Catalysis Letters Vol. 89, Nos. 1–2, July 2003 (© 2003)

Highly active Au/TiO$_2$ catalysts for low-temperature CO oxidation: preparation, conditioning and stability

B. Schumacher[a], V. Plzak[b,*], M. Kinne[a], and R.J. Behm[a]

[a]*Department of Surface Chemistry and Catalysis, University of Ulm, D-89069 Ulm, Germany*
[b]*Centre for Solar Energy and Hydrogen Research, Helmholtzstr. 8, D- 89081 Ulm, Germany*

Received 28 January 2003; accepted 6 May 2003

Using a modified deposition–precipitation procedure and a new reductive conditioning method, Au/TiO$_2$ catalysts with small metallic Au particles (<2 nm) and a very high activity for low-temperature CO oxidation were prepared. The particles are stable during reaction; a decreasing activity is caused by the accumulation of by-products on the catalyst.

KEY WORDS: supported catalyst; catalyst activation; catalyst deactivation; CO oxidation; selective CO oxidation; particle size; Au/TiO$_2$; TEM; DRIFTS; XPS; XRD; kinetic measurements.

1. Introduction

Previous studies have shown that highly dispersed metal oxide–supported Au catalysts are very active for various oxidation and hydrogenation reactions, in particular, the CO oxidation [1–3]. Especially Au/TiO$_2$ has shown an extraordinary activity even at temperatures as low as 90 K [4]. Commonly, these catalysts are prepared by coprecipitation or deposition–precipitation, followed by an activation procedure involving calcination in air at 200–400 °C, which is considered to give the most active catalysts [5–8]. We have shown previously, however, that catalysts prepared via a modified deposition–precipitation (MDP) procedure reveal a similar or even higher activity as ones prepared by the above procedures [9]. Its experimental simplicity and high reproducibility make this method attractive for industrial applications also.

In the present paper, we report on highly active Au/TiO$_2$ catalysts for low-temperature CO oxidation, which were prepared using this method. We will introduce a new activation procedure. By comparison with catalysts conditioned via the conventional calcination procedure, we will demonstrate that the new conditioning method leads to an improved activity of the resulting catalysts. It results in very small particle sizes, below the value of 2.5–3.5 nm given by Haruta and coworkers [10,11], Valden *et al.* [12], and Maciejewski *et al.* [13], respectively, for the most active particles. In addition, we investigated the chemical state of the Au particles and the stability/ageing behavior of the catalysts. Since Au/TiO$_2$ catalysts could be attractive CO oxidation catalysts for the cleanup of reformer gas from CO impurities in feed streams for polymer membrane (PEM) fuel cells [14], we will focus on a reaction temperature of 80 °C, the working temperature of these fuel cells.

2. Experimental

2.1. *Preparation of the* Au/TiO$_2$ *catalysts*

The TiO$_2$ powder (anatase, Sachtleben VP9413/3, annealed in air at about 700 °C for 30 min; TiO$_2$ particle sizes 21–25 nm) was suspended in water at 60 °C. To this suspension, an aqueous solution of $HAuCl_4 \bullet 4H_2O$ was added, while stirring at constant temperature. During this process, the suspension was kept constant at a pH of about 5.5 by adding 0.16 M Na_2CO_3 solution. After an additional 30 min of continuous stirring, the precipitate was cooled, filtered and washed. Careful washing is important to avoid Na contamination (Na concentrations $> 0.5\%$ were found to significantly decrease the activity of different Au catalysts). The filtrate was then dried overnight at room temperature under vacuum. Since in a number of experiments we have found that depending on the used metal oxide (Fe_2O_3, TiO_2, CeO_2, Co_3O_4) only part of the Au (50–95%) is deposited on the oxide particles, accurate values for the actual Au metal loading were determined by inductively coupled plasma atom emission spectroscopy (ICP-AES). Three different Au/TiO$_2$ samples denoted AuTi(A), AuTi(B) and AuTi(C) were used in this study. AuTi(A) and AuTi(B) are identical samples investigated to examine the reproducibility of our results. AuTi(C) is also prepared in a similar way, but with a higher Au loading (4.5 wt% Au instead of 2.4 wt%). The BET surface areas of the different catalysts were determined to be 50 m^2 g^{-1} ((AuTi(A), AuTi(C)) and 65 m^2 g^{-1} for AuTi(B) respectively.

---

* To whom correspondence should be addressed.

1011-372X/03/0700–0109/0

Two different conditioning procedures were applied: (i) conventional conditioning by calcining in 10% O_2/90%N_2 at 400 °C for 30 min as described in the literature [5,11] and (ii) a new reductive conditioning procedure involving annealing in H_2/N_2 at 200 °C. For comparison, we also evaluated a catalyst dried at 120 °C in N_2 overnight.

2.2. *Catalyst characterization*

Details of the procedures and experimental setup for the microscopic, spectroscopic and catalytic characterization of the catalysts have been reported elsewhere [9]. In short, the Au particle sizes were determined both by transmission electron microscopy (TEM) using a Philips CM 20 microscope (200 kV) and by X-ray diffraction (XRD) (Siemens 2000) via the Scherrer equation, recording difference spectra and averaging over Au(111) and Au(200) reflections. The oxidation state of the gold particles was evaluated via X-ray photoelectron spectroscopy (XPS) (PHI 5800 ESCA system), using monochromatized Al Kα radiation. Catalytic activities were measured in a quartz micro-reactor with on-line gas chromatography detection (Dani GC 86.10HT) under differential flow conditions, except for the deactivation measurements, which were performed under integral flow conditions. All catalytic measurements were performed at atmospheric pressure and a gas flow of 60 NmL min^{-1}. High-purity reaction gases (CO 4.7, O_2 5.0, H_2 5.0 and N_2 6.0 from Westphalen) were used. *In situ* IR measurements on CO adsorption were performed using a Magna 560 spectrometer (Nicolet), in a DRIFTS configuration with a Harricks cell (HV-DR2). Typical amounts of catalysts were about 50 mg for DRIFTS experiments and 1 mg for kinetic studies. All experiments were carried out at 80 °C and atmospheric pressure.

3. Results and discussion

3.1. *Physical characterization after conditioning*

After conventional conditioning (calcination at 400 °C), TEM imaging resolves particle sizes of about 2.5–3 nm (see table 1), which is, according to Refs [10–13,] the most active Au particle size. In contrast, after reductive conditioning at 200 °C, the Au particles were much smaller, with diameters around 1.8 nm (table 1). As is evident from the TEM image in figure 1, the particles are homogenously distributed over the catalyst, with a very narrow particle-size distribution. Similarly, small particle sizes were also found for other Au-supported catalysts upon the reductive conditioning procedure (e.g., Au/Fe_2O_3, Au/CeO_2, Au/Co_3O_4). The smaller particle sizes are not only a result of the lower conditioning temperature but also of the reactive atmosphere and the conditioning time. For instance, Daté *et al.* [15] found 2.4-nm-sized Au particles after calcination in air for 4 h at 200 °C and 3.5 nm particles after calcination at 300 °C. It is important to note that the particle size does not vary for loadings of 2.4 and 4.5% Au, respectively (see table 1).

Table 1
Particle sizes of different Au/TiO$_2$ catalysts after calcination at 400 °C and after reductive treatment at 200 °C

Catalysts	TEM (nm)	XRD (nm)
AuTi(A)$_{calc}$	3.0 ± 1.1	2.9 ± 0.3
AuTi(B)$_{calc}$	2.6 ± 0.9	2.7 ± 0.2
AuTi(C)$_{calc}$	2.6 ± 0.8	2.6 ± 0.1
AuTi(A)$_{red}$	–	1.7 ± 0.1
AuTi(B)$_{red}$	1.8 ± 0.5	1.8 ± 0.2

To examine the chemical state of the Au particles after conditioning we performed XPS measurements on the catalyst and compared these spectra with results obtained on an untreated catalyst. Au(4f) spectra for AuTi(C) are shown in figure 2; the other samples gave similar results. In order to avoid radiation-induced changes of the catalyst composition, in particular, of the untreated and the dried samples, respectively, the spectra were recorded rather quickly, resulting in a relatively high noise level. The untreated sample gives a

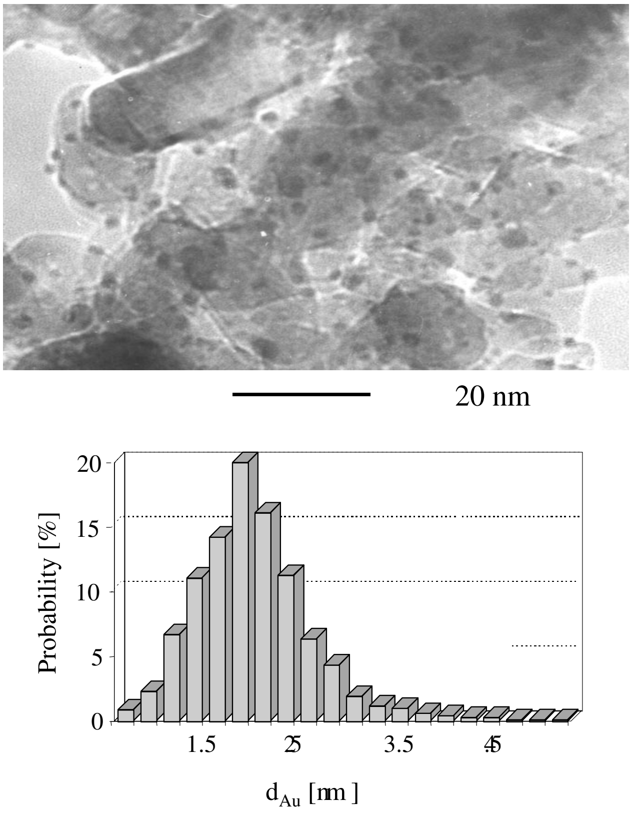

Figure 1. TEM image and particle size distribution of the AuTi(B) catalyst after reductive conditioning at 200 °C (mean Au particle size ~ 1.8 nm).

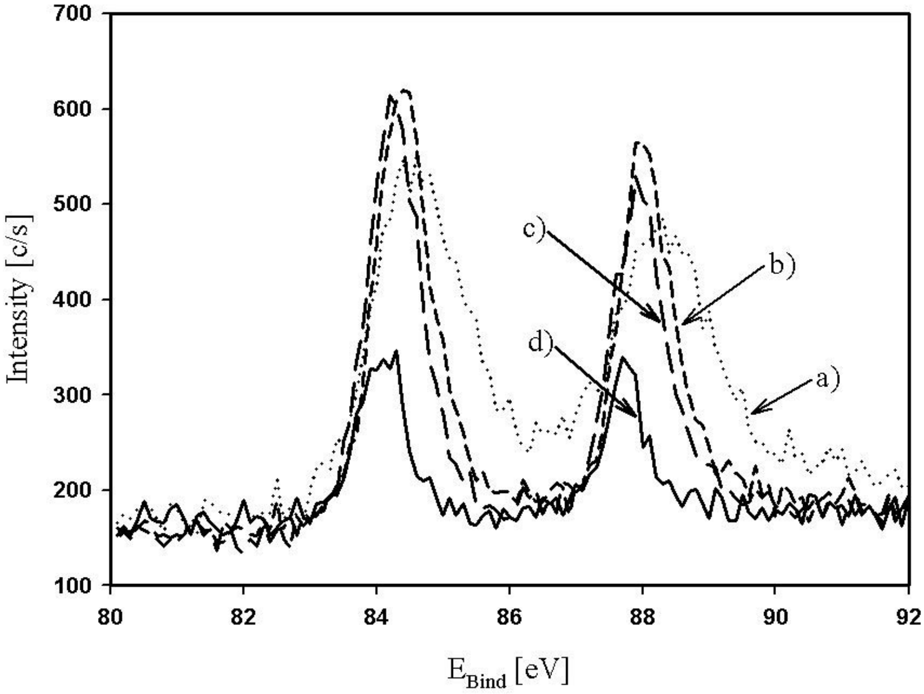

Figure 2. Au(4f) peak areas of photoelectron spectra of the AuTi(C) catalysts (a) after preparation, (b) after drying at 120 °C overnight, (c) after reductive conditioning at 200 °C in H_2/N_2 and (d) after calcination at 400 °C.

very broad signal with a peak maximum at about 85 eV (curve 2a), which is in good agreement with literature data for cationic gold on oxide supports [16]. From the large peak width, it is evident that different Au species contribute to this signal. After drying the sample overnight at 120 °C, the signal changes considerably (curve 2b). The peak is significantly narrower and is shifted to a lower binding energy (BE 84.3 eV). The shift of the Au(4f) peak may originate from two reasons: (i) from a reduction of the cationic Au species (initial state effect) and/or (ii) from the increasing size of the metallic Au particles (final state effect) [17,18]. In our case, most probably both processes are contributing to the spectra. (It should be noted that the composition of the dried sample, i.e., the contribution of ionic Au species, depended sensitively on the pretreatment, ageing history, etc. of the sample.) This trend is continued when the sample is reduced at 200 °C (curve 2c). Now the BE of the Au(4f) signal is at about 84.1 eV, in good agreement with data for small Au^0 particles (1.4 nm, 84.0 eV) [18]. The small difference in BE of 0.1 eV is attributed to the very small particle size of the Au particles in the latter reference. Furthermore, the intensity of the signals is decreased, supporting the above assumption of Au particle growth. Finally, after conventional conditioning (calcination at 400 °C in 10%O_2/90%N_2), the BE and the FWHM of the peaks remain nearly identical, but the signal intensity is further decreased (curve 2d), indicating a pronounced particle growth. These findings are in excellent agreement with the TEM/XRD results compiled in table 1, according to which smaller gold particles have been found after reductive conditioning. Essentially, identical results were obtained for other catalyst samples. The XPS results are supported by thermogravimetric measurements, which show similar weight losses during oxidative and reductive conditioning.

We conclude that both after calcination and after the reductive conditioning procedure, gold is completely reduced to metallic particles, while after drying at 120 °C overnight, there is still a significant amount of cationic Au present.

3.2. *Activity and long-term stability of the* AuTiO$_2$ *catalyst*

3.2.1. *Catalytic activity*

The activities of the differently conditioned catalysts for CO oxidation in ideal reformer gas (1 kPa CO and O_2, 75 kPa H_2, rest N_2) are plotted in figure 3. Turnover frequencies (TOFs) were calculated from Au mass-specific rates using the average particle size. The reductively conditioned Au/TiO$_2$ catalyst with Au particle sizes of about 1.7 nm shows a significantly higher rate and also a higher TOF number than the conventionally treated sample with particle sizes about 2.5–3 nm, contrasting the results reported by Refs [10–13], in which samples with the latter particle sizes were found to be most active. A higher activity for smaller particle sizes was observed also in measurements on other Au/MeO$_x$ catalysts in our laboratory. The lowest

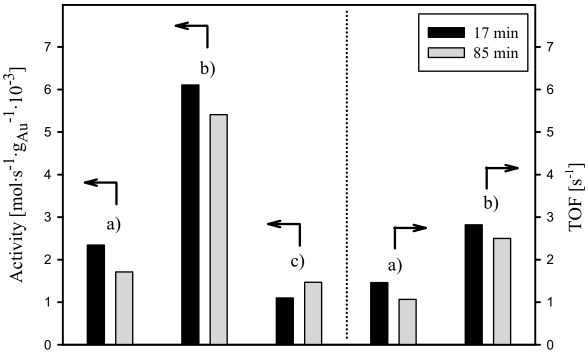

Figure 3. Rates (left axis) and TOFs (right axis) for CO oxidation in ideal reformer gas (1 kPa O_2, CO, 75 kPa H_2, rest N_2) at 80 °C after 15 min and after 85 min on differently treated Au/TiO$_2$ catalysts (Au/TiO$_2$(A)). (a) After calcination at 400 °C, (b) after reductive conditioning at 200 °C in H_2/N_2 and (c) after drying in N_2 overnight at 120 °C.

activity is found for the dried Au catalyst. (Since both TEM imaging and XRD did not resolve Au particles, only mass-specific rates are available in this case). This result is interesting insofar as this is the only sample containing both cationic and metallic Au species based on XPS, indicating that cationic Au species are not *per se* beneficial for the CO oxidation activity. In addition, we observed an activity increase for this catalyst during the first 2 h on steam, in contrast to the other samples. Similar effects were also discovered by Daté *et al.* [15] who found that leaving a low-temperature conditioned Au/TiO$_2$ sample in the reactor for a few days increases the activity. Since our results show a significant increase in activity upon reductive activation (see above), we expect similar trends also during reaction in a H_2- or CO-containing atmosphere and therefore attribute this activation to a decrease in the amount of cationic Au species owing to the reduction by H_2 or CO. On the basis of the significantly higher activity of the reduced catalyst compared to the calcined sample (see figure 3), which was also found for other catalysts, and considering the much smaller particle sizes of the reduced samples (see table 1), we conclude that the higher activity of the reduced samples originates from a particle-size effect. Chemical effects appear unlikely because of the similar composition of the reduced and calcined samples, respectively, as detected by XPS.

Finally, we compare the activity of these catalysts with the activities of highly active Au catalysts reported in the literature (see, e.g., Ref [11] and values given therein). Correcting for the temperature difference by using an average activation energy of 30 kJ mol^{-1}, we find that (for comparable experimental conditions) the activity of the calcined catalysts is comparable with the activities reported there, and that the activity of the reduced catalyst is at least by a factor of 2 higher than those values. This underlines the fact that the activity of the reduced catalysts is high not only on a relative scale, compared to the calcined catalysts in our study, but also on a general scale, compared to the rates of highly active Au catalysts reported in the literature.

3.2.2. Stability/ageing

The long-term stability of the different catalysts was evaluated by following their activity over 1200 min (figure 4). For better comparison clarity, all curves were normalized to an initial activity of 100%, independent of their absolute activities. As can be seen, the deactivation behavior is nearly identical for all three samples. There is a strong decrease in the activity at the beginning of the reaction, followed by a stabilization in the later stages (1000 min). A similar behavior was also observed for other Au/MeO$_x$ catalysts in our laboratory [9]. Owing to the potential application of Au/TiO$_2$ catalysts for the removal of CO from H_2-rich reformer gas in PEM fuel cell feed streams, we investigated the deactivation behavior in a H_2-rich atmosphere (1 kPa CO, 1 kPa O_2, 70 kPa H_2, rest N_2). As evident from figure 4, there is practically no change in the deactivation behavior.

To gain more information on the physical origin of the deactivation process, we recorded TEM images of the catalysts before and after the long-term measurements. Surprisingly, the size of the Au particles did not change during the reaction, and therefore an aggregation or sintering of the Au particles can be excluded. The underlying reason for the catalyst deactivation must therefore be sought in different effects. For this reason, we followed the reaction by *in situ* DRIFT measurements, monitoring the CO adsorption behavior during the reaction. These measurements were performed both in H_2-rich (composition see above) and H_2-free (1 kPa CO and O_2, rest N_2) atmosphere at 80 °C over a calcined and a reduced catalyst (Au/TiO$_2$(A)), respectively. Figure 5(a) shows spectra recorded after 5-min, 90-min, and 1200-min reaction on the calcined sample in H_2-free atmosphere; figure 5(b) shows the corresponding spectra recorded during reaction in H_2-rich atmosphere. In both

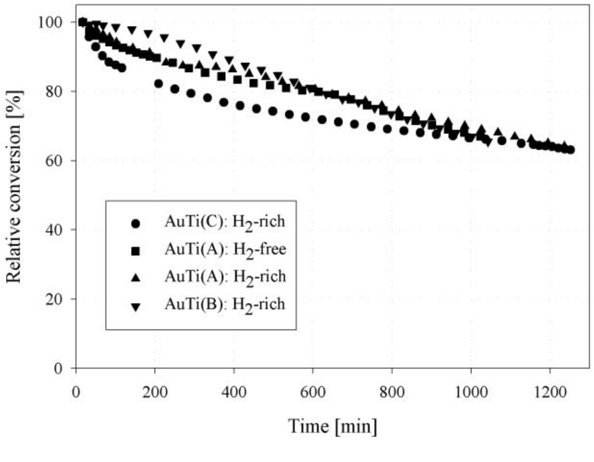

Figure 4. CO conversion over AuTi(A), AuTi(B) and AuTi(C) in H_2-rich and H_2-free atmosphere (only for AuTi(A)) as a function of reaction time, up to 1200 min. (All rates are normalized to an initial conversion of 100%.)

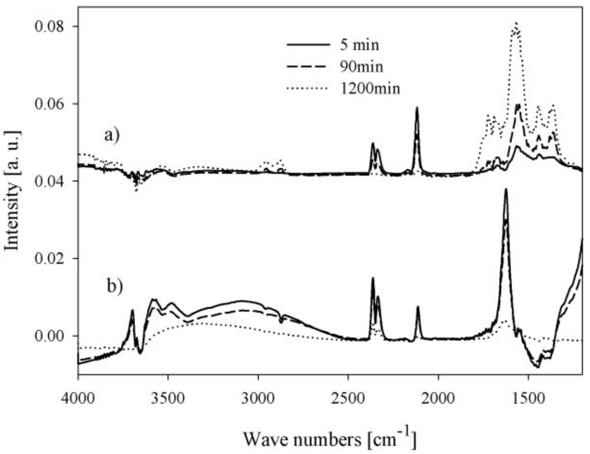

Figure 5. *In situ* DRIFT spectra obtained during CO oxidation over AuTi(A) in (a) H$_2$-free and (b) H$_2$-rich atmosphere, after 5 min, 90 min, and 1200 min.

atmospheres, we find characteristic signals for adsorbed CO and for CO$_2$ at ~2112 cm^{-1}, 2362 cm^{-1} and 2335 cm^{-1}. The intensity of these signals decays significantly with time; after 1200 min, it is reduced to a few percent of the initial intensity. Hence, the amount of CO adsorbed in steady state decreases considerably during the reaction, which provides a plausible explanation for the decay in activity.

The reason for the decreasing CO$_{ad}$ coverage is found upon inspecting the spectral regions below 1700 cm^{-1}. In H$_2$-free atmosphere, we find the evolution of pronounced peaks, which are attributed to adsorbed carbonate and formate species. The peaks at 1690 cm^{-1} and 1586 cm^{-1} are assigned to bidentate carbonate species on TiO$_2$ [19,20]. The peak at 1440 cm^{-1} is characteristic for monodentate carbonate or bulk carbonates [5,19], and the doublet between 1350 cm^{-1} and 1400 cm^{-1} is tentatively attributed to formates [19,21]. Finally, the signals at 2953 cm^{-1} and 2881 cm^{-1} are attributed to C–H vibrations of formates [19]. Along with the decay of the CO and CO$_2$ peaks during the reaction, the formate and carbonate peaks increase significantly. On the basis of these data, we conclude that the deactivation of the Au/TiO$_2$ catalyst during reaction in H$_2$-free atmosphere is mainly caused by the growth of carbonate and formate species, which increasingly cover the surface of the catalyst and act as catalyst poison. Since CO adsorption on the Au particles is strongly affected, these species must partly overgrow the Au particle surface. Their large total amount, which can be determined by TPD, indicates, however, that a significant fraction is deposited on the oxide support.

A completely different picture is found in H$_2$-rich atmosphere, in which no significant contributions from carbonate or formate bands can be detected. Instead, strong water signals at 1630 cm^{-1} and 2500–3300 cm^{-1} and of hydroxy groups 3600–3800 cm^{-1} are visible (figure 5(b)). Surprisingly, however, the intensity of all of these bands does not increase during the reaction but decreases with time, together with the CO and CO$_2$ signals. The evolution of water is also confirmed by thermal desorption experiments, suggesting water as catalyst poison. We do not understand at present, however, the decay of these signals with time, leaving this as a preliminary explanation. Additional experiments are in progress. Hence, although the deactivation behavior is comparable in both atmospheres, completely different by-products or intermediates are detected on the catalysts' surface. For the reductively conditioned sample, the results are, in principle, identical. The only major difference between the reduced and the calcined sample is a much higher intensity of the CO and CO$_2$ signals on the former catalyst. This correlates well with the higher activity of the reduced sample.

Finally, we studied the ageing of Au/TiO$_2$ catalysts in ambient atmosphere, evaluating the Au particle size via XRD at different times for up to one year. The results for freshly prepared reductively conditioned catalysts stored under different conditions are displayed in figure 6. Samples stored in the dark at 7 °C (refrigerator) did not change significantly with time for up to one year, increasing only from 1.7 to 2.3 nm. The situation is completely different for samples stored in daylight (ca. 22 °C). XRD measurements show a steady growth of the Au particles, reaching particle sizes of about 5 nm.

To reduce the catalyst ageing, we tried to stabilize the catalysts by an additional calcination treatment (400 °C, 30 min, in air), after the reductive conditioning. This leads to an average particle size of about 2.1 nm, i.e., the particles are still significantly smaller than those obtained after conventional conditioning. If these post-calcined catalysts are stored in the dark, they change only very little, reaching about 2.4-nm particle size. Hence, the post-treatment has little effect on the catalyst ageing under these conditions. Keeping the catalyst in daylight, however, we find a significant difference: for the post-calcined catalyst, the Au particle growth is much slower. Even after one year, the particle size is

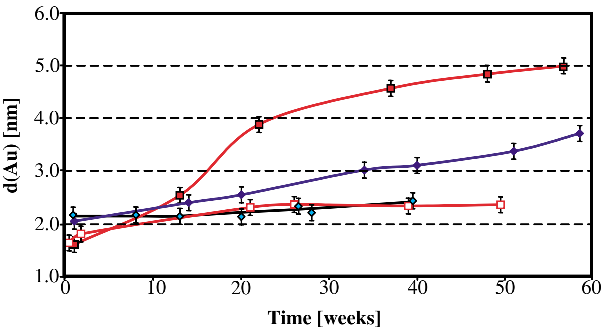

Figure 6. Evolution of the Au particle sizes over one year for catalysts stored in the dark (7 °C) (□) or under daylight (22 °C) (■), or first calcined at 400 °C and subsequently stored in the dark (7 °C) (◇) or under daylight (22 °C) (◆).

below 4 nm. These results illustrate the importance of proper storing conditions.

4. Conclusion

We have shown that highly active Au/TiO_2 CO oxidation catalysts can be prepared by a modified deposition–precipitation procedure. The maximum activity of these catalysts is obtained after applying a newly developed reductive conditioning method that results in catalysts with Au particle sizes of about 1.7 nm. Both conventional conditioning (calcining at 400 °C) and the new reductive conditioning procedure result in fully reduced, metallic Au particles, in contrast to catalysts dried at 120 °C in N_2. The much higher activity of the former samples suggests small metallic Au particles and not ionic Au species as the (more) active species for CO oxidation. The deactivation of the catalysts during reaction, both for H_2-free and H_2-rich reaction atmospheres, is caused by the accumulation and deposition of by-products on the catalyst's surface and not by sintering of the gold particles. Natural ageing can be reduced by storing the catalyst in the dark.

Detailed studies on the CO oxidation mechanism and on the influence of H_2 and other co-reactants (CO_2, H_2O) are currently being carried out in our laboratory.

Acknowledgments

We gratefully acknowledge the financial support by the Deutsche Forschungsgemeinschaft (Be 1201 Be/9-1).

References

[1] M. Haruta, Catal. Surv. Jpn. 1 (1997) 627.

[2] G.C. Bond and D.T. Thompson, Gold. Bull. 33 (2000) 41.

[3] G.C. Bond and D.T. Thompson, Catal. Rev.—Sci. Eng. 41 (1999) 319.

[4] F. Boccuzzi and A. Chiorino, J. Phys. Chem. B 104 (2000) 5414.

[5] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet and M. Delmon, J. Catal. 144 (1993) 175.

[6] Y. Iizuka, H. Fujiki, N. Yamauchi, T. Chijiiwa, S. Arai, S. Tsubota and M. Haruta, Catal. Today 36 (1997) 115.

[7] J.D. Grunwaldt and A. Baiker, J. Phys. Chem. B 103 (1999) 1002.

[8] F. Boccuzzi, A. Chiorino, M. Manzoli, P. Lu, T. Akita, S. Ichikawa and M. Haruta, J. Catal. 202 (2001) 256.

[9] M. Schubert, V. Plzak, J. Garche and R.J. Behm, Catal. Lett. 76 (2001) 143.

[10] G.R. Bamwenda, S. Tsubota, T. Nakamura and M. Haruta, Catal. Lett. 44 (1997) 83.

[11] M. Haruta, Catal. Surv. Jpn. 1 (1997) 61.

[12] M. Valden, X. Lai and D.W. Goodmann, Science 281 (1998) 1647.

[13] M. Maciejewski, P. Fabrizioli, J.D. Grunwaldt, O.S. Becker and A. Baiker, Phys. Chem. Chem. Phys. 3 (2001) 3855.

[14] M.J. Kahlich, H.A. Gasteiger and R.J. Behm, J. Catal. 182 (1999) 430.

[15] M. Daté, Y. Ichihashi, T. Yamashita, A. Chiorino, F. Boccuzzi and M. Haruta, Catal. Today 72 (2002) 89.

[16] A.M. Visco, F. Neri, G. Neri, A. Donato, C. Milone and S. Galvagno, Phys. Chem. Chem. Phys. 1 (1999) 2869.

[17] L. Zhang, R. Persaud and T.E. Madey, Phys. Rev. B 56 (1997) 10549.

[18] H.G. Boyen, G. Kästle, F. Weigl, B. Koslowski, C. Dietrich, P. Ziemann, J.P. Spatz, S. Riethmüller, C. Hartmann, M. Möller, G. Schmid, M.G. Garnier and P. Oelhafen, Science 297 (2002) 1533.

[19] M.A. Bollinger and M.A. Vannice, Appl. Catal., B 8 (1996) 417.

[20] J.D. Grunwaldt, M. Maciejewski, O.S. Becker, P. Fabrizioli and A. Baiker, J. Catal. 186 (1999) 458.

[21] G. Busca, J. Lamotte, J.C. Lavalley and V. Lorenzelli, J. Am. Chem. Soc. 109 (1987) 5197.