

Catalysis by Gold Nanoparticles

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Gold catalysts have superior activity in CO and other oxidations at low temperatures. Both a small (~ 5nm) particle size and the presence of a partly reducible oxide (ceria or a transition metal oxide) have a beneficial effect on the catalyst performance. The present paper reviews our recent studies focused on understanding the specific role of the Au particle size and that of the oxide (MO). Our personal viewpoint on gold catalysis is outlined. The effects of Au particle size and of the oxidic additive are distinguished by using several alumina-supported gold catalysts having different gold particle sizes and various oxidic additives. The most active catalyst in CO oxidation is the multicomponent catalyst Au/MgO/MnO_x/Al₂O₃ with MgO being a stabilizer for the Au particle size and MnO_x being the cocatalyst. This catalyst also exhibits good performance in selective oxidation of CO in a hydrogen atmosphere, a reaction relevant for the development of polymer electrolyte fuel cell technology.

In its bulk form, gold has been regarded to be chemically inert towards chemisorption of reactive molecules such as oxygen and hydrogen. Consequently, pure gold was considered to be an uninteresting metal from the point of view of catalysis. The most noticeable exception to this was its use as a 'diluent' for an active metal: the addition of the inert gold to an active metal such as platinum affects to a significant extent the selectivity of the catalyst (1). However, recently, gold catalysts have attracted a dramatic growth of interest, since gold was reported to be extremely active in the oxidation of carbon monoxide if deposited as nanoparticles on partly reducible oxides. It is in particular the pioneering work of Haruta *et al*, which has stimulated research in this area (2). Early work performed with gold catalysts has been reviewed by Bond (3) and by Hutchings (4). For recent reviews on gold catalysis see references 2 and 5 - 7.

A large range of chemical reactions are now known to be catalysed by gold catalysts including total and selective oxidation, and reduction of nitrogen oxides. Based on the growth of the number of papers and patents dealing with gold-based catalysts for a range of potential applications in pollution control, chemical processes and development of fuel cells, it can be concluded that there may be a bright future for gold-based catalysis.

In the present paper we discuss some of our research on catalysis by gold (8 - 14), and in particular, the following topics will be discussed:

- a) the effect of the gold particle size and the role of the oxidic additive;
- b) the selective oxidation of CO in the presence of hydrogen, a reaction relevant to hydrogen fuel cell applications.

Experimental

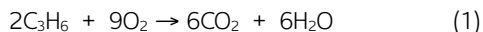
All the catalysts discussed in this paper are supported on γ -alumina, the gold loading is 5.0 wt%. The gold catalysts were prepared by homogeneous deposition precipitation using urea as precipitating agent. The advantage of the use of alumina as support is the high stability of the catalysts up to relatively high temperatures (10, 11). The following techniques were used for characterization of the catalysts: X-ray diffraction, high resolution transmission electron microscopy with facilities for chemical analysis by EDX, atomic absorption spectroscopy and ¹⁹⁷Au-Mössbauer effect spectroscopy. For details of catalyst preparation and characterization, the experimental set-up and the activity measurements, see references 10 - 14. The flow rate used was 40 ml min⁻¹, GHSV 2500h⁻¹. The gold and metal oxide (MO) phases are well dispersed on the alumina support and the HRTEM/EDX results point to close contact between the gold and MO phases.

Results and Discussion

1 Synergistic and Particle Size Effects

New regulations in the United States, Japan and Europe will make it mandatory that automotive emissions decrease substantially from current levels. Consequently, there is a strong incentive to develop improved catalysts with better oxidation activity at low temperatures, since most of the hydrocarbons and CO are emitted immediately following the cold start of engines (15).

A possible option may be the application of gold catalysts, making use of their superior activity in oxidation of CO and hydrocarbons at low temperatures. This is clearly illustrated in Figure 1 which indicates the conversion of propene over three types of alumina supported catalysts, *viz* CeO_x/Al₂O₃, Au/Al₂O₃ and the multicomponent catalyst consisting of both Au and CeO_x, Au/CeO_x/Al₂O₃ (16):



For all of the gold catalysts the average particle size is 3.0 nm. Clearly, the multicomponent catalyst is much more active at low temperatures than the monocomponent ones. It should be noted that the γ -Al₂O₃ support itself is not active under the conditions used in the experiments shown in the Figure 1. The presence of such a *synergistic* effect has been reported before for highly dispersed gold catalysts supported on reducible and catalytically active supports such as FeO_x, CoO_x, TiO_x and MnO_x for a number of reactions (2 - 14). Hence, the interesting observation is that gold-based catalysts are more active if:

- the gold particle is nanosized, *ie* of the order of ca 5 nm, and
- the gold particles are combined with an oxidic catalyst (MO_x).

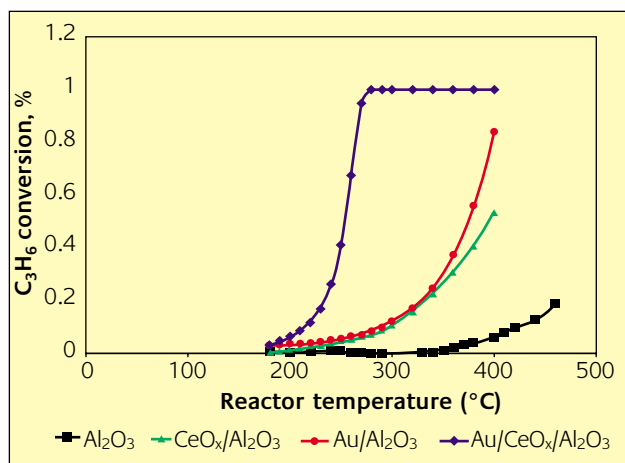
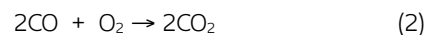


Figure 1

Synergistic effect - oxidation of propene over γ -Al₂O₃, CeO_x/Al₂O₃, Au/Al₂O₃ and Au/CeO_x/Al₂O₃ (16)

In order to distinguish the effects of gold particle size and the presence of MO, a comparative study was performed on the behaviour of several gold-based catalysts in CO oxidation:



Some of the results are shown in Figure 2. All the catalysts examined had γ -Al₂O₃ as the support. The pure MO_x/Al₂O₃ catalysts are not very active in low-temperature CO oxidation. No significant CO conversion was found below 150°C, a temperature at which full conversion is reached over a Au/Al₂O₃ catalyst with 4nm Au particles (not shown in the figure). The CO oxidation activity of the alumina-supported metal oxides decreases in the order: CoO_x > FeO_x > MnO_x > NiO_x > CrO_x >> MgO and ZnO. Addition of MO_x to Au/Al₂O₃ greatly influences the CO conversion in the low temperature region. Since none of the selected MO_x was found to be active at these low temperatures, the activity enhancement must be due to either changes in the gold phase or to synergistic effects between gold and the MO_x. To illustrate the large beneficial effect of MO_x addition, the temperatures

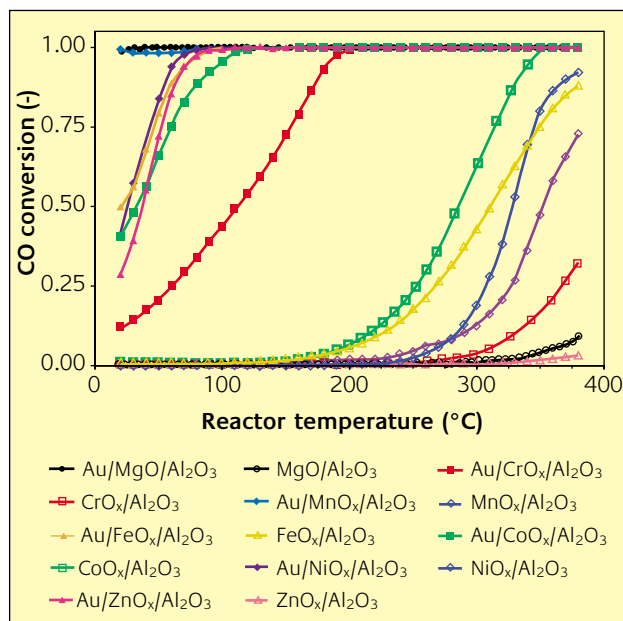


Figure 2

CO oxidation over gold-based catalysts:

Au/MgO/Al₂O₃ and MgO/Al₂O₃

Au/CrO_x/Al₂O₃ and CrO_x/Al₂O₃

Au/MnO_x/Al₂O₃ and MnO_x/Al₂O₃

Au/FeO_x/Al₂O₃ and FeO_x/Al₂O₃

Au/CoO_x/Al₂O₃ and CoO_x/Al₂O₃

Au/NiO_x/Al₂O₃ and NiO_x/Al₂O₃

Au/ZnO_x/Al₂O₃ and ZnO_x/Al₂O₃

The CO conversion over Au/MgO/Al₂O₃ and Au/MnO_x/Al₂O₃ is 100% in the whole temperature range studied

Gold loading = 5%

Atomic ratio Au : M (= Mg, Cr, Mn, Fe, Co, Ni and Zn) = 1 : 1

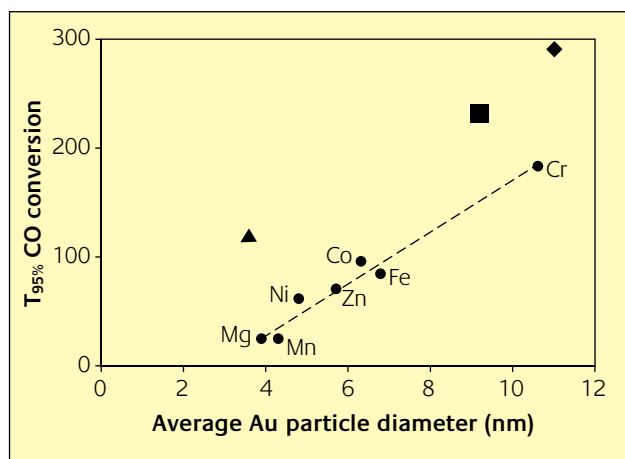


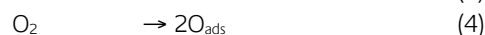
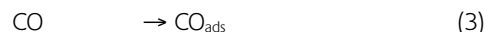
Figure 3

Temperature needed for 95% CO conversion versus the average gold particle size of Au/Al₂O₃ calcined at 300°C (▲), Au/Al₂O₃ calcined at 600°C (■), Au/Al₂O₃ calcined at 900°C (◆) and Au/MO_x/Al₂O₃ (●) catalysts. The three Au/Al₂O₃ catalysts have been calcined at 300, 400 and 600°C in order to change the average Au particle size

needed for 95% CO conversion (T 95%) are plotted versus the average gold particle size as determined from XRD line broadening. Figure 3 summarizes the results obtained for seven multicomponent Au/MO_x/Al₂O₃ and three monocomponent Au/Al₂O₃ catalysts with an average gold particle size between 4 and 11nm. The gold particle size of the three Au/Al₂O₃ catalysts was varied by heating a standard Au/Al₂O₃ catalyst in an oxygen atmosphere at 300, 400 and 600°C. In this way the average particle size increases from 3.6nm via 9 to 11nm.

The results clearly demonstrate that small gold particles (< 5nm) are required for high activity. This observation is in line with literature data (2, 5 - 7, 17 - 19). The addition of MO_x has a large beneficial effect on the activity at low temperatures. This effect is larger than can be expected from the presence of stable small Au particles alone. For example, the Au/MnO_x/Al₂O₃ catalyst with an average particle size of 4.2 ± 1.4 nm has a T 95% that is 100 degrees lower than that found for Au/Al₂O₃ with an average particle size of 3.6 ± 1.4 nm. In fact, the CO conversion over Au/MnO_x/Al₂O₃ is higher at ambient temperature than the CO conversion over the Au/Al₂O₃ catalyst at 150°C. Most probably, the role of MO_x is twofold. Firstly, the oxide (in particular, MgO) may stabilize the small size of the gold particles throughout preparation and activity measurements (promoter effect). Secondly, the oxide may actively take part in one of the steps involved in the catalytic cycle (ie it acts as a co-catalyst).

The dominant mechanism of CO-oxidation at low temperatures over the platinum group metals (PGMs) is that of a Langmuir-Hinshelwood type between adsorbed CO and adsorbed O (15):



The mechanism of the CO oxidation reaction on gold catalysts is not fully understood. In the opinion of the present authors the mechanism on Au/Al₂O₃ may be similar to that on the platinum group metal (PGM) catalysts. If this is so, the difficult step is the dissociative adsorption of O₂ on gold, step 4. Gold is not very active in the O-O bond scission. However, O adatoms are stable on gold at room temperature. The beneficial effect of the addition of a transition metal oxide may be that the MO_x supplies the O needed for the reaction. The reaction may occur at the Au-MO_x interface with CO adsorbed on Au reacting with O on MnO_x. The O-vacancies on MO_x will then react with O₂ and the catalytic cycle is completed. An alternative explanation is that O atoms spill over to the gold surface and then react with adsorbed CO according to step 5.

Large synergistic effects have been reported earlier for combinations of Pt or Pd with reactive metal oxides (15, 20, 21). An example is shown in Table 1 for CO oxidation over Pt catalysts. Pt/CoO_x/SiO₂ and Pt/CoO_x/Al₂O₃ belong to the most active Pt catalysts investigated in our laboratories. Even at room temperature CO is oxidized. The high activity of Pt/CoO_x/SiO₂ in CO oxidation is related to the absence of CO inhibition effects at low temperatures (22). At temperatures up to about 200°C Pt surfaces are almost inactive for CO oxidation because the whole Pt surface is covered with CO. Oxygen cannot adsorb and dissociate on a CO-covered Pt surface. At higher temperatures this CO-inhibition disappears because some of the CO desorbs, resulting in oxygen adsorption and reaction. On the multicomponent Pt catalysts CO inhibition does not occur, the transition metal oxide

Table 1 Temperature (°C) Needed for 50% O₂ or CO* Conversion at Several CO/O₂ Ratios after a Reductive or an Oxidative Treatment

Catalyst	Pretreatment	Ratio CO:O ₂		
		1:1	2:1	3:1
Pt/CoO _x /SiO ₂	Reduction	15	26	29
	Oxidation	101	103	103
Pt/MnO _x /SiO ₂	Reduction	94	114	125
	Oxidation	150	173	162
Pt/SiO ₂	Reduction	175	212	204
	Oxidation	187	210	210

CO conversion starts between 300 and 350°C over CoO_x/SiO₂ and MnO_x/SiO₂ catalysts. However, 50% conversion was not reached over these catalysts at 400°C, the maximum temperature used in these series of experiments

* Conversion of O₂ for reducing and stoichiometric gas mixtures, and conversion of CO for oxidizing gas mixtures.

supplies the O needed for the reaction. It is likely that the reaction takes place at the Pt-MO_x interface (22).

Some of the gold-based catalysts are clearly superior to the Pt-based catalysts. For example, full conversion of CO is reached over Au/MnO_x/Al₂O₃ below room temperature, whereas a temperature of 100°C is needed for complete conversion over Pt/CoO_x/SiO₂. In the opinion of the present authors the superior activity of the Au-based catalysts is related to the low Au-O and Au-CO bond strengths.

The gold catalysts could be used as a start-up automotive catalyst because of the short warm-up period required to heat the catalyst to the temperature at which it becomes effective. Alternatively, new generations of automotive three-way catalysts based on gold might be feasible, since Au-based catalysts are also able to reduce nitrogen oxides (8, 9, 23).

2 Selective Oxidation of CO in the Presence of Hydrogen

The hydrogen-air PEM (Polymer Electrolyte Membrane) fuel cell is potentially an attractive and clean energy source for vehicle propulsion and auxiliary power units. However, it is not practical to store hydrogen in large quantities aboard a vehicle. Hydrogen storage and distribution can be avoided by producing hydrogen locally (on-board) from gasoline, methanol or natural gas via steam-reforming, or partial oxidation combined with water-gas shift reaction processes. A major problem is the presence of a few per cent of CO in the hydrogen product stream. It decreases the efficiency of the fuel cell by CO-poisoning of the Pt-based electrode at the operating temperature of the fuel cell, typically 60-100°C. The most promising approach to reduce the CO concentration to acceptable levels is by selective catalytic oxidation (SCO) of CO, *ie* reaction (2). Hence, an efficient catalyst must be highly active in CO oxidation at temperatures compatible with the operation of the PEM fuel cell and very selective to CO₂ formation. The selectivity is defined as the ratio of oxygen used for CO oxidation over the total oxygen concentration which includes the oxygen loss due to H₂O formation:



For a number of reasons these catalyst requirements - high activity in CO oxidation at 60-100°C and almost no hydrogen oxidation - are hard to meet:

- a) reaction (6) is faster than reaction (2) on most of the noble metal catalysts;
- b) in the relevant temperature range CO oxidation is very slow on Pt and Pd due to CO inhibition (15).

Results reported in the literature show that CO can be

oxidized in preference to hydrogen in the temperature range of 100-200°C over Al₂O₃ supported Ru, Rh, and Pt catalysts (24 - 27). The interesting observation is that CO oxidation is enhanced by the presence of hydrogen. Possible mechanisms include the effect of hydrogen on the heat of adsorption of CO and interaction of the hydroxylated Al₂O₃ support with CO adsorbed on Pt (25). For Pt catalysts an optimum in activity and selectivity was found at 200-250°C (24, 25). At lower temperatures (desired temperature ~ 70°C) CO oxidation was rather slow due to CO inhibition of oxygen adsorption. At a higher temperature the selectivity decreased because CO desorption enables hydrogen adsorption and oxidation.

We have studied SCO of CO over various multicomponent Au-Pt-, Rh-, Pd- and Ru-based catalysts. Some of the results obtained over gold-based catalysts are summarized in the present paper. For more details see references 13 and 14.

Gold catalysts are promising candidates for SCO for two reasons:

- 1) They exhibit an extraordinarily high activity in CO oxidation in the low temperature range relevant for fuel cell applications.
- 2) The catalysts have another unique property: the rate of CO oxidation exceeds that of hydrogen oxidation in the relevant temperature range (13, 14, 28).

Results obtained for four alumina-supported Au-based catalysts will be discussed here: Au, Au/MnO_x, Au/MgO with very small gold particles and the multicomponent Au/MgO/MnO_x catalyst. All these catalysts are able to oxidize CO at room temperature with the multicomponent catalyst being the most active: 100% conversion at 20°C. Hydrogen is also oxidized over these catalysts. However, as shown in Table 2, significantly higher temperatures are needed for hydrogen oxidation compared to CO oxidation. When hydrogen is present in the feed, the behaviour of the catalysts towards CO oxidation changes. Figure 4 shows the conversion of CO, hydrogen and oxygen for a mixture H₂ : CO : O₂ = 4 : 2 : 1. This composition was chosen because it contains just enough oxygen to oxidize all the CO, if hydrogen does not participate in any oxidation reaction. Up to 50°C relatively high CO conversions are obtained as was the case for measurements without hydrogen in the feed. However, at higher temperatures hydrogen oxidation starts at the expense of CO oxidation. Over the most active catalysts, Au/MgO and Au/MgO/MnO_x all the oxygen is consumed, even at 20°C. Depending on the composition of the catalyst, hydrogen conversion exceeds that of CO at temperatures between 150 and 250°C. At temperatures higher than 300°C CO oxidation increases again.

The presence of CO distinctly suppresses the oxidation of hydrogen at low temperatures over all four of the catalysts. For example, over Au/MgO the hydrogen conversion at 20°C

Table 2 CO and Hydrogen Oxidation over Alumina Supported Gold Catalysts. Gold Loading 5wt%

Catalyst	Average Au Particle Size (nm)	CO oxidation		H ₂ oxidation	
		α CO	T 50% (°C)	α H ₂	T 25% (°C)
Au	3.6 ± 1.4	0.22	57	0.16	63
Au/MnO _x	9.2 ± 2.7	0.49	35	0.19	102
Au/MgO	2.2 ± 1.0	0.59	< 20	0.41	< 20
Au/MgO/MnO _x	2.7 ± 1.0	1.00	< 20	0.19	57

Conversion α at 20°C and temperature needed for a conversion of 25% hydrogen and 50% (CO). Ratio CO/O₂ = 1 and H₂/O₂ = 4. Reactant flow 40 ml/min⁻¹, GHSV = 2500 h⁻¹ with a mixture of H₂, CO and O₂ in helium (96 vol%)

in the absence of CO in the feed is 0.45 (see Table 2) and in the presence of CO it is zero. The CO₂ selectivity of Au/MgO and Au/MgO/MnO_x is higher than 90% in the temperature range of interest for fuel cell applications (up to 100°C).

However at temperatures higher than 100°C the CO₂ selectivity of Au/MgO decreases rapidly with increasing temperature. This decrease of selectivity is much slower using the multicomponent Au/MgO/MnO_x catalyst.

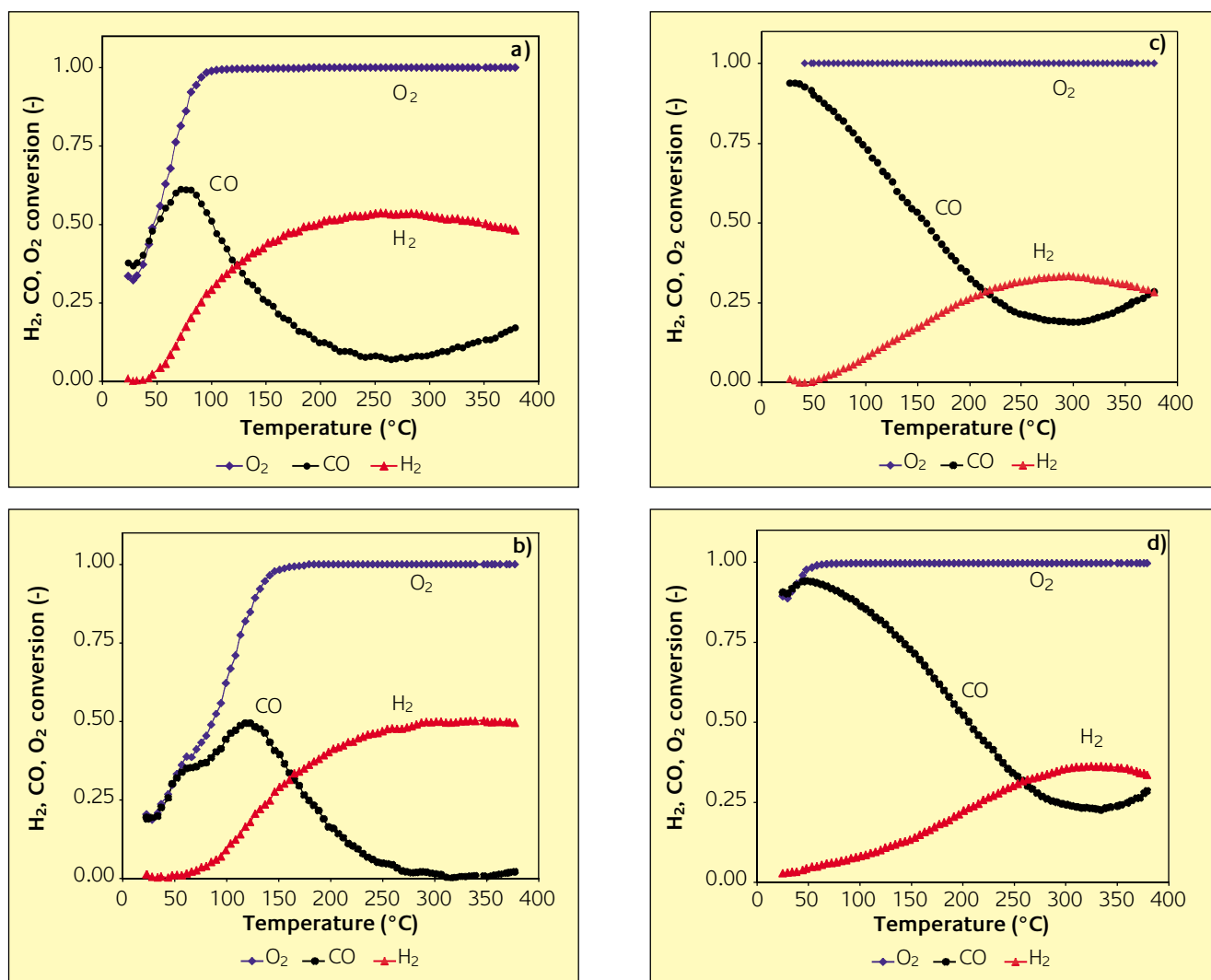


Figure 4

Conversion of CO (●), H₂ (▲) and O₂ (◆) versus temperature over (a) Au/Al₂O₃, (b) Au/MnO_x/Al₂O₃, (c) Au/MgO/Al₂O₃ and (d) Au/MgO/MnO_x/Al₂O₃. Au loading 5wt% Au: M (M = Mg and Mn). Atomic ratio = 1 : 5. The Au : Mg : Mn atomic ratio was 1 : 5 : 5 in the case of Au/MgO/MnO_x/Al₂O₃. (Adapted from (13))

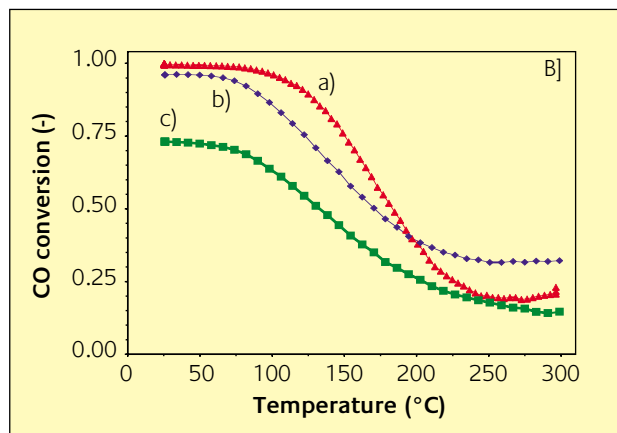
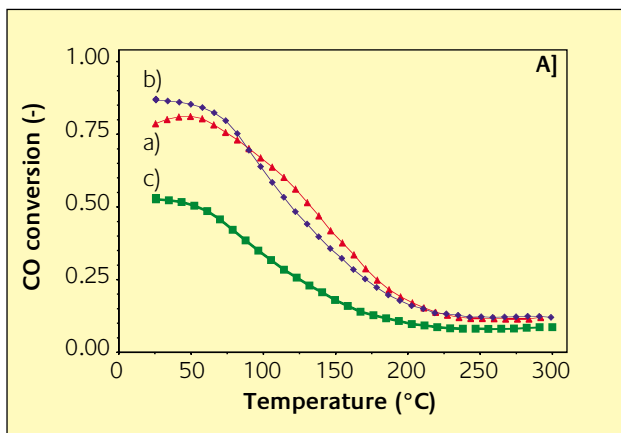


Figure 5

CO conversion in hydrogen rich feed: over: A] Au/MgO/Al₂O₃ B] Au/MgO/MnO_x/Al₂O₃

70 vol% H₂ and CO + O₂ (1.2 vol%) in helium (~29 vol%) Au loading 5 wt%; Au : Mg atomic ratio 1 : 5; Au : Mg : Mn atomic ratio 1 : 5 : 5; a) λ = 4, b) λ = 2 and c) λ = 1

Table 3 CO Conversion at 70°C for Three Values of λ (see text) in 70 vol% Hydrogen.

Catalyst	λ = 4	λ = 2	λ = 1
Au/MgO/Al ₂ O ₃	0.77	0.81	0.45
Au/MgO/MnO _x /Al ₂ O ₃	0.99	0.95	0.72

Feed composition: H₂ (70 vol%) and CO+O₂ (1.2 vol%) in helium (29 vol%)

The high CO oxidation activity of Au/MgO is mainly due to the presence of small gold particles. Its performance in CO oxidation can be enhanced by the addition of MnO_x. Another beneficial effect of MnO_x addition is that the high activity of Au/MgO in hydrogen oxidation is lowered by the presence of MnO_x.

All the results discussed up to now have been obtained in a diluted hydrogen atmosphere. Figure 5 and Table 3 show results obtained under more realistic conditions for the two most promising catalysts viz Au/MgO/Al₂O₃ and Au/MgO/MnO_x/Al₂O₃. These experiments were performed in a mixture of H₂ (~ 70 vol%) and O₂ + CO (1.2 vol%) in helium (~ 29 vol%) using three different O₂ : CO molar ratios (λ = 1, 2 and 4). The parameter λ is defined as the concentration of O₂ in the feed divided by the concentration of O₂ needed to oxidize completely all the CO in the feed:

$$\lambda = \frac{O_2, \text{ initial}}{2 \text{ CO, initial}} \quad (7)$$

The results clearly show that a large excess of hydrogen results in a lower CO conversion. Under these conditions more oxygen is needed to increase the CO conversion (higher λ) at the expense of the CO₂ selectivity. Similar effects have been reported for Pt/Al₂O₃, Ru/Al₂O₃ and Rh/Al₂O₃: an increase in hydrogen partial pressure leads to a significant lowering of the

CO₂ selectivity (24 - 27). The addition of MnO_x to Au/Mg/Al₂O₃ improves the CO conversion and CO₂ selectivity over the whole temperature range studied for all values of λ used.

Based on the results discussed, the following model is proposed for the oxidation of CO in a hydrogen atmosphere. In our opinion gold nanoparticles have an intrinsic activity in CO oxidation and in hydrogen oxidation according to the same mechanism that has been established for PGMs (15). For CO oxidation the relevant steps are 3, 4 and 5 and for H₂ oxidation (6) steps 8, 9 and 10:



In this view gold nanoparticles have the ability to dissociate O₂ (step 9) and H₂ (step 8). Some recent results obtained in our laboratory support this proposal. It was found that the rate of the hydrogen-deuterium exchange reaction (11) is much faster over Au/Al₂O₃ catalysts, active in H₂ and CO oxidation, than over Al₂O₃ (29):



The significant differences between Au and the PGM catalysts are the lower heat of CO adsorption and the lower binding energies of H and O on Au combined with the slower rate of dissociative adsorption of oxygen and hydrogen on gold.

The mechanism proposed includes adsorption of CO on the small, mainly metallic, gold particles. At low temperatures hydrogen adsorption is blocked by CO (T < 100°C). At higher temperatures the CO coverage becomes small, allowing more hydrogen to dissociate and react with oxygen resulting in a decrease in the selectivity towards CO₂. An

increase in λ , ie upon lowering the CO partial pressure, may induce a similar effect. At low temperatures most of the O may originate from the lattice of MnO_x. At these temperatures the reaction most likely occurs at the Au-MnO_x interface. The multicomponent Au/MgO/MnO_x/Al₂O₃ catalyst has the best performance in SCO of CO. The presence of MgO enables the formation of small, highly dispersed, and thermally stable gold particles on γ -Al₂O₃ which are highly active in CO and H₂ oxidation. The CO oxidation activity is improved by adding MnO_x. In addition, the hydrogen oxidation on these multicomponent catalysts is suppressed, leading to an overall increase of CO₂ selectivity in the temperature range relevant for fuel cell applications (~ 70°C).

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About the Authors

Ben Nieuwenhuys is the principal investigator and supervisor of the research group at Leiden Institute of Chemistry, Leiden University in The Netherlands, where the investigations described here were undertaken. He has more than 170 publications on various surface chemistry topics and heterogeneous catalysis. The research programme of the group focuses on the understanding of heterogeneous catalysis on the atomic level; and, in particular, the relationship between activity, selectivity of the catalyst and the structure/composition of sites present on the surface. These goals are achieved by correlating results of experiments on model systems using the surface science approach with those obtained on high surface area ('real') catalysts.

Ruud Grisel was a PhD student at the Leiden University before he moved to ASM (Advanced Semiconductor Materials) in 2001. He will defend his PhD thesis entitled 'Supported Gold Catalysts for Environmental Applications' in June 2002.

Kees-Jan Weststrate investigated the activity of gold and other noble metal catalysts in the selective oxidation of CO in the presence of H₂ for his MSc thesis. From April 2002 he has been working on his PhD. His research involves the study of carbon species on noble metal surfaces during different reactions, such as partial oxidation of methane to syn-gas.

Andrea Gluhoi joined the Heterogeneous Catalysis and Surface Science Group in 2000 as a PhD student. Before 2000 she worked as a researcher at the National Institute for

Research and Development of Isotopic and Molecular Technologies at the Cluj Napoca, Romania for three years. Her main research interest is in the influence of support and additives on the catalytic activity and selectivity of gold-based catalysts in oxidation and reduction reactions.

References

- 1 V. Ponec and G.C. Bond, in 'Catalysis by Metals and Alloys', eds. B. Delmon and J. T. Yates, Stud.Surf.Sci.& Catal., Elsevier Sci./Amsterdam, 1995, **95**
- 2 M. Haruta, *Catal. Today*, 1997, **36**, 153
- 3 G.C. Bond, *Catal. Today*, 2002, **72**, 5; G.C. Bond, *Gold Bull.*, 2001, **34**, 117
- 4 G.J. Hutchings, *Gold Bull.*, 1996, **29**, 123
- 5 D.T. Thompson, *Gold Bull.*, 1998, **31**, 111
- 6 G.C. Bond and D.T. Thompson, *Catal. Rev. - Sci. Eng.*, 1999, **41**, 319
- 7 M. Haruta and M. Date, *Appl. Catal. A*, 2001, **222**, 427
- 8 M.A.P. Dekkers, M.J. Lippits and B.E. Nieuwenhuys, *Catal. Lett.*, 1998, **56**, 195
- 9 M.A.P. Dekkers, M.J. Lippits and B.E. Nieuwenhuys, *Catal. Today*, 1999, **54**, 381
- 10 R.J.H. Grisel, P.J. Kooyman and B.E. Nieuwenhuys, *J. Catal.*, 2000, **191**, 430
- 11 R.J.H. Grisel and B.E. Nieuwenhuys, *Catal. Today*, 2001, **64**, 69
- 12 R.J.H. Grisel, J.J. Slyconish and B.E. Nieuwenhuys, *Topics in Catal.*, 2001, **16/17**, 425
- 13 R.J.H. Grisel and B.E. Nieuwenhuys, *J. Catal.*, 2001, **199**, 48
- 14 R.J.H. Grisel, C.J. Weststrate, A. Goossens, M.W.J. Crajé, A.M. van der Kraan, and B.E. Nieuwenhuys, *Catal. Today*, 2002, **72**, 123
- 15 B.E. Nieuwenhuys, *Adv. Catal.*, 1999, **44**, 49
- 16 A. Gluhoi and B.E. Nieuwenhuys, to be published
- 17 S.K. Tanielyan and R.L. Augustine, *Appl. Catal.*, 1992, **A85**, 73
- 18 M. Valden, S. Pak, X. Lai and D.W. Goodman, *Catal. Lett.*, 1998, **56**, 7
- 19 S. Tsubota, T. Nakamura, K. Tanaka and M. Haruta, *Catal. Lett.*, 1998, **56**, 131
- 20 Y.J. Mergler, A. van Aalst, J. van Delft and B.E. Nieuwenhuys, *Appl. Catal.*, 1996, **B10**, 245
- 21 G.C. Bond, M.J. Fuller and L.R. Mulloy, Proc.6th Int. Congr. Catal., 1976, A26
- 22 Y.J. Mergler, J. Hoebink and B.E. Nieuwenhuys, *J. Catal.*, 1997, **167**, 305
- 23 A. Ueda and M. Haruta, *Gold Bull.*, 1999, **32**, 3
- 24 M. Watanabe, H. Uchida, H. Igarashi and M. Suzuki, *Chem. Lett.*, 1995, 21
- 25 M.J. Kahlich, H.A. Gasteiger and R.J. Behm, *J. Catal.*, 1997, **171**, 93
- 26 S.H. Oh and R.M. Sinkevitch, *J. Catal.*, 1993, **142**, 254
- 27 M.L. Brown, A.W. Green, G. Cohn and H.C. Anderssen, *Ind. Eng. Chem. Res.*, 1960, **52**, 841
- 28 R.H. Torres Sanchez, A. Ueda, K. Tanaka and M. Haruta, *J. Catal.*, 1997, **168**, 125
- 29 H.S. Vreeburg, J.W. Bakker and B.E. Nieuwenhuys, unpublished results.