Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 122 (2007) 365–369

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Au–TiO_2 catalysts stabilised by carbon nanofibres

Nina Hammer, Ingvar Kvande, De Chen, Magnus Rønning *

Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, Norway

---

Abstract

The catalytic activity and stability in the water–gas shift reaction have been tested for Au-based catalysts prepared by deposition of Au from colloid solutions. The supports that have been used are TiO_2, TiO_2 supported on carbon nanofibres (CNF) and CNF. Thermal treatments of the samples show that the Au particle size depends on the support material and hence the interaction between the Au particles and the support. *In situ* X-ray absorption spectroscopic (XAS) measurements during the water–gas shift reaction show no changes in the first Au–Au coordination number for the catalysts containing CNF. Furthermore, improved short-time stability is obtained compared to the $AuTiO_2$ catalysts. The improved stability is achieved by the CNF stabilising small TiO_2 particles and hence prevent subsequent sintering of the Au particles.

Keywords: Water–gas shift; Au/TiO_2; Carbon nanofibres; Catalyst stability

---

1. Introduction

The water–gas shift (WGS) performance of supported gold catalysts is mainly governed by three factors; the method of preparation, gold particle size and the nature of the support material. A wide range of support materials has been examined, such as TiO_2 [1–3], CeO_2 [4–6], Fe_2O_3 [7–9], ZrO_2 [10], ZnO [11] and ThO_2 [12]. Preparation of Au/Fe_2O_3 [13] and Au/TiO_2 [1] by deposition–precipitation gives more active catalysts than preparation with co-precipitation. Moreover, crystalline metal oxides have been observed to exhibit higher activity than amorphous oxides. This is also the case for mixed oxide supports [14]. Venugopal et al. [15] found a higher activity for the bimetallic Au–Ru supported on iron oxide over a wide temperature range compared to Au/Fe_2O_3 and Ru/Fe_2O_3.

A challenge for Au nanoparticles is their lack of stability. The agglomeration of gold particles during operating conditions [14] and blocking of the active sites by formation of surface carbonate [16] are believed to contribute to the instability. The stability is also influenced by the support material. A higher stability is observed for Au/TiO_2 compared to Au/Co_3O_4, which shows relatively rapid deactivation [14]. Yan et al. [17] have reported that a significant enhancement in the stability of gold particles against sintering can be achieved by using brookite as catalyst support. Grisel et al. [18] found that the CO conversion over Au/MnO_x/Al_2O_3 is higher at ambient temperatures than for a Au/Al_2O_3 catalyst at 150 °C. They suggested a dual role of MnO_x. The oxide may stabilise the gold particles and may also take part in one of the steps involved in the catalytic cycles. Fu et al. [19] have investigated the stability of Au/CeO_2 catalysts in the WGS reaction under realistic conditions. The catalysts showed a drop in the conversion of approximately 20% the first 10 h and a slow further decay in activity. They explained the deactivation by the reduction of surface area in the oxide. However, cyclic temperature operations in the gas stream identified a stability problem due to cerium-hydroxycarbonate formation.

The use of carbon nanofibres (CNF) as a support material in heterogeneous catalysis has attracted growing interest due to their specific characteristics. The CNF are resistant to acid/base media and precious metals can easily be recovered by burning off the support. The material also provides a relatively high surface area which may promote high dispersion of the metals [20]. However, preparation of small Au particles on CNF is not straightforward. Deposition–precipitation leads to agglomeration of the Au particles ($>$50 nm) during the synthesis when $HAuCl_4$ is used as a precursor [21]. To obtain a high dispersion on CNF the Au precursor has to be converted to the metallic form as part of the initial preparation. The scope of the present

---

* Corresponding author. Tel.: +47 73 59 41 21; fax: +47 73 59 50 47.
E-mail address: ronning@chemeng.ntnu.no (M. Rønning).

0920-5861/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.cattod.2007.03.006

work is to examine the effect of CNF as a support material for Au-based catalysts in the WGS reaction.

2. Experimental

CNF with fishbone structure were synthesized in a fixed-bed reactor at 600 °C using a Ni-hydrotalcite derived catalyst. The procedure is described by Yu et al. [22]. The CNF were treated in acid to remove the Ni catalyst from the preparation and also to introduce surface functional groups which act as anchoring sites for the metals. CNF were refluxed in concentrated nitric acid for 1 h followed by filtration, washing in distilled water and drying at 100 °C for 12 h. The acid treatment was performed twice.

The catalysts supported on CNF have been prepared in two steps; first deposition of the TiO_2 onto the CNF followed by deposition of gold. In addition, an $AuTiO_2$ catalyst prepared by the same method was made for comparison.

TiO_2 was prepared by hydrolysis of a $TiCl_4$ solution by adding polyethylene imine (PEI) to the solution. The mixture was covered with aluminium foil and kept at 70 °C in an oven. After 40 min the white precipitate began to appear and the CNF were added. The mixture was stirred and refluxed at 70 °C for another 2 h. The suspension was filtrated, washed with ethanol and dried for 12 h at 100 °C. A more detailed description of this preparation procedure is given by Sun et al. [23].

The Au sol was prepared by reduction of chloroaurate(III) ions in a partially hydrolysed tetrakis(hydroxymethyl)phosphonium chloride (THPC) solution following the procedure reported by Duff et al. [24]. 0.2 M NaOH and THPC (1.2 ml of 80 wt.% THPC in water diluted to 100 ml) were added to the required amount of continuously stirred distilled water. After 2 min a 43 mM $HAuCl_4$ solution was added. Dispensing the gold(III) solution into the alkaline THPC mixture yielded a rapid colour change from yellow to orange-brown indicating formation of the gold sol. The support was dispersed in 50 ml water and the Au sol was added dropwise. The pH was adjusted to 2 by 0.2 M HNO_3 and the suspension was stirred for 1 h. The mixture was filtered and no colour could be observed in the filtrate. The same washing procedure as stated above was performed. All catalysts have been dried at 100 °C for 12 h.

Various thermal treatments have been investigated for the samples. The TiO_2CNF support material for the sample denoted $AuTiO_2$CNF_Red has been pre-reduced at 300 °C in H_2 for 2 h before deposition of the Au colloids. All the samples except $AuTiO_2$CNF have been treated in nitrogen at 300 °C for 1 h after the preparation and will be denoted CT.

The BET-surface area determination was performed in a Beckman Coulter SA 3100 Surface Area Analyzer. Prior to the measurements the samples were degassed at 150 °C for 3 h.

Elemental analysis (X-ray fluorescence, XRF) was performed to verify the sample composition.

Transmission electron microscopy (TEM) was used to obtain the average particle sizes. The analyses were performed on a JEOL 2010F electron microscope with an acceleration voltage of 200 kV. The sample powder was suspended in chloroform using an ultrasonic bath. The sample was spread onto a Cu-grid coated with holey carbon.

XAS data were collected using the facilities of the Swiss-Norwegian Beamlines (SNBL) at the European Synchrotron Radiation Facility (ESRF), France. Spectra were collected at the Au-L_3 edge (11919 eV) in fluorescence mode using a Lytle type water-cooled furnace for the *in situ* treatment of the samples. An Au foil (thickness 3 μm) was used for energy calibration and as an internal standard. The XAS data analysis program WinXAS 3.1 [25] was used for background subtraction and normalisation of the spectra. Model fitting was carried out with *EXCURV98* using curved-wave theory and *ab initio* phase shifts [26,27]. The EXAFS spectra were least squares fitted in k space using k^2 weighted data [28].

The WGS activity measurements were performed in a fixed-bed reactor at atmospheric pressure. The temperature range was 190–310 °C and the catalyst amount was 100 mg or 300 mg. The reactor was fed with 50 ml/min CO, 50 ml/min H_2O and 50 ml/min nitrogen. The analytical grade of the gases was 99.999% and no further purification was performed. The product stream was analyzed with an Agilent 3000 micro-gas chromatograph. The catalytic activity was calculated from the carbon balance and expressed as the rate of disappearance of CO. The stability of the catalysts was studied at 310 °C using the same conditions as above.

3. Results and discussion

The physical data of the samples are presented in Table 1. The surface area of the CNF is approximately 75 m^2/g and remains unchanged after deposition of Au. The deposition of titania leads to an increase in the surface area which may be

Table 1
Physical data for the samples

Sample	S_{BET} (m^2/g)	Au[a] (wt.%)	Cl[a] (wt.%)	E_a (kJ/mol)	d_p (nm)	TiO_2[a] (wt.%)
$AuTiO_2$_CT	143	3.3	0.15	34.4	8.2[b]	96.7
$AuTiO_2$CNF_Red_CT	104	1.8	0.23	46.1	2.0[b]	10.8
AuCNF_CT	75	1.5	n.m.[c]	15.4	4.7[b]	–
$AuTiO_2$CNF_CT	111	0.9	0.28	27.4	5.8[b]	10.4
$AuTiO_2$CNF	125	1.7	0.07	34.4	1.8[d]	20.1

[a] Determined from XRF.
[b] Particle size (d_p) determined from TEM.
[c] n.m.: not measured.
[d] Particle size (d_p) determined from EXAFS.

beneficial for the dispersion of Au. TiO_2 deposited on CNF contains mainly mesopores and the unsupported TiO_2 has a much higher fraction of micropores. TEM images (not presented here) show that the Au is selectively deposited on titania [21]. The Au particle size in the colloid solution is approximately 2 nm. An increase in particle size can be seen by comparing the as-prepared samples and the thermally treated. The increase in particle size is probably related to the high content of Cl^- in the samples. Chloride is known to have a sintering effect on the Au particles during thermal treatments and hence suppress the catalytic activity [29]. However, $AuTiO_2CNF$_Red_CT exhibits a different behaviour. The average particle size is similar to $AuTiO_2CNF$, which has not been thermally treated. Lopez et al. [30] have reported that adhesion of Au to TiO_2 requires oxygen defects or possible steps or adatoms. The distribution and dynamics of the oxygen vacancies will determine the dispersion and shape of the Au particles. This can imply that a pre-reduction of the TiO_2/CNF provides more adhesion sites for the Au colloid particles and hence prevents Au particle growth. The TiO_2 is predominantly in the anatase phase and only traces of rutile can be observed. The particle size of the oxide is approximately 10 nm for all the samples.

The catalysts are active in the WGS reaction in the temperature range 190–300 °C. Fig. 1A shows the reaction rates as a function of temperature. The activity of AuCNF_CT is very low and the presence of titania significantly increases the catalytic activity. It has been suggested that the active sites for CO oxidation are located at the Au–TiO_2 interface creating a synergy effect between TiO_2 and Au [31]. This is also reflected in the present WGS activity measurements which show that both the Au particles and the oxide have to be present in order to obtain high activity. The measurements show that the catalysts do not need any activation. On the contrary, the sample without thermal treatment is more active during the temperature scan. The sample has a smaller average particle size and hence a higher catalytic activity. However, the deactivation at 310 °C is more severe than for the thermally treated sample.

The catalytic activity of $AuTiO_2CNF$_Red_CT is lower during the temperature scan compared to the other samples. The activity continues to increase with time on stream (TOS). This shows that pre-reduction of the TiO_2CNF has a negative effect on the initial catalytic activity. Andreeva et al. [32] have studied the effect of pre-reduction of Au supported on ceria and ceria-alumina. They reported that pre-reduction had a negative impact on the activity. However, re-oxidation of the support restored the activity. Their results also demonstrated that the water vapour in the reaction was able to restore the catalytic activity completely for ceria supported catalysts and partially for ceria-alumina supports. The final size and shape of the gold particles is determined by the interface energy between the Au particles and the TiO_2 surface and the oxygen vacancies contribute to this interface energy [30]. Since both reducing and oxidising components are present during the WGS reaction it is not possible to determine if Ti^{3+} or Ti^{4+} is beneficial for the reaction. However, a change in the vacancy density affects the dispersion and shape of the Au particles, and therefore presumably also the catalytic activity [30].

The stability measurements presented in Fig. 1B shows that the gold particles supported on TiO_2/CNF display a higher stability than with the TiO_2 support. The loss of catalytic activity is related to a more pronounced decrease in surface area of unsupported TiO_2 compared to TiO_2/CNF and hence a decrease in the dispersion of the Au particles. A minor initial deactivation can also be seen for the CNF-containing samples before they become relatively stable. The improved stability may also be due to TiO_2 supported on CNF creating a stronger interaction with the Au particles and thereby stabilising the particles at the reaction conditions.

Results from the *in situ* XAS measurements during the water–gas shift reaction [28] are listed in Table 2. There are only minor changes in the first Au–Au coordination numbers after the reaction. Since the particle size is reflected in the coordination number this shows that the CNF have a positive effect for stabilising the Au particle size [33].

Arrhenius plots of the WGS reaction rates are given in Fig. 2A and the calculated apparent activation energies are presented in Table 1. The Arrhenius plots indicate that there are two temperature regions. However, the plot for $AuTiO_2CNF$_Red_CT is nearly linear over the entire range. Haruta [34]

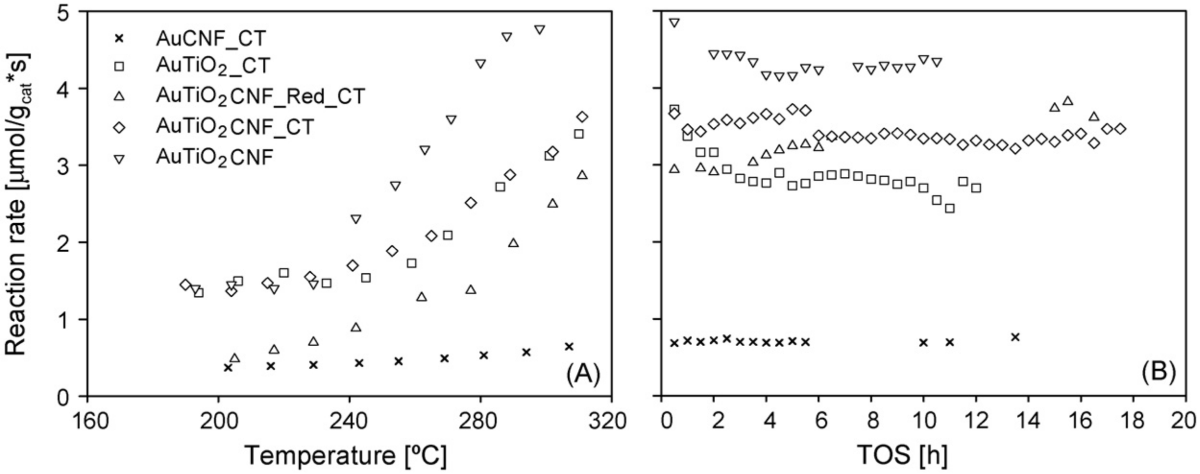

Fig. 1. (A) Reaction rates as a function of temperature for the water–gas shift reaction and (B) subsequent stability measurements at 310 °C.

Table 2
Results from the EXAFS analysis

Sample	Shell[a]	Before WGS reaction			After WGS reaction		
		N[b]	R (Å)[c]	$2\sigma^2$ (Å^2)[d]	N[b]	R (Å)[c]	$2\sigma^2$ (Å^2)[d]
AuCNF_CT	Au–Au	10.2	2.86	0.015	10.8	2.86	0.015
AuTiO_2CNF_CT	Au–Au	11.3	2.86	0.016	10.4	2.86	0.015
AuTiO_2CNF_Red_CT	Au–Au	8.9	2.85	0.019	8.6	2.84	0.020
AuTiO_2CNF	Au–Au	8.3	2.84	0.022	8.0	2.84	0.018

[a] First Au–Au coordination sphere.

[b] Coordination number.

[c] Interatomic distance.

[d] Debye–Waller type factor—N: ±20%; R: ±0.02 Å.

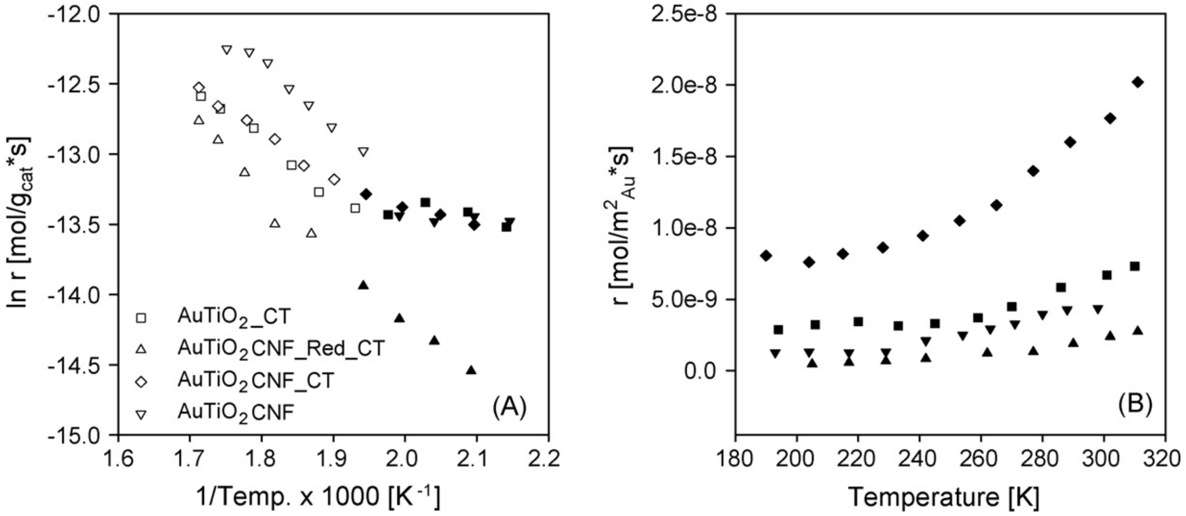

Fig. 2. (A) Arrhenius plots for the various catalysts examined in the water–gas shift reaction. Filled symbols are used for data obtained in the temperature range 190–250 °C. Data obtained from 250 °C to 300 °C are labelled with the same open symbol and (B) reaction rate per square meter per second as a function of temperature.

have reported that for CO oxidation on Au/TiO_2 there are several temperature regions where different kinetics can be observed, together with markedly different apparent activation energies. This is also the case for the Au based catalysts in the water–gas shift reaction where changes in the apparent activation energies as a function of the temperature have been reported [15]. The apparent activation energies in Table 1 are calculated from the high-temperature region in Fig. 2A. The activation energies range from 27 kJ/mol to 46 kJ/mol. The calculated values for AuTiO_2CNF_CT and AuTiO_2CNF show that the activation energies are lower for the thermally treated sample. This indicates that a heat treatment procedure is needed to create a stronger interaction between Au and titania. The activation energy for AuTiO_2_CT is approximately the same as for AuTiO_2CNF. The largest E_a is observed for AuTiO_2CNF_Red_CT and corresponds well with the lower catalytic activity observed for this sample in spite of the small particle size.

In an attempt to study the impact of the thermal treatment on the catalytic activity, the reaction rate per square meter Au per second was determined. The results are presented in Fig. 2B. Spherical Au particles were assumed in the calculation of the surface area. The relatively high activity of the AuTiO_2CNF sample demonstrates that no activation process is necessary for obtaining activity. However, a higher activity is obtained for the thermally treated catalysts albeit lower Au loading and larger particle size. This means that an activation procedure of the catalysts is beneficial for obtaining improved interaction with the support. Studies of Au-based catalysts have shown that the catalytic activity depends on the calcination temperatures [35].

4. Conclusions

The preparation of Au nanoparticles on carbon supports is not a trivial task. The deposition of Au from colloid solution is an appropriate method for Au catalysts supported on TiO_2/CNF and CNF. Thermal treatment leads to an increase in particle size. This increase in particle size is more pronounced for Au supported on TiO_2 than for Au supported on TiO_2/CNF. This indicates that the surface properties of TiO_2 are distorted by the CNF. Especially, the pore structure of the TiO_2 supported CNF is altered compared to TiO_2, since a larger fraction of mesopores is observed.

Pre-reduction of the support is beneficial for deposition of Au, although a lower initial activity is achieved, indicating that the samples should be further treated before the reaction.

It can be concluded from the EXAFS analyses that CNF are effective as a support material to prevent sintering of the Au particles during the water–gas shift reaction. Moreover, Au supported on TiO_2/CNF show higher stability than Au on TiO_2

prepared from hydrolysis. This is most likely due to the higher surface area which contribute to stabilisation and improved dispersion of the oxide and hence the Au particles.

The catalytic activity significantly improves when TiO_2 is present in the catalytic material, compared to Au deposited directly on CNF. This shows that both Au and the oxide have to be present in order to obtain a high catalytic activity in the WGS reaction.

Acknowledgements

The Norwegian University of Science and Technology (NTNU) is acknowledged for the financial support. We thank the Research Council of Norway for financial support through Grant No. 158516/510 (NANOMAT). We acknowledge the project team at the Swiss-Norwegian Beam Lines (SNBL) at ESRF for their assistance.

References

[1] H. Sakurai, A. Ueda, T. Kobayashi, M. Haruta, Chem. Commun. (1997) 271.
[2] V. Idakiev, T. Tabakova, Z.-Y. Yuan, B.-L. Su, Appl. Catal. A 270 (2004) 135.
[3] F. Boccuzi, A. Chiorino, M. Manzoli, D. Andreeva, T. Tabalova, L. Ilivers, V. Idakiev, Catal. Today 75 (2002) 169.
[4] Q. Fu, A. Weber, M. Flytzani-Stephanopoulos, Catal. Lett. 77 (2001) 87.
[5] T. Tabakova, F. Boccuzzi, M. Manzoli, J.W. Sobczak, V. Idakiev, D. Andreeva, Appl. Catal. B 49 (2004) 73.
[6] G. Jacobs, P.M. Patterson, L. Williams, E. Chenu, S. Sparks, G. Thomas, B.H. Davis, Appl. Catal. A 262 (2004) 177.
[7] D. Andreeva, V. Idakiev, T. Tabakova, A. Andreev, J. Catal. 158 (1996) 354.
[8] A. Venugopal, M.S. Scurrell, Appl. Catal. A 258 (2004) 241.
[9] S.T. Daniells, M. Makkee, J.A. Moulijn, Catal. Lett. 100 (2005) 39.
[10] V. Idakiev, T. Tabakova, A. Naydenov, Z.-Y. Yuan, B.-L. Su, Appl. Catal. B 63 (2006) 178.
[11] T. Tabakova, V. Idakiev, D. Andreeva, I. Mitov, Appl. Catal. A 202 (2000) 91.
[12] T. Tabakova, V. Idakiev, K. Tenchev, F. Boccuzzi, M. Manzoli, A. Chiorino, Appl. Catal. B 63 (2006) 94.
[13] D. Andreeva, T. Tabakova, V. Idakiev, P. Christov, R. Giovanoli, Appl. Catal. A 169 (1998) 9.
[14] D. Andreeva, Gold Bull. 35 (2002) 82.
[15] A. Venugopal, J. Aluha, D. Mogano, M.S. Scurrell, Appl. Catal. A 245 (2003) 149.
[16] C.H. Kim, L.T. Thompson, J. Catal. 230 (2005) 66.
[17] W. Yan, B. Chen, S.M. Mahurin, S. Dai, S.H. Overbury, Chem. Commun. (2004) 1918.
[18] R. Grisel, K.-J. Weststrate, A. Gluhoi, B.E. Nieuwenhuys, Gold Bull. 35 (2002) 39.
[19] Q. Fu, W. Deng, H. Saltsburg, M. Flytzani-Stephanopoulos, Appl. Catal. B 56 (2002) 57.
[20] P. Serp, M. Corrias, O. Kalck, Appl. Catal. A 253 (2003) 337.
[21] N. Hammer, I. Kvande, V. Gunnarsson, B. Tøtdal, X. Xu, D. Chen, M. Rønning, Au–TiO_2 catalysts on carbon nanofibres prepared by deposition-precipitation and from colloid solutions, Catal. Today (2007), doi:10.1016/j.cattod.2007.03.001.
[22] Z. Yu, D. Chen, B. Tøtdal, A. Holmen, Mater. Chem. Phys. 92 (2005) 71.
[23] J. Sun, M. Iwasa, L. Gao, Q. Zhang, Carbon 42 (2004) 885.
[24] D.G. Duff, A. Baiker, P.P. Edwards, J. Chem. Soc. Chem. Commun. (1993) 96.
[25] T.J. Ressler, J. Phys. IV 7 (C2) (1997).
[26] EXCURV98 CCLRC Daresbury Laboratory computer program.
[27] S.J. Gurman, N. Binsted, I. Ross, J. Phys. C 17 (1984) 143.
[28] N. Hammer, I. Kvande, D. Chen, M. Rønning, Identification of valence shifts in Au during the water-gas shift reaction, Topics in Catal., doi:10.1007/s11244-007-0235-6.
[29] S. Ivanova, C. Petit, V. Pitchon, Gold Bull. 39 (2006) 3.
[30] N. Lopez, J.K. Nørskov, T.V.W. Janssens, A. Carlsson, A. Puig-Molina, B.S. Clausen, J.-D. Grunwaldt, J. Catal. 225 (2004) 86.
[31] M.A. Bollinger, M.A. Vannice, Appl. Catal. B 8 (1996) 147.
[32] D. Andreeva, I. Ivanova, L. Iieva, M.V. Abrashev, Appl. Catal. A 302 (2006) 127.
[33] G. Colón, M.C. Hidalgo, J.A. Navío, Catal. Today 76 (2002) 91.
[34] M. Haruta, Cattech 6 (2002) 102.
[35] S. Tsubota, T. Nakamura, K. Tanaka, M. Haruta, Catal. Lett. 56 (1998) 131.