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Nanoporous Gold: From an Ancient Technology to a High-Tech Material

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Nanoporous Gold: From an ancient technology to a high-tech material. A comprehensive introduction into fabrication, characterization, and applications

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CHAPTER 8

Surface Chemistry and Catalysis

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Abstract

In this chapter we will report on the catalysis with nanoporous gold (npAu). Beginning with a comprehensible introduction to the concept of catalysis, we will establish the broader background of the research on the surface chemistry and catalysis with npAu. In the following sections, we will discuss the interaction of prime reactants such as O₂, CO, and alcohols, such as methanol and ethanol, with gold surfaces. Here, we focus on experimental work performed under ultra high vacuum (UHV) conditions, dealing with single crystals and npAu. Oxygen is discussed first; it is a key reactant which “activates” the gold surface for a variety of chemical reactions, as for example the oxidation of CO at low temperatures but also mechanistically more complex reactions, such as the oxidation of alcohols. The following sections will treat the latest insights regarding the ambient pressure catalysis with npAu. We will discuss the gas-phase catalysis of npAu with the emphasis on the low temperature oxidation of CO and alcohols, especially emphasizing the correlation to model experiments under UHV conditions, which help to understand the reactions on a molecular level. We will also cover aspects of the liquid phase catalysis with npAu reporting on two exemplary and important reactions. In the last sections, we will treat the surface modification of npAu with metal oxides; this latter subject being an upcoming focus on a specific design of the material for catalytic applications.

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8.1 Introduction

The history of chemical catalysis started about 200 years ago in the early 19th century, along with the evolution of chemical science. One can say that the concept of catalysis in chemistry is nearly as old as the atomic theory published by John Dalton in 1806. Scientists made the observation that a chemical reaction would not proceed unless a material such as for example a metal was present. Seemingly, it was only the presence of this material which “magically” facilitated the chemical reaction as it was neither consumed nor its physical state changed. In 1836 the Swedish scientist Jöns Jacob Berzelius tried to combine those observations and dubbed it as catalysis. He said that the “*catalytic power means that substances are able to awake affinities that are asleep at this temperature by their mere presence*”.

Most people nowadays probably know the term catalysis from the automotive catalyst also dubbed automotive converter which became a self-evident part of the exhaust gas management in modern cars, for example converting poisonous constituents such as carbon monoxide or nitrogen oxides in non-poisonous carbon dioxide and nitrogen. Not so commonly known is that catalysts in the form of biological molecules such as enzymes are the very bases for life itself or that in modern chemical industry the vast majority of products are produced with the aid of catalysts. The reason for this is that a catalyst can provide the very handle and control of a chemical conversion. Life would not be possible with exact control of chemical reactions inside the biological cell.

Today we know that it is the specific interaction, the chemical bonding of the catalyst and the reactants in the course of chemical reaction which opens a specific kinetic pathway for the reaction. Noteworthy a catalyst will not change the thermodynamic restraints of a reaction such as the free enthalpy ΔG and as a consequence the equilibrium of the reaction. For example, the

oxidation of carbon monoxide to carbon dioxide using molecular oxygen remains exactly as exothermic ($\Delta H^\circ \sim -283$ kJ/mol) whether it is catalyzed or not. But it is the temporary chemical bonding of at least one of the reactants with the catalyst which opens a “faster” pathway for the reaction. In this way the course of reaction is altered so that the activation energy of the overall reaction is lowered and the reaction proceeds faster and at lower temperatures, respectively. Thus, in the light of green chemical technologies, novel energy harvesting, and storage concepts, catalysis plays a central role.

Depending on whether the catalyst and the reactants form a homogeneous compound (one liquid phase) or they form a heterogeneous compound consisting of least two different phases (gas/liquid/solid phase), one distinguishes between homogeneous and heterogeneous catalysis. As nanoporous gold is a solid which inevitably forms heterogeneous compounds with the reactants, we will forthcoming refer only to heterogeneous catalysis (either liquid or gas).

In heterogeneous catalysis the reactions take place on the very surface region of the catalyst (see Figure 8.1). Reactants will have to impinge on the catalyst surface and being chemically bonded, i.e. “chemisorbed” in order to become activated for a specific chemical reaction. The chemistry of the catalyst surface thus is of crucial importance for the catalytic performance in terms of activity and selectivity of the catalyst. In order to achieve high catalytic activity, one has to balance out the strength of the chemical bond formed. This is also dubbed as the principle of Sabatier. In order to achieve an activation of the adsorbed molecule, it has to be chemically bonded and electron density has to be transferred from the catalyst surface into and out of the bonds within the adsorbed reactant (“activation”) on the one hand. On the other hand, in order to achieve high enough turn over, the reactants must not stick too strongly to the surface in order to avoid poisoning of the catalyst by blocking of the available active sites.

[Figure 8.1 near here]

Considering the group of transition metals one can draw a simplistic curve, the so called volcano curve which reflects the ideal catalytic activity as a function of the position of the particular metal in the periodic table of the elements. In this simple picture with increasing atomic number (i.e. “from left to right”) the strength of chemisorption (formally the heat of adsorption) decreases. The bonding of for example oxygen with metal surface such as Ti is too strong as to allow a high enough turn-over. Yet, with increasing atomic number (e.g. from Ti to Cu) the bonding becomes weaker allowing a high enough turn-over, before the chemisorption becomes too weak as to observe appreciable catalytic activity. As an easy measure this curve can explain why so many highly catalytically active metals can be found in the middle, meaning the groups 8-10 of the periodic table of the elements (Fe, Co, Ni, Pd, Pt).

Although Au can be found in close neighborhood of these metals, in the group 11 (Cu, Ag, and Au) it is distinguished by its nobleness and exceptional weak interaction with adsorbates.¹ First reports on gold as an active catalyst being even superior to other metals were published for the hydrogenation of olefines in the 1970s by Bond et al.², later in the mid 1980s for the low temperature oxidation of CO by Haruta et al.³ or for the chlorination of olefins by Hutchings et al.⁴. Gold was formerly rather known as “catalytically dead” due to its apparent inertness. The interaction of gold surfaces with reactants, such as hydrogen or molecular oxygen is very weak¹; as a consequence gold remains in its metallic form without showing any sign of for example corrosion but also was considered to be a poor catalyst, for the reasons explained above. Remarkably, if gold is in the form of very small particles in the range of a few nanometers on a

suitable oxidic support it may indeed be catalytically highly active. The reason for this kind of behaviour was controversially discussed throughout the last two decades.^{5, 6} Especially the chemisorption and activation of molecular oxygen is hardly detectable on pure gold surfaces and strongly profits from the presence of the oxidic support and the nanosized particles.

In 2006 Zielasek et al.⁷ and 2007 by Ding et al.⁸ independently discovered that unsupported nanoporous gold is a highly active catalyst for the low temperature oxidation of CO. This came as a bit of surprise, as npAu is neither made up of nanoparticles nor contains an oxidic support material which was thought to be essential for high catalytic activity so far. At first, it was speculated whether that abundance of low coordinated surface atoms within the material is the source of its high catalytic activity revealing the genuine catalytic activity of pure nanostructured but unsupported gold.^{8, 9} Later reports focused on the remaining traces of the less noble metal, such as Ag, that remain in small quantities below 1 at% in the material after preparation.¹⁰ Since metals such as Ag and Cu, which can also be used for generation of npAu, are known to chemically bond molecular oxygen, very much in contrast to Au, it is very likely that their presence contributes to the catalytic activity.¹¹⁻¹³ Nevertheless, the overall catalytic characteristics of the material in terms of activity and selectivity was found to be governed by the surface chemistry of Au alone, for example it was observed that CO oxidation takes place at temperatures well below 0 °C⁷ and the highly selective oxidation of alcohols proceeds already at room temperature¹⁴.

Among others it is the weak interaction with adsorbates that enables high activity at low temperatures making gold a great candidate for a predictable and green catalytic concept.¹⁵ The absence of an oxidic support material reduces the degree of complexity of the surface chemistry and catalysis of npAu. Recent studies showed that insights from well-controllable UHV studies

can be directly transferred to npAu catalysts working under ambient pressure conditions npAu.¹⁴

¹⁶ Latest developments reported on the combination of npAu with small amounts of metal oxides such as TiO₂ and a greatly enhanced catalytic activity.^{11, 17}

In the following sections we will summarize and report on the various catalytic applications of npAu starting with surface chemistry and principles derived from UHV model studies followed by applied studies under ambient pressure conditions in the gas and in the liquid phase. First, we will discuss the interaction of the gold surface (single crystals as well as npAu) with oxygen, as this is the key for oxidation reactions and the source of reactivity. We will then discuss the reaction of oxygen with carbon monoxide and alcohols, increasing the complexity of reaction by adding the possibility to form several products. In the latter case not only the activity of the catalyst but also its selectivity will be discussed and interpreted on a molecular level. Following these sections we will report on important work in the liquid phase, the oxidation of d-glucose and non-carbon based compounds, organosilanes to organoliansols. We will conclude with examples of tuning and designing the catalytic activity of the npAu by doping with metal oxides such as titania. The latter modification of the material is a very remarkable example of the wide structural and chemical adjustability of npAu.

8.2 Surface Chemistry of Au

The key element of any catalytic cycle is the interaction, namely the bonding and activation of the particular reactant on the catalysts surface.¹⁸⁻²³ Perhaps due to its early industrial relevance and the lack of suitable experimental techniques, for a long time the use and application of catalysts outweighed the scientific understanding of the underlying molecular processes on the catalyst surface. Experimental techniques as well as theoretical approaches such as DFT (density

functional theory) calculations to investigate the key steps of catalysis on the atomic level were developed only in the last 4 to 5 decades, aiming at closing this important knowledge gap. For example, in the early stages of the 20th century the development of the “Haber-Bosch process” for the catalytic generation of ammonia from hydrogen and nitrogen, one of the most important catalytic processes until today, was honored with two Nobel Prizes (in 1918 for Fritz Haber and 1931 for Carl Bosch). But it took almost hundred years, until in 2007 another Nobel Prize was awarded to Gerhard Ertl for his contribution to derive an atomistic understanding (inter alia) of this catalytic process.

The biggest hurdle to overcome in the study of adsorption and binding of chemical entities on surfaces is to prepare and conserve clean adsorbate free surfaces over the duration of the experiment (at least several minutes). From simple kinetic gas theory one can derive that at 1 mbar of gas pressure (for example He) in the order of 10^6 monolayers (ML, equivalent of a one atomic thick layer) gas molecules impinge on the metal surface per second. Even if only a fraction of those molecules stick to the surface, it will be covered within milliseconds. As a result pressures in the range of 10^{-10} mbar – a regime called ultrahigh vacuum - are necessary to study clean and well characterized (single crystalline) surfaces. The required experimental techniques and appliances were developed since the 1950th leading to the establishment of a new scientific field, the *surface science*.

8.2.1 Interaction of Au with Oxygen

The presence of active oxygen is the first and the key step in the catalytic cycle for oxidation reactions over gold surfaces. The presence of oxygen on Au surfaces was found to be mandatory for inducing reactivity.²⁴⁻²⁶ Although gold based catalysts have been deployed as catalysts for a

variety of oxidation reactions at ambient pressures, the activation and the dissociation of molecular oxygen which is the natural source for (atomic) oxygen in these experiments seems unclear. First experiments in the 1970th indicated some dissociation of molecular oxygen at temperatures above 500 °C on flat single- and polycrystalline gold surfaces²⁷⁻²⁹, yet, later experiments showed that the presence of hardly detectable amounts of impurities such as calcium were critical.³⁰ It is widely agreed that the activation barrier for the splitting of molecular oxygen on Au is very high³¹ so that thermal activation leads to desorption from the surface rather than dissociation of the oxygen molecule. The dissociation probability of molecular oxygen on flat gold surfaces was assessed to be below 10^{-6} .³² As a consequence, molecular oxygen remains mostly physisorbed, for example, on Au(110) surfaces at 28 K and desorbs at temperature below 60 K under ultra-high vacuum conditions.³³

In order to study atomic oxygen on Au surfaces different techniques were developed to overcome the activation barrier for splitting of molecular oxygen for example by irradiation of physisorbed layers of molecular oxygen with electrons³³, O₂ ion bombardment³⁴, decomposition of NO₂³⁵, oxygen atom impingement³⁶ or catalytic decomposition of ozone^{27, 37, 38}. All these techniques result in chemisorbed atomic oxygen, yet, also induce different surface morphologies. For example when sputtering the surface with oxygen ions the surface becomes rough and a pit and mound structure evolves due to the impact of the ions on the surface.^{39, 40} In this way, oxygen atoms can be implanted well below the surface of the metal.³⁹

In contrast, the comparatively mild catalytic decomposition of ozone on gold surfaces was shown to lead to about 1 monolayer of atomic oxygen on the surface.^{41, 42} As revealed by scanning tunneling microscopy (STM) studies from Friend et al. on Au(111) surfaces, the surface reconstruction is lifted after deposition of oxygen and small gold oxide clusters in the

size of about 2 nm are created (Figure 8.2).²⁴ With increasing coverage of oxygen (> 0.3 ML) and temperature (400 K) the clusters aggregate and build two-dimensional arrays of oxide on the surface. It was found that the initially formed small oxygen gold clusters are the most reactive ones.⁴³ The fact that these clusters are indeed gold-oxygen compounds was verified by reacting the oxygen with CO at low temperatures. The small clusters could be still detected, yet, without oxygen contained.²⁴

Temperature programmed desorption studies (TPD)⁴⁴ and photoemission experiments (XPS) on Au(111) and Au(110) surfaces confirmed at least two different oxygen species on the gold surface generated in this way: one very reactive and more weakly bonded oxygen, dubbed as “chemisorbed oxygen” and corresponding to the cluster like oxide found by STM, and another slightly tighter bonded oxygen species called “surface oxygen” corresponding to the two-dimensional, more ordered oxygen structures. Theoretical studies do not exclude the presence of subsurface oxygen at elevated temperatures and oxygen pressures²⁴, yet, it has not clearly been detected in experiments so far.

[Figure 8.2 near here]

Latest studies on npAu surfaces using highly resolved photoemission spectroscopy and ozone decomposition support that these oxygen species can also be formed on npAu surfaces. Due to the low pressure required for this studies, ozone was used as a source of chemisorbed atomic oxygen.⁴⁵ Yet, an interesting difference was noticed: in contrast to flat Au surfaces where with increasing coverage of oxygen the ordered two-dimensional “surface oxide” prevails, the oxygen on npAu remains rather disrupted as “chemisorbed oxygen” even at high coverages. A possible explanation is that the absence of larger crystallite facets on the strongly curved npAu surface

prevents ordering of the oxygen species. This is noteworthy, especially in light of the higher activity of this disrupted chemisorbed oxide and may also contribute to the high catalytic activity found in ambient pressure studies.

8.2.2 Interaction of Au with CO

In general, CO is molecularly adsorbed on Au surfaces. This means that the scission of the CO bond leading to atomic carbon or oxygen is not detected.⁴⁶⁻⁴⁸ The adsorption and bonding of CO on Au surfaces was found to strongly depend on the local geometry, namely the coordination number (CN) of the surface atoms with the tendency to form a stronger bond with decreasing coordination of the surface atom. For example, Gottfried et al. studied adsorption of CO on flat Au(110) surfaces and found weakly bonded physisorbed CO desorbing well below 100 K as well as smaller quantities of stronger bonded chemisorbed CO desorbing above 100 K.⁴⁷ The latter one was assigned to CO adsorbed on low coordinated surface atoms consistent with the observation that the fraction of this chemisorbed CO increased after sputtering and roughening of the surface, respectively. At least two different chemisorbed CO species can be identified by their desorption temperatures at around 120 K and 170 K.⁴⁸ Various experimental^{31, 47-50} as well as theoretical studies^{12, 49} showed that this chemisorbed CO is bonded to surface atoms with a coordination number of 7 and below, corresponding to atoms at steps (CN 7) and kink/defect sites (CN 6). CO physisorbed on terraces (CN 9) generally desorbs at temperatures well below 100 K.

As mentioned in the introduction, the bonding (chemisorption) of molecules on the catalyst surface is critical for the “activation” of the molecule and thus the catalytic activity. The presence of step and kink sites can be expected to greatly facilitate the catalytic oxidation of CO,

accordingly. Specifically, nanostructured materials such as npAu contain a large fraction of low coordinated surface atoms due to the presence of curved surfaces and the absence of large crystalline facets. Indeed, when exposing npAu to CO at low temperatures (e.g. liquid nitrogen temperature) one observes large quantities of chemisorbed CO desorbing at temperatures above 120 K, corresponding to CO bonded to step and kink sites.⁵¹ In the presence of coadsorbed oxygen, further desorption at temperatures above 200 K is observed (Figure 8.3). Theoretical calculations confirmed that the co-adsorption of, for example, atomic oxygen can further increase the binding energy of CO on the Au surface. As a first result, the bonding and activation of CO on the npAu surface strongly profits from the large fraction of low coordinated surface atoms and the co-adsorption of atomic oxygen.

[Figure 8.3 near here]

8.2.3 Alcohol Oxidation

The selective oxidation of alcohols plays an important role in the production of a wide range of bulk and commodity chemicals/materials, as alcohols can be synthesized by conventional petro chemistry or are derived from renewable resources such as landfill gas, biomass or municipal waste.⁵² Using gold as a selective and green catalytic material for the selective oxidation of alcohols has gained considerable interest (a more detailed discussion can be found in chapter 8.3.2). In case of alcohols, various bonds such as C-H, C-C and C-O bonds can be subject to catalytic activation/scission. A metal which activates all bonds equally may be very active for the oxidation, but poorly selective resulting in full combustion. Examples for such reactive catalytic elements are Pt and Pd. On Au and Ag surfaces the breaking of the C-H bond, however, is greatly

hampered⁴⁶, making these two materials interesting candidates for the selective oxidation of alcohols. And indeed, Ag is employed as the catalyst in commercial oxidation of, for example, methanol to the corresponding aldehyde, formaldehyde.⁵²⁻⁵⁴

The corresponding reactivity of gold surfaces for the oxidation of various alcohols was intensively investigated during the last 25 years.⁵⁵ Friend et al. used temperature programmed reaction spectroscopy (TPRS) to investigate the molecular transformation of alcohols on Au surfaces.⁵³ In these experiments the reactants are adsorbed on the metal surface at low temperature (~100 K) and the reaction products desorbing from the metal surface are monitored by mass spectrometry while linearly increasing the sample temperature. The desorption temperature of the particular products is correlated to the specific activation barrier of formation (this technique is limited to reactions where desorption of the products is not the rate limiting step). In combination with other techniques, such as infrared spectroscopy and isotope labeling, a mechanistic picture of the reactions on the surface can be derived.⁵³

In case of Au surfaces no reactivity can be observed in the absence of atomic oxygen, pre-adsorbed on the surface. As soon as atomic oxygen is present, though, a very rich and selective surface chemistry evolves (figure 8.4). At first, in a Brønstedt type acid-base reaction the alcoholic proton of the alcohol reacts with atomic oxygen on the surface and forms an adsorbed alkoxy group (RO-Au). In a next step this surface bonded alkoxy can be subject to further deprotonation by scission of the alcoholic C-H bond (β -elimination), by reaction with either surface oxide or with an adjacent alkoxy. The resulting surface bonded aldehyde can (a) react with an adjacent alkoxy forming the corresponding coupling product, the ester (e.g. methyl formate) (b) desorb from the surface resulting in “free” aldehyde (e.g. formaldehyde), or (c) be further oxidized to the carboxylate (e.g. formate), eventually leading to the full combustion

product the CO₂. The tendency to form the aldehyde by β-hydrogen elimination increases with increasing carbon chain length of the alcohol. As this is considered to be the rate limiting step it determines the overall selectivity of the reaction.²⁵ In case of methanol which contains only one C atom, the rate for β-elimination is the lowest resulting in low concentrations of formaldehyde that will predominantly react with methoxy, to form the ester, methyl formate. This is very much in contrast to Ag where the formaldehyde is the favored product. With increasing chain length (e.g. ethanol, propanol, and n-butanol) the formation of the aldehyde is favored and the product distribution will change, in favor of the formation of aldehyde.

[Figure 8.4 near here]

8.3 Gas-Phase Catalysis over Nanoporous Gold

In order to study the catalytic activity of catalysts under “working conditions” higher i.e. ambient pressures are typically deployed. The catalyst is placed in a reactor with environmental and temperature control and the reactants are either fed continuously into (and out of) the reaction chamber (“continuous flow reactor”) or the reactor containing the reactants is sealed for a specific reaction time (“batch type reactor”). In any event, the reactants will continuously be able to react with the catalysts surface and a large number of catalytic cycles can be investigated. In the following, gas-phase catalytic experiments will be reported which were mainly obtained in a continuous flow reactor (as for example described in ref. 14). This type of steady-state fixed-bed tubular flow reactor is especially suitable to determine activity and kinetics of catalytic reactions.⁵⁶ In the studies reported below, the monolithic npAu samples were in the form of free standing membranes (e.g. disks with a diameter of 5 mm and a thickness of 200 to 300 μm) so that the reactant gases could diffuse into and out of inner sections of the material from all sites.

8.3.1 CO Oxidation

The catalytic oxidation of CO with molecular oxygen certainly represents one of the most investigated reactions in heterogeneous catalysis combining a great relevance from an application as well as from a fundamental point of view. The oxidation of harmful CO to non-poisonous CO₂ plays an important role in exhaust gas cleaning (e.g. in the automotive converter). The superior activity of gold for low temperature oxidation of CO and hydrocarbons compared to typical metals used in car catalysts (Pt, Pd, Rh) may solve the issue of the very low efficiency of the converter during the cold start-up period. Consequently, intense research efforts were initiated in this respect.^{36, 57, 58} As of recent, first commercial Au based automotive converters are available (NS Gold™ from Nanostella Inc.). Additionally, the ability of gold to selectively oxidize CO in the presence of H₂ renders applications in hydrogen fuel cell applications promising.⁵⁹ Very small quantities of CO present in the hydrogen feed gas poison the Pt electrode catalyst over time; an efficient removal by oxidation with an Au catalyst thus represents a viable solution to this problem. Besides this technological potential, the oxidation of CO was widely used for investigations of the surface chemistry. A more detailed description of this topic and the interaction of CO with Au surfaces can be found in chapter 8.2.2. Due to the comparatively structural simplicity of this diatomic molecule, the oxidation resulting in only one product, it is particularly suitable as a test reaction probing the catalytic activity of a material for oxidation reactions.

The first reports on the catalytic activity of npAu consequently emphasised the oxidation of CO with molecular oxygen. In 2006 and 2007 two groups independently reported on the remarkable activity of npAu for this reaction at temperatures as low as – 30 °C.^{7, 8} Depending on

the preparation conditions and the storage of the sample, the material need to be “activated” before conversion of CO was detected. A pre-treatment and activation, respectively, of the catalyst is not uncommon in ambient pressure catalysis and refers to a potential cleaning and structural/chemical evolution of the catalyst surface so that the actual catalytically active surface evolves and the “active sites” on the catalysts surface become available. It seems however that right after preparation of npAu samples no activation period is necessary and samples can be active from the very first moment on.⁸ In other investigations, the sample was exposed to a stream of CO and oxygen at temperatures above 60 °C for a period of hours before activity was detected.¹⁰ The fact that no activation could be observed when no CO was present in the feed points towards a reaction, possibly a reduction, of the surface which leads to the catalytically active state. On the other hand, when samples were stored for a longer period of time (several weeks), longer activation periods were necessary, an observation which implies a concurrent cleaning procedure.

However, after activation of the npAu catalyst it shows stable conversion of CO over the range of several hours and days. A typical curve for the conversion of CO adding different quantities of oxygen to the feed gas is depicted in Figure 8.5. The conversion of CO increases with increasing supply of reactants until saturation is reached. In these experiments no poisoning or decline of conversion at or above a certain concentration of either CO or oxygen was detected in contrast to other transition metals, such as platinum or palladium at these temperatures.

As already pointed out in chapter 8.2.1, the bonding of molecular oxygen on Au surfaces is very weak and the probability of dissociation, leading to reactive atomic oxygen on the surface, is very low. Although different theoretical studies predict that in case of low coordinated Au atoms the bonding of molecular oxygen becomes stronger⁶⁰⁻⁶² this is not a straight forward

explanation for the high catalytic activity of npAu. Different than in case of Au particles which were found to be only active for gas-phase CO oxidation when the particle diameter was smaller than 5 nm the ligaments in npAu can be 10 times larger, between 40-50 nm in diameter and still highly catalytically active. The catalytic activity of npAu rather scales with the surface area of the material.¹⁷ Accordingly, other possible ways of an efficient activation of molecular oxygen were discussed.^{10, 63} After dealloying of the material, small fractions of the less noble constituent in the starting alloy remain in the material. For example, when dealloying Au-Ag alloys, the concentration of residual Ag in the bulk is virtually below 1 at%. This is possibly below the detection limit of for example energy dispersive x-ray spectroscopy (EDX), often applied in combination with scanning electron microscopy (SEM) for morphological and compositional characterization. In some studies this low concentration of the less noble constituent obviously was an obstacle when identifying possible contributors to the catalytic activity of the material. However, surface sensitive x-ray photoelectron spectroscopy (XPS) at the outer surface of the npAu material revealed that the Ag is present and can be enriched at the surface of the material to several percent (see Figure 8.5).^{10, 45} From thermodynamic considerations it is clear that during the corrosion the activity of the Ag ions in the solution is not zero and - although becoming very small - some Ag has to remain in the Au material. By a careful choice of the preparation conditions (e.g adjusting the time of dealloying or the potential for corrosion) one can adjust the amount of residual Ag within the material. In this way, samples containing amounts of up to about 15 at% of Ag were prepared. The upper limit of Ag remaining in the material is given by the formation of a homogeneous three dimensional porous structure. The samples used in this study contained different amounts of Ag, yet, showed all a similar homogeneous size of ligaments and pores in the range of 30 nm throughout the cross section of

the particular npAu disk. Experimental results testing those samples for the CO oxidation are shown in Figure 8.5. The general trend was that with increasing Ag content the activity for CO oxidation increased. This finding is in line with results from bimetallic Au-Ag particles, where the combination of Au and Ag was found to be more active than either one alone. Depending on the preparation conditions and the type of support a fraction of Ag between 10 at% and about 40 at% was found to be optimal in case of CO oxidation.^{64, 65}

[Figure 8.5 near here]

Besides the overall activity of the catalyst, the kinetics of the reaction in terms of the reaction constant and the reaction order are important means of characterization of a catalytic system.⁶⁶ To determine the kinetic parameters of the reaction, double logarithmic plots of the activity as a function of the partial pressure were used.^{10, 16} As inferred from Figure 8.6 the apparent reaction order of O₂ is close to 0.5 for all investigated samples, while the reaction order of CO is close to 1, in some studies lower values close to 0.7 were reported.^{10, 66} Considering mass transport phenomena⁶⁶, these results correspond to an actual reaction order of 0 for O₂ and between ~ 0 and 1 for CO. A reaction order of zero implies fast saturation of adsorption sites for oxygen, either owing to strong interaction (large adsorption enthalpy) or a very limited number of active sites. This is compatible with a model where O₂ is primarily adsorbed on Ag sites which constitute the minority sites on the catalyst surface. On the other hand, a reaction order close to 1, as was measured for CO, implies that the adsorption i.e. the supply of CO from the gas phase is rate limiting, either because of a weak interaction (low adsorption enthalpy) or a large number of available sites for adsorption. This is compatible with CO adsorption primarily taking place on Au sites which constitute the majority of the npAu surface. However, with respect to different

amounts of Ag within the material no substantial change in the reaction order of O₂ was observed. This in turn implies that even though the overall activity is altered for increasing amounts of residual Ag the reaction mechanism is not noticeably changed. A potential spill over of oxygen onto the Au surface site or a reaction at special surface sites (e.g. containing adjacent Au and Ag sites) may dominate the characteristics.

[Figure 8.6 near here]

An experiment further highlighting the surface chemistry of npAu is the influence of additives such as water on the catalytic conversion. Water does only weakly adsorb (physisorb) on metal surfaces, especially on Au surfaces. Only if oxygen is present, the water molecule can be activated to transiently form OH species.⁶⁷ This effect is discussed to have an impact on the activity of surface bonded oxygen, e.g. by disrupting the oxygen layer which leads to higher activity.⁴³ In case of supported gold catalysts, water can amplify the reaction rate by orders of magnitude.⁶⁸ Here, it is however mostly the interaction with the oxidic support (such as TiO₂) which is thought to cause this effect.^{69, 70} In case of npAu and a stoichiometric supply of reactants, the conversion of CO is increased by about 100 % just by adding 0.01 vol% water to the gas stream.¹⁶ Neither the apparent reaction orders nor the activation energy was altered when increasing the water content in the gas feed. When no oxygen was present, the reaction immediately ceased; accordingly, water is not an additional source for oxygen. This finding implies that water works as a co-catalyst; it is not consumed in the process as it is not contained in the products or educts. Nevertheless, it amplifies the total activity of the catalyst. These experimental results are compatible with the observed reactivity of Au surfaces^{67, 71} and prove

that support free metal catalysts working under ambient conditions are influenced by moisture as well.

8.3.2 Oxidation of Alcohols

As already pointed out in chapter 8.2.3, the oxidation of alcohols represents a key catalytic conversion in the industrial production of commodity and bulk chemicals in the range of tens of millions of tons per year in volume.⁵² Materials generated from alcohols touch our very daily life in the form of plastics and paints, carpets and many more. Products such as PET bottles, DVDs or the dashboard in the car are generated on the basis of alcohols such as methanol. The methyl alcohol (methanol or wood alcohol) is the smallest alcohol containing just one carbon atom and has the formula CH_3OH . Since the early stages of industrial production of alcohols methanol was the alcohol gaining the main emphasis and also provided a starting point for the generation of longer chain alcohols such as ethanol and butanol. In the early stages of industrial generation of this alcohol from about 1830 it was generated by dry distillation of wood and was dubbed wood alcohol, accordingly. With the onset of petrochemistry in the beginning of the 20th century the source of methanol shifted to natural gas. Interestingly, the development of the according process involved iron as a catalyst and was strongly correlated to the industrial production of ammonia using the Haber-Bosch process (see introduction to chapter 8.2) at the BASF in Germany. Until now the vast fraction of methanol (and many other industrial alcohols, accordingly) is generated from synthesis gas, a mixture of CO and H_2 which is generated from cracking of natural gas.⁵² In light of the ever increasing costs of these resources and their forecasted shortage it is very likely that we will see another shift in generation of this so important alcohol towards renewable and green resources. It is of particular importance that today considerable amounts of methanol are

already generated from those sustainable resources like landfill gas, biomass degradation or simply from waste.⁷² Methanol constitutes a viable green resource for chemicals and fuels, accordingly.

The oxidation of methanol to formaldehyde and formic acid via the hydrolysis of methyl formate constitutes one of the major processing routes for methanol. Both chemicals are generated from methanol in the range of several thousand tons (formic acid) to millions of tons per year (formaldehyde).^{73, 74} It comes without further reasoning that both processes are critical in view of selectivity, waste generation, and energy consumption. The catalytic research focuses on *green* and *sustainable* catalytic concepts using renewable, ubiquitous and non-hazardous resources, consuming just a minimum of energy, for example needed for heating the reactor. Two catalytic materials are of considerable interest regarding the selective oxidation (in contrast to total oxidation): Ag and Au, as they break foremost the O-H bond of the alcohol (see chapter 8.2.3). Indeed crystalline Ag or Ag gauze are employed as industrial catalysts for the generation of formaldehyde by selective oxidation of methanol using molecular oxygen with a conversion of nearly 100 % at temperatures of about 700 °C.⁷³ As can be deduced from model experiments, Au is supposed to be a very selective catalyst for the generation of methyl formate and formic acid, accordingly. The current industrial process for the generation of methyl formate is based on the carbonization of methanol using metallic sodium as a catalyst. Several publications during the last decade focused on gold based catalysts as part of a “greener” catalytic process using the selective oxidation of methanol with molecular oxygen, the ideal resource for reactive atomic oxygen.⁷⁵⁻⁸² Most of this work emphasized the liquid phase oxidation of alcohols using gold particles in the size range of a few nanometers on oxidic supports. The activity and selectivity of the reported processes are very promising, reaching turn-over frequencies (TOF) in the order of

$0.1 \text{ s}^{-1} - 0.2 \text{ s}^{-1}$.^{78, 80, 82, 83} Still, issues which constitute problems for nanometer sized gold particles on oxidic supports are: sintering of particles, contamination and unclear role of the support material. A further obstacle is the low activity of the catalysts in the absence of base as co-catalysts.

NpAu as an unsupported gold catalyst constitutes a very interesting catalyst for this type of reaction. First experimental work in 2010 focused on the gas-phase oxidation of methanol using molecular oxygen.¹⁴ The npAu was found to be a highly active catalyst for this type of reaction already at temperatures as low as 20 °C (Figure 8.7). Beside small amounts of CO₂ stemming from the total oxidation of methanol, the only detected product was methyl formate. As anticipated from UHV experiments (chapter 8.2.3) the ester is formed by coupling of the surface bonded methoxy and formaldehyde on the npAu surface. As the tendency to undergo β -hydrogen elimination is less pronounced for methanol on Au surfaces, the selectivity is governed by the fast reaction of methoxy and aldehyde. The selectivity for the formation of the coupling product was close to 100 % under the experimental conditions (temperatures below 100 °C, oxygen concentrations between 1 vol% and 50 vol%). The activity in terms of TOF for this reaction was in the range of 0.2 s^{-1} and very comparable to the ones of highly active supported catalysts, yet, without the need of additional base as a co-catalyst. Additionally, by usage of a continuous flow reactor and deployment of methanol in the gas phase made a recovery of the catalyst, as for example necessary in a batch-type approach, obsolete. This finding gained considerable interest as the experimental conditions applied do reflect an exemplary green catalytic process.¹⁵ Importantly, the surface chemistry during reaction can be anticipated and predicted based on the mechanistic understanding derived from UHV model experiments.⁸⁴

[Figure 8.7 near here]

However, this pattern of reactivity is not restricted to methanol but can be extended to the gas-phase oxidation of longer chain alcohols such as ethanol or n-butanol containing 2 and 4 carbon atoms, respectively.⁸⁵ By using npAu as a catalyst and molecular oxygen, both alcohols can be oxidized already at temperatures well below 100 °C. Yet, the product distribution is considerably altered. In case of ethanol, the aldehyde (acetaldehyde) as well as the coupling product (ethyl acetate) are observed in almost similar proportions (Figure 8.7). In case of oxidation of n-butanol, no coupling but exclusively the formation of the aldehyde (n-butanal) was detected in the entire temperature range (up to 180 °C). In general, the activity in terms of TOF was found to decrease with increasing chain length, too. While the TOF in case of methanol oxidation was in the range of 0.2 s⁻¹, it decreases to 0.01 s⁻¹ in case of ethanol oxidation and 0.008 s⁻¹ for the oxidation of n-butanol (all numbers determined at 80 °C). Although for the latter two cases the activity of the catalyst was not tested for a maximum conversion (e.g. by supplying higher amounts of reactants possibly reaching a maximum of activity), the trend underlines that the activity decreases with increasing chain length. Ding et al. reported TOFs in the range of 0.1 s⁻¹ in case of aerobic gas-phase oxidation of benzyl alcohol to benzaldehyde over npAu. Yet, temperatures above 200 °C were necessary to achieve TOFs in this range.⁸⁶ This observation can be similarly made using supported Au catalysts.⁷⁸ However due to different supports and experimental conditions, a straight forward correlation between the observed activities as a function of the chain length of the alcohol is in these cases very difficult. With respect to unsupported npAu a possible explanation for the decreasing activity for the long chain alcohols is the more pronounced tendency to form a carboxylate species with increasing chain length.²⁵

As the experiments are performed at low temperatures and very dry conditions (5 ppm of water in the feed gas), preventing a reaction of water forming the free acid, this carboxylate species may block active sites on the surface.

The concept of oxygen mediated coupling reactions on the npAu surface can be further explored by cross (x)-coupling of two different alcohols or even two different species such as an alcohol and an aldehyde. For example, when co-dosing similar proportions of methanol and acetaldehyde the x-coupling product of both is observed (exclusively), the methyl acetate.¹⁴ This can be understood in terms of the reactivity of the aldehyde on the surface, rapidly reacting with the surface bonded methoxy. The competing β -hydrogen elimination of methoxy, on the other hand, which would lead to the formaldehyde and the self-coupling is largely suppressed due to the comparatively higher activation barrier of this step.²⁵ But also two different alcohols can be co-dosed and the cross coupling products are formed. When methanol and ethanol are co-dosed only the methyl acetate is observed, stemming from the x-coupling of methoxy and acetaldehyde on the surface.⁸⁵ The formation of either ethyl formate or methyl formate is not detected; both reactions are suppressed due to the higher activation barrier for β -hydrogen elimination of methoxy.

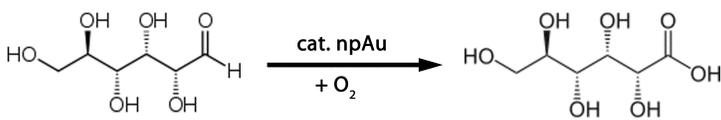
After all, the oxidation and coupling of alcohols over npAu shed light on a rich surface chemistry of Au towards selective and predictable oxidation reactions. Basic principles of reactivity can be understood and anticipated based on model experiments under UHV conditions. Especially the absence of an oxidic support material and the extended gold type surface of npAu opens the door for this correlation.

8.4 Liquid Phase Catalysis

In many cases the vapor pressure of one of the reactants is low and it is more convenient and practical to investigate the catalytic activity in the liquid phase. Regarding the interpretation of the surface chemistry and the underlying mechanism the situation is mostly distinguished from the gas phase catalysis due to the inherent higher concentration of spectator species on the surface. For example, catalysts such as gold nanoparticles on a carbon support which do not show any catalytic activity for CO oxidation in the gas phase can become catalytically active in the liquid phase.⁸⁷⁻⁹⁰ In these cases the abundance of hydroxyl groups in the liquid (water) phase is discussed to bridge the impediment of activation of molecular oxygen.⁹⁰ The liquid phase catalysis by npAu is a still evolving field; critical parameters (e.g. Ag or Cu concentration) may play a very different, as the case may be even no role anymore. In the following, we will discuss two recent and well-studied examples of the catalytic aerobic oxidation in liquid phase, namely the oxidation of organosilanes and d-glucose. Both reactions are important from an academic as well as from an industrial point of view. They are suited to demonstrate the broad potential of npAu as a catalyst also in liquid phase.

8.4.1 Aerobic Oxidation of D-Glucose

The oxidation of d-glucose is the exclusively used reaction to derive gluconic acid. This acid is a natural compound in the human body as part of the carbohydrate metabolism. It is also used for example in the food industry as an acidity regulator (E574) or in cleaning products as a mild acid. The annual production of gluconic acid amounts to about 60,000 tons.⁹¹



(Equation 8.1)

Besides biotechnological production (i.e. fermentation) using enzymes such as *Aspergillus niger* and *Gluconobacter suboxydans* the catalytic oxidation of glucose using molecular oxygen and metal catalysts is a viable alternative.^{91, 92} Finely dispersed Pt group metals on oxidic supports, such as alumina, or activated charcoal (carbon black) were employed for this reaction since the 1970s.^{82, 93} The fast decay of catalyst activity and the insufficient selectivity of these catalysts fueled an ongoing research on an alternative catalyst design. The lack of reactivity of Au surfaces with respect to the unfavorable activation of C-H and C-C bonds was already discussed in the context of oxidation of alcohols, such as methanol and ethanol, in the chapters 8.2.3 and 8.3.2. Accordingly, Au as a promising highly selective catalyst was investigated for this type of reaction. In 2002 Biella et al. reported finely dispersed Au on carbon supports being highly selective and active catalysts for this type of reaction already at temperatures in the range of 330 K using molecular oxygen and water as solvent. Carbon appeared to be the support of choice regarding liquid phase oxidation reactions; this is noteworthy as in the case of gas phase oxidation reactions carbon is known as an inert support leading to poor catalytic activity. Besides a different mechanism of activation of molecular oxygen in the liquid phase⁹⁰, it seems that an inert support material such as carbon prevents strong sticking and thus poisoning of the catalyst by either the reactants or intermediates and thus leads to higher activity. Rossi et al. demonstrated that the absence of a support is even most favorable.⁹⁴ Unsupported colloidal gold particles in the size of about 3.6 nm were astonishingly active for glucose oxidation.⁹⁴ The detected turn-over frequency (TOF) was in the range of 14 s^{-1} , thus about fourteen times higher than the maximal TOF measured on supported gold particles⁹⁵. This high activity was achieved by using glucose not only as a reactant but also as stabilizing agent so that the gold colloids were

stable but “naked” particles. Unfortunately, the high activity of particles led to deactivation within just minutes due to sintering of particles from 3.6 nm to over 10 nm in size.

In 2008 Ding et al. demonstrated that unsupported nanoporous gold is an active and stable catalyst for this type of reaction, too.⁹⁶ The experiments were performed in a glass reactor containing a solution of 0.1 M d-glucose and 20 mg crushed npAu. The pH of the solution was controlled and adjusted, respectively, using an automated potentiometric titrator. The oxygen was bubbled through the reaction solution from underneath. Every hour a small volume of the mixture was sampled and the conversion determined. The resulting conversion over time is depicted in Figure 8.8. Noteworthy, the selectivity of the oxidation reaction was found to be close to 100 %, this means that almost no isomerization into fructose or other biproducts was detected.

[Figure 8.8 near here]

The reaction proceeded already at very mild temperatures slightly above room temperature (303 K). As expected for a chemical reaction, the conversion of reactants proceeded faster with rising temperature. By increasing the temperature to 323 K the conversion was doubled and resulted in appreciable yields. The pH value of the reaction media was found to be critical for catalytic conversion. As was also reported for supported Au particles, alkaline conditions were favorable for the reaction ($\text{pH} > 7$).⁹⁷ In case of npAu a pH of 9 was found to be optimal as the activity was not only the highest but the conversion of glucose also increased over the entire duration of the experiment. Besides the catalysts activity and selectivity it is the stability of the self-contained nanostructure of npAu which renders this material so interesting. The catalytic

conversion using the same sample of npAu in two subsequent experiments (7 hours duration each) was found to be virtually the same (Figure 8.8). This finding is well in line with scanning electron micrographs of the sample before and after reaction showing no increase in pore or ligament size (30 nm) which would indicate ripening. Noteworthy, also npAu samples containing smaller (e.g. 6 nm wide) ligaments were prepared. Those samples initially showed higher catalytic activity owing to the increased specific surface area, yet, lesser catalyst stability. For example the ligaments in the range of 6 nm increased to about 15 nm after 7 hours of catalytic conversion with accordingly reduced activity. Although the activity of npAu in this study was somewhat lower than that of (supported) gold catalysts – likely owing to the higher specific surface area of such catalysts – it shows very promising catalyst stability. Using molecular oxygen as the oxidizing agent and water as the solvent also makes it an environmentally benign process.

8.4.2 Oxidation of Silanes

Hitherto, we reported exclusively on the aerobic oxidation of carbon based entities, such as methanol, ethanol, or glucose, a transformation which is of outmost importance in academic as well as industrial organic chemistry. Interestingly, in 2010 Asao et al. reported on the oxidation and hydrolysis, respectively, of silicon based compounds such as organosilanes to organosilanoles using npAu (Equation 8.4.2). In the periodic table silicon (Si) is positioned in the same group (14) as carbon and contains the same number of valence electrons. As a consequence some aspects of its chemistry such as the tendency to form tetrahedral compounds with the valence number of 4 are similar to carbon. Organosilanes are derived from silanes (e.g. SiH_4), yet, one or more hydrogen atoms are replaced by an organic entity. Silanols, or silicon based

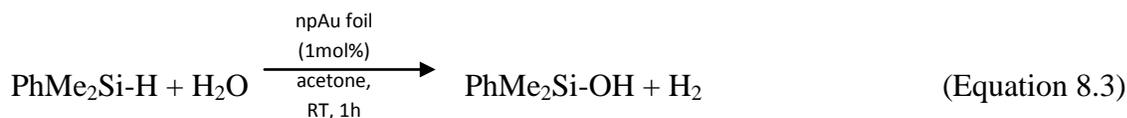
alcohols, can be derived by oxidation/hydrolysis of silanes according to the following equation:



Traditionally, silanols are used as building blocks in synthetic chemistry to generate for example metallasiloxanes.^{98, 99} Very similar to the acidity of alcohols discussed in chapter 8.2.3, the proton of the OH group can react in a Brønstedt type acid-base reaction forming a Si-O-Metal bond. Those compounds are called metallasiloxanes. Several attempts aimed at the synthesis of ceramics using for example metallasiloxanes as precursors.^{100, 101} Silanols tend to polymerize forming longer chain Si-O-Si entities (such as in ceramics) by splitting off water. When using the appropriate silanol containing a specific organic group one can generate various silicon based polymers.¹⁰² A recent review of the chemistry of organosilanols can be found in ref.¹⁰².

As oxidizing agent for the oxidation of organosilanes, chemicals, such as ozone, AgNO₂ or KMnO₄, have been used, just to name these few.¹⁰² However, molecular oxygen or water as oxidizing reactants would be preferable (according to Equation 8.2), since they are of course non-poisonous, non-hazardous and inexpensive and the resulting by-products, hydrogen or water, are non-polluting, too. In 2009 Kaneda et al. reported that gold nanoparticles are suitable and very active catalyst for this type of reaction.¹⁰³ Recently, Asao et al. used 40 μm thin nanoporous gold foil in liquid phase to oxidize various organosilanes.¹⁰⁴ Just giving one example, by using finely dispersed 1 mol% of npAu as a catalyst dimethylphenylsilanol was derived within one hour at room temperature with nearly 100 % yield (Equation 8.3). The turn-over-frequency for this reaction was calculated to be about 3 s⁻¹. Importantly, the npAu catalyst

could be recycled and reused several (i.e. more than 5) times.



When using a gold foil with the same dimensions instead of the npAu foil the activity dropped drastically, implying that the surface area and the nanostructure of the material play a decisive role. However, the exact mechanism of the catalytic conversion has not yet been clarified.

8.5 Surface Modification of Nanoporous Gold by Metal Oxides

The self contained nanoporous structure of npAu opens further options for the preparation of high performance materials by modifying it with certain additives. Of particular advantage is the high electrical and thermal conductivity of the bicontinuous monolithic structure of npAu leading to a large range of interesting applications. For example Qian et al. demonstrated that by coating npAu with alumina the optical properties of the materials can be tuned.^{105, 106} Ding et al. demonstrated that by applying titania particles on the npAu outer surface a very interesting photocatalytic electrode material can be generated.¹⁰⁷

The combination of npAu with metal oxides for catalytic applications is a very promising approach for several reasons. First, pure gold lacks the ability of efficiently activating molecular oxygen which is the natural source for reactive atomic oxygen. In case of npAu this obstacle can be overcome by traces of a less noble metal (Ag, Cu) in the material. As shown for gold nanoparticles by combining gold with metal oxides such as titania or iron oxide highly active oxidation catalysts can be generated, too.¹⁰⁸ Accordingly, metal-oxides are interesting additives, possibly leading to even more active oxidation npAu catalysts. Second, nanostructured metals

are prone to temperature activated rippling and coarsening of structures limiting the applicability at high temperatures. Especially in case of gold the inherent instability of nanosized structure leads to fast deactivation at elevated temperatures. Biener et al. recently demonstrated that by coating npAu with for example Al_2O_3 the nanostructure of npAu can be conserved even at temperatures of 1000 °C while ligaments in pure npAu start coarsening already at temperatures of about 200 °C. This opens the door for applications such as in automotive converters.

In general two different ways of depositing metal oxides in the nanoporous structure of npAu are possible: A) deposition from the gas phase e.g. by chemical or physical vapor deposition techniques (ALD, CVD, PVD) or B) deposition from liquid phase, meaning by immersion of npAu samples into a solution containing either the metal oxide or a viable precursor. In the following, we will report on two examples showing how modification of npAu with metal oxides can lead to highly active and stable catalysts . Obvious choices for additives are reducible metal oxides like TiO_2 , CeO_2 or FeO_x as these materials are known to lead to high activity in case of gold nanoparticle based systems.

8.5.1 Gas-Phase Deposition: ALD Modified Nanoporous Gold

Atomic layer deposition (ALD) was shown to be an especially dedicated gas phase deposition technique for the coating of high aspect ratio materials.^{109, 110} In case of free standing films of npAu with a thickness of 200-300 μm and a pore size of about 30 nm, the aspect ratio - this is the length of the pore referred to its diameter - amounts to several thousands. The slow diffusion of molecules into inner sections of the material is a major obstacle when aiming at a conformal coating of the inner surface and avoiding clogging of pores close to the outer surface. ALD consists of self-limited surface reactions (i.e. chemisorption) of precursors (see Figure 8.9). By

separately dosing reactants the maximal amount of material deposited during one cycle of ALD is ideally only 1 monolayer. This limitation makes ALD an ideally suited technique for conformal coating of high-aspect ratio materials.

In the first study of this kind, Biener et al. deposited TiO_2 inside the npAu to generate a highly catalytically active material. Titania was chosen as an exemplary reducible oxide leading to highly active gold based catalytic materials. For deposition a well-established process using titanium tetrachloride (TiCl_4) and water (H_2O) ALD was deployed. TiCl_4 exhibits a sufficiently high vapor pressure so that reasonable partial pressures in the gas phase can be realized already at temperatures slightly above 100 °C. The molecule readily reacts (hydrolyzes) with water and hydroxyl groups on the surfaces forming a “ $\text{Cl}_3\text{Ti-O-Au}$ ” layer. As there are no hydroxyl groups left on the surface after reaction, residual TiCl_4 not chemisorbed to the surface can be removed by pumping and purging of the system, respectively. By subsequently dosing water, the residual chloride groups are removed by hydrolysis and a first “ $(\text{HO})_2\text{OTi-O-Au}$ ” layer is formed. This corresponds to one cycle of ALD. The impeded mass transport in and out of the pores can be accounted for by prolonged purge and pump times (i.e. 90 s). The average growth rate for the TiO_2 deposition was about 0.07 nm per ALD cycle. Considering the {101} lattice spacing of the Ti anatase phase of 0.35 nm¹¹¹ this would correspond to roughly 1/5 of a monolayer as an equivalent of a closed layer of titania on the surface.

The impact of the titania coating on the temperature stability of the material was investigated by annealing (Figure 8.9). While pure npAu samples start coarsening at around 200 °C, the titania coated samples (30 cycles of titania ALD) showed enhanced stability up to temperatures of 600 °C. This lower temperature as compared to for example alumina coated samples is in line with the comparatively lower crystallization temperature of titania of 370 °C¹¹² as compared to

alumina $\sim 950\text{ }^{\circ}\text{C}$ ¹¹³. At this temperature, the initially amorphous layer of titania transforms into titania crystallites (anatase) leading to the break-up of the initial film.

After this initial break-up of the continuous titania film, it was found that the samples were catalytically active. Note that titania itself is not catalytically active meaning that a closed layer of approximately 2 monolayer thickness (e.g. after 10 cycles of ALD) on the gold surface is not expected to show detectable activity.¹¹⁴ Yet, after the break-up of the film and the formation of titania particles on the npAu surface, catalytic activity evolves. The activity for CO oxidation (measured at $60\text{ }^{\circ}\text{C}$) of the titania modified sample was noticeably amplified by a factor of about 5 as compared to the pure npAu (Figure 8.9). The enhanced catalytic activity of the TiO_2/npAu system is likely due to an increased activation of molecular oxygen as this is the reaction step with probably the highest activation energy and thus most hampered on pure gold surfaces (see considerations in chapter 8.2.1).

[Figure 8.9 near here]

8.5.2 Liquid-Phase Deposition

Aside from deposition of metal oxides through the gas phase as reported in the previous chapter, another viable route is the deposition of either the metal oxide or its precursor from solution. The advantage of these bench-top techniques is that they are connected with a significantly reduced experimental and instrumental demand. Ding et al. first used the deposition of TiO_2 particles suspended in ethanol in 2009.¹⁰⁷ Although the majority of particles were larger than the pores and accordingly were only deposited on the very outer surface of the npAu material, the resulting electrode material showed very promising photocatalytic performance.

Wittstock et al. deployed a comparable technique to generate TiO₂/npAu composite materials for catalytic gas phase CO oxidation.¹¹ Titania particles in the form of a commercially available powder (e.g. TiO₂ nanopowder from Sigma Aldrich, particle sizes below 100 nm) were suspended in ethanol (here 2.5 g/mL). Droplets of this suspension were applied to the outer surface of a free standing npAu membrane (200 to 300 μm thick). The membrane was subsequently rinsed to remove excess of particles from the outer surface. Scanning electron micrographs (SEM) showed that the majority of particles were clearly deposited on the outer surface of the material. Yet, the catalytic activity for CO oxidation was enhanced by about a factor of 5 as compared to an un-modified npAu sample. Transmission electron micrographs showed that also particles in the size of 10 nm are contained in the titania powder. It is reasonable that particles smaller than the ligament size can be sucked into the pores and thus deposited even below the outer surface while being suspended in the ethanol due to capillary action.

[Figure 8.10 near here]

Besides direct application of titania particles the application of a precursor is a another viable means to generate TiO₂/npAu composites. Wichmann et al. demonstrated that by using titanium isopropoxide (TTIP) which is a liquid at room temperature conformal coating of TiO₂ in npAu can be achieved.¹¹⁵ After immersion of a free standing membrane (disk with a diameter of 5 mm and a thickness of about 250 μm) in a TTIP solution and subsequent calcination at 400 °C the npAu (inner-) surface was abundantly covered with TiO₂ particles in the size of about 5 nm. Quantification by EDX showed a content of about 3.5 wt% of titania inside the npAu structure

(e.g. 30 μm below the outer surface). The catalytic activity of these TiO_2/npAu samples was greatly enhanced as compared to the pure npAu (Figure 8.10). Besides being highly active, the nanostructure of the oxide modified npAu system could be preserved at temperatures as high as 400 $^\circ\text{C}$ (Figure 8.10). Even in sections of the membrane being 100 μm far from the outer surface of the membrane a stabilization of the ligaments could be observed (Figure 8.10). However, in those deep sections a bimodal ligament size distribution indicated a lower coverage of the surface and thus reduced stabilization. This is in line with a reduced amount of titania detected by EDX in deeper sections of the membrane (e.g. 1 wt% as compared to 3.5 wt% close to the outer surface). As a result of the stabilization of the nanostructure, the TiO_2/npAu samples showed considerable catalytic durability at high temperatures; for example at 250 $^\circ\text{C}$ the catalytic activity for CO oxidation did not considerably decrease over the period of several days. In a similar attempt Wichman et al. showed that this approach can be expanded to other metal oxides such as praseodymia (PrO_x). Immersion of a npAu membrane in a solution of $\text{Pr}(\text{NO}_3)_3$ in ethanol (20 g/L) and subsequent calcination to 500 $^\circ\text{C}$ lead to deposition of praseodymia particles inside the pores on the npAu surface. In this case the catalytic activity of the composite material was enhanced for CO oxidation, too (Figure 8.10).

Summing up, the combination of the npAu material with a suitable metal oxide indeed can result in highly active catalytic materials with superior stability and durability, especially at elevated temperature. This opens the door for high temperature applications as for example in automotive converters which was an obstacle for gold based catalysts so far. However, it is noteworthy that by coating the npAu surface with metal oxides a reversed situation as for example opposed to oxide supported metal nanoparticle catalyst is realized. Comparing the systems in detail may also contribute to the mechanistic understanding of both systems.

8.6 Summary and Remarks

In this chapter we reported on the various aspects of the surface chemistry and catalysis of npAu. We first discussed the interaction of oxygen with pure gold surface as this is the starting point for the catalytic activity of gold surfaces. Yet, the dissociation of molecular oxygen which is the natural source for oxygen as it is abundantly contained in the surrounding atmosphere (about 20 vol%) has a very low probability and is hardly detectable on pure gold surfaces. It is observed that in case of npAu this hurdle can be overcome by small traces of the residual less noble component (Cu or Ag) which is contained in the material after preparation. The oxygen species present on the npAu surfaces (prepared by decomposition of ozone) are the same as one can observe on single crystalline surfaces.

In the following we discussed two classes of gas phase catalytic reactions of molecular oxygen with increasing complexity: first, the reaction of CO and second, various alcohols with increasing chain length (methanol, ethanol, etc.). In both cases we discussed the reactivity in terms of activity and selectivity in strong correlation with results obtained from UHV studies. A pattern of reactivity can be found and explained on the molecular level. It is the extended gold surface and the absence of any support material which makes this material an ideal candidate for transferring knowledge gained from UHV studies to a catalyst working under “real world” ambient pressure conditions. We subsequently discussed two well studied and important catalytic reactions performed in the liquid phase, the oxidation of glucose and organosilanes over npAu. Both reactions exemplify the potential of npAu as a versatile catalyst combining activity with durability and good recyclability.

In the last section we discussed latest research on the chemical functionalization of the npAu

surface with metal oxides. The bicontinuous and monolithic structure of npAu makes it particularly attractive for a material design involving the npAu as an active and tunable scaffold. We reported on latest work using liquid and gas phase deposition techniques decorating the npAu surface with metal oxides such as titania or praseodymia. In both cases, the catalytic activity for CO oxidation can be drastically amplified. Additionally, by putting metal oxides on the gold surface its mesoscopic structure can be conserved at temperatures of several hundred degrees Celsius. This opens the door for catalytic applications at elevated temperatures as for example in the automotive converter.

The catalysis with npAu is only roughly five years old, starting with the first publication of its activity for the low temperature CO oxidation in 2006. Yet, in those last five years several fascinating discoveries were made, resulting in more than 40 papers as of today¹¹⁶, covering the catalytic conversion of various compounds. Most importantly, in several cases the reactivity of the npAu could be interpreted and thus anticipated on the molecular level based on models derived from UHV and DFT model studies. This is the very fundament for a future development of the material for catalytic applications. Future work will have to be devoted into three directions, the discovery of new catalytic reactions (including hydrogenation reactions), an ongoing effort to correlate and understand the surface chemistry based on models of the molecular transformations on its surface and last but not least a material design aiming at an optimized performance of the material in terms of activity, selectivity but also durability and recyclability as all of them determine the economic viability of the entire catalytic process. Given the fact that the efforts of the last five years will continue in a comparable manner, one can anticipate further considerable progress in all three fields within the next years.

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