Catalysis Letters Vol. 90, Nos. 1–2, September 2003 (© 2003)

The water-gas shift reaction over Au-based, bimetallic catalysts. The Au-M (M=Ag, Bi, Co, Cu, Mn, Ni, Pb, Ru, Sn, Tl) on Iron(III) oxide system

Akula Venugopal[a], James Aluha[b], and Mike S Scurrell[b,*]

[a]*Catalysis and Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad, India–500 007*
[b]*Molecular Sciences Institute, School of Chemistry, University of Witwatersrand, Johannesburg, PO Wits 2050, South Africa*

Received 30 April 2003; accepted 7 July 2003

The bimetallic Au-M/Fe_2O_3 catalysts were prepared by deposition coprecipitation method with Au/M atomic ratio of 1. All the catalysts were measured for WGS reaction and characterized by TPR/TPO studies. Ruthenium- and nickel-modified catalysts showed higher WGS activities compared to the other systems including unmodified Au/Fe_2O_3 at low temperature (100 °C). At higher temperature (240 °C), ruthenium-, nickel-, bismuth-, lead-, copper-, silver-, thallium- and tin-modified catalysts were more active than unmodified Au/Fe_2O_3. Manganese- and cobalt-modified catalysts were less active than unmodified Au/Fe_2O_3. TPR analyses indicated a shift in reduction temperature in the bimetallic catalysts, suggesting a degree of interaction between gold and the second metal.

KEY WORDS: gold; water-gas shift; iron oxide; silver; bismuth; cobalt; copper; manganese; nickel; lead; ruthenium; tin; thallium.

1. Introduction

Catalysis by gold continues to attract considerable attention [1], and a major part of the effort expended to date on the development and understanding of gold-based catalysts has concerned catalyst systems with potential application in various environmental applications [2]. The use of supported gold systems for CO removal in the hydrogen feed to fuel cell applications for the removal of carbon monoxide, as well as for the synthesis of fine chemicals, is currently a topic of considerable interest. The removal of carbon monoxide by selective oxidation or by low-temperature water-gas shift is the principal option that has been considered. Despite much work being carried out on the behavior of gold catalysts, there has been almost no report of the action of promoters for gold or, in more general terms, the action of bimetallic systems, in marked contrast to the considerable body of research devoted to this topic for other related metals, for example, the platinum group elements. We have recently attempted to conduct studies in this area, using the water-gas shift reaction (WGSR) as a suitable test reaction that is also of potential commercial interest.

Bimetallic gold catalysts were not much studied for the low-temperature water-gas shift reaction. The low-temperature water-gas shift activities of gold catalysts mainly depend on the redox properties of the support metal oxide used [1,2], and it has been found that reducible oxides such as ceria, titania and ferric oxide are found to be attractive as support materials for Au systems for the conversion of carbon monoxide by means of the WGSR at low temperatures [1,2]. The method of preparation (which is again dependent on the pH, preparation temperature, precipitating agent and type of the precursor used for the active component) of supported Au catalysts has pronounced effect on the activity behavior [3]. The low-temperature water-gas shift activity of Au/Fe_2O_3 has been reported [4].

In assessing the likely influence of a second metal, consideration of those elements associated with water-gas shift activity provides one starting point. For example, in the early work of Grenoble *et al.* [5] on alumina-supported metals, water-gas shift activity was relatively high in the case of copper, rhenium, cobalt, nickel and platinum. Ruthenium/iron oxide has recently been examined as a water-gas shift system [6,7]. While the work of Basinska *et al.* [6] suggests that this system is active at relatively high temperatures (300–350 °C), work in our laboratories indicates that much lower temperatures (100–120 °C) can be used and, indeed, in preliminary studies on mixed metal Au–Ru/iron oxide catalysts, we suspect that ruthenium is the more active component of the two metals [7]. Other elements selected by us in the present study were chosen on the basis of scouting studies and, anticipating our presently reported results, include some rather surprising components such as bismuth, lead, silver and thallium. Au/Fe_2O_3 incorporating these four elements are more active than the unmodified Au/Fe_2O_3 catalyst when rates are compared at 240 °C.

---

* To whom correspondence should be addressed.
E-mail: scurrell@aurum.wits.ac.za

In this investigation, we have prepared the bimetallic Au-M/Fe_2O_3 catalysts, examined them for WGSR and conducted some preliminary characterization work using TPR/TPO methods. It should be mentioned here that the pure α-Fe_2O_3 support did not show any water-gas shift (WGS) activity under the reaction conditions adopted, although at temperatures higher than those used in the present work (100–240 °C), some activity has been detected. Similarly, the iron oxide used did not display any methanation activity under the conditions employed here.

2. Experimental

All the bimetallic catalysts were prepared by deposition coprecipitation method using chloroauric acid, $HAuCl_4 \cdot xH_2O$, ferric nitrate hexahydrate, $Fe(NO_3)_3 \cdot 6H_2O$ and M = metal-nitrate solutions except for ruthenium and thallium (for Au-Tl/Fe_2O_3 and Au-Ru/Fe_2O_3 catalysts, where thallium acetate, or ruthenium trichloride, $RuCl_3 \cdot xH_2O$ respectively were used) modified catalysts. In a typical method, the ferric nitrate was precipitated using dilute ammonium hydroxide solution at a pH of 8.8–9.0. The gel was kept for vigorous stirring for 3 h, and on the preformed ferric hydroxide gels in separate batches, the required amounts of gold and second metal, M (M = Ru, Cu, Ag, Co, Ni, Sn, Tl, Mn, Pb, Bi) nitrate or chloride were deposited simultaneously with the addition of ammonium hydroxide solution. The total metal content, i.e., Au + M was maintained constant at 5 mass%, and in all catalysts the Au/M atomic ratio was 1 (see table 1). The pH of the gels were maintained to be about ~8.8 for all the samples. Preliminary tests were carried out in order to check the precipitation of the modifying metal nitrate in the pH range below 9.0. The gels were washed thoroughly with hot distilled water until the pH reached to about 7.0 and the cakes were filtered, dried at 120 °C/16 h subsequently calcined in air at 400 °C/3 h. The TPR/TPO studies were analyzed under identical conditions using a purpose-built microreactor using 5 vol% hydrogen in argon for the TPR runs and 5 vol% oxygen in helium for the TPO runs. The microreactor was heated at a standard rate of 8 °C min^{-1} and the sample temperature recorded by means of a thermocouple placed in the sample bed. Thermal conductivity was used to measure hydrogen or oxygen concentrations in the exit stream relative to the inlet stream. The quantitative analysis of hydrogen and oxygen uptakes was obtained by calibration of the analysis system using a standard silver oxide sample (Micromeritics) in place of a catalyst sample for the TPR/TPO/TPR runs. The calcined catalysts were used for the WGSR measurements and for the TPR/TPO analyses as well. For activity measurements, about ~0.5 g of sample was loaded in a tubular reactor in between the two plugs of glass wool and pretreated in air at 400 °C/30 min prior to the reaction. All the samples were stabilized before the activity measurements. In a typical experiment, the catalyst samples were exposed to the reaction mixture with a flow rate of carbon monoxide of 57.5 $cm^3\ h^{-1}$ ($p_{CO} = 5.88$ kPa) and a flow rate of water of 920 $cm^3\ h^{-1}$ ($p_{H_2O} = 94.1$ kPa) up to a reaction temperature of 380 °C at a ramping rate of 1 °C min^{-1} and maintained at this temperature for 1 h. During this stabilization period, the $T_{1/2}$ (temperature at which 50% conversion of CO was observed) was noted. After stabilization, the reactor temperature was reduced to 100 °C and WGSR activities were recorded at various reaction temperatures. The experimental errors in the activity measurements were ±2% unless otherwise stated. The activity data are collected only after 3 h of continuous operation, and the activities were calculated on the basis of the degree of conversion of CO per gram of catalyst. The calculations of conversion were based both on CO consumption and cross-checked with the CO_2 production level. Our approach means that integral

Table 1

Composition of catalysts Au-M/Fe_2O_3 and calculated and experimental hydrogen consumptions expected for various reduction processes

M =	Ru	Ni	Bi	Pb	Cu	Ag	TP	Sn	Mn	Co
Au mass (%)	3.31	3.85	2.43	2.44	3.78	3.29	2.46	3.12	3.91	3.85
M mass (%)	1.69	1.15	2.57	2.56	2.12	1.71	2.54	1.88	1.09	1.15
H (due to Au)[a]	252	293	185	186	288	251	187	238	298	293
H (due to M)[b]	250	196	184	124	334	79	186	317	199	195
H (total)[c]	502	489	369	310	622	330	373	555	497	488
H (TPR)[d]	585	593	609	n.m.	670	404	525	n.m.	435	565
H (excess)[e]	83	104	240	–	48	74	152	–	–62	77
Percentage support reduction[f]	4.0	5.0	11.5	–	2.3	3.5	7.3	–	–	3.7

[a] Hydrogen consumption in μmol g^{-1} expected for Au_2O_3 reduction to Au.

[b] Hydrogen consumption in μmol g^{-1} expected for M_2O_3 or MO reduction to M.

[c] Total hydrogen consumption expected.

[d] Measured hydrogen consumption (see table 2).

[e] Excess hydrogen consumption.

[f] Percentage reduction $Fe_2O_3 \rightarrow Fe_3O_4$ corresponding to excess hydrogen consumption.

rates have been used. However, the highest conversion levels observed at 100 °C (obtained with the Au-Ru/iron oxide catalyst) correspond to about 10% conversion and, therefore, all rates reported here for this reaction temperature may be considered to have been obtained under differential conditions.

3. Results

3.1. *WGS activity measurements*

We have tried to evaluate the influence of a second metal on Au/Fe_2O_3 catalyst for the water-gas shift activities at different reaction temperatures (table 2). With an increase in reaction temperature, the WGS rates normally increased. Only in the case of the Au-Mn sample did the WGS activity decrease with an increase in reaction temperature above 360 °C. We attribute the decrease in WGS activity to structural changes occurring in this catalyst and the formation of $Mn(CO_3)_2$ [8]. Cobalt-modified catalysts exhibited relatively low activities at all temperatures studied. Au-Ru bimetallic catalyst has shown high activity compared to the other systems, though as stated in Venugopal *et al.* [7], much of this activity can probably be attributed to the separate contributions from ruthenium and gold, with only a weak synergistic effect due to gold–ruthenium interactions. The copper- and silver-modified Au/Fe_2O_3 catalysts also showed relatively low activities at low temperature, but were more active than the unmodified sample when comparison was carried out at high reaction temperatures. At both low and high reaction temperatures, the ruthenium- and nickel-modified catalysts were more active than the unmodified sample. The bismuth-modified sample was slightly less active than the unmodified sample at low reaction temperature. Continuing with the comparison of activities at low temperature, lead- and tin-modified catalysts were less active, with copper, silver, thallium and manganese samples being still less active, relative to the unmodified sample. At high reaction temperatures, ruthenium- and nickel-modified catalysts exhibited higher activities than the unmodified sample, but all other modified catalysts were also more active, with the exception of the manganese- and cobalt-containing samples. In summary, the WGS activities were found to be, Au-Ru $\geq$ Au-Ni > Au > Au-Bi > Au-Sn > Au-Pb > Au-Mn $\geq$ Au-Cu > Au-Tl > Au-Co > Au-Ag at 100 °C, with the range of activities spanning two orders of magnitude, and Au-Ru > Au-Ni > Au-Bi > Au-Cu > Au-Pb > Au-Ag > Au-Tl > Au-Sn > Au > Au-Mn > Au-Co at 240 °C, with activities spanning one order of magnitude.

It is noted that, although the gold contents of the various catalysts are not completely identical (table 1), the range of gold content is close to 1.6 : 1 at most, and it is, therefore, considered extremely unlikely that the relative WGS activates observed are due to differences in the gold contents of the various solids. In fact, there is no correlation between WGS activity and gold content at either low reaction temperature or high reaction temperature. Promotion effects are considered to be responsible for differences in activities, though we cannot decide at this stage of our investigation on the relative contributions that might arise from chemical (electronic) effects and effects due to differences in gold dispersion. What is clear is that components such as bismuth, lead and thallium that often exert a poisoning effect on catalysis by metals are, in fact, associated in this work with an enhancement in the activity of gold.

Table 2
WGS rates over bimetallic Au-M/Fe_2O_3 (M = Tl, Sn, Bi, Ag, Co, Mn, Cu, Ni, Pb, Ru) catalysts at various reaction temperatures

Catalyst Au-M/Fe_2O_3 M =	$^a r_{100\,°C} \times 10^8$	$^b r_{240\,°C} \times 10^8$	$T_{1/2}$ °C	$^c H_2$ uptake in TPR
Ru	14	125	175	585
Ni	10	103	208	593
Au [d]	8			
Bi	2	65	225	609
Pb	0.65	59	270	n.m
Cu	0.24	63	262	670
Ag	0.18	53	275	404
Tl	0.22	49	292	525
Sn	0.79	41	326	n.m
Au[d]		35		
Mn	0.55	20	345	435
Co	0.20	13	353	565

Note: *r:* rate measured on the basis of the degree of conversion of CO i.e., fractional conversion of CO multiplied by flow rate of CO per gram of catalyst.
n.m: not measured.
[a] WGSR rates at a reaction temperature of 100 °C in mol s^{-1} $g_{cat}{}^{-1}$.
[b] WGSR rates at a reaction temperature of 240 °C in mol s^{-1} $g_{cat}{}^{-1}$.
[c] Hydrogen consumptions are in μmol $g_{cat}{}^{-1}$, measured by means of TPR analyses in the temperature range 30–500 °C.
[d] Rate data for Au/Fe_2O_3 taken from reference [7].

The specific mechanism by which such an enhancement occurs requires in-depth investigations, which are now in progress.

The presented data must be taken as indicative of relative activities, since no attempt has yet been made to examine detailed kinetics. For example, it is not clear whether the apparent promotional effects are due to some form of direct interaction between gold and the second element, or whether interactions between the second element and the iron oxide support are involved. However, at this stage, we can make the observation that this is not the first time that some surprising effects in gold catalysis have been observed. Thus, there is an increasing awareness that gold catalysts tend to be far less sensitive to poisoning relative to the platinum group elements [9].

From the data presented in table 2, we note that estimation of the activation energy of the WGSR, or more correctly, the temperature coefficient of rate, since we have not conducted detailed examination of reaction kinetics, has the lowest value of ca. 17 kJ mol^{-1} for the Au/Fe_2O_3 catalyst. The highest value is 65 kJ mol^{-1} observed for the Au-Ag/Fe_2O_3. The interpretation of these energy values must first await the securing of detailed data on the kinetics of the reaction, but it is of interest to note that the value found for the unmodified gold catalyst is close to the values of 21 kJ mol^{-1} reported in Venugopal *et al.* [7] and 26 kJ mol^{-1}, estimated from the data presented by Andreeva *et al.* [4], for the water-gas shift reaction on Au/Fe oxide. A further comparison with the data of Andreeva *et al.* [4] concerns the absolute rates of reaction. A rate of 5.0×10^{-5} mol $g_{cat}{}^{-1}$ s^{-1} at 120 °C can be estimated from the data presented in Andreeva *et al.* [4], and this is higher than our rate now reported (8.0×10^{-8} mol $g_{cat}{}^{-1}$ s^{-1} at 100 °C) by a factor of about 600. The Au : Fe atomic ratio in the catalyst [4] is quoted as 1 : 22, which indicates a gold loading on the iron oxide of close to 10 mass% corresponding to $Au(Fe_2O_3)_{11}$. In addition, the partial pressures of carbon monoxide and water are higher [4] than those employed by us by factors of about 8 and 3 respectively. These differences may, at least in part, account for the higher activity reported in Andreva *et al.* [4], but, since detailed kinetics and information on activity as a function of gold loading are not available, it is difficult to draw firm conclusions at this stage.

Ruthenium- and nickel-modified catalysts, in particular, might have been expected to produce some methanation. In all our work reported here, no methane was detected in the exit stream under any conditions. The analysis system was capable of detecting this product and indeed we have seen such behavior in other ruthenium-based systems. For example, methanation is seen with ruthenium-hydroxyapatite systems, though not with gold-hydroxyapatite [10]. With Ru-hydroxyapatite, however, the methanation activity was severely reduced at higher H_2O/CO feed ratios [10], and a similar inhibiting effect of water may perhaps account for a lack of such activity for this reaction in the present work. A further reason may be that gold is perhaps able to inhibit the reaction; this is a speculative suggestion since we have no direct evidence that this may be the case.

3.2. *TPR analysis*

The bimetallic Au catalysts have not been well explored for the low-temperature WGS reaction. In the present study, an attempt has been made to understand some aspects of the surface structure of Au-M/Fe_2O_3 catalysts by means of TPR analyses. The TPR studies of the Au-M/Fe_2O_3 bimetallic catalysts involved analysis up to 500 °C at a ramping rate of 8 °C/ min. All samples were calcined in air at 400 °C before the analyses were conducted. The TPR profiles are shown in figure 1. We have reported that bulk Au_xO_y, prepared by precipitation from a solution of chloroauric acid with sodium carbonate or sodium hydroxide, showed a low-temperature reduction signal at 195 °C and a shoulder at 146 °C, along with a sharp signal at 232 °C [11]. Bulk α-Fe_2O_3 showed two distinct reduction profiles, one at 413 °C and a high-temperature peak at 666 °C. On the other hand, the Au/Fe_2O_3 showed four reduction signals at 223, 375, 658 and 755 °C [11]. It was inferred that the presence of gold tends to catalyze the reduction of some of the iron present in the ferric oxide support. It is evident that the presence of reduction peak centered at 350 °C is observed in the TPR profiles of all the bimetallic catalysts. Such a peak may be attributed to the reduction of bare α-Fe_2O_3 species indicating no influence of either Au or M (M=Ru, Ni, Bi, Cu, Ag, Tl, Mn, Co) on the reduction peak at 350 °C. None of the bimetallic catalysts showed any reduction signals below 200 °C except the ruthenium- and cobalt-modified samples. However, our earlier studies on the bulk gold oxide showed a low-temperature reduction signal at 130 °C [11]. The low-temperature peaks centered at 105 °C and at 170 °C are observed over Au-Ru/Fe_2O_3 catalyst. Similarly, copper-modified catalyst showed two thermo-reduction peaks at 130 °C and at 175 °C. Whereas the Au-Ni/Fe_2O_3 catalyst has shown a small broad feature centered at 150 °C, the sharp signals shifted toward high temperatures, i.e. 210 °C. This sharp reduction signal at 210 °C appeared in the nickel- and silver-modified catalysts, and in the case of bismuth-, cobalt- and manganese-modified Au/Fe_2O_3 catalysts, it is found as a shoulder. It is also observed that the sharp reduction signal in Au-Tl/Fe_2O_3 shifted toward high temperatures, i.e. 275 °C.

The low-temperature peaks (in the temperature range 105–300 °C) may be attributed to (1) the reduction of gold oxidic species, (2) the reduction of oxidic species of

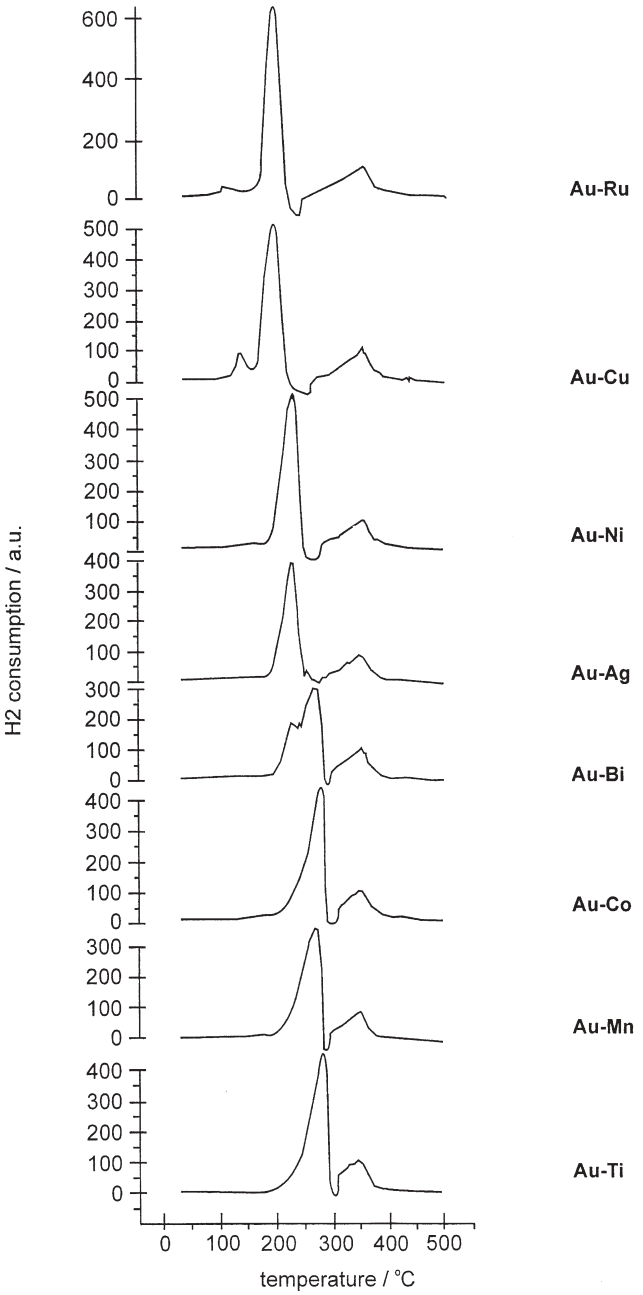

Figure 1. TPR profiles of various Au-M/Fe_2O_3 samples. Catalysts were subjected to calcination at 400 °C prior to the TPR runs being conducted.

the second metal and (3) partial reduction of the iron cations present in the support. It is not easy to distinguish which reduction processes correspond to these different processes, and it may well be that all three types of reductions take place concurrently to a greater or lesser extent, depending on the nature of the modifier metal, M. Comparison of the total hydrogen consumption (table 2) with the calculated consumption levels (table 1) based on stoichiometric reduction of Au_2O_3 to Au and reduction of M_2O_3 or MO (depending on the nature of M) to M reveals that the TPR data is consistent with a full reduction of the Au and M oxidic components, and the excess consumption would then be attributed to a partial reduction of the ferric oxide support, with the extent of this partial reduction being in the range 2.3–11.5% for conversion of ferric oxide to magnetite. Only in the case of the manganese-modified sample is the TPR hydrogen consumption insufficient to account for full reduction of the gold and manganese oxides. In fact, reduction of some of M species is not likely to occur at such low temperatures. This is true, for example, for M=Bi, Pb, Sn and Tl. Overall, the TPR data suggest that the Au and M components may well be interacting since there is no consistent peak or peaks that can be attributed to the reduction of gold oxide. However, the picture is not clear, and the absence of peaks clearly attributable to gold oxide may be partly explained if the gold is, in fact, already in a substantially reduced state, even after calcination at 400 °C. The work of Wang *et al.* [12] suggests that on Au/Fe oxide catalysts, prepared in a manner similar to our own samples, calcination at temperatures in excess of 300 °C result in a considerable fraction of the gold being in the zero valent state. Their TPR data then indicate an absence of peaks in the 100–200 °C region, which are otherwise clearly present. It is also apparent from other work performed in our laboratories [7] that the reduction of ferric oxide to magnetite in gold and gold–ruthenium catalysts during water-gas shift conditions is substantial enough to be readily detectable by means of XRD. The fact that in all our samples the TPR peak in the approximate range 200–300 °C is roughly similar in shape but displaced as far as temperature is concerned suggests that a common process is involved. The two common factors relating to all our samples are (1) the presence of gold and (2) the presence of iron oxide. At this stage, it is not easy to decide whether the major TPR peak lying in the range 200–300 °C is attributable to the reduction of gold oxide species or to a partial reduction of the iron oxide lattice, catalyzed by the presence of gold [13], but especially in view of the data reported by Wang *et al.* [12], we believe that a significant part of the hydrogen consumption seen at temperatures in the 100–200 °C range is due to the reduction of gold species. Further investigations are now in progress in order to secure a more definitive interpretation of the TPR studies on the variously modified catalysts.

4. Conclusions

The temperature-programmed reduction and oxidation studies suggest that a direct interaction between gold centers and the modifier could take place in these solids. Ruthenium- and nickel-modified Au/Fe_2O_3

catalysts showed higher WGS activities at both 100 °C and 240 °C compared to the other systems. In addition, although all remaining catalysts were less active than Au/Fe_2O_3 at 100 °C, they were more active than Au/Fe_2O_3 at 240 °C with the exception of manganese- and cobalt-modified samples, which had lower activities than that of Au/Fe_2O_3 at both 100 and 240 °C. The sample reduction behavior is dependent on the nature of the modifier metal, and the extent of reduction (of the iron oxide to magnetite) lies between 19 and 32%. From TPR studies, it is likely that at least partial reduction of the catalyst will take place under conditions of the water-gas shift reaction, especially at higher reaction temperatures.

Surprisingly, modifier elements bismuth, lead and thallium are found not to act as poisons for gold in the WGSR at 240 °C. In fact, a degree of promoter action is indicated at this reaction temperature. Whether these elements are able to promote gold catalysis in a more general sense must await the outcome of further investigations now in progress. Gold-ruthenium catalysts are the most active at all temperatures studied and, in line with our previously reported results, it is likely that ruthenium components in these catalysts dominate any contribution from the gold present. A similar dominating contribution might well arise in the case of nickel at high reaction temperatures, though a promotional effect cannot be ruled out for the WGSR run at low temperatures.

Acknowledgments

Akula Venugopal is grateful to the University of Witwatersrand for the provision of a postdoctoral fellowship. In addition, financial assistance from Anglogold is acknowledged, and thanks are also due to project AuTEK (sponsored by Anglogold and Mintek) for their assistance in the form of a gold loan.

References

[1] G.C. Bond and D.T. Thompson, Gold Bull. 33 (2000) 41.
[2] M. Haruta and M. Date, Appl. Catal., A 222 (2001) 427.
[3] M. Haruta, A. Ueda, S. Tsubota and R.M. Torres Sanchez, Catal. Today 29 (1996) 443.
[4] D. Andreeva, V. Idakiev, T. Tabakova and A. Andreev, J. Catal. 158 (1996) 354.
[5] D.C. Grenoble, M.M. Estadt and D.F. Ollis, J. Catal. 67 (1981) 90.
[6] A. Basinska, A. Nowacki and F. Domka, React. Kinet. Catal. Lett. 66 (1999) 3.
[7] A. Venugopal, J. Aluha, D. Mogano and M.S. Scurrell, Appl. Catal., A 245 (2003) 149.
[8] A. Venugopal and M.S. Scurrell, unpublished observations.
[9] D.T. Thompson, Appl. Catal., A 243 (2003) 201.
[10] A. Venugopal and M.S. Scurrell, Appl. Catal., A 245 (2003) 137.
[11] A. Venugopal and M.S. Scurrell, Appl. Catal., A in press.
[12] G.Y. Wang, H.L. Lian, W.X. Zhang, D.Z. Jiang and T.H. Wu, Kinet. Catal. 43 (2002) 433.
[13] D. Andreeva, Gold Bull. 35 (2002) 82.