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Supported gold catalysts studied with ^{197}Au Mössbauer effect spectroscopy

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Abstract

Gold catalysts supported on TiO_2 and TiO_2/SiO_2 have been studied with ^{197}Au Mössbauer spectroscopy. During the preparation of the Au/TiO_2 catalyst the formation of metallic particles is observed. The presence of ionic gold in active gold catalysts is not observed. The spectra can be interpreted in terms of bulk-like contributions from the inner-core atoms plus contributions from the outermost atoms at the surface of the particles.

Keywords: Mössbauer spectroscopy; Gold catalysts

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1. Introduction

Bulk gold is regarded to be catalytically inactive. However supported gold nanoparticles were found to have catalytic activity for different reactions [1–5]. Various studies have been performed to clarify the nature of the activity of these supported gold particles [6]. In these studies the catalytic activity has been attributed to: (i) the highly abundant metal/support interface, (ii) the presence of ionic gold or (iii) coordinatively unsaturated gold atoms at the surface of small clusters. Clearly the catalytic properties can be dependent on the electronic structure of the gold particles. ^{197}Au Mössbauer effect spectroscopy is a valuable microscopic tool to characterize this electronic structure. Previous ^{197}Au Mössbauer work on supported gold catalysts already has shown the suitability of this technique [7–9].

In the present study, the investigations concentrate on Au/TiO_2 catalysts which showed an extremely high selectivity towards propene epoxidation [3]. Although a lot of research has been already done to unravel the catalytic mechanisms of these materials, a lot of questions are still unanswered. The most important one regards the nature of gold as the active phase in the catalysts. Kobayashi et al. [9] concluded from their Mössbauer study that the Au^{I} state might be the active phase in CO oxidation catalysts, while Grisel et al. [4,5] deduced from IR, XRD and transmission electron microscopy (TEM) results that ionic gold was absent in these catalysts, and that metallic gold seems to be more important.

Since it is element-selective and sensitive to the local surroundings of the atoms ^{197}Au Mössbauer effect spectroscopy is an excellent probe. This sensitivity makes it possible to resolve different metal sites within the catalyst particles and thereby differentiate

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between metal atoms at the surface and atoms in the inner-core of the particles. In previous work [10–13], extensive knowledge of the electronic structure of gold and platinum molecular cluster compounds and colloids with well-defined particle sizes [14–17] was obtained using both ^{197}Au Mössbauer absorption and emission spectroscopies. From these investigations information could be obtained on Au atoms at the surface of the particles with respect to the known isomer shift/quadrupole splitting (IS/QS) combinations for ionic Au compounds. In the case of Au the IS, which is proportional to the s-electron density at the nucleus, varies with the density of the 6s- and 5d-electrons roughly as 8.0 mm/s per 6s-electron [18] and -1.6 mm/s per 5d-electron (due to screening of the s-electrons [19]), respectively. The QS, which is proportional to the electric field gradient (EFG) over the nucleus, gives information on the coordination of the atom (degree of symmetry). In addition, the vibrational characteristics of the Au atoms in combination with other size-effects were studied [10–13].

In the present ^{197}Au Mössbauer study we extend our earlier presented investigations on supported gold catalysts [20]. Our goal is to investigate the differences and systematics in a series of Au-containing catalysts, especially the presence or absence of ionic gold in the catalysts. Spectra have been recorded during the preparation (calcination) stage of the Au/TiO$_2$ catalyst, as well as from as prepared fresh Au/TiO$_2$ and Au/TiO$_2$/SiO$_2$ catalysts and a spent Au/TiO$_2$ catalyst (propene epoxidation). The results will be compared to literature data on gold catalysts and gold compounds.

2. Experimental

Mössbauer spectra have been recorded in transmission geometry. The applied ^{197}Au gamma ray sources were obtained by irradiating enriched platinum powder (97.4% ^{196}Pt) with thermal neutrons for 24 h. This results in a 200 MBq Mössbauer source due to the reaction $^{196}\mathrm{Pt} + \mathrm{n} \rightarrow {}^{197}\mathrm{Pt}$, which is followed by $^{197}\mathrm{Pt} \rightarrow {}^{197}\mathrm{Au}^{+} + \beta^{-} + \bar{\nu}_e + 0.6\,\mathrm{MeV}$. The beta-decay process has a half-life of 18.3 h and determines the half-life of the ^{197}Au Mössbauer source. The ^{197}Au nucleus, left behind in an excited state, decays to the ground state by emission of the 77.3 keV gamma photon that is used for Mössbauer spectroscopy. Both source and absorber were cooled to a temperature of 4.2 K. The source velocity has been calibrated by a Michelson interferometer. All IS values are given according to this (absolute) velocity scale. For detection of the transmitted photons a high purity Ge detector has been used. Although the high resolution of this detector should enable us to discriminate between the 77.3 keV gamma ray line and the 77 keV X-ray line of mercury, both lines partially overlap (caused by the high intensity of the source). Furthermore, the position of both lines slightly changes as a function of the activity of the source (i.e. as a function of its age). Due to the combination of these two effects, it is impossible to filter out the gamma ray line in a reproducible way. Therefore we choose to include the neighbouring X-ray line in the window of preferred energy instead of trying to filter out exactly the Mössbauer line. In this way we lose some intensity in the resonant spectrum, typically about 15–30%. This is an acceptable loss because the gain in reproducibility makes it possible to compare the resonant absorption areas of the various spectra.

Catalysts containing 1 wt.% Au were prepared by deposition–precipitation of Au(OH)$_3$. A AuCl$_3$ (Fluka) solution was added dropwise to a suspension of the support at pH 10 [3]. As supports TiO$_2$ (P25, Degussa) and TiO$_2$/SiO$_2$ were used. The TiO$_2$/SiO$_2$ (0.1 monolayer TiO$_2$) support was prepared by reaction of titanium(IV)ethoxide (Fluka, 97%) in 2-propanol with surface hydroxyl of SiO$_2$ (Davisil 646, Aldrich). All catalyst samples were centrifuged and washed with at least 10 times their own volume of distilled water. Finally the catalyst samples were dried at 373 K and calcined at 673 K for 4 h. The catalysts were tested in a flow setup equipped with a fixed-bed reactor. Activity and selectivity data are reported elsewhere [3]. TEM was used to determine the gold particle size using a Philips CM30T electron microscope with an LaB$_6$ filament as the source of electrons operated at 300 kV. Samples were mounted on a microgrid carbon polymer supported on a copper grid by placing a few droplets of the suspension of ground catalyst in ethanol on the grid, followed by drying at ambient conditions.

In addition the effect of the calcination temperature on the Au/TiO$_2$ catalyst has been studied. Five stepwise calcined Au/TiO$_2$ catalysts with intended gold loading of 1 wt.% after calcination at 673 K have been

Table 1
Overview of the samples calcined at 673 K[a]

Sample	Mean diameter	Surface intensity (%)	Remarks
Au/TiO_2	5.2 ± 1.1 nm	10	Active
Au/TiO_2	ND[b]	10	Spent
Au/TiO_2/SiO_2	3.2 ± 1.0 nm	22	Active, slower deactivation

[a] All samples contain 1 wt.% gold. The mean diameters are determined with TEM. The third column gives the relative intensity of the surface contribution found in the Mössbauer spectra. The surface contribution is also referred to as the non-bulk contribution present next to the bulk contribution.

[b] Not determined.

prepared by deposition–precipitation of $Au(OH)_3$ on TiO_2 as mentioned above. The chloride was removed with water from the white paste of suspended TiO_2 and Au species and the paste was dried in a centrifuge. One sample was taken from this batch (the 293 K sample). From the rest of the batch three different samples were taken to be then treated at different temperatures. All the samples from 373 to 573 K had an 8 h drying treatment at 373 K. The 423 K sample had this drying treatment after an extra treatment of 4 h at 423 K, and the 473 K sample after an additional treatment of 4 h at 473 K. The 573 K sample has been prepared from the measured 423 K sample by treating it 2 h again at 423 K to remove unwanted water (due to sample handling in air and cryostat) and 4 h at 573 K as final treatment.

In Tables 1 and 2 the investigated catalysts have been compiled. One sample of the 1 wt.% Au/TiO_2 catalyst has been used in the propene epoxidation process.

Table 2
Overview of the stepwise calcined samples[a]

Sample	Calcination treatment	Spectral contribution of metallic Au (%)
Au/TiO_2, 293 K	No treatment	0
Au/TiO_2, 373 K	8 h, 373 K	12
Au/TiO_2, 423 K	8 h, 373 K; 4 h, 423 K	37
Au/TiO_2, 473 K	8 h, 373 K; 4 h, 473 K	88
Au/TiO_2, 573 K	8 h, 373 K; 4+2 h, 423 K; 4 h, 573 K	100

[a] The second column shows the duration and the temperatures at which the samples have been treated. The third column gives the relative intensity of the metallic Au contributions found in the Mössbauer spectra.

3. Results and discussion

In Figs. 1 and 2 the measured Mössbauer spectra are shown for the different samples. The results of the analyses of the spectra, as well as the decomposition in subspectra, are included in these figures. All spectra have been analysed using a decomposition in as few subspectra as necessary. Although in a first approach all fitting parameters were left free, in the analyses presented here a single line has been fixed at −1.22 mm/s, which is the IS value of bulk metallic Au. The remaining intensity in the spectra has been fitted with a maximum of three additional lines (singlets and/or doublets). In previous reported work (see e.g. [10–17]) it was shown that the Mössbauer spectrum of a metallic nanoparticle can be divided into two parts: a contribution due to the metallic core of identically coordinated atoms (inner-core site) and one or more contributions from the surface shell (one atom layer thick). In some cases the contributions from metal atoms of differently coordinated sites in the surface shell could be distinguished. Using this approach, we can attribute the observed single lines at −1.22 mm/s

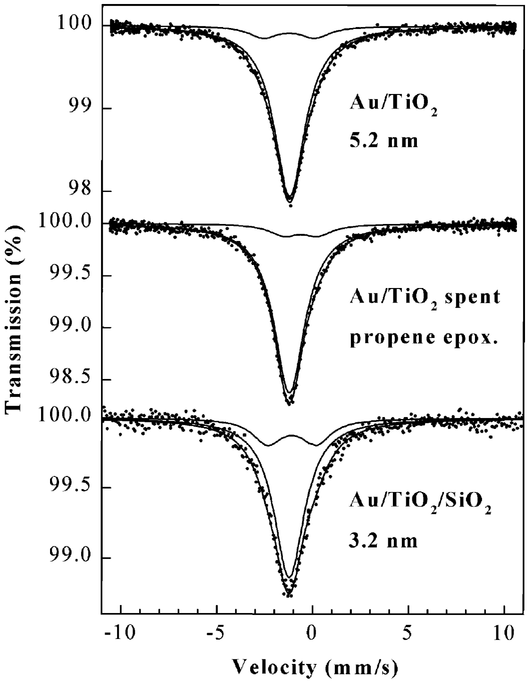

Fig. 1. Mössbauer spectra for the samples calcined at 673 K (see Table 1) recorded at $T = 4.2$ K.

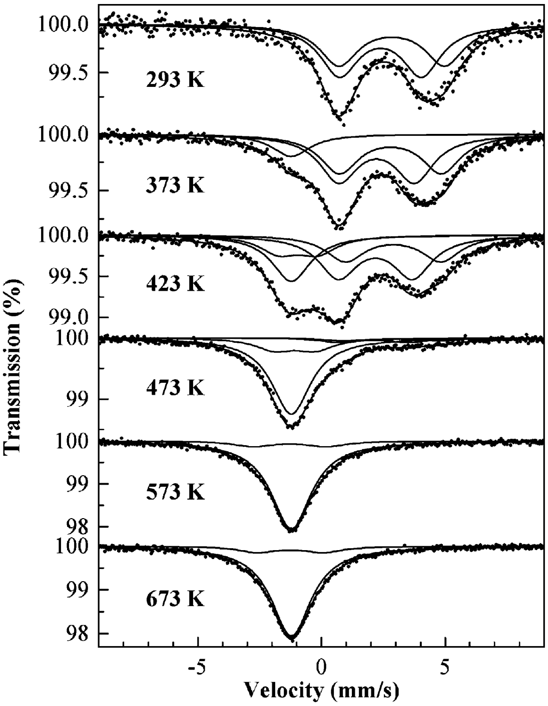

Fig. 2. Mössbauer spectra for the stepwise calcined Au/TiO_2 samples (see Table 2) recorded at $T = 4.2$ K. The lowest spectrum, marked as 673 K, is taken from Fig. 1 for comparison.

to the inner-core sites (also called bulk contribution) and the other contribution(s) to the surface site(s).

The main question regarding the surface sites is whether they can be attributed to ionic gold species or not. To address this question, the sets of IS and QS values obtained for the contributions of the surface sites have been plotted in Fig. 3. Also the IS $= -1.22$ mm/s and QS $= 0$ mm/s for bulk metallic Au is presented in this figure. The grey background regions indicate the values that are most commonly measured for Au compounds and should be regarded as guides to the eye [21]. In Table 3 the IS and QS values extracted from the spectra in Figs. 1 and 2 are given, as well as the relative intensities of the different spectral contributions. Interestingly, it can be seen that for the 673 K calcined samples, also the IS values for all the surface contributions are concentrated around that of bulk metallic Au. Moreover, almost all IS/QS combinations do not fit within the regions that are known for the ionic Au^{I} or Au^{III} species. Hence the observed behaviour of the surface sites can more likely be explained in terms of a metallic surface layer with an IS value close to bulk and QS values depending on the symmetry of the local coordination of the surface atoms. The same behaviour has been seen with gold catalysts on alumina-based supports [20]. So we are led to conclude that ionic species do not play an important role neither in the fresh samples nor in the spent catalyst. This interpretation of the spectra agrees with the investigations on molecular Au and Pt clusters and colloids that showed that surface sites can be best described as asymmetrically coordinated but metallic atom shells [12,13]. Although we find some surface contributions in the Mössbauer spectra that look like Au^{I} species (Fig. 3), in our opinion, it is not allowed to conclude from single values that these contributions should be strictly assigned to Au^{I} as reported in Ref. [9].

From Fig. 1 it can be clearly seen that nevertheless only a minor difference is visible in the surface contributions of a fresh and a spent Au/TiO_2 catalyst. A small difference in IS and QS is found, probably due to a slight change in the symmetry of the local coordination of the surface atoms. Comparison of the fresh (active) Au/TiO_2 and Au/TiO_2/SiO_2 catalysts in Fig. 1 clearly shows a smaller bulk contribution for the latter due to the smaller mean particle size (5.2 vs. 3.2 nm). This shows directly the particle size effect in spectra: the relative intensity in the spectra of the bulk contribution is proportional to the mean diameter of the particles (as expected for a surface-to-volume ratio). The surface contributions of these different supported catalysts do not show mentionable differences in their parameters.

In Fig. 2 an interesting evolution of spectra can be seen for the stepwise calcined Au/TiO_2 samples. From top to bottom a gradual decrease of the non-bulk contributions, situated on top of the Au^{III}-region in the IS/QS plot (Fig. 3), is observed. From the IS/QS combinations it is not possible to match these positions with a known Au compound. The non-bulk contributions found in these precursor samples do not seem to be the remnants of $Au(OH)_3$ precursor, as can be checked in literature [8,22]. Support influences on the $Au(OH)_3$ compound could be the cause of this deviation. At the same time the increase of the bulk contribution with increasing calcination temperature appears very clearly. At higher temperatures starting

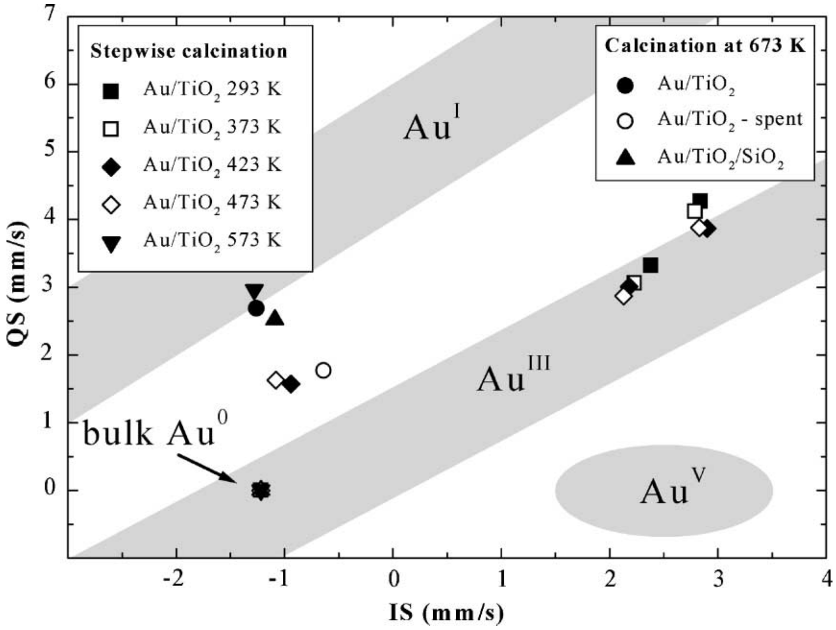

Fig. 3. IS vs. QS plot showing the sets of values extracted from the measured spectra. The values for the bulk contributions are all coinciding with the point referred to as 'bulk Au^{0}'. The grey background regions indicate the values that are most commonly measured for Au compounds, corresponding to the known valence states in gold: Au^{I}, Au^{III} and Au^{V}. As can be seen in the plot two areas are present in which the values are distributed: an area close to the IS for bulk whose values can be referred to as metallic-like, and an area in the Au^{III}-region close to IS = 2.6 mm/s, QS = 3.6 mm/s whose values can be referred to as ionic.

Table 3
Mössbauer parameters extracted from the measured spectra[a]

Sample	Metallic inner-core		Metallic surface		Ionic species		Ionic species	
	IS (*I*, %)[b]	QS	IS (*I*, %)[b]	QS	IS (*I*, %)[b]	QS	IS (*I*, %)[b]	QS
Calcination at 673 K								
Au/TiO$_2$	−1.22 (90)	0	−1.26 (10)	2.69				
Au/TiO$_2$ spent	−1.22 (90)	0	−0.64 (10)	1.77				
Au/TiO$_2$/SiO$_2$	−1.22 (78)	0	−1.09 (22)	2.52				
Stepwise calcination								
Au/TiO$_2$ 293 K					2.38 (55)	3.32	2.84 (45)	4.27
Au/TiO$_2$ 373 K	−1.22 (12)	0			2.23 (48)	3.06	2.79 (40)	4.12
Au/TiO$_2$ 423 K	−1.22 (22)	0	−0.94 (15)	1.57	2.18 (39)	3.01	2.90 (24)	3.87
Au/TiO$_2$ 473 K	−1.22 (69)	0	−1.08 (19)	1.63	2.13 (7)	2.87	2.83 (5)	3.88
Au/TiO$_2$ 573 K	−1.22 (91)	0	−1.28 (9)	2.96				

[a] All IS and QS values are given in mm/s.
[b] The values in brackets are the relative intensity (*I*, %) of the different contributions found in the Mössbauer spectra.

at 423 K, a similar surface contribution as in the spectra of the fully calcined samples emerges. At 573 K the spectrum resembles already closely the calcined catalyst at 673 K. However to clean the catalyst from redundant species, the standard treatment of the catalyst is performed at higher temperature of 673 K. The catalyst does not show negative side effects (sintering) from this cleaning [3].

4. Conclusions

The stepwise calcination of a Au/TiO_2 catalyst has been investigated with ^{197}Au Mössbauer effect spectroscopy. With increasing calcination temperature a gradual formation of metallic gold at the expense of an ionic Au^{III}-like species is clearly evidenced. We suggest that this phenomenon may provide an explanation for previous reports on the presence of ionic gold in Au catalysts on the basis of ^{197}Au Mössbauer experiments. Also calcined catalysts with gold particles of about 3–5 nm supported on TiO_2 and TiO_2/SiO_2 have been characterized. From the measured spectra we can conclude that the presence of ionic gold atoms, situated in the surface layer, in active Au catalysts suggested in the literature is not confirmed. The spectra can be explained in terms of an inner-core (bulk-like) component plus a surface contribution with an IS close to bulk and QS values determined by the local atomic coordination. So a disturbed but still metallic surface layer is more consistent with the Mössbauer results.

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References

[1] M. Haruta, Catal. Today 36 (1997) 153.
[2] M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, J. Catal. 115 (1989) 301.
[3] T.A. Nijhuis, B.J. Huizinga, M. Makkee, J.A. Moulijn, Ind. Eng. Chem. Res. 38 (1999) 884.
[4] R.J.H. Grisel, B.E. Nieuwenhuys, Catal. Today 64 (2001) 69.
[5] R.J.H. Grisel, P.J. Kooyman, B.E. Nieuwenhuys, J. Catal. 191 (2000) 430.
[6] G.C. Bond, D.T. Thompson, Catal. Rev.-Sci. Eng. 41 (1999) 319.
[7] B. Nkosi, N.J. Coville, G.J. Hutchings, M.D. Adams, J. Friedl, F.E. Wagner, J. Catal. 128 (1991) 366.
[8] F.E. Wagner, S. Galvagno, C. Milone, A.M. Visco, L. Stievano, S. Calogero, J. Chem. Soc., Faraday Trans. 93 (1997) 3403.
[9] Y. Kobayashi, S. Nasu, S. Tsubota, M. Haruta, Hyperfine Interact. 126 (2000) 95.
[10] F.M. Mulder, T.A. Stegink, R.C. Thiel, L.J. de Jongh, G. Schmid, Nature 367 (1994) 716.
[11] F.M. Mulder, R.C. Thiel, L.J. de Jongh, P.C.M. Gubbens, Nanostruct. Mater. 7 (1996) 269.
[12] P.M. Paulus, A. Goossens, R.C. Thiel, G. Schmid, A.M. van der Kraan, L.J. de Jongh, Hyperfine Interact. 126 (2000) 199.
[13] P.M. Paulus, A. Goossens, R.C. Thiel, A.M. van der Kraan, G. Schmid, L.J. de Jongh, Phys. Rev. B 64 (2001) 205418.
[14] G. Schmid, L.F. Chi, Adv. Mater. 10 (7) (1998) 515.
[15] G. Schmid, J. Chem. Soc., Dalton Trans. 7 (1998) 1077.
[16] G. Schmid, Clusters and Colloids, VCH, Weinheim, 1994.
[17] L.J. de Jongh (Ed.), Physics and Chemistry of Metal Cluster Compounds, Kluwer Academic Publishers, Dordrecht, 1994.
[18] H.D. Bartunik, G. Kaindl, in: G.K. Shenoy, F.E. Wagner (Eds.), Mössbauer Isomer Shifts, North-Holland, Amsterdam, 1978, p. 525.
[19] J.O. Thomson, F.E. Obenshain, P.G. Huray, J.C. Love, J. Burton, Phys. Rev. B 11 (1975) 1835.
[20] A. Goossens, M.W.J. Crajé, A.M. van der Kraan, A. Zwijnenburg, M. Makkee, J.A. Moulijn, R.J.H. Grisel, B.E. Nieuwenhuys, L.J. de Jongh, Hyperfine Interact., in press.
[21] H.H.A. Smit, R.C. Thiel, L.J. de Jongh, Z. Phys. D 12 (1989) 193.
[22] G.J. Long (Ed.), Mössbauer Spectroscopy Applied to Inorganic Chemistry, Plenum Press, New York, 1984, p. 577.