (c), (f) no removal of gas phase CO signal as well as details of the OH (a), (d) and CO (b), (e) gas phase CO signal removed regions. The catalyst (15–20 mg) was diluted 1:2 with α-Al_2O_3.

[12], we do not see any evidence of surface formate species in these measurements. Based on a qualitative correlation between increasing presence of surface carbonates and decreasing activity, the deactivation of the Au/TiO_2 catalysts during reaction in H_2-free atmosphere at 80 °C is mainly attributed to the growth of surface carbonates, which increasingly cover the catalyst support [12,16,38].

Characteristic peaks at 3724 and 3675 cm^{-1} are attributed to isolated OH groups [57–59]. An additional peak at 1616 cm^{-1}, corresponding to adsorbed water, is formed after 10 min of the reaction. The intensity of the water signal increases with ongoing reaction, while that of the OH signal at 3725 cm^{-1} decreases to about 50% of the initial intensity over 1200 min on stream. This points to OH consumption and H_2O formation during the reaction, which was also observed previously on similar P25-TiO_2 [49] and anatase-based catalysts [12].

The picture is completely different for reaction in H_2-rich atmosphere at 80 °C (Fig. 5d–f), where we detected only very small contributions from bidentate carbonates (ν(C=O)) [56] at 1559 cm^{-1}, which increase in the first minute of the reaction and then remain constant during CO oxidation over 1200 min reaction. This goes along with an almost constant signal intensity of both CO_2 and linearly adsorbed CO_{ad} during the reaction. Pronounced water signals are visible at ~1620 cm^{-1} and 2500–3300 cm^{-1}, which increase in the first minute of the reaction and stay about constant afterward. Hence, under reaction conditions, the surface contains significant amounts of adsorbed water, which are accumulated directly at the beginning of the reaction due to the significant water production on the little diluted catalyst under these reaction conditions (see also Fig. 4c), and then remain about constant in coverage (adsorption–desorption equilibrium).

The spectra recorded during reaction at 180 °C (Fig. 6) are distinctly different from those obtained at 80 °C reaction temperature (Fig. 5). Linearly adsorbed CO (CO_{ad}) is not detected any more at this high reaction temperature, neither in H_2-free atmosphere (Fig. 6b) nor in H_2-rich atmosphere (Fig. 6e), indicative of very low steady-state CO_{ad} coverages. Furthermore, signals of gaseous CO_2 (2363 and 2335 cm^{-1}) appear in both reaction atmospheres, whose intensity stays about constant in both cases (decrease by ~1% over 1000 min). The lower intensity of these signals at 180 °C than at 80 °C, despite of the higher CO_2 formation rate at 180 °C, will be discussed in the next section. In the carbonate region below 1700 cm^{-1}, we again find the evolution of surface carbonates adsorbed on the TiO_2 support in H_2-free atmosphere, with signals at 1528 cm^{-1} (ν(C=O) of bidentate carbonate), 1423 cm^{-1} (ν_{as}(COO) of monodentate carbonate), and 1371 cm^{-1} (ν_s(COO) of monodentate carbonate) [24,56]. The intensities of the signals related to adsorbed carbonates increase significantly during the reaction, but less strongly than those during the reaction at 80 °C. In contrast, for reaction in H_2-rich atmosphere, surface carbonate species are essentially absent.

In both reaction atmospheres, we furthermore resolve a distinct peak at 1615–1620 cm^{-1}, which is related to adsorbed H_2O (see above and [52,59,60]). This peak decreases during the reaction in H_2-free reaction mixture (Fig. 6c), while in H_2-rich atmosphere (Fig. 6f) it increases. Apparently, for reaction at 180 °C, desorption of water overcompensates the formation of water via conversion from hydroxyl groups to water, which was observed during the reaction at 80 °C (Fig. 5c). For reaction in H_2-rich atmosphere, in contrast, water formation due to H_2 oxidation is much more pronounced and results in an initial increase of the adsorbed water species with time, despite the higher desorption rate compared to reaction at 80 °C, until finally steady-state conditions are reached after 1000 min.

These results fully support our previous conclusion that deactivation of the Au/TiO_2 catalyst in H_2-free atmosphere (Fig. 1) is mainly related to the build-up of surface carbonate species, which is less pronounced at higher temperatures. For reaction in H_2-free atmosphere, surface carbonate formation is much less pronounced at 80°C, most likely due to a H_2O-assisted more facile decomposition of these species, and essentially absent at 180 °C. Qualitatively, this agrees with the observed lower tendency for deactivation during CO oxidation in H_2-rich reaction atmosphere (see Fig. 1). Similar observations were reported also for the PROX reaction on Au/Fe_2O_3 catalysts, and tentatively assigned to the H_2O-assisted formation of bicarbonates, which are thermally less stable [10,20–22]. Furthermore, we expect that the significant H_2O formation in H_2-rich reaction atmosphere also contributes directly to the deactivation, reducing the activity for CO oxidation during the build-up of the H_2O adlayer [23,49,50,61–63], until the content of adsorbed H_2O on the catalyst surface reaches steady-state conditions. A quantitative separation of these two contributions, however, is hardly possible from the present data. Because of the complex correlation between H_2O surface content and CO oxidation activity, with an increase in activity at H_2O contents of $\leqslant$100 ppm in the reaction mixture and a decrease in activity with further increasing H_2O content (>3000 ppm) [49,50,63], the effect of adsorbed H_2O on the deactivation behavior is expected to be more complicated, which also agrees with the observed change from decreasing deactivation up to 140 °C and the higher deactivation again at 180 °C (in H_2-rich reaction atmosphere).

3.2.2. Temperature-dependent changes in H_2-free and H_2-rich atmosphere

Finally, temperature-dependent changes in the adlayer during reaction in H_2-free and H_2-rich atmosphere in the range 80–180 °C are illustrated in the two sequences of DRIFT spectra in Fig. 7, which were recorded after initial deactivation at 180 °C (1200 min), after the measurements presented in Fig. 6. Complete spectra without removal of CO gas phase contributions are presented in the bottom panels (Fig. 7c and f), details of the spectral regions for OH groups (Fig. 7a and d) and CO species (Fig. 7b and e, after removal of the CO gas phase contributions) in the top panels.

In both gas mixtures, the trends are comparable. The most significant finding in these sequences of spectra is that the signal of linearly adsorbed CO in H_2-free atmosphere and H_2-rich atmosphere, at 2125 and 2108 cm^{-1}, respectively, decreases in intensity in the temperature range 80–140 °C, and is completely absent at higher temperatures. The decreasing CO coverage at higher temperatures is mainly attributed to higher desorption rates. At temperatures >140 °C, the steady-state CO_{ad} coverages are below the detection limit. The oxidation product CO_2, with peaks at 2363 and 2336 cm^{-1}, appears at all temperatures. The decrease of the CO_2 signal with increasing temperature, which is in contrast to the increasing activity for CO oxidation, results from the increase of the CO_2 gas phase concentration due to thermal effects (reduced density of the gas phase in the reactor at higher temperatures). Accordingly, the CO_2 signals cannot be used for estimating the temperature dependence of the CO_2 production rate. For reaction in H_2-free atmosphere, the increase in CO_2 formation with temperature is apparently compensated by these thermal effects, and the decrease in CO_2 intensity is only small. For CO oxidation in H_2-rich atmosphere, where under integral reaction conditions, as they are given for the present amount of catalyst, the CO oxidation rate was found to decrease with temperature at higher temperatures, these two effects are acting in the same direction and the decrease in CO_2 intensity with temperature becomes much more pronounced than that in H_2-free atmosphere.

In the spectral region of 1300–1600 cm^{-1}, the build-up of surface carbonates is observed at 80 °C. With increasing temperature, the amount of surface carbonates decreased, which agrees with the expected increasing decomposition of these species at elevated temperatures (see previous section). Considering the decreasing tendency for deactivation in H_2-free reaction mixtures at higher temperatures, these results agree very well with our previous conclusion that the formation of surface carbonates is the main cause for the deactivation of these catalysts. For reaction in H_2-rich atmosphere, the carbonate coverages and hence the tendency for carbonate formation are significantly lower at comparable temperatures than during reaction in H_2-free atmosphere, which agrees well with our finding of a significantly lower tendency for deactivation in the H_2-rich reaction atmosphere compared to the H_2-free one. Furthermore, the intensity of the carbonate-related signals also decays with increasing temperature, and already at 120 °C, surface carbonates cannot be detected any more under present reaction conditions. For reaction in H_2-rich atmosphere, surface carbonate formation also plays a role for the deactivation at lower temperatures, but not at temperatures $\geqslant$120 °C. Hence, for reaction in this atmosphere, the accumulation of H_2O on the catalyst surface and its effect on the CO oxidation activity are more important and seem to be dominant at temperatures $\geqslant$120 °C.

In agreement with our findings in Figs. 5 and 6, also the intensity of the H_2O-related signals and hence the amount of adsorbed H_2O_{ad} decreases with increasing temperature, which reflects the increasing H_2O_{ad} desorption rates at higher temperatures. As expected (see also Figs. 5 and 6), the absolute signal intensities and amounts of H_2O_{ad} are much higher during reaction in H_2-rich atmosphere than in H_2-free atmosphere.

In total, these data fully support the conclusions on the decisive role of surface carbonate formation for the deactivation of the Au/

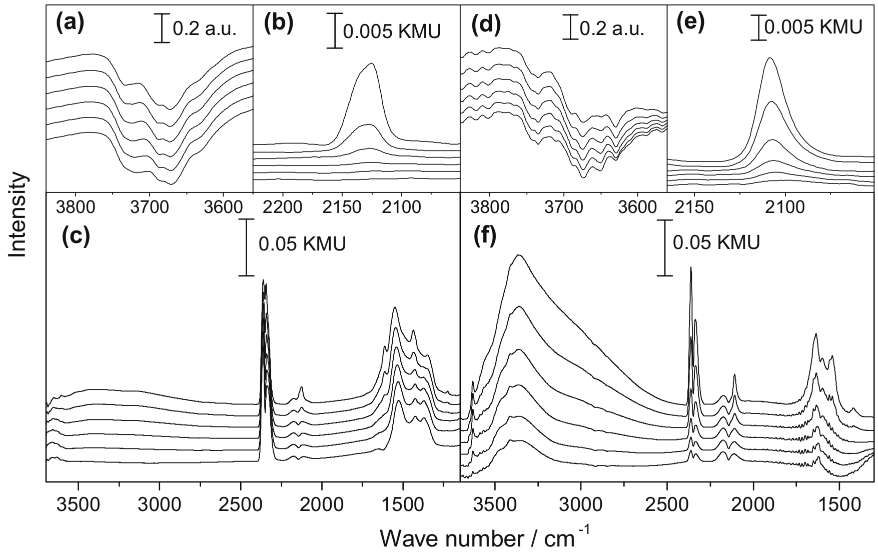

Fig. 7. Sequences of DRIFT spectra recorded during CO oxidation at various temperatures (a–c) in H_2-free atmosphere (1 kPa CO, 1 kPa O_2, balance N_2; left panel) and (d–f) in H_2-rich atmosphere (1 kPa CO, 1 kPa O_2, 75 kPa H_2, balance N_2; right panel). The spectra were recorded after conditioning and CO oxidation for 20 h at 180 °C, keeping the sample for 1.5 h at each temperature (from bottom to top: 180, 160, 140, 120, 100, and 80 °C). Each panel shows the complete spectrum (c), (f) no removal of gas phase CO signal as well as details of the OH (a), (d) and CO (b), (e) gas phase CO signal removed regions. The catalyst (15–20 mg) was diluted 1:2 with α-Al_2O_3.

TiO_2 catalysts during CO oxidation in H_2-free atmosphere derived in the last section. Furthermore, they also reflect a more pronounced temperature dependence of the CO_{ad} signal during reaction in H_2-free atmosphere than in H_2-rich atmosphere, which correlates with the lower activation barrier for CO oxidation in the latter reaction atmosphere. Nevertheless, the considerable decrease in the steady-state CO_{ad} coverage also in H_2-rich atmosphere is considered to be the main cause for the pronounced decrease in selectivity with temperature (see Section 3.1.3), due to higher accessibility of active reaction sites to adsorbed hydrogen.

4. Summary

Kinetic and in situ DRIFTS measurements on the CO oxidation behavior on P25-Degussa-based Au/TiO_2 catalysts, which were performed at elevated temperatures in the range between 80 and 180 °C and in idealized H_2-free as well as in H_2-rich reaction atmosphere, led us to the following conclusions on the effect of increasing reaction temperatures:

1. In both reaction atmospheres, the activity increases with increasing temperature. For reaction in H_2-free atmosphere, the temperature dependence can be described by a simple Arrhenius-type behavior, with an apparent activation barrier for CO oxidation of 30 ± 3 kJ mol^{-1}. The linear relation between $\ln r$ and $1/T$ over the entire temperature range indicates that the rate-limiting steps (CO oxidation, CO desorption) do not change in that temperature range. In H_2-rich mixtures, this is less clear, and the slight curvature in the $\ln r$ vs. $1/T$ relation may point to a change in rate-limiting step(s) with increasing temperature. In the lower temperature range, an apparent activation energy of 18 ± 3 kJ mol^{-1} is derived, which decreases with temperature. In addition, the rapidly increasing O_2 consumption results in an apparent decrease of the CO oxidation rate with increasing temperature in the higher temperature regime, simulating even a negative apparent activation energy for CO oxidation, if the catalyst dilution is not sufficient to maintain differential reaction conditions over the entire temperature regime also for O_2.
2. For reaction in H_2-free gas mixture, the deactivation decreases with temperature. For reaction in H_2-rich gas mixture the deactivation decreases with temperature up to 140 °C and then increases again. Under all conditions tested, however, the deactivation is more pronounced in the absence of H_2 (78% (80 °C) → 29% (180 °C)) than in the presence of H_2 (15% (80 °C) → 0% (140 °C) → 13% (180 °C)).
3. In H_2-rich gas atmosphere, the selectivity for CO oxidation decreases strongly with increasing temperature, from ~60% at 80 °C to <15% at 180 °C. This precludes application of Au/TiO_2 catalysts for applications for catalytic removal of CO from H_2-rich gas mixtures, e.g., from feed gases for low temperature fuel cells, at higher temperatures.
4. Also at higher temperatures, up to 180 °C, deactivation is related to reversible modifications of the catalyst surface rather than to irreversible Au particle sintering, which can be excluded from TEM measurements. For reaction in H_2-free reaction atmosphere, deactivation is clearly correlated with the build-up of surface carbonates. The decreasing deactivation at higher temperatures coincides with less carbonate formation, possibly due to increasing (oxidative) carbonate decomposition. Furthermore, the conversion of OH groups into adsorbed water during the reaction, which is much more pronounced at 80 °C than at 180 °C, may further affect the deactivation behavior. During reaction in a H_2-rich mixture, formation of surface carbonates is much less pronounced and essentially absent at $T \geqslant 120$ °C, presumably due to an H_2O-induced destabilization of surface carbonates. In this case, adsorbed water is the main reason for deactivation. The significant rates for H_2O formation in H_2-rich atmosphere lead to much higher contents of adsorbed H_2O than in H_2-free atmosphere, in particular at 80 °C. With increasing temperature, the content of adsorbed H_2O decreases, due to an increasing H_2O removal from the reactor. The complex correlation between CO oxidation activity and adsorbed water content results in a non-linear relation between the temperature-dependent deactivation and adsorbed H_2O content.

In total, raising the reaction temperature up to 180 °C has a distinct influence on the reaction and deactivation behavior of P25-based Au/TiO_2 catalysts in the CO oxidation and PROX reaction, which also allow conclusions on mechanistic aspects in the lower temperature regime.

Acknowledgments

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