Catalysis Today 181 (2012) 26–32

Contents lists available at SciVerse ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

# Gold catalysis: Effect of particle size on reactivity towards various substrates

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ARTICLE INFO

*Article history:*
Received 15 March 2011
Received in revised form 22 July 2011
Accepted 17 August 2011
Available online 9 December 2011

*Keywords:*
Gold catalysis
Single crystal
Nanoparticle
Size effect

ABSTRACT

In this contribution the general rules and the exceptions in the area of gold catalysis are discussed in order to establish a correlation between the size of the catalytically active element and its reactivity towards different classes of substrate molecules. The general behaviour of gold is that it is inactive in massive form while it can be used as a highly active catalyst when downsized. Throughout this paper experimental data from different sources are collected to proof that – according to this general behaviour – small molecules (CO, NO, etc.) can be activated only on small nanoparticles or roughened Au(1 1 1) surfaces, whereas Au(1 1 1) single crystals or extended metal films are active in the reaction of large molecules. This observation defines the applicability area of gold nanoparticles and the activity of large gold surfaces, films or single crystals.

The above effect can be modulated by interfacial interaction between gold species and active oxide either if gold is deposited directly on them or is supported on inactive oxides (such as model $SiO_2$/Si(1 0 0) or high surface area amorphous or mesoporous silica) with minute amounts of promoter oxide. The oxide may invoke electronic interaction and simultaneously the defect structure of oxides likely has a key issue in the formation and stabilization of Au nanoparticles.

On the other hand, it turned out that in some cases – independently of the interface – the key issue is the available gold area of Au nanoparticles dictating the reaction rate of a substrate.



## 1. Introduction

Investigation of small metallic particles in the 1–10 nm size range is a very active area in solid state physics and chemistry. Studies on these systems provide information about the development of the electronic structure of materials in the size range between isolated atom and bulk solid. Knowledge on size dependence of the electronic structure is very important in order to understand the enhanced catalytic activity and the special optical or magnetic properties observed in small particles.

Research on metal nanoparticles has long been pursued. Among the most spectacular results is the case of gold which was found to be an inert metal in massive form, while reactivity of gold nanoparticles, e.g. activity in catalysis, was greatly enhanced. This behaviour was observed very consistently from the early, pioneering works in reactions involving small molecules such as $H_2$, CO, $O_2$ and $CO_2$. Although this general rule states that the prerequisite for catalytic activity is the particle size diminished to the nanometric range, there are examples for reactions which are catalyzed by extended gold structures, involving even single crystal surfaces.

These exceptions are in the primary focus of this contribution. An extensive literature survey is presented, in order to establish a correlation between the size of the catalytically active gold structure and the properties of the class of molecules which can be transformed over the given gold structure. This correlation allows identification of the applicability range of gold-containing catalysts with active elements of various size ranging from nanoparticles to single crystals or films, pointing out which aspects of the electronic structure of the catalyst play a role in defining its activity in a given type of reaction.

Consequences of interfacial interaction between gold catalysts and oxide supports are often the deciding factors determining the performance of a given catalyst. A brief account on these issues will also be given, with particular emphasis on processes involving large reactant molecules.

## 2. Pioneering observations

Pioneering works by Galvagno and associates [1–3] dealt with the preparation of silica and magnesia supported gold catalysts by wet impregnation or ion-exchange techniques. The gold size was below 10 nm. Oxygen adsorption was found to take place at 200 °C at 3 mbar pressure with a stoichiometry corresponding to Au/O = 2. As the temperature increased from 200 to 400 °C, the adsorption

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0920-5861/$ – see front matter © 2011 Published by Elsevier B.V.
doi:10.1016/j.cattod.2011.08.037

became reversible [1]. In isotopic exchange reaction of molecular oxygen supported gold presented high activity and massive uptake of labelled oxygen by the solid phase. Au/MgO was one order of magnitude more active than $Au/SiO_2$. The activation of support oxygen for the isotopic exchange reaction was related to an interaction between gold and support [1].

$SiO_2$, $Al_2O_3$ and MgO supported gold was active in NO reduction by $H_2$, there was an effect of the support on the reaction selectivity to $N_2$.

Ru–Au bimetallic catalysts supported on $SiO_2$ and MgO were also intensively studied [4]. For $RuAu/SiO_2$ chemisorption and XPS experiments showed a surface composition similar to the bulk. Interestingly, Ru surface enrichment was observed in Ru–Au bimetallic particles supported by MgO [5]. The XPS and hydrogen chemisorption data showed that the fraction of surface Ru atoms enhanced on decreasing the bulk Ru/Au atomic ratio. These conclusions were also supported by an IR study of CO chemisorbed on the same samples. It was suggested that the strength of the metal–support interaction can affect the surface composition of multimetallic supported systems. In the reduced Au/MgO there is a relevant amount of Au(III)–O and possibly Au(I)–O bonds (approximately 70% Au metal and 30% Au oxides), thus suggesting that a Au/MgO interaction occurs.

In hydrogenolysis of propane and ethane the activity of silica supported ruthenium decreased by two orders of magnitude with addition of gold [4]. However, the activity for the oxygen transfer between $^{14}CO$ and $CO_2$ on Au/MgO sample was two orders of magnitude higher than that of the Ru/MgO and AuRu/MgO samples. The affinity of the Au surface for oxygen increased with decreasing particle size. The degree of dispersion of Au was found to influence the rate of the catalytic reaction [3]. The effect of the addition of Au to Ru/MgO on the rate of reaction between cyclopropane and hydrogen was also measured. Increased activity related to one surface Ru atom was observed on gold containing samples [6], while Au/MgO was found to be inactive up to 350 °C.

Galvagno and Parravano also tested the bimetallic samples (Pt–Au) [7] supported on $SiO_2$. The rate of the $^{14}C$ equilibration between benzene and cyclohexane was found to be independent of surface composition of the Au–Pt particles for samples with total metal content constant, while for samples with increasing gold content the rate increased upon addition of Au to Pt. They explained the behaviour of the latter samples by the Au–Pt interaction, responsible for the enhancement of the reactivity of Pt.

The conclusion concerning this early stage of employing gold is that on small (up to 10 nm size) nanoparticle molecules such as oxygen, CO, hydrogen and NO, easily interact with gold surface, even if a larger molecules (e.g. cyclohexane) is adsorbed sidewise. On the contrary, hydrogenolysis of hydrocarbons including cracking is prevented by gold if bimetallic $RuAu/SiO_2$ catalyst is used.

## 3. Mystery of gold in bimetallic catalysts: diluent or active component

As was indicated in the previous part gold nanoparticles (in the range of 5–10 nm) were found always active in some hydrocarbon reactions, in NO hydrogenation and in oxygen isotope equilibration, but some groups observed controversy in the behaviour.

The role of gold in bimetallic catalysts was disputed from the early days. It may act as an inert diluent, causing the change of the ensemble site size. On the other hand, gold may also be involved in the reaction in a more direct way. The answer is still not a unique one, as it turns out from studies on bimetallic nanoparticles or single crystal model catalysts. In this section we highlight reactions which used bimetallic single crystal or thin film catalysts.

Epitaxial gold layers decreased the activity of the Pt(1 1 1) surface in skeletal transformation of n-hexane in proportion to the gold coverage because of the reduction of the available platinum surface area, without substantial selectivity changes. When surface alloys having smaller Pt ensembles were formed by heat treatment of epitaxial Au layers on Pt(1 1 1), it became more active than pure Pt(1 1 1) [8]. Large increases in the isomerisation rate of n-hexane and simultaneous exponential decrease of hydrogenolysis and aromatization rates with increasing gold concentration led to high selectivity for isomerisation. These effects are caused by changes in the bonding of organic molecules that are induced by structural alterations of the Pt(1 1 1) single-crystal surface.

Cyclohexane dehydrogenation was investigated on the Au–Pt(1 1 1) surface alloys as catalysts [9]. Benzene production was found to be strongly enhanced by Au, reaching a maximum at a surface composition of 50 atom% Au and declining thereafter. The Pt(1 1 1) crystal face did not produce detectable amounts of cyclohexene, its formation by the single crystal being completely attributable to the crystal edges. The addition of gold to the Pt(1 1 1) surface also induced production of cyclohexene. Surfaces containing about 90 atom% Au were the most active. Somorjai is undoubtedly true as the various surface reactions are affected in various ways. The gold as inert component was assumed to decrease the Pt ensemble size if added in increasing amount. However, we may not exclude the role of large Au domains for the reaction.

The picture becomes more complicated when Pt–Au alloy films is subjected to investigation in H/D exchange in cyclopentane [10]. At 350 °C sintered films are composed of two phases: a Pt-rich phase (97% Pt) and an Au-rich phase (18% Pt). The surface of the films is formed by the Au-rich phase for all concentrations within the miscibility gap (97–17% Pt). For higher gold concentration the Pt content in the surface decreases below that of the Au-rich phase. The authors compared the changes of cyclopentane-$d_1$ and cyclopentane-$d_{10}$ species as a function of Pt content. The $d_1$ species dominate at very diluted Pt content which proves that multiple C–H bond forms only on Pt surface site. According to the authors it is difficult to arrive at definite conclusion on Pt–Au films. The most likely explanation is that gold is not active in the C–H bond rupture, rather it affects by changing the size of the platinum active site (geometrical approach). As one will see later hydrogen adsorption takes place on supported alloys.

On the contrary to the behaviour of single crystal and film, in which in most cases the reaction rate was enhanced with addition of gold, the nanoparticles affects the reaction differently.

Skeletal reactions of neopentane (geometrically different from cyclohexane) have been studied over a range of supported platinum–gold catalysts [11]. The rate also rose with increasing gold content. Here gold is considered as an inert diluent and the behaviour is interpreted in terms of two different reaction mechanisms which require different types of active sites. Here again there is an activity increase with gold content which could be one of the active sites for the neopentane.

Isomerization, dehydrocyclisation and hydrogenolysis reactions of n-pentane and n-hexane were also studied on supported Pt and Pt–Au alloys [12]. By increasing the gold content there are various mechanisms operating. Characteristic changes in selectivity towards the different reactions were observed when Pt was compared with alloys in various composition ranges. From the comparison of the n-pentane and n-hexane reactions it is possible to suggest a self-consistent picture of the mechanisms involved. For the alloys the reaction mainly proceeds via a one-site isomerisation mechanism. Catalysts are comparable to small particle catalysts and show cyclisation and isomerisation mainly via a cyclic mechanism. On small Pt–Au particles the hydrogen adsorption also plays important role [13]. Hydrogen adsorption data on highly dispersed

Pt–Au catalysts of wide range of composition led to the conclusion that equilibrium surface enrichment by gold was achieved. At higher pressures, some hydrogen could be adsorbed on surface gold atoms, probably as a result of spillover from the platinum component. The temperature programmed desorption (TPD) profiles on platinum–gold were independent of gold content; to a first approximation the gold acted as an inert diluent. The implications of this result for the mode of hydrogen chemisorptive bonding are discussed.

Somorjai and coworkers studied the gold–palladium nanoparticles in CO oxidation using highly sophisticated experimental technique [14]. Au–Pd nanoparticles (8–11 nm in diameter) in various compositions were synthesized by using colloidal chemistry. The characterization showed that the as synthesized AuPd (with 0.25 and 0.5 gold atomic ratio) bimetallic species had gradient alloy structures with Au-rich cores and Pd-rich shells. The simultaneous composition and structure in the surface region (2–3 layers to the bulk from the particle surface) were studied with ambient pressure-XPS under $CO/O_2$ reaction in the mbar pressure regime. Under the reaction at 200 °C the surface region was Au-rich (~70% by Au). All $Au_xPd_{1-x}$ ($x = 0.25$, 0.5, 0.75) nanoparticle catalysts had higher turnover rates for the model $CO/O_2$ reaction than pure Pd and pure Au nanoparticles. The Pd-rich Au–Pd nanoparticles showed the highest turnover rates. Interestingly, the Au-rich Au–Pd nanoparticles exhibited steady-state turnover rates which are intermediate to those of the Pd-rich bimetallic nanoparticles.

Supported gold, palladium and gold–palladium catalysts have been used to oxidatively dehydrogenate cyclohexane and cyclohexenes to their aromatic counterpart [15]. The authors found that the order of reactivity was Pd ≥ Au–Pd > Au supported on $TiO_2$. Attempts were made to lower the reaction temperature while retaining high selectivity. Increasing the temperature in this case improved conversion at a detriment to the benzene selectivity. Oxidative dehydrogenation of cyclohexene over Au–Pd/$TiO_2$ or Pd/$TiO_2$ catalysts was found to be very effective. These results indicated that the first step in the reaction sequence of cyclohexane to cyclohexene was the slowest step. These initial results suggest that in a fixed-bed reactor the oxidative dehydrogenation in the presence of oxygen, palladium and gold–palladium catalysts are readily able to surpass current literature examples and with further modification should yield even higher performance.

## 4. Gold nanoparticles versus large gold crystal face

As is obvious from the previous part, gold in form of small nanoparticles has unique properties. Accordingly, gold has a uniquely high catalytic activity in, e.g. CO oxidation and other reactions found by Haruta [16] and many authors as reviewed in numerous publications like in Refs. [17–19]. The previous works assumed that gold is an inert diluent in platinum and palladium and the result was the testing of ensemble and ligand sites. First Ponec called our attention that the practical catalysts consist of very small particles and its behaviour is different from large alloy particles [20].

In this part we try to call the attention of the reader for the difference of the two types of gold species.

When gold is downsized there is a drastic change in the physical properties, primarily in the electronic structure which has been already summarized [21,22]. This was indicated by the valence band spectra measured by UPS [23]. As the gold size diminished the peak at 2 eV in the UPS spectra disappeared. Similar effect could be observed in the core level X-ray photoelectron spectra indicated by a shift of 0.5 eV in the binding energies towards the higher energies. By high temperature treatment the particle size of gold increased, electronic structure typical of bulk gold restored accompanied with diminished rate of reaction in CO oxidation.

On the other hand, on Au(1 1 1) single crystal surface there is no reaction as CO chemisorption does not take place. To adsorb CO on the Au(1 1 1) surface high CO pressures (>1 mbar) are needed, but adsorption drives surface restructuring and roughening [24]. CO adsorption on the well-annealed Au(1 1 1) surface is largely suppressed. It was demonstrated that CO adsorption on the Au(1 1 1) surface can be increased by controlling the length of steps and that the weakly adsorbed CO induces irreversible morphological changes of the surface. Introducing surface defects drastically increases the amount of adsorbed CO. The gold surface patterned by one atomic layer deep vacancy islands reveals a significant increase in the overall number of monatomic steps.

Similar results were obtained on studying CO adsorption by means of sum frequency generation technique [25–27]. When modelling gold catalysts, one usually encounters with difficulties related to the general inertness of the single crystalline Au faces. Nevertheless, this surface still can be used as a starting point for a model catalyst, if some structural complexity is introduced by an appropriate surface modification as described [26]. In this paper the CO adsorption properties of an Au(1 1 1) single crystal surface modified by ion bombardment were investigated by photoelectron spectroscopy, sum frequency generation vibrational spectroscopy and scanning tunnelling microscopy in pressures ranging from ultrahigh vacuum to 1 mbar.

According to STM images (Fig. 1), sputtering transformed the surface into a three dimensional structure with pit and mound-like elements. The ion bombardment increased the density of steps significantly, while the typical terrace width was considerably reduced, especially at the side walls of the pits and mounds. Nevertheless, still (1 1 1) terraces remained the dominant morphological elements.

Spectroscopic evidence such as work function measurements, UPS and XPS experiments confirmed the formation of stable CO adsorbates on the roughened surface at low temperatures, which completely desorbed around 190 K. The UPS measurement suggested an electronic interaction between the CO adsorbates and the substrate surface states (Fig. 2). Vibrational spectra showed that CO adsorbs on top of Au atoms leading to a coverage-dependent frequency around 2120–2110 $cm^{-1}$ (Fig. 3). Estimation of the adsorbed CO amount from XPS data and statistics of the morphological elements created by sputtering derived from STM images revealed a very strong correlation between the surface density of the CO adsorbates and the number of Au atoms belonging to step edges, corroborating that step edge sites are responsible for the CO binding capacity of the bombarded Au(1 1 1) surface. Computational studies by density functional theory confirmed the role of the low coordinated Au atoms in CO adsorption and suggested a correlation between the coordination number of the binding site and the CO stretching frequency.

The ion bombardment roughened Au(1 1 1) surface was found to spontaneously relax towards the atomic order of the smooth surface even below room temperature. Our spectroscopic investigations as well as STM measurements (Fig. 1) provided evidence for the significant acceleration of this reordering in the presence of CO, which leads to the gradual elimination of the CO binding sites. A positive correlation was established between the reordering kinetics and the applied CO pressure.

An alternate way to introduce complexity into a model catalyst is to deposit a thin layer of oxide onto a smooth metal substrate resulting in a so-called inverse catalyst. Indeed, the properties of Au(1 1 1) single crystal, i.e. its high activity in converting larger molecules, can be fully changed if using patches of a decorating oxide [28]. A good example is the water–gas shift reaction (WGS) which is an important reaction for the production of molecular

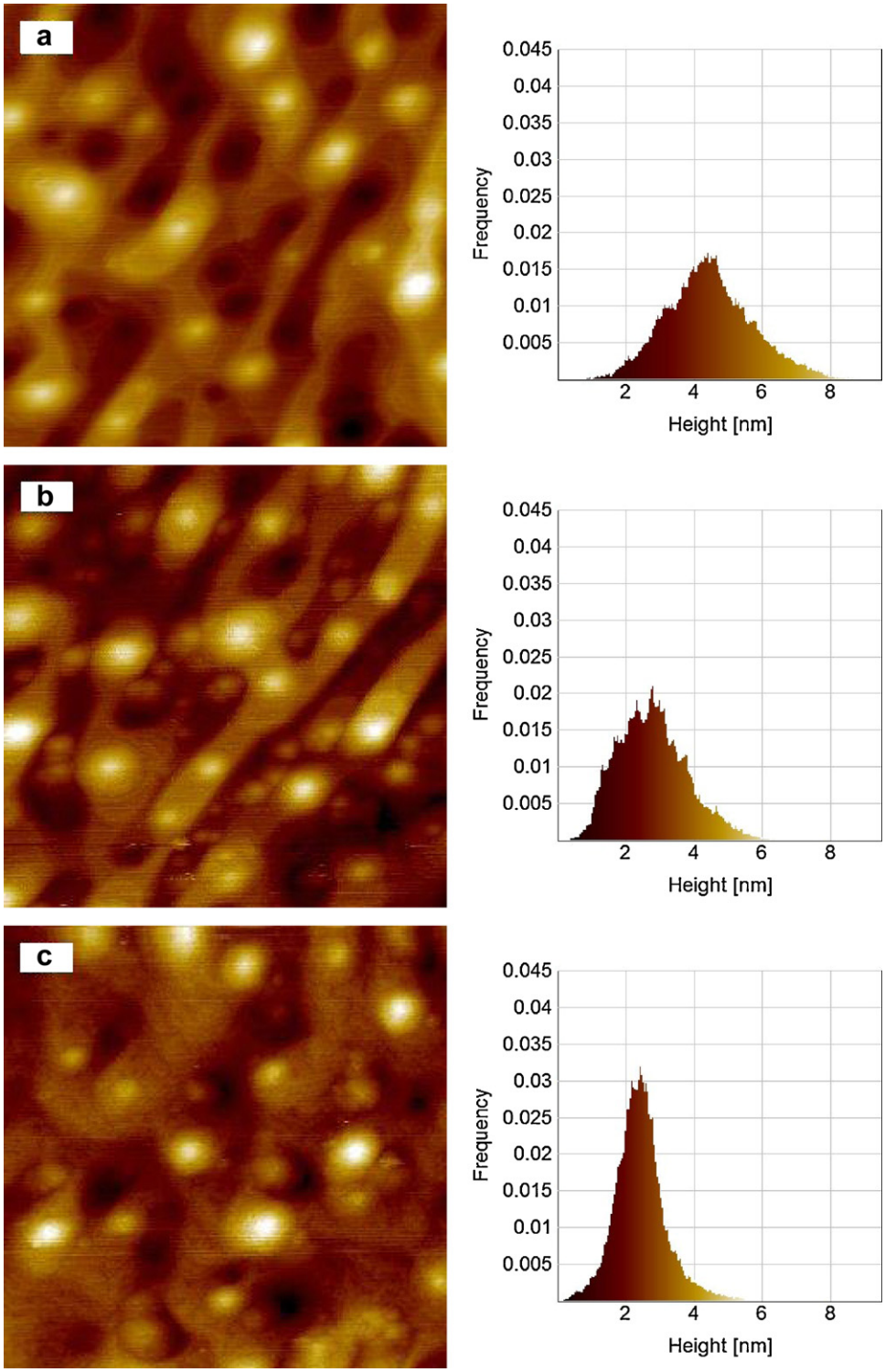


**Fig. 1.** 200 nm × 200 nm STM images of the sputter modified Au(1 1 1) surface (a): immediately after 3 keV $Ar^+$ ion bombardment, (b): after 60 min CO exposure at $10^{-4}$ mbar and (c): after 60 min CO exposure at 1 mbar. The *z*-scale can be derived from the corrugation, which was 8.6 nm in (a), 6.8 nm in (b) and 5.8 nm in (c). Graphs on the right show the height distribution (measured from the lowest point) of the pixels of the images. All treatments and STM measurements were carried out at room temperature. Reprinted from Ref. [26] with permission. © 2010, American Chemical Society.

$H_2$ from CO and $H_2O$. An inverse $CeO_x$/Au(1 1 1) catalyst exhibits a very good WGS activity. Several potential intermediates including formates (HCOO), carbonates ($CO_3$) and carboxylates (HOCO) were considered. Adsorption of HCOOH and $CO_2$ is used to create both HCOO and $CO_3$ on the $CeO_x$/Au(1 1 1) surface, respectively. On the $CeO_x$/Au(1 1 1) catalysts, the presence of $Ce^{3+}$ leads to the dissociation of $H_2O$ to give OH groups, which interact with CO. When there is an abundance of $Ce^{4+}$, the OH concentration is diminished and the likely intermediates are carbonates.

$CeO_2$/Au(1 1 1) was investigated by STM [29]. Cerium metal nanoparticles on gold have limited reactivity towards molecular oxygen and $NO_2$, due to the formation of Ce–Au alloys. Their

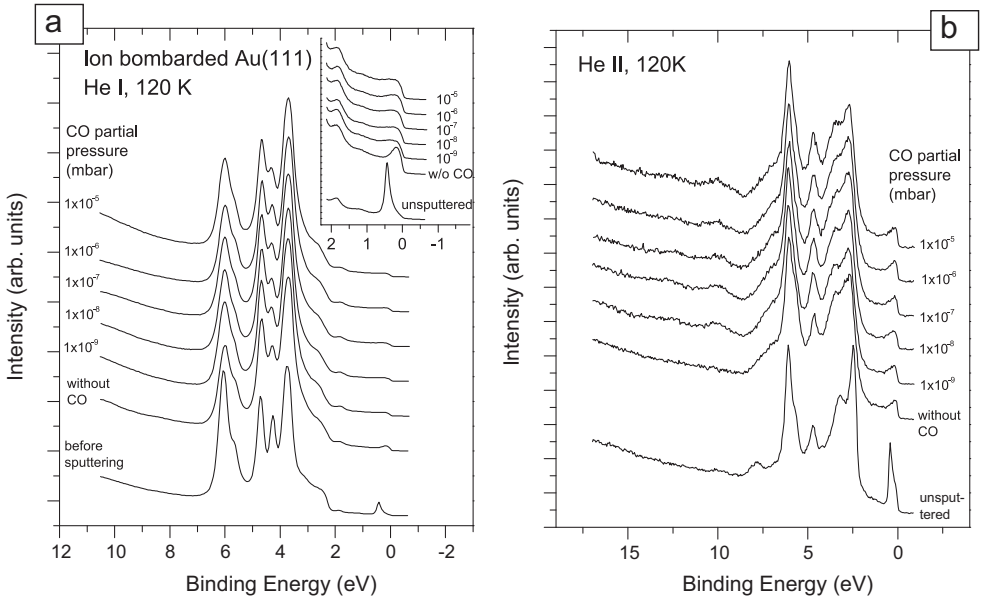


**Fig. 2.** Valence band UPS spectra of Au(1 1 1) modified by 3 keV 10 min $Ar^+$ ion bombardment measured during exposure to different partial pressures of CO. All spectra were taken in normal emission at 120 K and are shifted vertically for clarity. For reference, the spectra of the intact Au(1 1 1) surface are also included. (a) He I (21.2 eV) excitation. *Insert*: enlarged view in the vicinity of the Fermi level. Note the effect of CO on the surface state related feature just below the Fermi level. (b) He II (40.8 eV) excitation. Note the weak bands at 10.0 and 12.5 eV due to the $5\sigma$-$1\pi$ and $4\sigma$ levels of the CO adsorbates.
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oxidation leads to formation of non-uniform substoichiometric three-dimensional (3D) oxide particles. Cerium metal deposition onto condensed multilayers of water or $NO_2$ generates fully oxidized but poorly ordered ceria particles after annealing. Ultra-thin flat and ordered ceria nano-islands were prepared by deposition of cerium metal on the gold surface at elevated temperatures under an oxygen background pressure. Atomically resolved images show an oxygen-terminated surface of $CeO_2$/Au(1 1 1) with oxygen vacancies.

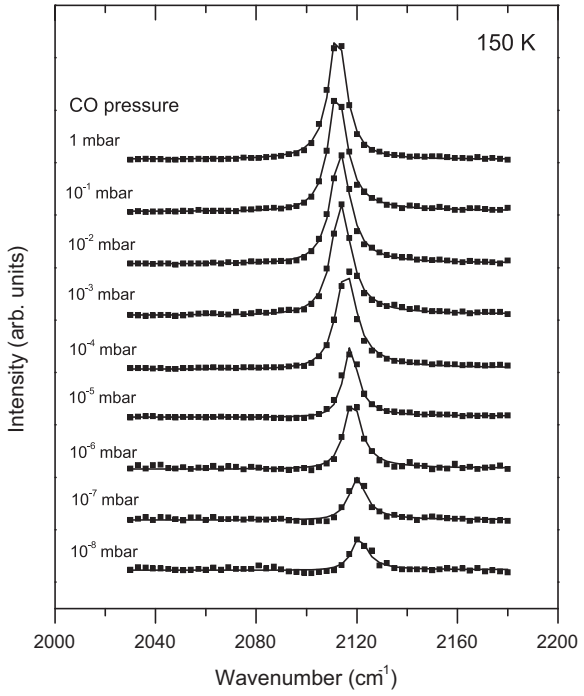


**Fig. 3.** (a) Sum frequency spectra of the sputter modified Au(1 1 1) surface exposed to different CO partial pressures. All spectra were taken in the *ppp* polarization combination. The CO vibration can be fitted with a single narrow peak with a frequency shifting towards lower values with increasing adsorbate amount, a typical characteristic of CO interacting with gold.
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Preliminary results on the CO adsorption properties of a $FeO_x$/Au inverse catalyst were presented in Ref. [27]. Iron oxide overlayers of 2 and 8 nm nominal thickness were prepared on MBE grown polycrystalline Au substrates by reactive evaporation. Low temperature sum frequency generation vibrational spectroscopy measurements indicated CO adsorbates on the 2 nm iron oxide covered sample with a frequency around 2103 $cm^{-1}$ (Fig. 4). On the contrary, no evidence for CO adsorption was found on either the 8 nm iron oxide covered sample or the bare Au substrate.

As shown above, small molecules, such as $O_2$, CO and $NO_2$, can be adsorbed on Au(1 1 1) provided that the large gold terraces are broken up either by roughening, or by depositing oxide patches.

On the other hand, the Au(1 1 1) surface itself is active if there are large molecules reacting. From this point of view, it is worth recalling the Sonagashira reaction, the cross-coupling of phenylacetylene and iodobenzene recently studied by Lambert school [30–32].

Temperature-programmed reaction measurements supported by STM have shown that phenylacetylene and iodobenzene react on smooth Au(1 1 1) under vacuum conditions to yield biphenyl and diphenyldiacetylene (Scheme 1). Roughened Au(1 1 1) is completely inert towards all three reactions, indicating the importance of crystallographically well-defined adsorption sites [31]. The reactants are initially present as essentially flat-lying molecules and the temperature threshold for Sonogashira coupling coincides with that for C–I bond scission in the iodobenzene reactant. Lambert explained that Sonogashira reaction occurs at the boundaries of islands of adsorbed reactants. These findings demonstrate unambiguously that the heterogeneous cross-coupling chemistry is an intrinsic property of extended, metallic pure gold surfaces.

As a continuation of the above work the authors found that the gold species deposited on lanthana was also active catalyst [30]. Atomically dispersed Au species were catalytically inert, whereas larger metallic gold nanoparticles (about 20 nm in size) were both active and very selective. Thus it is metallic gold that provides the catalytically active sites. $Au^0$ nanoparticles supported on silica,

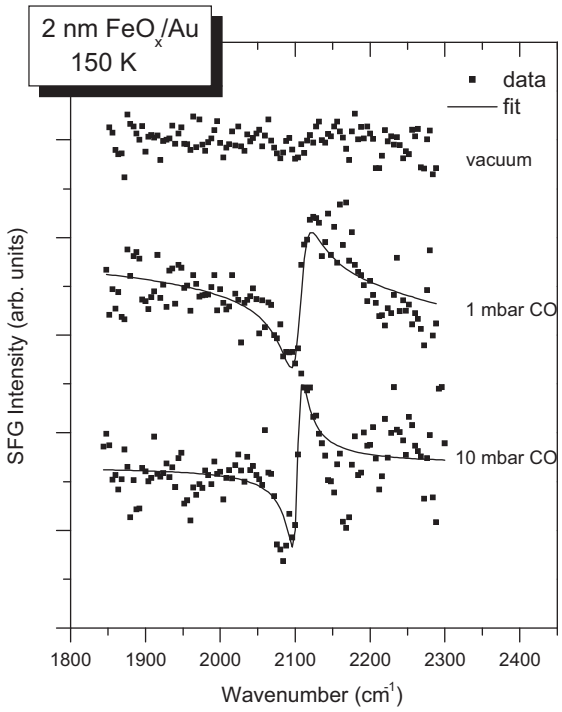


**Fig. 4.** Sum frequency spectra of the CO stretching region for 2 nm iron oxide film deposited on gold at 150 K at different CO pressures. For reference, the spectrum measured in vacuum is also shown. Spectra were taken in the *ppp* polarization combination.

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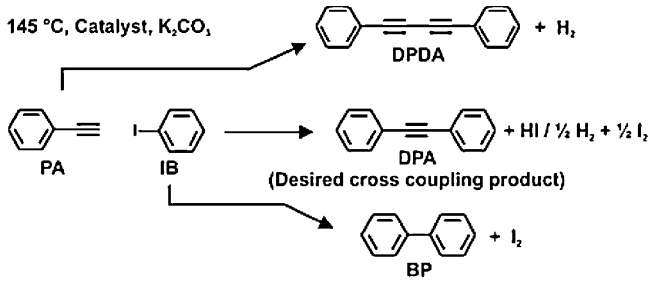
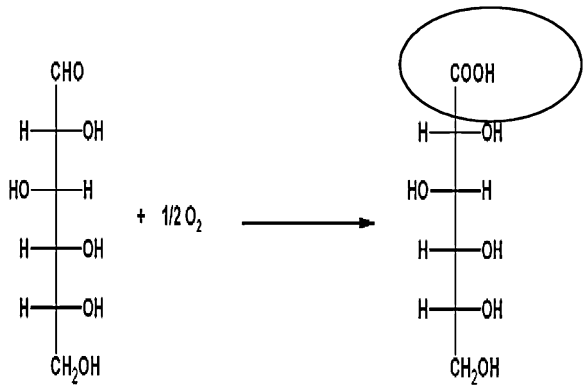
$\gamma$-alumina, and BaO were active but relatively unselective; however, as with lanthana, ceria-supported $Au^0$ nanoparticles showed high selectivity which was ascribed to SMSI effects and hydrogen spillover.

Many efforts have been made to oxidize selectively the aldehyde group of D-glucose to produce gluconic acid (Scheme 2) which is a high value product for fine chemical industry [33]. Although the effect is not as pronounced as for Au(1 1 1), correlation was found between the $T_{50\%}$ in CO oxidation and reaction rate in glucose oxidation. The higher the temperature of 50% CO conversion the lower the activity of the sample is. The more active samples in CO oxidation are less active samples in glucose oxidation as Fig. 5 shows. In the oxidation of glucose – as a larger molecule – silica and carbon supported samples were more effective than the reducible oxide supported samples and higher activity was observed over catalysts with larger gold particles on each support.

From the literature data and from own experiments it becomes obvious that gold reactivity primarily depends on the surface structure. The term of nano structured catalysis on gold nanoparticles




**Scheme 1.** Coupling reactions of iodobenzene and phenylacetylene to yield both the desired Sonogashira cross-coupling product diphenylacetylene (DPA) and the two homocoupling side products diphenyldiacetylene and biphenyl [30].




**Scheme 2.** Selective glucose oxidation.

is indeed devoted to special substrates like small size molecules, CO, and NO. and sometimes in the case of larger molecules, like cyclohexene when the adsorption requires an active site of small size (remember Kemball introduce the side-wise adsorption for these molecules). Furthermore, CO cannot be adsorbed on a smooth gold single crystal, but this surface is active when it becomes disordered. In other words, the presence of highly undercoordinated sites rather than the overall electronic structure of the gold ensemble determines the reactivity of gold towards small molecules.

Nevertheless, activation of small molecules on smooth Au(1 1 1) is still feasible, provided that the surface is promoted by, e.g. preadsorbed atomic oxygen, as excellently summarized by Carabineiro and Nieuwenhuys [34].

On the contrary, in certain cases involving large molecules (like the Sonogashira reaction) the reaction is feasible only on structurally well-ordered sites. Similar considerations are valid for the n-hexane isomerisation reaction because the reactivity increases on Au/Pt(1 1 1) with increasing gold content. These processes, where molecules should be laid down flat to the surface in order to be activated, clearly cannot be termed as nanocatalysis. Instead, the surface electronic structure of large gold ensembles may be responsible for activation of the reactants.

## 5. Modulation of gold by oxide support

Earlier we published an article in which we tried to convince the reader about the role of the support [35]. Regarding the gold nanoparticles, the Au/oxide interface determines the CO oxidation activity of the gold nanoparticles which is strongly affected by the length of the Au-oxide perimeter regarded as the active phase. The activity of the Au/oxide perimeter depends on the size of Au particles and also on the nature, size and morphology of the oxide component. It has been established that interaction of gold nanoparticles deposited on either model $SiO_2$/Si(1 0 0)

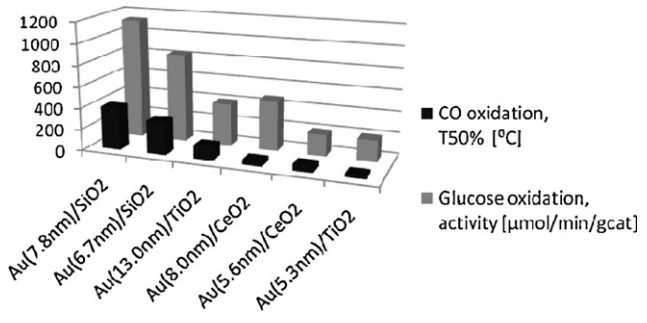



**Fig. 5.** Temperature of 50% conversion of CO oxidation (black bars) and the activity of glucose oxidation (grey bars) over various catalysts.

and amorphous or mesoporous silica with minute amounts of amorphous promoter oxide like $FeO_x$, $TiO_2$ and $CeO_2$ dramatically increases the gold activity in CO oxidation. The amorphous oxide not only enhances electronic interaction, but also stabilizes the nano-size gold particles. The defect structure may be important for the formation and stabilization of very small Au particles.

Au(1 1 1) sample can also be activated by doping gold surface with "active" oxides, usually a transition metal oxide. In oxidation reactions one of the crucial steps is the activation of oxygen. The $O_2$ dissociation has not been observed on gold surfaces and it is a very difficult process according to DFT calculations. It has been shown that the "active" oxygen can be supplied by the metal oxide which may also play an important role in the formation of carbonates, formates and carboxyl species in CO oxidation. An examplary discussion of these issues can be found in Hrbek's works [28,29] for ceria on Au(1 1 1). The importance of doping gold nanoparticles supported on $SiO_2$ by $TiO_x$ [36], $CeO_2$ [37] or $FeO_x$ [38] deposit and more recently the use of novel Au–$ZrO_2$ yolk–shell catalysts were found to exhibit a surprisingly high activity in CO oxidation even though the gold particle size is about 15 nm. $TiO_2$-doping shows further significant activity enhancement [39].

The modification is concerned mainly with changing selectivity. An excellent example is given by Lambert for the Sonogashira reaction: the activity is controlled by the particle size (supported on $Al_2O_3$, BaO, $SiO_2$) while lanthanum oxide is the best for receiving the optimum selectivity.

The selectivity could be controlled also by particle size. Selective hydrogenation of acetylene or 1,3 butadiene on palladium could be good examples. If support-free palladium was used initially the sample was not selective, while on supported catalyst the sample was initially selective [40]. As the reaction progressed the supported Pd became less selective due to enlarged palladium sites, whereas the unsupported palladium catalyst became more selective owing to the carbonaceous deposit formation. On the unsupported sample initially acetylene underwent dissociative adsorption and the carbonaceous surface became more selective. For further evidence we refer to other examples [41,42].

## 6. Conclusions

The general rules and the exceptions in the area of gold catalysis have been discussed. We have established the activity and selectivity criteria, in particular for gold catalyst, which is valid for various substrates. Accordingly, large molecules require a larger surface area or single crystal for activation, while small molecules can be reacted on small nanoparticles.

This conclusion is based on experimental data from various sources indicating that small molecules (CO, NO, etc.) can be activated only on small nanoparticles or roughened Au(1 1 1) surfaces, i.e. in the presence of considerable structural disorder, whereas well-ordered Au(1 1 1) single crystals or extended metal films are active in the reaction of certain large molecules.

The above effect can be modulated by interfacial interaction between gold species and active oxide. The oxide may invoke electronic interaction and simultaneously the defect structure of oxides likely has a key issue in the formation and stabilization of Au nanoparticles. The activity of the Au/oxide perimeter depends not only on the size of the Au particles, but also on the size and morphology of the oxide component (amorphous or crystalline structure, various polymorphs) regardless of whether it is supporting Au nanoparticles or decorating them.

On the other hand, it turned out that in some cases – independently of the interface – the key issue is the available gold area of Au nanoparticles dictating the reaction rate of a substrate.

## Acknowledgement

The authors are indebted for the National Science and Research Grants (OTKA T-68052 and NNF 78837) for financial support.

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