Available online at www.sciencedirect.com
SCIENCE DIRECT®

Catalysis Today 90 (2004) 175–181

CATALYSIS TODAY

www.elsevier.com/locate/cattod

The beneficial effect of the addition of base metal oxides to gold catalysts on reactions relevant to air pollution abatement

Andreea C. Gluhoi [a], Shawn D. Lin [b], Bernard E. Nieuwenhuys [a,*]

[a] *Department of Heterogeneous Catalysis and Surface Chemistry, Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands*
[b] *Department of Chemical Engineering, Yuan Ze University, Taiwan, Republic of China*

Abstract

The present paper reviews some of our recent studies concerning reactions relevant to air pollution abatement over gold based catalysts. In particular, the following reactions will be discussed:

1. CO oxidation.
2. Total oxidation of hydrocarbons.
3. Reduction of NO.
4. Reduction of N_2O.
5. Selective oxidation of CO in an atmosphere of hydrogen, in relation to the development of polymer electrolyte fuel cell technology.
6. Selective oxidation of NH_3.

Large synergistic effects have been found by combining Au/Al_2O_3 with a transition metal oxide (TMO) or ceria for all the reactions studied in our laboratory. One of the most efficient gold-based catalysts that we developed is based on alumina-supported combinations of Au, CeO_x and Li_2O. Our model is that most of the chemistry is taking place at the interface of gold and the partly reducible oxide CeO_x. The cocatalyst CeO_x can provide the O needed for oxidation reactions. The non-reducible alkali or alkali-earth metal oxide functions as a promoter. It enables the formation of small, highly dispersed, and thermally stable gold particles on γ-Al_2O_3.

As a general conclusion, supported gold catalysts are highly active in both oxidation and reduction reactions. The selectivity can be steered into the desired direction by using the right additive.

Keywords: Monometallic; Alkali-earth metal oxide; Hydrocarbons

1. Introduction

Noble metal catalysts, in particular Pt and Pd, are used already for many years with major applications in the chemical and petroleum industry, and, in the last 25 years, automotive pollution control. The noticeable exception is gold. This noble metal has almost no applications in catalysis although it is much more abundant than the other noble metals. Some early studies indicated that gold catalysts have some activity for various reactions [1–3]. However, gold-based catalysts did not exhibit any advantage over the Pt group metal catalysts. In general, it was believed that due to its nobility gold would not have any future as an active component of commercial catalysts. However, because of its alleged inertness, gold was considered as a useful additive to monometallic catalysts in order to improve the selectivity. Recent results suggest that this century may become the golden age for gold-based catalysts. The two areas where gold has industrial potential are:

1.1. *Bimetallic catalysts. Gold-an inhibitor of undesired reactions*

In particular, Sachtler and van Santen [4], Sinfelt [5] and Ponec and Bond [6] demonstrated that the addition of a group IB metal (Cu, Ag, Au) to a group VIII metal results

---

* Corresponding author.
E-mail addresses: sdlin@saturn.yzu.edu.tw (S.D. Lin), b.nieuwe@chem.leidenuniv.nl (B.E. Nieuwenhuys).

0920-5861/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.04.025

in major selectivity effects in catalysis. It was realized that geometric factors play a crucial role in determining selectivity [4,6]. For some reactions surface sites are required consisting of a number of adjacent active group VIII metal atoms. Other reactions, however, require sites consisting of just a few, or even a single active metal atom. As a consequence, the former reactions will be more sensitive that the latter to inclusion of inactive atoms in the surface. Although this early research regarding bimetallic catalysts was very successful in terms of fundamental understanding of metal catalysis in general, it did not yet result in the application of new generations of metal catalysts based on Group VIII and IB metals.

Recently, a number of papers renewed the interest in the possible application of bimetallic catalysts consisting of an active metal and gold that acts as a "diluent" for the active metal. Hydrogen is produced by steam reforming of natural gas (which is primarily methane) over a nickel catalyst:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \tag{1}$$

and the H_2 content is increased by means of the water gas shift reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{2}$$

Undesired side reactions on the nickel catalysts used for steam reforming of methane results in *coking*, the formation of a graphitic overlayer on the surface. In practice, sulfur compounds in the feed result in partial covering of the Ni-surface with sulfur. In this way, the Ni catalyst surface is diluted by S and the side reactions resulting in coking are suppressed. Besenbacher et al. suggested an elegant way to avoid graphite formation [7]. The addition of a small amount of gold to the nickel catalyst leads to the formation of a nickel–gold surface alloy. The presence of gold "dilutes" the nickel surface and prevents the formation of C–C bonds, the first step in graphite formation. The bimetallic Ni-Au catalyst has a slightly lower activity than the pure Ni catalyst. However, deactivation by coking is suppressed resulting in an improved catalyst lifetime.

In the forthcoming years we may expect the development of novel bimetallic catalysts based on the "traditional" noble metals and gold. As an example, BP Chemicals announced a new process for making vinyl acetate monomer from ethylene, acetic acid and oxygen using Pd/Au catalysts [8].

1.2. Gold-based catalysts with gold as active component

Until 15 years ago it was believed that gold is too inert to be an active constituent of metal catalysts. However, recently, gold catalysts have attracted an enormous growth of interest, thanks to the pioneering work of, in particular, Haruta and co-workers who showed that gold-based catalysts are extremely active in the oxidation of carbon monoxide if gold is present as nanoparticles on a support [9–11]. Gold nanoparticles on partly reducible oxides were found to exhibit CO oxidation activity even at sub-ambient temperatures (200 K).

Following their first publications the number of papers dealing with gold catalysis has grown in an exponential way. It has been demonstrated that gold-based catalysts exhibit catalytic activity for a wide range of different reactions: NO_x reduction, CO and CO_2 hydrogenation, NO oxidation, water gas shift reaction, alkene epoxidation, total oxidation of hydrocarbons including methane and selective oxidation of CO and hydrocarbons. Recently, some authors reported on the effect of the Au^0/Au^{3+} nanoparticles on CO electrooxidation [12], as well as the performance of bimetallic Au-Pd/SiO_2 catalysts for CO oxidation [13]. For comprehensive reviews on gold catalysis we refer to [1–3,10,11,14–16].

The present paper reviews some of our recent studies concerning reactions relevant to air pollution abatement over gold based catalysts. In particular, the following reactions will be discussed:

[1] CO oxidation.
[2] Total oxidation of hydrocarbons.
[3] Reduction of NO.
[4] Reduction of N_2O.
[5] Selective oxidation of CO in an atmosphere of hydrogen, in relation to the development of polymer electrolyte fuel cell technology, using steam reforming or partial oxidation of gasoline, methanol or natural gas to produce hydrogen. CO oxidation is needed to reduce the CO concentration to acceptable levels. An efficient catalyst must be highly active in CO oxidation at temperature compatible with the operation of the PEM fuel cell (∼70 °C) and very selective to CO_2 formation.
[6] Selective oxidation of NH_3.

The oxidation of ammonia can proceed via three overall reactions:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \tag{3a}$$

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \tag{3b}$$

$$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O \tag{3c}$$

Reaction (3a) is the so-called Ostwald process used to produce nitric acid. Reaction (3b) is potentially an ideal technology to remove ammonia from waste gases and reaction (3c) for the production of N_2O.

2. Experimental and catalyst characterization

The catalysts are γ-alumina supported multicomponent catalysts consisting of gold (5 wt.%) and one or more base metal oxides. Various kinds of base metal oxides have been added to the noble metal including transition metal oxides (TMOs), rare earth metal oxides and (earth) alkali metal oxides.

Details of the preparation procedure were given elsewhere [17]. Briefly, the mixed oxides MO_x/Al_2O_3 or

Table 1
Characterization of gold-based catalysts

Sample	Au loading (wt.%)	d^{a}_{Au} (nm)	d^{b}_{Au} (nm)
Au/Al_2O_3	4.7	4.3 ± 0.1	5.5 ± 0.2
$Au/MnO_x/MgO/Al_2O_3$	4.5	<3	3.5 ± 0.2
$Au/CeO_x/Al_2O_3$	4.5	<3	4.5 ± 0.3
$Au/Li_2O/Al_2O_3$	4.0	3.3 ± 0.1	3.0 ± 0.2
$Au/Li_2O/CeOx/Al_2O_3$	4.6	<3	3.0 ± 0.1
$Au/Rb_2O/Al_2O_3$	4.2	7.0 ± 0.5	7.5 ± 0.1
$Au/Rb_2O/CeO_x/Al_2O_3$	4.5	<3	2.5 ± 0.3
$Au/CeO_x/ZrO_x/Al_2O_3$	3.2	<3	6.5 ± 0.1
$Au/ZrO_x/Al_2O_3$	3.2	3.1 ± 0.2	–

d^{a}_{Au}: average size of gold particles of fresh catalysts (XRD); d^{b}_{Au}: average size of gold particles of fresh catalysts (HRTEM).

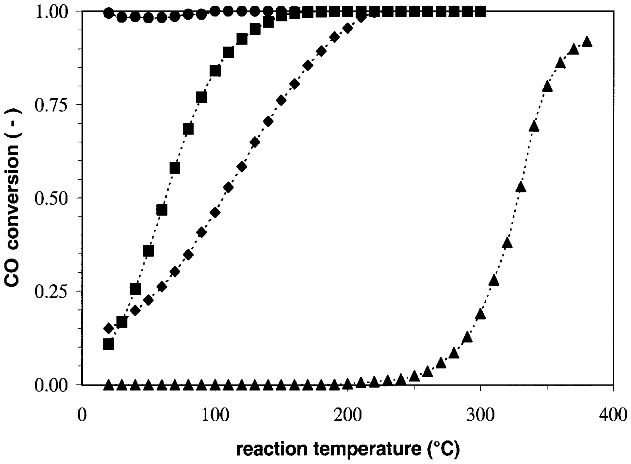

Fig. 1. CO conversion versus temperature ($CO:O_2 = 1:1$) over prereduced Au/Al_2O_3 (■), Au/Al_2O_3 calcined at 400 °C (◆), MnO_x/Al_2O_3 (▲) and $Au/MnO_x/Al_2O_3$ (●) (adopted from [21]).

$M^{I}O_x/M^{II}O_x/Al_2O_3$ were prepared by vacuum impregnation of γ-Al_2O_3 with the corresponding nitrates. For this purpose, the dehydrated γ-Al_2O_3 was impregnated under vacuum with a certain volume of an aqueous solution of the nitrates that corresponds to the pore volume of the amount of the support used. The intended M:Al atomic ratio has been set to 1:15. After drying and calcination at 350 °C, the mixed oxides were used as supports to deposit gold. 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. 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, diffuse reflectance UV–VIS spectroscopy and ^{197}Au-Mössbauer effect spectroscopy.

The reduction and oxidation reactions were carried out in a lab-scale fixed bed reactor. The feed gases were controlled by mass flow controllers. All the gases were 4 vol.% in He. The effluent stream was analysed on-line by mass-spectrometry and/or gas chromatography. The flow rate used was 40 ml min^{-1}, GHSV 2500 h^{-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.

The results of the various characterization methods suggest that the gold particles are mainly in the metallic state. The gold loading and the average particle size of some of the catalysts used in this study are summarized in Table 1.

3. Results and discussion

3.1. Oxidation of CO and hydrocarbons

New regulations in the United States, Japan and Europe will make it mandatory that automotive emissions decrease substantially from current levels. Therefore, 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 [18].

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 Figs. 1 and 2, which indicate the conversion of CO and propene over various types of alumina supported catalysts:

$$2\,CO + O_2 \rightarrow CO_2 \tag{4}$$

$$2\,C_3H_6 + 9O_2 \rightarrow 6CO_2 + 6H_2O \tag{5}$$

It is generally accepted that for CO oxidation a very strong size effect exists, small gold particles being more active than the bigger ones [2,3,10,15]. A similar size-dependency is found for C_3H_6 oxidation. For example, $Au/Rb_2O/Al_2O_3$, with a gold particle size of ~7 nm is significantly less active than the gold catalysts with smaller Au particles. In addition to the effect of the Au particle size on the catalytic activity of Au-based catalysts, another effect appears to be extremely important: the presence of certain types of additives. Figs. 1 and 2 clearly illustrate the presence of a large synergistic

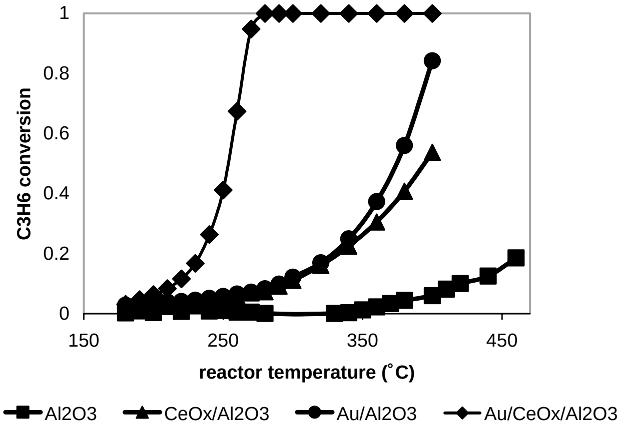

Fig. 2. Synergistic effect—oxidation of propene over γ-Al_2O_3, CeO_x/Al_2O_3, Au/Al_2O_3 and $Au/CeO_x/Al_2O_3$ (adopted from [13]).

effect, *i.e*. the multicomponent catalysts Au/MnO_x/Al_2O_3 and Au/CeO_x/Al_2O_3 are more active than the monocomponent ones. 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 [1–3,10,19–27]. A model for the large synergistic effect will be discussed in Section 4. It should be noted that γ-Al_2O_3 support itself is not active under the conditions used in the experiments shown in the Figs. 1 and 2.

3.2. Selective oxidation of CO in the presence of hydrogen

The hydrogen–air polymer electrolyte membrane (PEM) 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, i.e. reaction (4).

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 CO_2 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 H_2O formation:

$$2H_2 + O_2 \rightarrow 2H_2O \qquad (6)$$

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 (4) 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 [18].

Results reported in the literature show that CO can be oxidized in preference to hydrogen in the temperature range of 100–200 °C over Al_2O_3 supported Ru, Rh, and Pt catalysts [28–31]. 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 Al_2O_3 support with CO adsorbed on Pt [29]. For Pt catalysts an optimum in activity and selectivity was found at 200–250 °C [28,29]. At lower temperatures (desired temperature ~70 °C) CO oxidation is rather slow due to CO inhibition of oxygen adsorption.

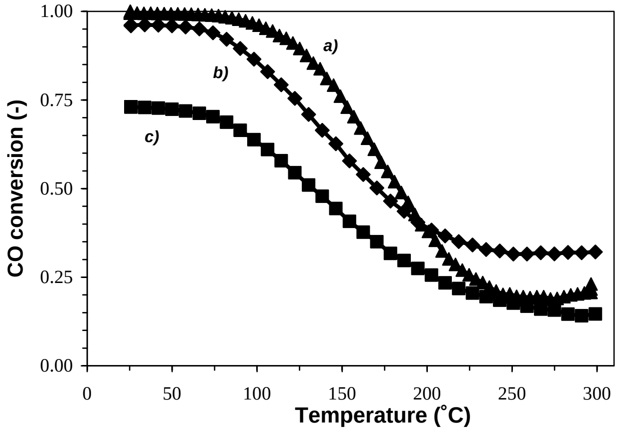

Fig. 3. CO conversion in hydrogen rich feed over Au/MgO/MnO_x/Al_2O_3 70 vol.% H_2 and CO + O_2 (1.2 vol.%) in helium (~29 vol.%); Au loading 5 wt.%; Au:Mg:Mn atomic ratio 1:5:5; (a) $\lambda = 4$, (b) $\lambda = 2$ and (c) $\lambda = 1$, $\lambda = ((O_2, \text{initial})/(2CO, \text{initial}))$ (adopted from [24]).

At higher temperatures the selectivity decreases because CO desorption enables hydrogen adsorption and oxidation.

We have studied SCO of CO over various multicomponent Au-based catalysts. Some of the results obtained over gold-based catalysts are summarized in the present paper. For more details see references [26] and [27].

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 [26,27,32].

Fig. 3 shows results obtained for Au/MgO/MnO_x/Al_2O_3 [27]. These experiments were performed in a mixture of H_2 (~70 vol.%) and O_2 + CO (1.2 vol.%) in helium (~29 vol.%) using three different O_2:CO molar ratios ($\lambda = 1, 2$ and 4). The parameter λ is defined as the concentration of O_2 in the feed divided by the concentration of O_2 needed to oxidize completely all the CO in the feed:

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

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 CO_2 selectivity. Similar effects have been reported for Pt/Al_2O_3, Ru/Al_2O_3 and Rh/Al_2O_3: an increase in hydrogen partial pressure leads to a significant lowering of the CO_2 selectivity [28–31]. The addition of MnO_x to Au/MgO/Al_2O_3 improves the CO conversion and CO_2 selectivity over the whole temperature range studied for all values of λ used [26,27].

Table 2
$T_{50\%}$ (N_2O/H_2) and $T_{50\%}$ and S_{N_2} (NO/H_2)

Catalyst	$N_2O:H_2$ (1:2)	$NO:H_2$ (1:1)	
	$T_{50\%}$ (°C)	$T_{50\%}$ (°C)	$S_{N_2}^{max}$, % (T, °C)
Au/Al_2O_3	111	74	74 (185 °C)
$Au/CeO_x/Al_2O_3$	56	73	74 (184 °C)
$Au/Li_2O/Al_2O_3$	75	43	82 (164 °C)
$Au/Li_2O/CeO_x/Al_2O_3$	52	39	86 (145 °C)

3.3. Reduction of NO and N_2O

The only NO reduction reactions discussed here are the reactions with hydrogen:

$$2NO + H_2 \rightarrow N_2O + H_2O \tag{8}$$

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O \tag{9}$$

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \tag{10}$$

$$N_2O + H_2 \rightarrow N_2 + H_2O \tag{11}$$

Supported gold catalysts convert nitric oxide in the presence of hydrogen to the following products: N_2O (at low temperature), N_2 (at intermediate temperature) and NH_3 (at high temperature). Nitrous oxide reduction over gold catalysts gives N_2 as the only N-containing product. The corresponding temperatures of 50% conversion obtained for both reactions are summarized in Table 2 for some selected catalysts. In addition, the maximum selectivity to N_2 and the temperature at which this maximum is reached are shown for the NO/H_2 reaction.

For both reduction reactions the catalytic activity of Au/Al_2O_3 is greatly enhanced by the oxidic additives.

In the absence of any reducing gas in the system no decomposition products of N_2O and NO were formed. It is suggested that the mechanism of N_2O reduction may involve hydrogen-assisted dissociative adsorption of N_2O to N_2 and O_{ads}. The adsorbed oxygen will then react with hydrogen to form water. The present results prove that reduction of N_2O to N_2 is enhanced in the presence of ceria. The presence of CeO_x might create new sites for N_2O dissociation at the gold/ceria interface. A striking result is that by addition of both an alkali metal oxide and CeO_x a dramatic increase in the catalyst performance is obtained. The main role of the alkali (earth) metal oxide is probably to prevent sintering of gold particles and the promoting effect increases with increasing basicity of the oxide [17].

For the NO/H_2 reaction the selectivity strongly depends on the reaction temperature and the nature of the support. A temperature below 100 °C favours N_2O formation; between 100 and 200 °C N_2 is the main product, and at higher reaction temperature, NH_3 is formed as a principal product. The $Au/Li_2O/CeO_x/Al_2O_3$ catalyst is very efficient in N_2O reduction and, hence, exhibits a higher selectivity to N_2 than Au/Al_2O_3. Again, possibly, hydrogen assists in NO decomposition. Based on the product distribution, it is suggested that at low temperature NO partly decomposes to N_2O and O_{ads}. At higher temperature, the amount of NO dissociatively adsorbed on the surface will increase and as a result, more N_2 will be produced via N combination. The atomic nitrogen might be hydrogenated in the presence of hydrogen to NH_x species and NH_3 is formed. The selectivity will then depend on the relative concentrations of adsorbed species on the surface, i.e. NO, N and NH_x. A similar mechanism has been established for PGM (Pt-group metals) [18,33]. The oxidic additives might create new sites for dissociative adsorption of NO.

Table 3
NH_3 oxidation by O_2: $T_{50\%}$, maximum selectivity to N_2 and N_2O, S_{N_2} and S_{N_2O} and d_{XRD}^{Au} (nm)

Sample	NH_3/O_2			d_{Au}^{a} (nm)
	$T_{50\%}$(°C)	S_{N_2} (%)	S_{N_2O} (%)	
Al_2O_3	>400	–	–	–
Au/Al_2O_3	>400	–	–	4.3 ± 0.1
$Au/CeO_x/Al_2O_3$	280	45	67	<3
$Au/Li_2O/Al_2O_3$	396	77	37	3.3 ± 0.1
$Au/Li_2O/CeO_x/Al_2O_3$	243	58	80	<3
$Au/CuO/Al_2O_3$	211	94	22	<3
CuO/Al_2O_3	268	99	–	–
$Li_2O/CeO_x/Al_2O_3$	>400	–	–	–

d_{Au}^{a}–average size of gold particles for fresh catalysts (XRD measurements).

3.4. NH_3 oxidation

Table 3 summarizes the $T_{50\%}$ (temperature needed for 50% conversion), the maximum selectivity towards N_2 and N_2O (the $S_{N_2}^{max}$ and $S_{N_2O}^{max}$ correspond to different temperatures) and the average gold particle size, d_{XRD}^{Au}, of some of the gold catalysts tested for NH_3 oxidation ($NH_3:O_2 = 1:1$). The obtained products were: N_2, N_2O and NO in different ratios. As a general trend, the catalysts that contain a TMO or an alkali metal oxide additive show a remarkable enhancement in catalytic activity.

The most active catalyst appears to be $Au/CuO/Al_2O_3$, with the oxidic additive (CuO) acting as co-catalyst. The activity and selectivity were very dependent on the type of support used. Together with $Au/CuO/Al_2O_3$, $Au/Li_2O/CeO_x/Al_2O_3$ is a very active catalyst for ammonia oxidation, but it produces large amounts of N_2O.

FT-IR studies showed that NH_3 adsorption might result in imide-like (–NH) adspecies, in addition to NH_4^+ (on Brønsted acid sites) and coordinated NH_3 (on Lewis acid sites) [34]. The presence of Au enhances the band intensity of imide-like adspecies, which may be responsible for the enhanced SCO activity in the presence of Au. The only exception is CuO/Al_2O_3 that shows significant SCO activity, but imide-like adspecies were not observed on this catalyst. The SCO on $Cu–Al_2O_3$ may occur via a different mechanism, for

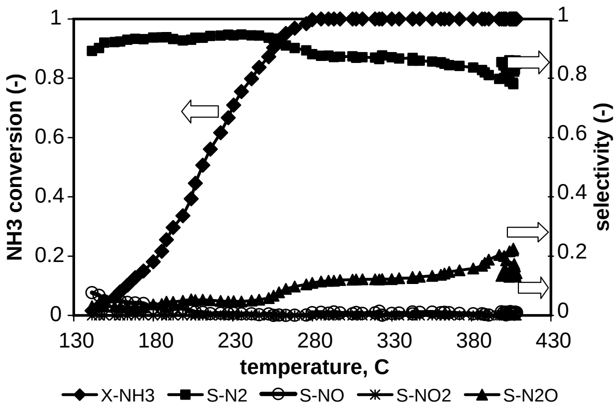

Fig. 4. NH_3 conversion versus temperature (NH_3:O_2 = 1, 2% NH_3 in He and 2%O_2 in He) over Au/CuO/Al_2O_3.

example via a Cu surface redox (or Mars and van Krevelen) mechanism [35]. The higher SCO activity of Au/Cu–Al_2O_3 compared to that of Cu/Al_2O_3 in ammonia oxidation may indicate a synergistic effect of Au-promoted imide-like intermediate and the reactivity of CuO-phase. An illustration of the behavior of Au/CuO/Al_2O_3 during ammonia oxidation is presented in Fig. 4.

Interestingly, the selectivity can be steered into the desired direction by using the right additives/cocatalysts. The Cu containing catalysts are highly selective to N_2 whereas the Au/Li_2O/CeO_x/Al_2O_3 catalyst is very selective to N_2O formation.

4. General discussion and conclusions

Large synergistic effects have been found by combining Au/Al_2O_3 with a transition metal oxide or ceria for all the reactions studied in our laboratory. One of the most efficient gold-based catalysts that we developed is based on alumina-supported combinations of Au, CeO_x and Li_2O. Our model is that for oxidation reactions most of the chemistry is taking place at the interface gold–CeO_x, i.e. the boundary region between Au and the partly reducible metal oxide that is accessible to the gas phase. The cocatalyst CeO_x can provide the O needed for oxidation reactions. This suggestion is consistent with literature data for CO oxidation on Au/TiO_2 [36]. The non-reducible alkali or alkali-earth metal oxide functions as a promoter. It enables the formation of small, highly dispersed, and thermally stable gold particles on γ-Al_2O_3. The exact role of the alkali or alkali-earth metal oxides has been speculated to be more than that of a structural promoter. Recent density functional theory calculations of Molina and Hammer [37] suggest that the role of MgO is twofold: (i) it acts as a structural promoter offering low coordinated gold sites; (ii) the oxide interacts with the adsorbates on the gold.

As a general conclusion, supported gold catalysts are highly active in both oxidation and reduction reactions. The selectivity can be steered into the desired direction by using the right additive.

Acknowledgements

The Netherlands organization for scientific research (NWO) is gratefully acknowledged for financial support, project numbers 99-037 and NOW–Russian–Dutch Research Cooperation 2002 #047-015-003.

References

[1] G.C. Bond, Catal. Today 72 (2002) 5.
[2] D.T. Thompson, Gold. Bull. 31 (1998) 111.
[3] G.C. Bond, D.T. Thompson, Catal. Rev. Sci. Eng. 41 (1999) 319.
[4] W.M.H. Sachtler, R.A. van Santen, Adv. Catal. 26 (1977) 69.
[5] J.H. Sinfelt, Catal. Sci. Technol. 1 (1981) 257.
[6] V. Ponec, G.C. Bond, Catalysis by metals and alloys, Stud. Surf. Sci. Catal. (1995) 95.
[7] F. Besenbacher, I. Chorkendorff, B.S. Clausen, B. Hammer, A.M. Molenbroek, J.K. Nørskov, I. Stensgaard, Science 279 (1998) 1913.
[8] http://www.bp.com/company_overview/technology/frontiers/fr04aug02/fr04leapavada.asp).
[9] M. Haruta, T. Kobayashi, H. Sano, N. Yamada, Chem. Lett. (1987) 405.
[10] M. Haruta, Catal. Today 36 (1997) 153.
[11] M. Haruta, CATTECH 6 (2002) 102.
[12] B.R. Cuenya, S.H. Baeck, Th.F. Jaramillo, E.W. McFarland, J. Am. Chem. Soc. 125 (2003) 12928.
[13] A.M. Venezia, L.F. Liotta, G. Pantaleo, V. La Parola, G. Deganello, A. Beck, Zs. Koppány, K. Frey, D. Horváth, L. Guczi, Appl. Catal. A 251 (2003) 359.
[14] T.V. Choudhary, D.W. Goodman, Top. Catal. 21 (2002) 25.
[15] R. Grisel, K.J. Weststrate, A.C. Gluhoi, B.E. Nieuwenhuys, Gold. Bull. 35 (2002) 39, references therein.
[16] G.Y. Wang, W.X. Zhang, H.L. Lian, D.Z. Jiang, T.H. Wu, Appl. Catal. A 239 (2003) 1.
[17] A.C. Gluhoi, M.A.P. Dekkers, B.E. Nieuwenhuys, J. Catal. 191 (2003) 197.
[18] B.E. Nieuwenhuys, Adv. Catal. 44 (1999) 49.
[19] G.J. Hutchings, Gold. Bull. 29 (1996) 123.
[20] M. Haruta, M. Date, Appl. Catal. A 222 (2001) 427.
[21] M.A.P. Dekkers, M.J. Lippits, B.E. Nieuwenhuys, Catal. Lett. 56 (1998) 195.
[22] M.A.P. Dekkers, M.J. Lippits, B.E. Nieuwenhuys, Catal. Today 54 (1999) 381.
[23] R.J.H. Grisel, P.J. Kooyman, B.E. Nieuwenhuys, J. Catal. 191 (2000) 430.
[24] R.J.H. Grisel, B.E. Nieuwenhuys, Catal. Today 64 (2001) 69.
[25] R.J.H. Grsiel, J.J. Slyconish, B.E. Nieuwenhuys, Top. Catal. 16–17 (2001) 425.
[26] R.J.H. Grisel, B.E. Nieuwenhuys, J. Catal. 199 (2001) 48.
[27] R.J.H. Grisel, C.J. Weststrate, A. Goossens, M.W.J. Crajé, A.M. van der Kraan, B.E. Nieuwenhuys, Catal. Today 72 (2002) 123.
[28] M. Watanabe, H. Uchida, H. Igarashi, M. Suzuki, Chem. Lett. 21 (1995) 21.
[29] M.J. Kahlich, H.A. Gasteiger, R.J. Behm, J. Catal. 171 (1997) 93.
[30] S.H. Oh, R.M. Sinkevitch, J. Catal. 142 (1993) 254.
[31] M.L. Brown, A.W. Green, G. Cohn, H.C. Anderssen, Ind. Eng. Chem. Res. 52 (1960) 841.

[32] R.H. Torres Sanchez, A. Ueda, K. Tanaka, M. Haruta, J. Catal. 168 (1997) 125.
[33] B.E. Nieuwenhuys, in: R.W. Joyner, R.A. Van Santen (Eds.), Elementary Steps in Heterogeneous Catalysis, Kluwer Publishers, 1993, 155 pp.
[34] S.D. Lin, A.C. Gluhoi, B.E. Nieuwenhuys, Catal. Today, in press.
[35] G. Ramis, L. Yi, G. Busca, M. Turco, E. Kotur, R.J. Willey, J. Catal. 157 (1995) 523.
[36] F. Bocuzzi, A. Chiorino, M. Manzoli, P. Lu, T. Akita, S. Ichikawa, M. Haruta, J. Catal. 202 (2001) 256.
[37] L.M. Molina, B. Hammer, Phys. Rev. Lett. 90 (2003) 206102.