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Catalysis Today 100 (2005) 49–54

CATALYSIS TODAY

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Chaos, oscillations and the golden future of catalysis

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Abstract

In this paper, three main activities of our research group in the past decade will be introduced:

(1) non-linear processes on surfaces, such as chaotic and oscillatory behaviour;
(2) the N-chemistry on noble metal surfaces;
(3) multi-component catalysts consisting of noble metals and metal oxides (MO).

Catalysis by gold will be discussed in some detail. Gold was formerly considered to be an uninteresting metal for catalysis. However, recent results suggest that there may be "a golden future" for gold-based catalysts. Progress in each of these fields will be discussed.

Keywords: Gold; Oscillations; Ammonia oxidation; Promoter; Additive; Ceria

1. Introduction

Over the past decades, heterogeneous catalysis has developed from a black box technology into a frontier area of modern physical science. It has been, in particular, surface science, with its powerful techniques of characterization, that has provided catalysis science with new concepts and insights into the mechanism of reactions at the molecular level. However, compared to, for example, molecular organic chemistry, our detailed understanding of catalytic mechanisms is still modest due to the complexity of surfaces of solid catalysts. A real catalyst usually contains several components and its surface composition and structure may change during the catalytic process. In situ techniques are now available that provide information on the catalyst surface under reaction conditions. The further development and improvement of in situ techniques will lead to a detailed understanding of heterogeneous catalytic reactions at the molecular level. Surface scientists usually utilize model catalysts with well-defined structure and composition. Catalytic reaction studies are carried out using these model catalysts and the catalyst surface is characterized before and after the reaction studies or in some cases in situ during the reaction.

The concept of "active sites" originally proposed by Hugh Taylor in 1925 is well established now. Research of, in particular, Somorjai showed that on metal surfaces, steps and kinks exhibit a very different activity than sites on terraces [1]. On oxide surfaces, defects also play a crucial role. The surface may be very mobile during reaction and its structure and composition may change during the reaction. Co-adsorption effects play a vital role in the catalytic action. Hence, understanding of mutual interaction effects of co-adsorbed species is of crucial importance. All these effects have a large effect on the kinetics and dynamics of surface reactions.

The approach used by the present authors is to study the same reactions on "real" supported catalysts and under low-pressure conditions on model catalysts. This approach has turned out to be very successful in understanding certain trends. As an example, we mention here the specific differences in behaviour of the various transition metals in various catalytic reactions [2].

The present paper will highlight some of our recent activities, in particular:

(1) the oscillatory behaviour of catalytic reactions [3–5];

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0920-5861/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.cattod.2004.12.022

(2) the N-chemistry on transition metal surfaces, in particular, the reduction of NO and N_2O, and the oxidation of NH_3 [6–9];
(3) catalysis by gold nanoparticles [10–13].

2. Non-linear behaviour of catalytic reactions over noble metal surfaces

The first observations regarding non-linear behaviour of NO_x ($x = 1$ and 1/2) reduction by hydrogen, both in the form of rate oscillations and spatio-temporal processes, have been reported by our group. The non-linear behaviour is manifested by oscillations in rate and selectivity on a macroscopic scale ($1\ cm^{-2}$) and spatio-temporal processes, such as diffusing reaction fonts and spirals observed by FEM/FIM and PEEM [3,4]. By means of synchrotron (fast and high resolution) XPS (with Baraldi et al. in Trieste), the composition of the surface layer was monitored in situ during an oscillatory cycle on Pt(1 0 0). Various N and O species have been detected on metal surfaces during NO reactions using fast XPS [7]. Based on in situ measurements, the mechanism of oscillatory behaviour on Pt(1 0 0) was elucidated [5].

Our interest was focused on understanding the phase shifts between oscillations of the partial pressures of the reactants and reaction products. As an example, Fig. 1 shows the oscillations of the partial pressures of N_2O, hydrogen and water during the reaction [14]:

$$N_2O + H_2 \rightarrow N_2 + H_2O \qquad (1)$$

For the related reaction:

$$N_2O + CO \rightarrow N_2 + CO_2 \qquad (2)$$

the products N_2 and CO_2 oscillate nearly in counter-phase and the reactants N_2O and CO produce counter-phase oscillations. Mathematical models were developed that can reproduce these phase shifts. Lateral interactions in the ad-layer play a crucial role. N_2O adsorption and decomposition are both affected by the decomposition product O_{ads}. In addition, N_2O influences the adsorption of CO and vice versa [15].

Future research in this field should be focused on understanding the lateral interaction of adsorbed species in detail. Clearly, in situ measurements are needed to learn the mechanism of non-linear behaviour of catalytic reactions.

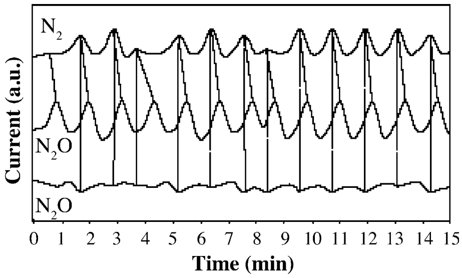

Fig. 1. Oscillations in the partial pressures of N_2O, H_2O and N_2 on Ir(1 1 0) surface at 460 K (N_2O pressure = 1×10^{-6} mbar; H_2:N_2O = 1.2; from [14]).

3. The N-chemistry on noble metal surfaces [6–8]—ammonia oxidation

Ammonia is oxidized via three overall reactions:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (3)$$

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad (4)$$

$$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O \qquad (5)$$

Reaction (3) is applied for the production of nitric acid, the Ostwald process. Reaction (4) is an attractive route to remove traces of the pollutant ammonia used for, for example, selective NO reduction in electricity plants. Possible mechanisms of the reactions (3)–(5) have been proposed in the literature. However, the mechanisms and, in particular, the selectivity are not understood.

In our project, the surface science approach is used to understand the selectivity, the differences in behaviour of the various metals and the influence of the surface structure. The decomposition and oxidation of NH_3 have been studied on the Ir(1 1 0), Ir(5 1 0), Pt(1 0 0) and Ru(0 0 0 1) surfaces. The activity and the selectivity of N_2 is higher on Ir(5 1 0) than on Ir(1 1 0) [6]. This enhanced reactivity may be due to the presence of Ir(1 0 0) terraces. Synchrotron XPS experiments were performed at ELETTRA/Trieste, using Ir(1 1 0) and Pt(4 1 0) [8]. Interestingly, five N component peaks were found. The temperature dependence and the comparison with the species found during the NO–H_2 reaction learn that the species are N, NH and various molecularly adsorbed NH_3 species. This confirms a mechanism based on stepwise dehydrogenation of NH_3. The thermal stability of these species in vacuum, in the presence of hydrogen and in the presence of oxygen was determined. During in situ measurements of ammonia oxidation, adsorbed NO was detected at $T < 550$ K. On the basis of the results, novel information is obtained regarding the mechanisms of reactions (3)–(5) [8].

Recently, we have developed gold-based catalysts with a very high selectivity towards one of the N-containing reaction products. These results will be briefly mentioned in Section 4.

4. The golden future of catalysis

Noble metal catalysts, in particular, Pt and Pd, have already been used for many years with major applications in the chemical and petroleum industry and, for 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 [16–18].

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 will be discussed now in more detail.

4.1. Bimetallic catalysts: gold—an inhibitor of undesired reactions

Many commercial catalysts are bimetallic or multi-component, or additives are used to improve their catalytic performance. The additives may act as promoters or inhibitors. Promoters are additives that improve the activity or the selectivity of the catalyst or increase the useful catalyst lifetime. Inhibitors are additives which are used to inhibit unwanted, chemical reactions and, hence, to improve the selectivity to the desired reaction or catalyst lifetime. This definition shows that the boundary between inhibitors and promoters is not always sharp. Inhibitors or promoters may also be formed during the catalytic reaction. As an example, a carbonaceous over-layer can be formed on the catalyst surface during a hydrocarbon reaction. This over-layer may greatly influence the catalyst performance. In particular, Sachtler and van Santen [19], Sinfelt [20], and Ponec and Bond [21] demonstrated that bimetallic systems exhibit major selectivity effects in catalysis. It was shown that the addition of a group IB metal (Cu, Ag, Au) to a group VIII metal results in a dramatic decrease in the activity of the latter for the rupture of C–C bonds in hydrogenolysis reactions of hydrocarbons. However, it has a much smaller effect on other hydrocarbon reactions, such as hydrogenation, dehydrogenation and isomerization of hydrocarbons. It had been realized that geometric factors play a crucial role in determining selectivity [19,21]. For some reactions, surface sites consisting of a number of adjacent active group VIII metal atoms are required. Other reactions, however, require sites consisting of just a few atoms, 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. In this context, it should be noted that bimetallic catalysts consisting of two group VIII metals are used for a number of important processes. Examples of commercial bimetallic catalysts include Pt–Rh and Pd–Rh based automotive three-way catalysts [2].

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:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (6)$$

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

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (7)$$

Undesired side reactions on the nickel catalysts used for steam reforming of methane results in coking, the formation of a graphitic over-layer 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 [22]. 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.

These studies also represent a great success of the fundamental surface science approach to heterogeneous catalysis.

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 have announced a new process for making vinyl acetate monomer from ethylene, acetic acid and oxygen using Pd/Au catalysts [23].

4.2. Gold-based catalysts with gold as active component

There are huge differences in the rates of catalytic reactions from metal to metal. When the activity of a given reaction is plotted versus, for example, the metal–oxygen bond strength or the heat of adsorption of oxygen, volcano-shaped curves are produced. This is directly related to the Sabatier principle or the Tanaka–Tamaru rule. For too weak adsorbate–surface bonds, the necessary bond-scission processes may be absent, or the ‘‘activation’’ of the adsorbed molecules is too weak. Hence, the reaction rate is low. If the surface bonds are too strong, the reaction intermediates block the adsorption of new reactant molecules and the reaction rate is low. For a good catalyst, the chemical bonds should be of intermediate strength, sufficiently strong to activate the adsorbed molecules and not too strong to assure short residence times of the intermediates and desorption of the reaction products. This requirement for intermediate bond strength results in volcano-shaped activity curves.

In the light of this consideration, the noble metal gold was believed to be too inert and, consequently, was considered to

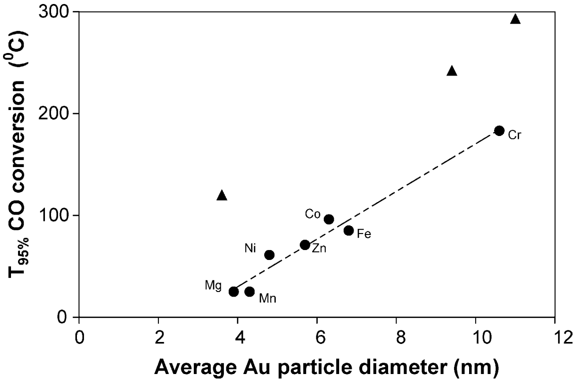

Fig. 2. Temperature needed for 95% CO conversion vs. the average gold particle size of Au/Al_2O_3 (▲) and $Au/MO_x/Al_2O_3$ (●) catalysts (from [11]).

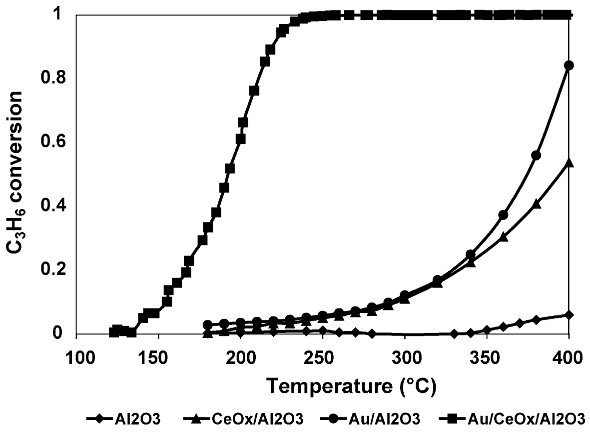

Fig. 3. Synergistic effect—oxidation of propene over γ-Al_2O_3, CeO_x/Al_2O_3, Au/Al_2O_3 and $Au/CeO_x/Al_2O_3$ (from [11]).

be an uninteresting metal from the point of view of catalysis. It was, therefore, an exciting discovery that nanoparticles of gold supported on metal oxides exhibit an extremely high activity for oxidation of CO at room temperature [24–26].

Fig. 2 illustrates the effect of the size of the gold particles and the large beneficial effect of MO_x addition (from [11]). The temperatures needed for 95% CO conversion ($T_{95\%}$) are plotted versus the average gold particle size. The figure summarizes the results obtained for seven multi-component $Au/MO_x/Al_2O_3$ and three mono-component Au/Al_2O_3 catalysts with an average gold particle size between 4 and 11 nm.

The results clearly demonstrate that small gold particles (<5 nm) are required for high activity. This observation is in line with other literature data [17,18,27–31]. 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 $Au/MnO_x/Al_2O_3$ catalyst with an average particle size of 4.2 ± 1.4 nm has a $T_{95\%}$ that is 100 °C lower than that found for Au/Al_2O_3 with an average particle size of 3.6 ± 1.4 nm. In fact, the CO conversion over $Au/MnO_x/Al_2O_3$ is higher at ambient temperature than the CO conversion over the Au/Al_2O_3 catalyst at 150 °C.

Since the initial studies, gold catalysis has become a rapidly developing topic of research. It has been demonstrated that gold-based catalysts exhibit catalytic activity for a wide range of different reactions including NO_x ($x = 1$ and 1/2) reduction, CO and CO_2 hydrogenation, NO oxidation, water gas shift reaction, alkene epoxidation, total oxidation of hydrocarbons and selective oxidation of CO and hydrocarbons. For comprehensive reviews on gold catalysis, we refer to [11,24,25].

At present, the commercial use of gold-based catalysts is still limited. It has been reported that gold catalysts are used for elimination of bad smells in toilets. The field of gold catalysis is currently undergoing an exciting period of discovery.

The interest in gold catalysis is a great stimulant for scientists in academia to focus their research on fundamental aspects of catalysis by gold: the role of the particle size, the effect of the partly reducible oxidic additive and of the promoters, the active site or the nature of the active species and, on the understanding of gold chemistry, in general.

In the laboratories of the authors, the research on catalysis by gold is focused on understanding of the fundamentals of gold catalysis: the effect of the gold particle size, the role of the partly reducible oxidic additive, the role of alkali and alkali-earth metal additives, the large synergistic effects found by combining gold and a transition metal oxide or ceria. Fig. 3 illustrates the presence of a huge synergistic effect. It shows the conversion of propene over three types of alumina-supported catalysts, viz. CeO_x/Al_2O_3, Au/Al_2O_3 and a multi-component catalyst consisting of both Au and CeO_x, $Au/CeO_x/Al_2O_3$:

$$2C_3H_6 + 9O_2 \rightarrow 6CO_2 + 6H_2O \quad (8)$$

For both gold catalysts, the average particle size is 3.0 nm. Clearly, the multi-component catalyst is much more active at low temperatures than the mono-component ones. The presence of such a synergistic effect has been reported before for highly dispersed gold catalysts supported on partly reducible oxides, such as FeO_x, CoO_x, TiO_x and MnO_x for a number of reactions [11]. Various reactions are studied in our laboratory including selective oxidation of CO in an atmosphere of hydrogen (in relation to the removal of traces of CO needed for the development of PEM fuel cells), oxidation of hydrocarbons, reduction of nitrogen oxides, selective oxidation of ammonia.

A synergistic effect, such as that illustrated in Fig. 3 has been found for all the reactions studied in our laboratory. One of the most efficient gold-based catalysts in both oxidation and reduction reactions that we have developed is based on alumina-supported combinations of Au, CeO_x and Li_2O. It was found that ceria plays a crucial role as a co-catalyst: it can supply oxygen whereas Li_2O acts as a promoter [13,32]. Our model is that most of the chemistry is taking place at the interface of gold and the partly reducible oxide CeO_x. Recent surface science studies of Freund support this model [33]. 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 [34] suggest that the role of MgO is two-fold: (i) it acts as a structural promoter offering low coordinated gold sites; and (ii) the oxide interacts with the adsorbates on the gold.

Interestingly, the catalytic behaviour of gold-based catalysts in NH_3 oxidation can be steered in the desired direction by using the right additive [35]. The gold catalyst with ceria and Li_2O exhibits a high catalytic activity and is very selective towards N_2O (80% at 400 °C). Other gold-based catalysts display a completely different selectivity towards the reactions (3)–(5) [35]. Hence, the product distribution depends on the nature of the additive.

At first glance, this high activity of gold-based catalysts seems in contradiction to the Sabatier principle. Hence, two questions of essential importance are: (1) what is the active site; and (2) what is the mechanism of the reaction. How are the molecules ‘‘activated’’?

Recent investigations have been directed towards elucidation of these questions. Models proposed to explain the high activity of gold-based catalysts include:

(1) the presence of specific sites present on gold nanoparticles, such as coordinatively unsaturated gold surface atoms or the existence of strain for metallic gold nanoparticles;
(2) an altered electronic structure of nanoparticles;
(3) the presence of ionic gold species;
(4) sites at the gold–oxide interface.

It has been suggested that the Au/MO_x perimeter defined as the boundary between Au, the oxide support MO_x and the gas phase may be crucial for activation of adsorbed molecules. It has also been suggested that the reaction solely takes place on the Au/MO_x perimeter with the dissociated oxygen atoms needed originating from MO_x. Our recent results show that CO and C_3H_6 can be oxidized over Au/CeO_x/Al_2O_3 in the absence of O_2 in the gas phase [13,32]. Hence, ceria can provide the oxygen needed for the oxidation reaction.

In addition to studies using ‘‘real’’ catalysts, well-defined gold-based ‘‘model’’ catalysts have been examined in a surface science oriented project. The intrinsic properties of gold surfaces have been investigated by using single crystal surfaces. We found that the reconstruction of Au(1 0 0) is lifted by NO at low temperature [36]. The reconstructed Au(1 0 0) surface is shown in Fig. 4 (from [37]).

For detailed studies of the chemical/catalytic properties of gold, the stepped Au(3 1 0) surface was selected. It turned out that the chemistry of gold is very rich at low temperatures. Our XPS and MS–TPD results show that NO decomposes on Au(3 1 0) at temperatures as low as 80 K and forms N_2O_{ads} and O_{ads} on the surface [38]. The N_2O formed desorbs around 160 K and O remains on the surface. These results prove the important role of steps in the reactivity of gold. Fig. 5 illustrates the interaction of NO with Au(3 1 0) [38].

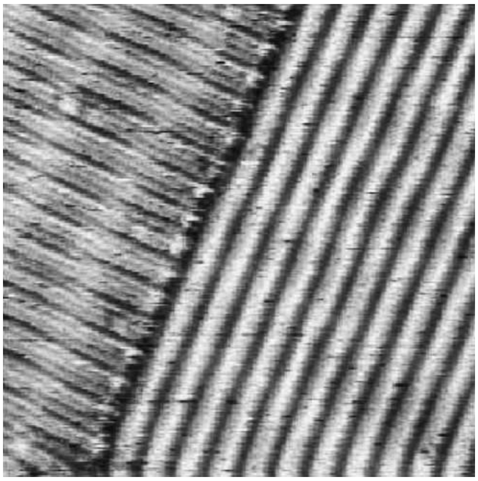

Fig. 4. A 26 nm × 26 nm STM image of hex reconstructed Au(1 0 0). Two different rotational domains of the hex reconstruction on a single terrace are imaged [37].

It is clear that essential knowledge on the mechanism of gold catalysis is still lacking. The increasing interest in gold catalysis has stimulated fundamental research. Hence, in the next decade, our knowledge on gold catalysis—the active site, the mechanism, the role of the particle size, the support/additive will increase and the results will lead to more practical applications. The authors are confident that the future of gold catalysis will be bright.

Possible catalytic applications being explored are abatement of pollutants from exhaust gases of automobiles, eliminations of VOCs, dioxins, ozone, nitrogen oxides, selective oxidation and reduction processes and in ‘‘fine chemistry’’ for production of desired products with high selectivity. Their low temperature CO oxidation activities may lead to the possible application of gold-based catalysts in fuel cells to eliminate traces of CO from hydrogen-rich mixtures produced by steam reforming of fuel, in gas sensors

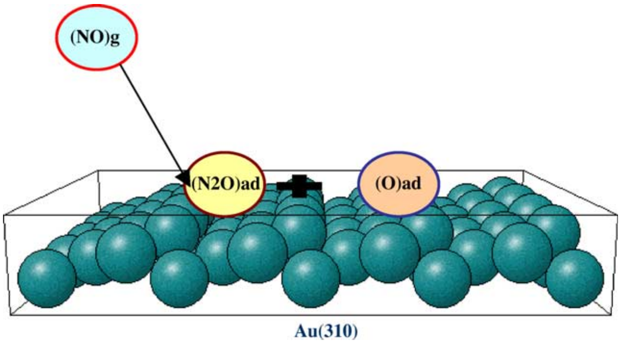

Fig. 5. NO interaction with Au(3 1 0) (from [38]).

and as a start-up automotive catalysts, because of the short warm-up period required to heat the catalyst to the temperature at which it becomes effective.

Acknowledgments

The Netherlands Organization for Scientific Research, NWO (Grants NWO/CW #99037 and NWO #047.015.003) are gratefully acknowledged for financial support.

References

[1] G.A. Somorjai, Chemistry in Two Dimensions: Surfaces, Cornell University Press, Ithaca, NY, 1981.

[2] B.E. Nieuwenhuys, Adv. Catal. 44 (1999) 259.

[3] C.A. de Wolf, B.E. Nieuwenhuys, Catal. Today 70 (2001) 287.

[4] S.A.C. Carabineiro, W.D. van Noort, B.E. Nieuwenhuys, Surf. Sci. 532 (2003) 96.

[5] A. Baraldi, et al., in preparation.

[6] S.A.C. Carabineiro, B.E. Nieuwenhuys, Surf. Sci. 532 (2003) 87.

[7] E.D.L. Rienks, J.W. Bakker, A. Baraldi, S.A.C. Carabineiro, S. Lizzit, C.J. Weststrate, B.E. Nieuwenhuys, Surf. Sci. 532 (2003) 120.

[8] C.J. Weststrate, E.D.L. Rienks, J.W. Bakker, C.P. Vinod, A. Baraldi, S. Lizzit, B.E. Nieuwenhuys, in press.

[9] S.A.C. Carabineiro, F.M.F. de Groot, L. Kjeldgaard, J.E. Rubensson, B.E. Nieuwenhuys, Surf. Rev. Lett. 11 (2004) 385.

[10] A.C. Gluhoi, M.A.P. Dekkers, B.E. Nieuwenhuys, J. Catal. 219 (2003) 197.

[11] R.J.H. Grisel, C.J. Weststrate, A.C. Gluhoi, B.E. Nieuwenhuys, Gold Bull. 35 (2002) 39, and references therein.

[12] A.C. Gluhoi, S.D. Lin, B.E. Nieuwenhuys, Catal. Today 90 (2004) 175.

[13] A.C. Gluhoi, N. Bogdanchikova, B.E. Nieuwenhuys, J. Catal. 229 (2005) 159.

[14] S.A.C. Carabineiro, B.E. Nieuwenhuys, Surf. Sci. 495 (2001) 1.

[15] N.V. Peskov, M.M. Slinko, S.A.C. Carabineiro, B.E. Nieuwenhuys, Catal. Today, submitted for publication.

[16] G.C. Bond, Catal. Today 72 (2002) 5.

[17] D.T. Thompson, Gold Bull. 31 (1998) 111.

[18] G.C. Bond, D.T. Thompson, Catal. Rev. Sci. Eng. 41 (1999) 319.

[19] W.M.H. Sachtler, R.A. van Santen, Adv. Catal. 26 (1977) 69.

[20] J.H. Sinfelt, Catal. Sci. Eng. 1 (1981) 257.

[21] V. Ponec, G.C. Bond, Stud. Surf. Sci. Catal. 95 (1995).

[22] F. Besenbacher, I. Chorkendorff, B.S. Clausen, B. Hammer, A.M. Molenbroek, J.K. Norskov, I. Stensgaard, Science 279 (1998) 1913.

[23] http://www.bp.com/company_overview/technology/frontiers/fr04aug02/fr041eapavada.asp.

[24] M. Haruta, Cattech 6 (2002) 102.

[25] G.C. Bond, D.T. Thompson, Gold Bull. 33 (2000) 41, and references therein.

[26] M. Haruta, T. Kobayashi, N. Yamada, Chem. Lett. 2 (1987) 405.

[27] M. Haruta, Catal. Today 36 (1997) 153.

[28] M. Haruta, M. Date, Appl. Catal. A 222 (2001) 427.

[29] S.K. Tanielyan, R.L. Augustine, Appl. Catal. A 85 (1992) 73.

[30] M. Valden, S. Pak, X. Lai, D.W. Goodman, Catal. Lett. 56 (1998) 7.

[31] S. Tsubota, T. Nakamura, K. Tanaka, M. Haruta, Catal. Lett. 56 (1998) 7.

[32] A.C. Gluhoi, H.S. Vreeburg, J.W. Bakker, B.E. Nieuwenhuys, Appl. Catal. A, in press.

[33] H. Freund, Invited lecture Gold 2003.

[34] L.M. Molina, B. Hammer, Phys. Rev. Lett. 90 (2003) 206102.

[35] S.D. Lin, A.C. Gluhoi, B.E. Nieuwenhuys, Catal. Today 90 (2004) 3.

[36] E.D.L. Rienks, G.P. van Berkel, J.W. Bakker, B.E. Nieuwenhuys, Surf. Sci. 571 (2004) 187.

[37] E.D.L. Rienks, Ph.D. thesis, Leiden University, 2004.

[38] C.P. Vinod, J.W. Niemantsverdriet, B.E. Nieuwenhuys, Appl. Catal. A, in press.