Catalysis by Unsupported Skeletal Gold Catalysts

ARNE WITTSTOCK* AND MARCUS BÄUMER

Institute for Applied and Physical Chemistry and Center for Environmental Research and Sustainable Technology, University of Bremen, 28359 Bremen, Germany

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CONSPECTUS

Catalysis is one of the key technologies for the 21st century for achieving the required sustainability of chemical processes. Critical improvements are based on the development of new catalysts and catalytic concepts. In this context, gold holds great promise because it is more active and selective than other precious metal catalysts at low temperatures. However, gold becomes only chemically and catalytically active when it is nanostructured.

Since the 1970s and 1980s, the first type of gold catalysts that chemists studied were small nanoparticles on oxidic supports. With the later onset of nanotechnology, a variety of nanostructured materials not requiring a support or organic stabilizers became available within about the last 10 years. Among these are gold nanofoams generated by combustion of gold compounds, nanotube membranes prepared by electroless deposition of gold inside a template, and corrosion-derived nanoporous gold. Even though these materials are macroscopic in their geometric dimensions (e.g., disks, cubes, and membranes with dimensions of millimeters), they are comprised of gold nanostructures, for example, in the form of ligaments as small as 15 nm in diameter (nanoporous gold, npAu). The nanostructure brings about a high surface to volume ratio and a large fraction of low coordinated surface atoms.

In this Account, we discuss how unsupported materials are active catalysts for aerobic oxidation reaction in gas phase (oxidation of CO and primary alcohols), as well as liquid phase oxidation and reduction reactions. It turns out that the bonding and activation of molecular oxygen for gas phase oxidations strongly profits from trace amounts of an ad-metal residue such as silver. It is noteworthy that these catalysts still exhibit the special gold type chemistry, characterized by activity at very low temperatures and high selectivity for partial oxidations. For example, we can oxidize CO over these unsupported catalysts (npAu, nanotubes, and powder) at temperatures well below water's freezing point ($-30\ °C$) and with turnover frequencies up to $0.5\ s^{-1}$ (at 30 °C). Yet, we can anticipate the surface chemistry of these unsupported and extended gold surfaces based on model experiments under UHV conditions. We have demonstrated this for the selective oxidation of primary alcohols at low temperatures employing npAu catalysts.

Chemists have paid growing interest to oxidation and reduction reactions in liquid phase catalysis, most suitable for synthetic organic chemistry. Early work on the aerobic oxidation of D-glucose in 2008 using Raney type npAu already showed the potential of this type of catalyst for liquid phase reactions. Since then, researchers have investigated further oxidation reactions (silanes to silanols) and reduction reactions of alkynes, as well as C−C coupling reactions ([4 + 2] benzannulation) and azo compound decomposition, with likely several more reactions to be reported in the next years. The advantage of this unsupported skeletal type of catalyst is its recyclability and retrievability without leaching of gold into the reaction medium, owing to its monolithic structure. Even though these materials contain nanoscopic structures, they are macroscopic in their geometric dimensions and pose no threat to the environment or health as discussed for other nanomaterials.
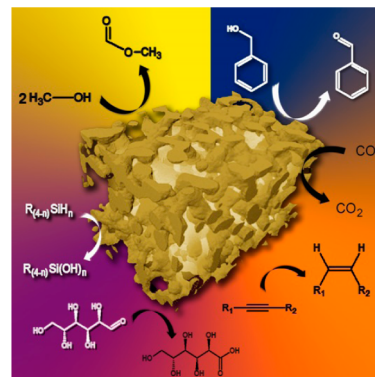
Introduction

The sustainable and green development of the chemical industry is a key scheme for the 21st century. The first oil crisis in 1973 raised awareness of the limited availability of energy and resources from traditional sources such as oil and gas for the first time. Again, it took almost 40 years to bring this issue back into the public attention. It is evident that improvements can only be achieved through technological innovations. Since catalysis plays a critical role in the production of the vast majority of bulk and commodity chemicals, it will be one of the key technologies for the development of a more sustainable industry. Besides further improvement

of existing catalysts, the development of novel catalysts and catalytic concepts is essential. Intriguingly, the most "noble" metal, gold, may play a central role in this context. For a long time, the use of gold was basically restricted to monetary assets and jewelry, and the technological importance of gold limited to conductive and inert coatings, for example, in electronics or brazing alloys.[1] Certainly, gold always played a prominent role in the natural sciences; Ernest Rutherford used a gold foil for proving his atomic theory in 1911.[2] Yet, the chemistry of gold and thus the use of gold in catalysis remained very limited, because bulk gold is very unreactive.[3] This changed with the onset of nanotechnology, and since the 1980s, gold in the form of nanoparticles has gained sustained and growing interest. The reason is gold's high activity and selectivity for catalytic reactions under mild and green conditions if nanostructured.[4] When in the right form (e.g., nanoparticles on a suitable oxidic support) gold at room temperature is more active than platinum for the aerobic oxidation of CO by orders of magnitude.[5] Besides its activity at low temperatures, gold is distinguished by its selectivity, since it does not attack C−C (single) or C−H bonds in organic compounds.[6] From an economic point of view, it is considerably cheaper than platinum or rhodium, that is, it is not a particularly expensive precious metal. Today, gold as a catalytic material reached first economic applications, for example, in automotive converters.[7]

The majority of research on gold catalysis, hitherto, was focused on supported gold nanoparticles.[10] Reasons for this are the established synthetic routines for the preparation of supported nanoparticles and the beneficial impact of the support on the catalytic activity.[11] Recent developments in nanotechnology, however, opened the door to a variety of unsupported nanostructured gold materials (Figure 1). Prominent examples are Raney type nanoporous gold,[1] gold foams formed by combustion,[8] gold tubes and membranes,[9] gold nanowire assemblies,[12] gold powder,[13] and colloidal gold in solution.[14] This Account will focus on a monolithic skeletal type of unsupported catalysts (cf. Table 1; for colloidal gold systems, we refer to a recent review article by Garcia and co-workers[14b]). This type of unsupported catalyst has great potential in catalysis, because of its advantageous physical properties. If prepared properly, it can provide very high surface to volume ratios, minimizing the dead bulk volume. At the same time, the material is heat and electrically conductive, making it an ideal candidate for electrocatalytic applications. In addition, it is a high strength material,[15] providing good abrasion resistance, for example, in a slurry reactor, or making catalytic coatings possible.[16] Its
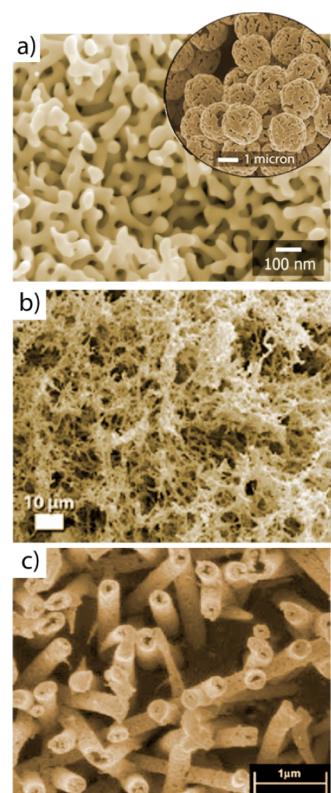

FIGURE 1. Examples of unsupported gold materials: (a) Corrosion-derived nanoporous gold consisting of a continuous pore and ligament structure on the order of 40 nm. This material can be applied as catalytic coatings (inset). (b) Nanogold foam prepared by combustion of a gold compound (reproduced from ref 8, copyright 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim). (c) Gold nanotube membrane prepared by electroless deposition of Au into a track etched polymer membrane (reproduced from ref 9, copyright 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

solid (monolithic) structure makes it a prime example of a recyclable and easily retrievable catalyst material.

Oxidation reactions under mild conditions are a central focus of research (Table 1). Since the first discovery of the catalytic activity of gold, the question about the conditions under which it becomes active, that is, binds and activates molecular oxygen, has been a matter of debate.[13c,17] In essence, the catalysis with gold requires a team, not only a nanostructured gold surface but also a set of "helpers" such as the support material or other metallic additives.[11] This also poses the important question under which circumstances unsupported gold materials are active catalysts.[18] While in liquid phase the presence of a reducing agent such as $NaBH_4$[12] or a base or just water for oxidation reactions[14b,19] can be sufficient and pure nanostructured gold material becomes active, the activation of molecular oxygen for gas phase oxidation reactions typically benefits strongly from traces of an additional metal such as Ag[18b,20] or the addition of metal oxides onto the gold surface.[21]

TABLE 1. Overview of Selected Unsupported Gold Catalysts, Their Characteristic Feature Size (for Example, Ligaments and Pores for Foams or Outer Diameter in Case of Nanotubes (in Parentheses Specific Surface Area)) and Catalytic Reactions for Which They Have Been Demonstrated To Be Active Catalysts

material	feature size	preparation	catalytic reaction
nanoporous gold	~40 nm (4−30 m^2/g)	corrosion of Au−X alloy	CO oxidation,[22] oxidation of primary alcohols,[23] benzyl alcohol,[24] glucose,[25] and organosilanes,[26] hydrogenation of alkynes[27] and quinolines,[28] [4 + 2] benzannulation,[29] decomposition of azo compounds[30]
gold foams	~50 nm (11 m^2/g)	combustion of Au compounds	CVD growth of carbon nanotubes[8]
gold nanotubes	200 nm (OD) (5.6 m^2/g)	electroless deposition inside polycarbonate matrix	CO oxidation[9]
gold powder	25−160 nm (2−4 m^2/g)	vacuum evaporation of gold metal	CO oxidation[13]

In this Account, we will discuss the gas phase and liquid phase catalysis of unsupported gold catalysts. The emphasis will be on the nanoporous gold (npAu), which has been more extensively researched than any other unsupported gold catalyst. This Account is organized as follows: We will first discuss heterogeneous gas phase catalysis, the aerobic oxidation of CO and alcohols. In the second part, we will summarize latest progress in employing unsupported npAu as a Raney type catalyst for a variety of reactions in synthetic organic chemistry. This section is labeled heterogeneous liquid phase catalysis, accordingly. Among the reported reactions, we will discuss oxidation and reduction reactions, as well as ring formation (C−C bonding) reactions.

Heterogeneous Gas-Phase Catalysis

The aerobic oxidation of CO is one of the prime reactions in heterogeneous catalysis. First of all, this reaction has industrial relevance in exhaust gas treatment and the automotive converter, removing poisonous CO from combustion exhaust. The activity of gold type catalysts for this reaction under milder conditions, exemplified by a reduced light off temperature by more than 100 °C compared with other precious metal catalysts (Pt, Rh, or Pd), resulted in increased research efforts making gold the promising candidate for solving the cold start-up period of the automotive converter.[17d,31] Indeed, one of the first commercial applications of gold today is in the form of the automotive converter (NS Gold from Nanostellar Inc.). Additional industrial relevance for gold and the oxidation of CO originates from its selectivity to oxidize CO in the presence of H$_2$ and thus remove this contaminant in fuel cell feed gas, which poisons the Pt electrodes.[32] In addition to its industrial relevance, CO oxidation is usually employed for probing and characterizing the catalytic activity because it is a widely studied reaction in particular under ultrahigh vacuum conditions.

The first reports about the catalytic activity of unsupported gold for this type of reaction were published in 1999 by Haruta and co-workers.[13a] A finely dispersed gold powder with particle size of 25−50 nm was investigated in a closed recirculation reactor. After introduction of reactants in a stoichiometric ratio (O$_2$/CO, 1:2), the reaction kinetics were monitored by measuring the pressure as a function of time at temperatures between −20 and +20 °C (CO + ^{1}/$_2$O$_2$ → CO$_2$). Unexpected at this point was that the catalytic activity of the seemingly pure gold was very similar to that of a supported catalyst (Au/TiO$_2$), which was only later explained by traces of a less noble metal (Ag) in the material from production of the gold fine powder.[13c] A few years later, Dumesic and co-workers reported on a gold nanotube membrane for catalytic oxidation of CO (Figure 1).[9] They prepared gold nanotubes with diameters of about 200 nm using a 10 μm thick track-etched polycarbonate matrix. Gold was deposited inside the pores by electroless deposition, the polycarbonate matrix was partially (2.3 μm) removed, exposing gold nanotubes on one side of the membrane. The resulting material was investigated for catalytic conversion of CO in a membrane reactor (O$_2$/CO ratio 1:1; setup, see Figure 2). This material was active already at temperatures of 300 K, increasing by a factor of 10 when water vapor was added to the gas stream (turnover frequencies, TOF, as high as 0.04 s^{-1}). Besides the influence of water on the activity of this unsupported gold catalyst, the preparation involving a metallic Ag layer for preconditioning of the matrix surface might have played a similar role as for the unsupported gold powder. It will be discussed in the following sections how very small quantities, fractions of a percent, of an ad-metal such as Ag can contribute to the catalytic activity of unsupported systems making them even more active than supported particle catalysts.

The most studied unsupported gold catalytic system is npAu (Figure 1).[1] This material is generated by corrosion of a Au alloy containing less noble metals such as Ag or Cu. While the less noble metal is removed, the gold forms a three-dimensional porous network of gold ligaments on the order of a few tens of nanometers, typically around 40 nm, but
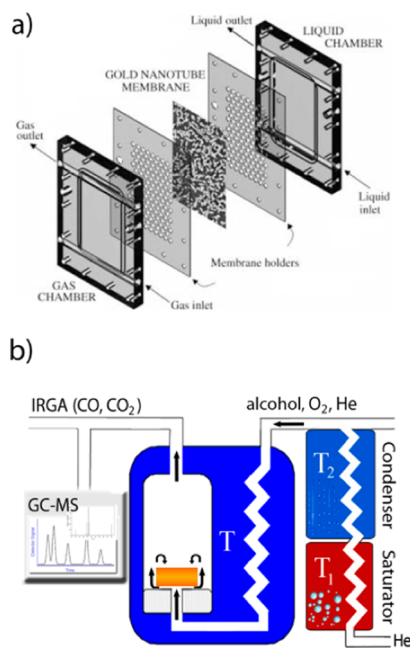
FIGURE 2. Schematics of reactors: (a) A membrane reactor for investigation of self-supported gold membranes.[9] This reactor consists of two chambers facing the membrane, one is filled with gas and the other one can be filled with liquid (reproduced from ref 9, copyright 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim). (b) Reactor schematic for investigating unsupported porous gold in a continuously operated plug flow reactor in gas phase. The gas stream is circulating around the sample; reactants and products are diffusing into and out of the porous network.

depending on the preparation technique also as small as ~15 nm. First reports on the catalytic activity of npAu for the oxidation of CO were published in 2006 and 2007 by the groups of Bäumer and Ding.[22] The material oxidizes CO already at temperatures as low as −30 °C with stable conversion over a period of days. The conversion of CO as a function of oxygen in the feed is depicted in Figure 3. The reaction of CO with oxygen increases with the supply of reactants. The reaction orders of CO and oxygen were found to be 1 and (close to) 0, respectively.[18b] No poisoning by either reactant, even when in excess, was detected, indicating that the adsorption of both reactants on the gold surface is not competitive. Indeed, the dissociation probability of molecular oxygen on pure gold surfaces is very low,[33] which seemingly contradicts the observed high activity. High resolution electron microscopy revealed that step and kink sites on the curved surface of the nanosized ligaments is comparable to that of 3−5 nm gold particles.[34] Step and kink sites are more reactive toward adsorption of CO[35] and are speculated to be beneficial for the chemisorption of O_2,[36] experimental studies of supported gold nanoparticles imply however that this is not the main route for O_2 activation.[11]

Careful analysis of the samples also showed small quantities of Ag (~0.6 atom %) remaining from the preparation of the material (Figure 3). In case of the oxidation of CO, the activity increases with increasing content of Ag in the bulk, by trend.[37b] In order to shed light on the apparent influence of Ag on the catalytic activity, Moskaleva et al. performed DFT calculations on representative Au surfaces containing different fractions of Ag.[20,37a] Especially the activation of molecular oxygen strongly profits from the presence of Ag atoms in the Au matrix. Schaefer et al. demonstrated that the Ag content on the surface of npAu is not a constant but rather a function of the chemistry on the surface (Figure 3).[38]

A further very important catalytic reaction from an industrial as well as from a mechanistic point of view is the aerobic oxidation of primary alcohols. The most industrially relevant alcohol is methanol, which is converted into its oxidation products on the order of millions of tons per year.[38] Recent progress toward a green generation of methanol from landfill gas or biomass degradations proves that this process has a great potential for becoming sustainable and green.[39] Additional effort accordingly has to be made for improving the catalytic oxidation of this alcohol.[40] In 2010 , the first reports about the catalytic oxidation of methanol with O_2 in the gas-phase under mild conditions using npAu were published.[23b] Aside from negligible amounts of the unwanted CO_2, the main product was methyl formate.[23b] The key to the reactivity of the extended gold surface is surface oxygen. This oxygen reacts with the methanol forming surface bonded methoxy (Figure 4). Further reaction of oxygen with the β-hydrogen of the methoxy results in formation of the aldehyde. Fast reaction of these surface species results in the coupling product methyl formate. As anticipated by model experiments,[41] the coupling product was almost exclusively formed using npAu catalysts for this catalytic conversion (<100 °C, 1−50 vol % O_2). This pattern of reactivity could be further extended to the oxidation of primary alcohols with longer carbon chains such as ethanol or n-butanol.[23a] The longer the carbon chain the higher the tendency to form the aldehyde by β-hydrogen elimination.[41] In case of n-butanol, the aldehyde (n-butanal) was formed with 100% selectivity. Even though these were not the first reports on the use of gold for the oxidation of alcohols (before gold nanoparticles dispersed, e.g., on titania were found be active for this reaction[42]), they gained considerable interest: the extended gold surface of the npAu provided an ideal platform for a predictable catalyst based on UHV model experiments.
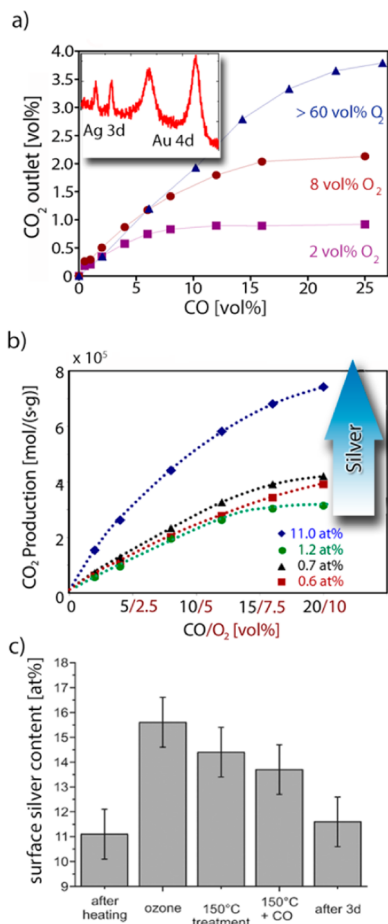
FIGURE 3. Catalytic oxidation of CO with molecular oxygen using the npAu catalysts. (a) The conversion increases with the supply of CO and oxygen (40 °C, 50 mL/min flow of gases, GHSV ≈ 50000/h). The inset depicts a photoemission spectrum (XPS) of the Ag 3d and Au 4f region of the npAu sample. (b) Samples prepared with increasing amount of residual Ag (bulk) show an increase of activity for CO oxidation. Reproduced from ref. 37a with permission from the PCCP Owner Societies. (c) The Ag present at or near the surface is a function of the environment.[38] While the as prepared sample (bulk ~0.5 atom % Ag) contains about 11 atom % Ag in the surface region (determined by XPS), it can be reversibly increased to nearly 16 atom % upon strong oxidation of the surface by ozone. Reprinted with permission from ref. 38. Copyright 2012 American Chemical Society.

Heterogeneous Liquid Phase Catalysis

In the last about 2 years, considerable progress has been made to investigate the reactivity of the Raney type npAu material for reactions in liquid phase. Besides important oxidation reactions of secondary alcohols,[43] glucose,[25] and organosilanes,[26] reduction reactions of alkynes[27] and quinolines,[28] also C−C ring formation reactions ([4 + 2] benzannulation)[29] and azo compound decomposition reactions[30] have been reported. This considerable growth in versatility of reactions underlines that gold, also in its unsupported form, has become an important material in chemical synthesis.
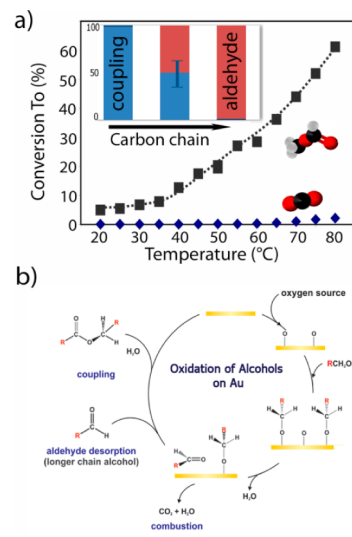

FIGURE 4. Oxidation of primary alcohols using npAu catalysts (disks of 5 mm diameter and 200 μm thickness) employing a constant flow reactor (Figure 2b). (a) The conversion of methanol to methyl formate ("coupling") already proceeds at 20 °C (1 vol % O_2 + 2 vol % methanol, 50 mL/min total flow, He carrier). (inset) selectivity as a function of the carbon chain length (methanol, ethanol, n-butanol). From ref. 23b. Reprinted with permission from AAAS. (b) Reaction scheme for the oxidative coupling of primary alcohols on Au.

The first reaction studied in liquid phase using npAu was the oxidation of D-glucose to industrially important gluconic acid.[25] Aside from biotechnological production, the role of precious metal catalysts for this oxidation reaction has been growing since the 1970s.[44] In 2002, Biella et al. reported on the use of supported gold for the selective and "green" aerobic oxidation of glucose (water as solvent, reaction at 330 K).[45] The activity of the gold catalyst could be considerably increased by 1 order of magnitude when unsupported colloidal gold was used, which, however, was prone to fast sintering and deactivation.[14a] In 2008, Ding et al. reported on the use of unsupported npAu for the aerobic oxidation of D-glucose (Figure 5).[25] They used 20 mg of crushed npAu and a 0.1 M D-glucose solution, which was constantly saturated by molecular oxygen. At a pH of 9 and at 323 K, the conditions were found to be optimal for catalytic activity resulting in a conversion of ~25% glucose with 100% selectivity. The npAu samples containing pores and ligaments in the range of 30 nm did not show growth of ligaments or degradation after repeated use for 7 h.

The oxidation of alcohols in liquid phase remains a challenging reaction. In 2012, Asao and co-workers reported on the selective aerobic oxidation of secondary aromatic and aliphatic alcohols and benzyl alcohol to the corresponding ketones in methanol.[43] The conversion was very selective, achieving yields of over 80%, and also was unaffected
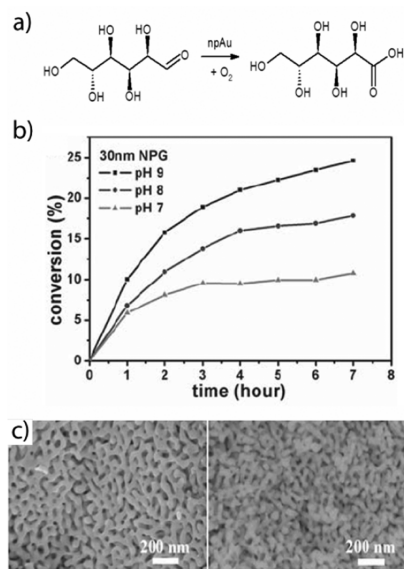
FIGURE 5. (a) The aerobic oxidation of D-glucose. (b) Run of conversion at 60 °C using 20 mg of npAu catalyst. (c) SEM before (left) and after (right) reaction. Reproduced with permission from ref 25. Copyright 2008 American Chemical Society).
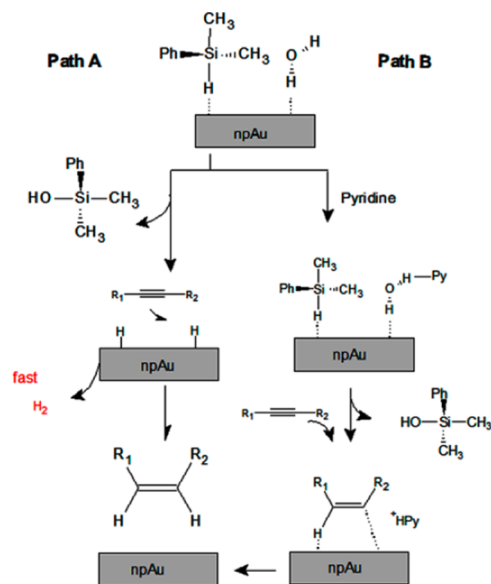

FIGURE 6. Reaction pattern of organosilanes and alkynes on npAu surfaces. Reaction with water results in the formation of the corresponding alcohols. The resulting surface bonded hydrogen can be used to selectively reduce alkynes to Z-alkenes. The recombination of atomic hydrogen to fast desorbing H_2 reduces the yield (path A). Addition of nitrogen containing compounds (pyridine, DMF; path B) increases the yield by formation of a reversible protonated ammonium species, which prevents recombination of surface bonded hydrogen.

by heteroatoms contained in the compounds. Methanol was employed as solvent and did not react. The activity of the catalyst in terms of turnover frequencies was on the order of ~0.015 s^{-1} (at 60 °C). Ding et al. studied the same reaction (benzyl alcohol oxidation) with npAu in the gas phase at over 200 °C.[24] The authors noted an increase of conversion and yield when pretreating the sample with NaOH. The addition of base was not investigated in liquid phase oxidation but might help to reach the higher activity as, for example, achieved in gas phase alcohol oxidation reactions.

Besides oxidation of organic compounds, the selective oxidation of silicon based compounds such as organosilanes to organosilanols is used in synthetic organic chemistry to generate chemical building blocks, for example, for the synthesis of metallasiloxanes and ceramics.[46] In 2010, Asao et al. reported on the use of unsupported npAu for the oxidation of organosilanes at room temperature employing water as the oxidant.[26] Among others, dimethylphenylsilane (PhMe$_2$SiH) could be oxidized to PhMe$_2$SiOH with 100% yield after just 1 h using thin npAu foil (100 nm thick, 1 mol %). The TOF for this reaction was calculated to be about 3 s^{-1}. Importantly the catalyst could be easily retrieved and reused several (>5) times. According to the derived mechanism of the reaction on the catalyst surface, the adsorbed silane reacts with the chemisorbed water generating two hydrogen atoms (Figure 6).[27] Of course, hydrogen is only metastable on gold surfaces[47] and is released as gaseous hydrogen.

In a subsequent study, the authors pursued the question whether the surface hydrogen could be used for hydrogenation reactions, circumventing the high dissociation barrier of molecular hydrogen on gold surfaces.[27]

Gold's niche in the hydrogenation of organic compounds, in particular alkynes, compared with more active hydrogenation catalysts such as Pd group metals, is its higher selectivity in terms of stereoselectivity (*E/Z* isomere) and overreduction (alkene vs alkane). In this context, already a few supported nanoparticle based gold catalysts demonstrated encouraging selectivity, resulting in only the semihdrogenated alkene, which is comparably weaker bonded and desorbs from the gold surface before being further reduced to the unfavored alkane.[48] The impeded activation of molecular hydrogen on unsupported pure gold surfaces could be circumvented by Asao and co-workers by using the reaction of the silanol and water generating atomic hydrogen on the gold surface. For example, phenylacetylene was hydrogenated to styrene with yields up to 96% after 2 h at 35 °C (2 mol % npAu, 2 equiv of H$_2$O and 1.5 equiv of PhMe$_2$SiH). Importantly, the authors noted a strong dependency of the yield on the solvent (DMF (dimethylformamide) ≫ CH$_2$Cl$_2$, THF (tetrahydrofuran)) or the addition of pyridine. This was attributed to the intermediate protonation of the nitrogen in these compounds
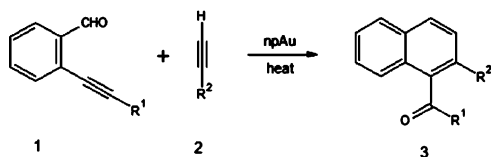
FIGURE 7. The [4 + 2] benzannulation of *ortho*-alkynylbenzaldehydes (**1**, R^1 = Ph, Bu) and alkynes (**2**, R^2 = Ph, Pr) resulting in naphthalene derivates (**3**).[29]

(pyridine, DMF) and the in situ formation of amines, which prevents recombination of atomic hydrogen on the catalyst surface as a competing side reaction (Figure 6). A wide range of alkynes could be selectively hydrogenated to the corresponding *Z*-alkenes with even better yields than Pd based catalysts. This intermediate formation of an amine, however, can be further used for the hydrogenation of nitrogen compounds such as quinolines.[28] In the absence of other alkynes and using unpolar solvents such as toluene, quinoline was hydrogenated to 1,2,3,4-tetrahydroquinoline with over 90% yield after 24 h at 80 °C.[28] These studies (refs 26−28) provide a very intriguing framework of molecular transformations on extended unsupported gold surfaces, combining oxidation reactions and hydrogenation reactions.

Aside from oxidation and reduction reactions, other types of reactions have been reported within the last one and a half years to be catalyzed by unsupported npAu, for example, C−C coupling reactions. This very challenging reaction in synthetic organic chemistry is a requirement for synthesizing larger carbon compounds. Homogeneous catalysis by Pd compounds led to a breakthrough in terms of chemo- and regioselectivty, which was recognized and honored by the Nobel Prize in chemistry in 2010. The [4 + 2] benzannulation reaction can be used for the synthesis of polysubstituted aromatic compounds. This reaction is catalyzed by Lewis-acidic gold compounds such as $AuCl_3$ in liquid phase with yields close to 100%.[49] In 2012, Inoue and co-workers reported on the use of npAu for this type of reaction (Figure 7).[29] Similar to the homogeneous Au catalysts, the npAu works as a Lewis acid; the alkyne group of **1** is chemisorbed and activated on the Au surface. The alkyne **2** reacts in a following step with the chemisorbed species yielding the reaction product **3** (for details about the proposed reaction mechanism, see ref 29). For example, using 40 μm thick npAu foil with pores and ligaments of 25 nm, *ortho*-phenylethylbenzaldehyde and phenylacetylene could be reacted to the naphthyl ketone with a yield of 64% within 2.5 h (20 mol % npAu, 150 °C, solvent o-$C_6H_4Cl_2$). Aside from the naphthyl ketone species, the decarbonylated naphthalene was detected, probably stemming from reaction of one of the intermediates with water. Importantly, the catalyst

was easily retrieved and reused for at least three times without apparent loss of activity.

Concluding Remarks

Unsupported gold catalysts were demonstrated to have encouraging potential in gas and liquid phase catalysis. These nanostructured gold materials can be generated by corrosion (nanoporous gold), vacuum evaporation (gold powder), combustion of precursors (nanogold foams), or templating (nanotube membranes). So far, a broad variety of reactions ranging from the industrially important oxidation of CO and primary alcohols all the way to synthetically relevant reactions such as the benzannulation have been studied. It can be anticipated that the scope of investigated reactions will further grow in the coming years. Unsupported materials provide several important advantages. They provide an extended gold surface without the need for any support or organic stabilizers. First studies already showed that their surface chemistry is thus predictable based on model studies under UHV conditions. Besides their electrical and heat conductivity, they provide good mechanical stability, for example, for slurry reactor applications. In all cases, the gold material could be easily retrieved from reaction, and no leaching was detected; good recyclability of the precious gold material is one of their key advantages. Noteworthy, these monolithic skeletal catalysts contain nanoscopic structures but are macroscopic in size; they, hence, pose no risk to the environment and health as discussed for other nanomaterials.

BIOGRAPHICAL INFORMATION

Arne Wittstock studied chemistry at the University of Bremen and performed his diploma thesis at the Krüss GmbH in Hamburg/Germany in 2006. He conducted his doctoral studies in the group of Marcus Bäumer (Institute for Applied and Physical Chemistry) and received his Ph.D. from the Department of Chemistry at the University of Bremen in 2010. Meanwhile he was visiting researcher at the Nanoscale Synthesis and Characterization Laboratory at the Lawrence Livermore National Laboratory in 2007−2008, where he returned in 2011 as a directorate postdoctoral associate in the physical and life sciences department. In 2013, he returned to the University or Bremen where he continues working on his habilitation in the field of nanostructured materials for catalytic applications.

Marcus Bäumer is professor at the Institute of Applied and Physical Chemistry of the University of Bremen where he leads a research group working on catalysis at nanostructured surfaces and innovative catalytic materials. He graduated in chemistry and received his Ph.D. at the Ruhr-University Bochum (Germany) in 1994. In the following, he carried out postdoctoral research at the

Ruhr-University, Stanford University (USA), and the Fritz-Haber-Institute (Berlin, Germany) in the field of surface science and model catalysis. In 2000, he received his habilitation in physical chemistry at the Technical University Berlin and became professor at the University of Bremen in 2002. The research of his group combining surface science and catalysis under ambient conditions is directed to the development of new catalysts by using novel synthesis techniques from material science and nanotechnology and the understanding of their catalytic properties at the atomic scale. His current research is focused on the use of nanoporous materials, colloidal nanoparticles, and rare earth oxide materials in heterogeneous catalysis.

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