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Nanoporous Gold Films as Catalyst

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Abstract

Nanoporous gold (NPG) is reviewed as a catalyst. Various preparation methods were first reviewed for NPG and its structure. Applications of this catalyst in CO oxidation, hydrogen oxidation, hydrogen production are discussed. Regarding CO oxidation, detailed studies on reaction mechanism and density functional theory (DFT) calculations were also reviewed. Not only as a model reaction but also practical aspects of removing CO residue in hydrogen stream are discussed. Beyond those simple reactions, the application of NPG to more complicated reactions such as alcohol oxidation is reviewed. Selective aerobic oxidation of gas-phase alcohols is first reviewed and reactions in liquid phase are discussed. Finally, future prospects of NPG as a catalyst for more complicated reactions such as organic synthesis are briefly discussed.

Keywords: nanoporous gold, catalysis, CO oxidation, hydrogen oxidation, selective oxidation of alcohol

1. Introduction

Recently, nanoporous gold (NPG) films have attracted significant interest in various fields such as catalysis, sensors, optics and electrochemistry due to their high catalytic activity, high conductivity, easy modification, high stability, tuneable porosity and good biocompatibility [1]. Compared to the regular gold films which are dense inside, NPG films have sponge-like or reticulate structures with nanometer-sized pores throughout the body of the film. The nanopores are typically 20–50 nm in size and can be as small as 5 nm depending on the preparation method (**Figure 1**). NPG films are typically prepared by selective etching of a less noble component from gold-containing alloys. Early studies on NPG structures could be found as early as 1960s, but NPG structures in the studies were prepared as a model system for studying the molecular mechanism of alloy corrosion [2]. From a technological point of view,

researchers began to explore and develop the potential of NPG for a variety of technological applications since the late 1990s.

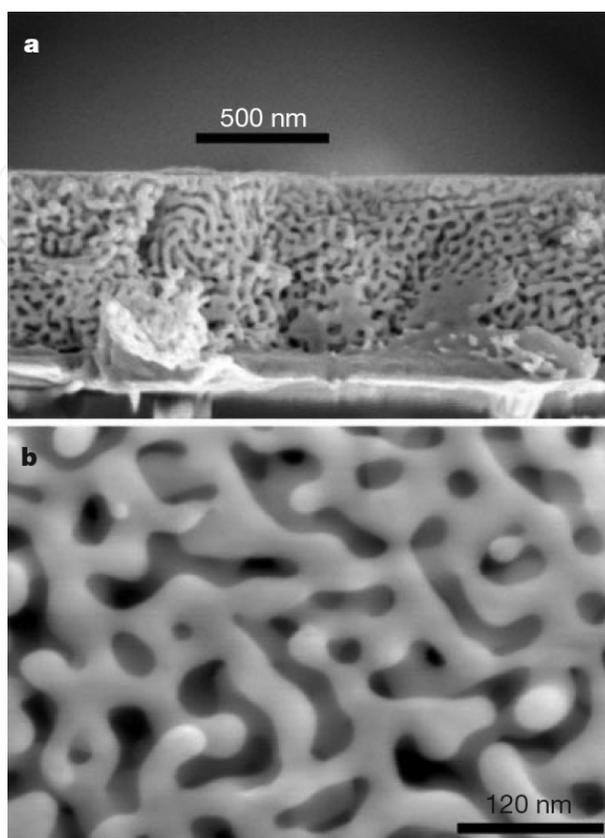


Figure 1. Scanning electron microscopy images of nanoporous gold film (a) cross sectional and (b) top view. NPG film was prepared by dealloying of $\text{Au}_{32}\text{Ag}_{68}$ (atom%) alloy in nitric acid. Reprinted with permission from Ref. [3]. Copyright 2001 Macmillan Magazines Ltd.

The catalytic activity of gold in the nanometer scale attracted great attention, most notably, in 1987 when Haruta et al. found the unexpected exceptional catalytic activity of nanometer-sized gold nanoparticles for CO oxidation even at below room temperature [4]. Before this discovery, gold was largely known to be very stable and inert. Bulk gold is a precious metal and does not have catalytic activity. Since then, numerous studies have been devoted to unravelling the catalytic properties of gold nanoparticles [5]. At the same time, immobilizing gold nanoparticles on a suitable support was gaining significance as it was apparent that they should be fixed somewhere to be used as a catalyst. Typically, carbon-derived materials such as carbon nanotubes and glassy carbon were used as support [6]. However, it was one of the intrinsic problems that immobilized gold nanoparticles were being detached from the support during reaction and it caused degradation of the catalytic activity of gold nanoparticle-supported composite catalyst. NPG plays a role in this aspect as it is a one-body film and there was no concern regarding the loss of catalyst materials [7]. Consequently, the catalytic activity of the NPG films drew considerable attention from the late 1990s. CO oxidation was the first model reaction tested using NPG as was the case for gold nanoparticles.

In this chapter, we have reviewed the recent advances in the field of catalytic properties of NPG films. First, we have briefly discussed the preparation and structure of NPG films. Then, studies on CO oxidation have been reviewed as this reaction has been extensively on NPG films. Hydrogen oxidation and production are much less studied on NPG films. Nonetheless, they are one of the important gas-phase reactions. Therefore, we have herein discussed studies regarding hydrogen oxidation and production on NPG films. After reviewing these reactions with simple molecules, we have reviewed reactions with more complicated molecules such as the selective oxidation of alcohols in the gas phase. Then, we have reviewed the most complicated reactions on NPG to date, that is, reactions in the liquid phase. Finally, we have elucidated the activation and stability of NPG films as a catalyst along with the concluding remarks and outlook.

2. Preparations of NPG structures

The typical method for NPG preparation involves preparation of a suitable gold alloy wire with a less noble component by drawing the melted alloy bulk. Then, the wire is immersed in a suitable etchant, and the less noble component is dealloyed [8]. Dealloying can be performed under free corrosion conditions, that is, without an applied bias, or it can be done under bias, typically less than 1 V above the standard electrode potential of the less noble component. Under free dealloying conditions, complete dealloying takes several hours to tens of hours. With bias, complete dealloying takes only a few minutes. During dealloying, dissolution and surface diffusion of surface atoms occur at the metal alloy/electrolyte interface [8]. Silver is the most commonly used less noble component. For silver, concentrated nitric acid (HNO_3) is commonly used as the etchant, as silver is corroded at all potentials in HNO_3 at low pH [8]. Other less noble components are Ag, Cu, Pd, Ni, Zn, etc. [9]. Recently, Si was also used as the less noble component and NPG structures were successfully prepared by etching Si out of Au-Si alloys [10]. We prepared NPG films from Au-Si alloys [11, 12].

The thickness of the drawn wire from the alloy bulk is typically in tens to hundreds of μm range. For catalytic applications, the thickness is more than necessary as catalytic reactions occur on the surface of catalyst. Valuable materials may get wasted if this thickness is maintained for NPG as a catalyst. Au-Ag leaves are available with a few nanometer thickness, but they are not easy to handle. Furthermore, after preparing NPG from the drawn wire or thin Au-Ag leaves, those free-standing NPG structures require to be attached to a suitable substrate for easy handling. If NPG films or leaves are to be used as an electrode, the substrate should also be conducting. Hence, we recently attempted to prepare a few hundred-nm-thick thin films of gold alloy using sputter deposition. In this case, the less noble component was Si. $\text{Au}_x\text{Si}_{1-x}$ thin films were prepared on silicon wafers. Si in the alloy was dealloyed by 3% HF solution [10]. NPG thin films prepared this way minimize the amount of gold in the structure and they can be readily connected to a measurement device such as an electrode [11, 12]. More detailed review on the preparation including dealloying and characterization of the prepared NPG films can be found in [13].

3. CO oxidation

CO oxidation has been the representative model reaction for investigating the catalytic efficiency of new catalyst materials due to its simple reactant molecules and a wealth of literature of the accumulated studies. Therefore, it was natural that researchers first attempted to test the catalytic activity of the NPG films for CO oxidation. Indeed, CO oxidation is also the most studied reaction in detail with NPG films. Early studies in 2006–2007 found that NPG films were very efficient for CO oxidation [14, 15]. The reaction proceeded at as low as -30°C . NPG films in the studies were dealloyed from Au-Ag alloy films. This observation was in line with the superior catalytic efficiency of gold nanoparticles for CO oxidation [16]. However, the structural difference between the NPG films and gold nanoparticles is enormous. Therefore, since the discovery of this superior catalytic efficiency of NPG films for CO oxidation, numerous studies have been devoted to elucidate the underlying origin of the superior catalytic efficiency [2, 17–19]. It is widely accepted that these peculiar properties of NPG come from atomic oxygen species adsorbed on the surface of NPG. Those oxygen atoms activate the adsorbing reactants on the catalyst surface. Bulk gold is inert because adsorbing molecules have very low sticking coefficients at typical reaction temperatures. On the surface of bulk gold, dissociation of oxygen molecules is even more difficult. NPG structures, on the contrary, do not have a negligible probability of adsorption of oxygen molecules and dissociation of the adsorbed oxygen molecules. Exact active sites for dissociative adsorption of one oxygen molecule into two oxygen atoms, however, are debatable. Initially, it was widely believed that under-coordinated surface atoms at the kink and step sites of the ligaments in the NPG structure were the active sites. It was natural to suspect this morphological effect for the high catalytic activity because numerous studies on the catalytic activity of gold nanoparticles on metal oxide supports showed that the under-coordinated surface atoms on the gold nanoparticles played a central role in the remarkable catalytic activities [18, 20]. However, because some residual silver atoms on NPG films always remained after dealloying of Au-Ag alloy, these residual Ag atoms were also assumed to be responsible for the dissociative adsorption (Figure 2) [21]. Bulk silver is known to bind oxygen molecules strongly and activate them in

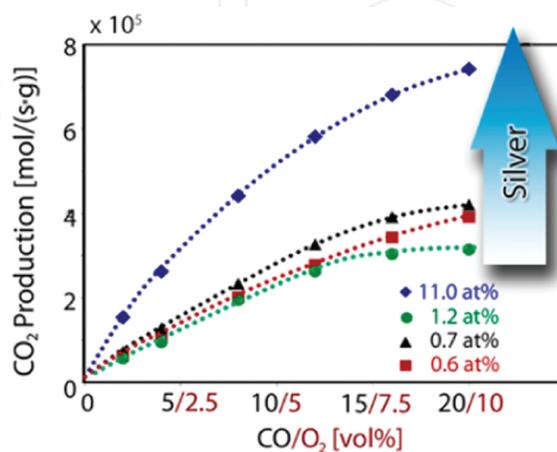


Figure 2. CO oxidation with molecular oxygen supply on NPG with varying silver residue content at 40°C . Reprinted with permission from Ref. [17]. Copyright 2011 the Royal Society of Chemistry.

contrast to the bulk gold surfaces [22]. Furthermore, NPG films dealloyed from Au-Cu alloy also showed some activity for CO oxidation which obviously did not contain any silver [23, 24].

An atomic scale TEM study with in situ observation revealed that a high density of atomic steps and kinks on the curved surface of ligaments of NPG structure were comparable to that of gold nanoparticles 3–5 nm in size (**Figure 3**) [20]. They found that these under-coordinated surface atoms were catalytically active sites during CO oxidation. Those surface atoms were also very mobile during the reaction and they rearranged to form {1 1 1} facets after reaction. This facet formation led to a lower density of atomic steps and structure coarsening accompanying catalyst deactivation (**Figure 3a** and **b**). However, when residual silver exists, they stabilized the atomic steps and kink sites by suppressing the facet formation during reaction (**Figure 3c** and **d**). In another in situ TEM study [25], they revealed coarsening mechanisms in the atomic scale during CO oxidation and found that chemical reactions stimulate the surface gold atoms at steps. The residual silver atoms and nanopore coarsening are directly associated with the rapid diffusion of these gold atoms and the surface segregation of those Ag atoms. The Ag atoms can suppress the {1 1 1} faceting dynamics and preserve the surface steps and kinks during reaction. They also found that the planar defects on the ligaments of NPG structures could hinder nanopore coarsening.

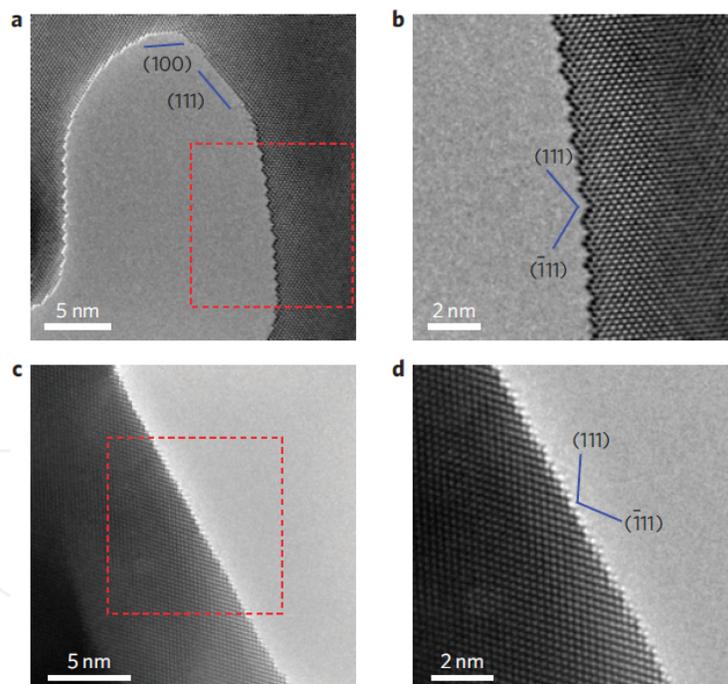


Figure 3. High-resolution TEM images of curved surface of NPG in atomic scale. (a) low silver-containing NPG (1.2 atomic%) in 1 vol% CO in an air mixture at 30 Pa at room temperature, (b) blow up image of (a), showing facet formation and reduced number of steps and kinks, (c) high silver containing NPG (20 atomic%), (d) blow up image of (a), showing suppression of facet forming and preservation of high density steps and kinks. Reprinted with permission from Ref. [20]. Copyright 2012 Macmillan Magazines Ltd.

Kameoka et al. studied the dominant factors for CO oxidation using NPG and found that the dominant factor can vary depending on the reaction temperature [26]. They prepared NPG

films by dealloying aluminium from Al_2Au with 10 weight% NaOH , HNO_3 and HCl . For NPG films etched by NaOH and HNO_3 , CO oxidation was dominated by different mechanisms at low ($<320\text{ K}$) and high ($>370\text{ K}$) temperatures. At low temperature, the perimeter interface of the residual Al species (AlO_x) on NPG was thought to be the main reaction sites, while a large number of lattice defects such as twins and dislocations were thought to be mainly responsible for the reaction at high temperature.

CO oxidation on NPG structures can be greatly enhanced by adding a little bit amount of water to the reactant gas stream. By adding as small as 0.01 vol% water vapour to the gas stream, CO_2 production rate increases by about 100% (**Figure 4a**) [27]. However, the apparent reaction order and activation energy did not change after the addition of water vapour (**Figure 4b**). Because the reaction stopped immediately when oxygen supply was ceased, it turned out that water vapour was not the source of oxygen, either. In this case, water was thought to be a co-catalyst. It is known that when oxygen atoms are present on gold surfaces at low temperatures ($<200\text{ K}$), adsorbing water molecules can be activated and form transient OH species [28]. Water vapour as a cocatalyst could be related to this finding.

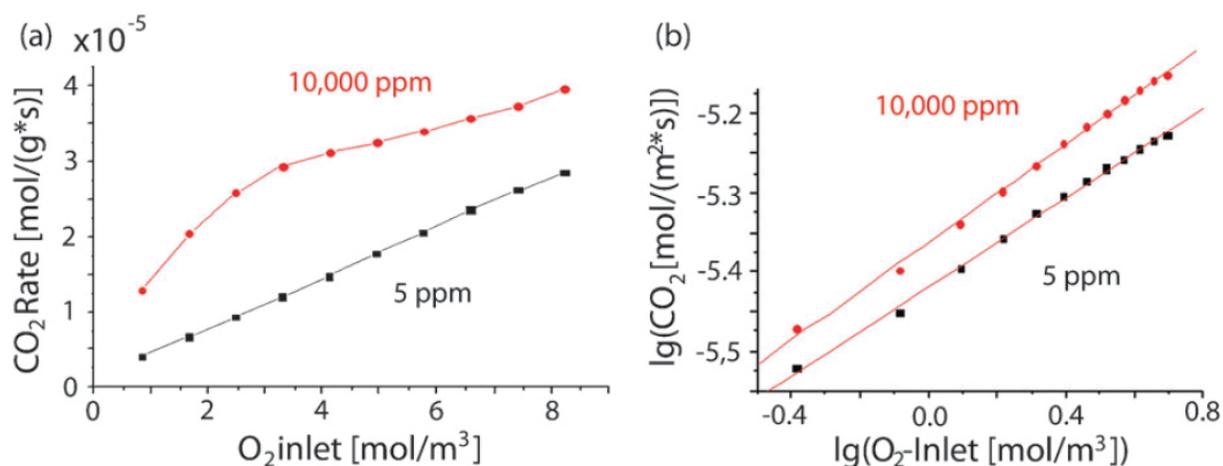


Figure 4. (a) Influence of water vapour on the rate of CO oxidation. Water vapour contents are shown in ppm numbers. 5 ppm of water is typical for dry reactant gas and 10,000 ppm corresponds to 0.01 vol%. (b) Double logarithmic plot showing the apparent reaction order. It is not dependent on the water content change. Reprinted with permission from Ref. [27]. Copyright 2010 PCCP owning societies.

Theoretical studies using DFT calculation on the reaction mechanism of CO oxidation on NPG were mostly focused on how the adsorbing oxygen molecules activate the reaction. The (1 1 1) and (1 0 0) Au surfaces are the most abundant surfaces on NPG structures and kink Au sites that connect (1 1 1) and (1 0 0) surfaces on NPG structures are assumed to be major active sites [29]. Especially, adsorption and dissociation of oxygen molecules could be enhanced on residual Ag atoms on NPG structures [22]. However, residual Ag did not lower the energy barrier of the $\text{CO} + \text{O}$ reaction [30] and an excessive Ag amount could be harmful for CO oxidation [29]. As for adsorbed CO species, they can induce O—O scission of the neighbouring OCOO^* intermediates to release CO_2 molecules (the CO self-promoting oxidation effect [31]) (**Figure 5**).

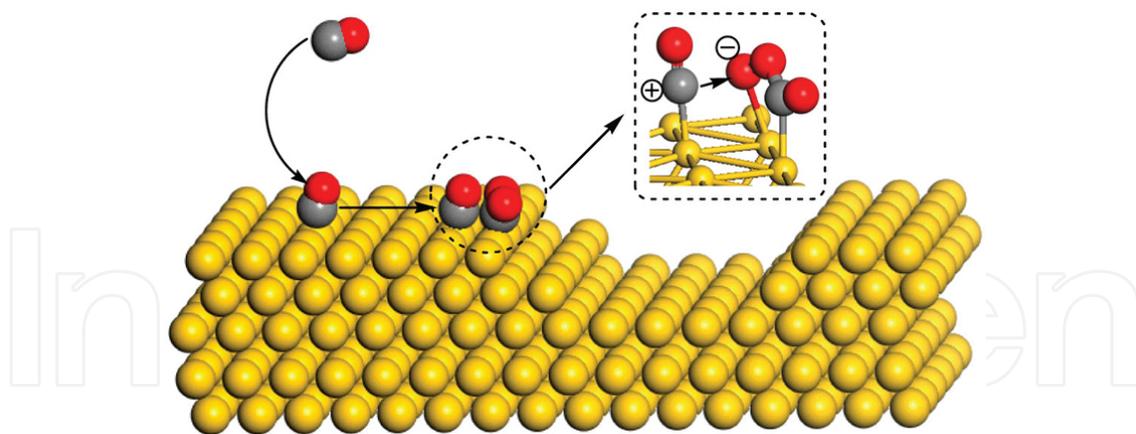


Figure 5. Illustration of adsorbed CO diffusion and reaction with OCOO' intermediate on stepped NPG surface. Reprinted with permission from Ref. [29]. Copyright 2015 American Chemical Society.

In most studies regarding CO oxidation on NPG, the reaction was treated as a model reaction to investigate the catalytic activity of the NPG structures and elucidate the reaction steps involved. In contrast to these studies, CO oxidation in hydrogen-rich stream on NPG was investigated as a practical application [32]. As the fuel of proton-exchange membrane fuel cells (PEMFCs), hydrogen is usually produced by steam reforming. The hydrogen produced contains a small quantity of CO (0.5–2.0%), and it is essential to remove those CO molecules from the hydrogen produced because CO molecules adsorb very strongly on platinum surface on the anode of PEMFCs and deactivate the electrode. As a catalyst for this preferential oxidation of CO (PROX) in hydrogen stream, NPG showed high activity and selectivity (low H₂ oxidation) at room temperature. Furthermore, selectivity of the reaction increased in the presence of CO₂ and H₂O. Interestingly, residual Ag did not seem to improve the catalytic activity of NPG. In this reaction, adsorbed oxygen molecules are assumed to be activated not by residual Ag atoms, but by reaction with hydrogen molecules to form highly oxidative intermediates. Adsorbing CO molecules readily react with those intermediates to form CO₂ and OH. The adsorbed OH would further react with adsorbing CO to form CO₂ and additional H atoms. Those H atoms on NPG would then react to form H₂ and desorb or react with the adsorbing O₂ molecules to form another highly oxidative intermediate. Residual Ag atoms were assumed to stabilize the catalytic activity and the structure of NPG.

4. Hydrogen oxidation and production

Fewer studies have investigated hydrogen oxidation using NPG as a catalyst compared to those on CO oxidation [12, 33]. In our lab in collaboration with Prof. Jeong Young Park's lab at KAIST (Korea Advanced Institute of Science and Technology), we studied hydrogen oxidation on NPG [12]. Previous studies on gold nanoparticles showed that hydrogen can be dissociatively adsorbed on low-coordinated atoms on the edge or corners of the nanoparticles. In NPG thin films, it is also known that under-coordinated surface atoms at the steps and kinks of gold ligaments are catalytically active sites. Then, we can expect that NPG thin films will

show catalytic activity even for hydrogen oxidation. Another factor for the catalytic activity of NPG films is the residual foreign atoms, most commonly silver, not etched during dealloying process. In order to investigate the effect of foreign atoms, we prepared NPG thin films from Au-Si alloy instead of the usual Au-Ag alloy as Si is assumed to be a much poorer catalyst for hydrogen oxidation. Below 300°C, no hydrogen oxidation was observed on silicon substrates [34]. In addition, we can remove all of Si from the dealloyed NPG surfaces because Si phases are segregated from the Au phase during Au-Si alloy formation [11]. On the contrary, NPG films with trace amounts of silver were observed to be much more active for hydrogen oxidation compared to pure NPG films [33].

In our study, the intrinsic catalytic activity of pure NPG dealloyed from Au-Si alloy was found to be low as was expected from other studies regarding H₂ or CO oxidation in the presence of H₂ [32, 33]. For gold nanoparticles dispersed on metal-oxide supports, enhanced catalytic activity is frequently ascribed to the active sites at the interface of gold nanoparticles and metal oxide surface. Some studies suggest that the interface not only serves as adsorption sites for reactant molecules, but also enables efficient activation of molecular oxygen [35]. For NPG films, depositing metal oxide particles was beneficial for improving catalytic activity [17]. Based on those previous studies, we deposited varying amounts of titania on our NPG films in order to investigate the effects of adding metal oxide particles for the catalytic activity of NPG (**Figure 6**). Titania was deposited using liquid-phase immersion deposition with TTIP solution in ethanol using 0.1, 0.5 and 1 weight% TTIP. With titania deposition, the overall catalytic activity of NPG films increased for H₂ oxidation, up to four times than that of bare NPG (**Figure 6a**). Turnover frequency comparison among NPG films with varying amount of titania showed that the catalytic activity was lowest for the 0.1 weight% TTIP precursor and highest for the 0.5 weight% TTIP precursor. Interestingly, the catalytic activity of 1 weight% TTIP precursor was lower than that of the 0.5 weight% TTIP precursor (**Figure 6a**). If we assume that the interface between the NPG surface and deposited titania particles has active sites for the reaction, it is possible that the reduction in catalytic activity is due to a corresponding decrease in the active TiO₂/NPG perimeter sites due to the higher surface coverage of titania. Based on this understanding, our proposed reaction mechanism was as follows: hydrogen

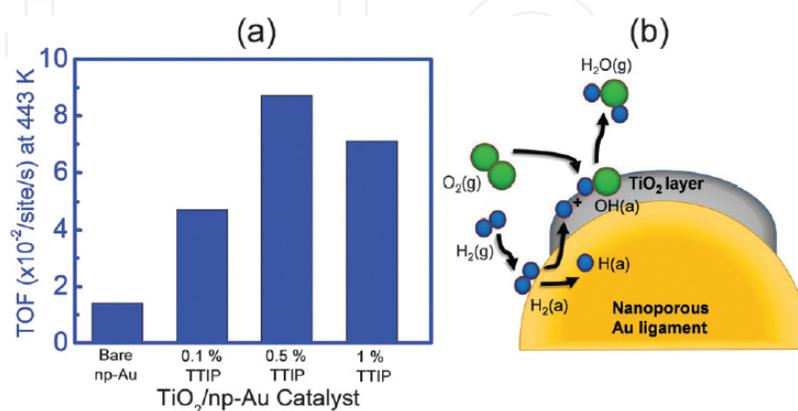


Figure 6. (a) Turnover frequency comparison for titania-deposited NPG films at 443 K under Hydrogen oxidation. (b) Schematic representation of hydrogen oxidation at the interface along the boundary of titania particles deposited on NPG surface. Reprinted with permission from Ref. [12]. Copyright 2015 the Royal Society of Chemistry.

molecules adsorb on the NPG/titania interface sites. They undergo dissociation and the resultant hydrogen atoms spill over to the titania. O₂ molecules adsorbed on the NPG/titania interface sites form Ti—OOH species that dissociate into Ti—O and Ti—OH species. The Ti—OH species finally hydrogenate to form H₂O molecules (**Figure 6b**).

Not only hydrogen oxidation, but also hydrogen production using water-gas shift (WGS) reaction was reported on NPG decorated with ceria [36]. In WGS reaction, one water molecule reacts with one CO molecule and produces one hydrogen molecule and one CO₂ molecule. It was shown that gold nanoparticles dispersed on ceria were very efficient for the WGS reaction [37]. Based on this finding, Shi et al. attempted the WGS reaction with NPG films decorated with ceria. Decorating NPG structure with metal oxide particles not only enhances catalytic activity, but also structural stability, which improves at high temperatures without coarsening of the nanopores and ligaments [7]. This structural stability is essential for the reaction because in this reaction, water molecules, not oxygen molecules, are used as an oxidant. In order to use water molecule as an oxidant, elevated temperature is needed. They investigated the catalytic activity of NPG/ceria at temperatures as low as 150°C and as high as 550°C (**Figure 7**). Ceria was prepared on NPG by impregnation and calcination. Ceria-covered NPG has structural stability up to 500°C, enabling low- as well as high-temperature WGS reactions. The catalytic activity was close to the highest ones reported so far. They attributed this exceptional catalytic activity to facile water dissociation on rich defect sites in ceria.

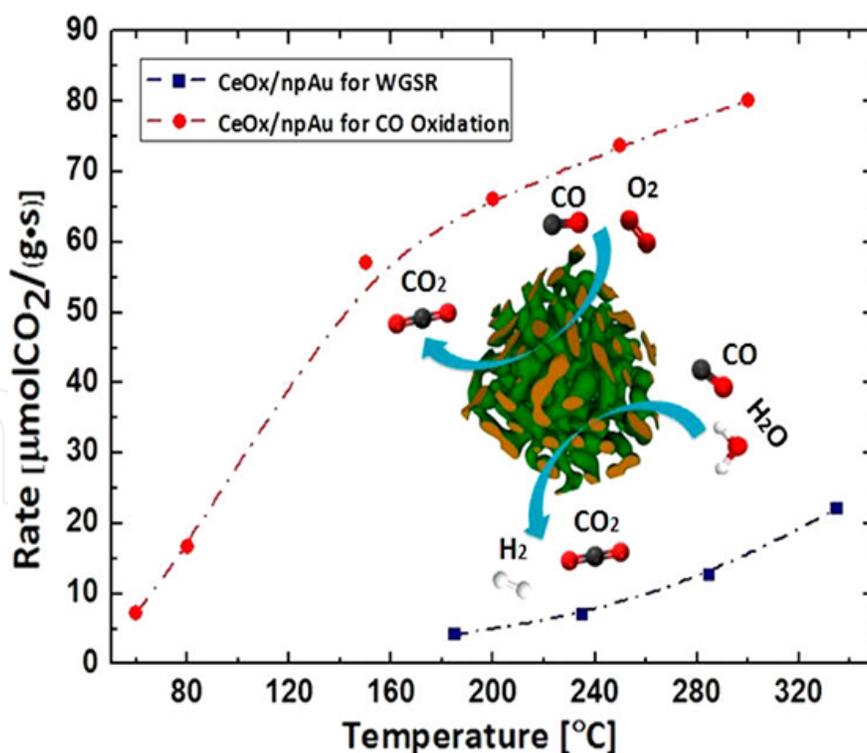


Figure 7. Comparison of reaction rates for WGS reaction (upper line) and CO oxidation (lower line) on ceria/NPG catalyst. Gas feeds are 2.9 vol% CO, 47.0 vol% O₂ in N₂ for CO oxidation and 4.2 vol% CO, 16.0 vol% H₂O in N₂ for WGS reaction. Reprinted with permission from Ref. [36]. Copyright 2014 American Chemical Society.

5. Oxidation of alcohols

The selective oxidation of alcohol is one of the important catalytic conversions in industry for a wide range of bulk commodity chemicals that are raw materials for various products for daily lives such as plastics and paints. Alcohols have been traditionally synthesized by petrochemistry but recently, intensive studies are focused on deriving alcohols from renewable resources such as landfill gas and biomass [1]. Gold-based catalysts are of particular interest in this aspect because molecular oxygen can be used as an oxidant for the selective oxidations, thereby implying greener processes replacing toxic oxidant chemicals in the conventional process [38]. With gold-based catalysts, it is also possible to work under environmentally benign conditions, that is, at low temperature ($<100^{\circ}\text{C}$) and under an ambient pressure. Regarding selectivity or oxidation power, the products of partial oxidations only weakly adsorb on gold-based catalysts, desorbing before being further oxidized. This delicate balance between oxidation power of gold and its relatively weak interaction with the reaction products provides gold with unique selectivity that cannot be obtained by typical catalytic materials such as Pt and Pd, on which full oxidation usually occur due to strong oxidation power. In an early work in 2010, Wittstock et al. showed that the NPG films were very effective for gas-phase partial oxidation of methanol to methyl formate with a very high selectivity of 97% at a temperature as low as 80°C and under an ambient pressure using molecular oxygen as an oxidant (**Figure 8**) [39]. The key to this reaction was the ability of the NPG surface to dissociate adsorbing molecular oxygen into oxygen atoms. In other words, high catalytic activity of NPG for this reaction was attributed to the atomic oxygen adsorbed on the NPG surface, thus forming surface-bound alkoxy species with adsorbing methanol.

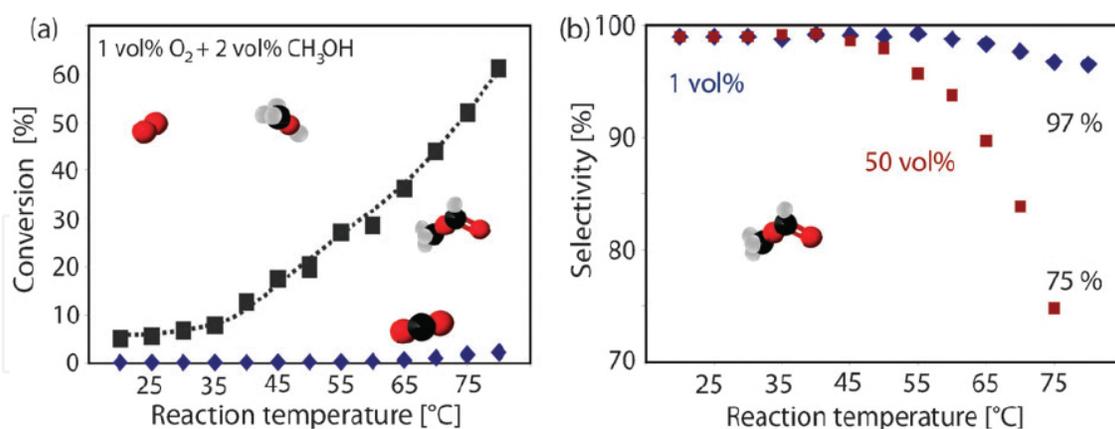


Figure 8. Oxidation of methanol on NPG showing (a) the activity and selectivity of the oxidation under continuous flow conditions at low temperature. The reaction shows high selectivity to methyl formate. In contrast to this, negligible amount of CO₂ is forming. (b) Temperature dependence of selectivity. For low oxygen partial pressure of 1 vol%, the selectivity remains high while it decreases for high oxygen partial pressure of 50 vol%. Reprinted with permission from Ref. [27]. Copyright 2010 PCCP Owner Societies.

In a subsequent study, they extended their study to aerobic oxidation and coupling of methanol (one carbon), ethanol (two carbons) and n-butanol (four carbons) on NPG under an ambient pressure and at a low temperature ($<100^{\circ}\text{C}$) [40]. They compared selectivity to coupling vs.

selectivity to aldehyde formation with an increasing chain length from methanol to *n*-butanol via ethanol and found that selectivity to aldehyde increased with an increasing chain length. For methanol, 100% product was the coupling product (methyl formate). For ethanol, 50% was the aldehyde product (acetaldehyde) and 50% was the coupling product (ethyl acetate). For *n*-butanol, no coupling product was obtained and the aldehyde product (*n*-butanal) was 100% (Figure 9).

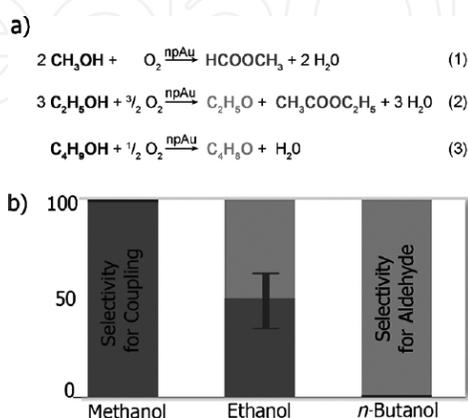


Figure 9. (a) Chemical formulas of oxidation and self-coupling of alcohols on NPG. (b) Selectivity towards the aldehyde (self-coupling product) vs chain length of the alcohol before reaction. Reprinted with permission from Ref. [40]. Copyright 2012 Wiley-VCH Verlag GmbH.

For higher alcohols, Ding et al. showed that benzaldehyde could be eco-friendly obtained from the selective oxidation of benzyl alcohol using molecular oxygen as an oxidant at a low temperature (<250°C) [41]. The conventional process involved organic chloride or toxic benzoic acid, thereby contaminating the environment. On NPG, selectivity to benzaldehyde was very high over 98%. Higher content of residual Ag did not improve the catalytic activity and selectivity of the reaction. However, NaOH-treated NPG showed drastically improved catalytic activity while preserving selectivity (Figure 10).

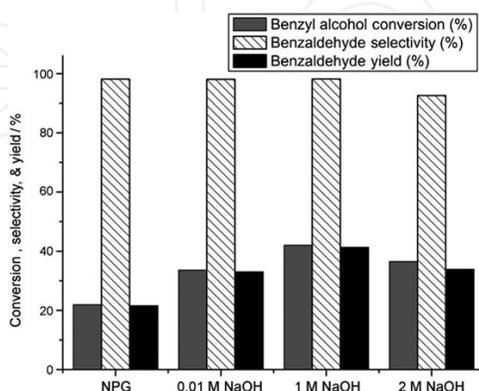


Figure 10. Comparison of conversion, selectivity and yield among bare NPG, NPG treated by various concentrations of NaOH for the gas-phase oxidation of benzyl alcohol. Reprinted with permission from Ref. [41]. Copyright 2012 Wiley-VCH Verlag GmbH.

While studying oxidative coupling of ethanol and 1-butanol on NPG, Friend et al. found that the catalytic activity of NPG films did not significantly depend on the ligament size of the NPG films [42]. This observation means that the under-coordinated gold atoms on the surface of NPG structure did not play a significant role for determining the catalytic activity of NPG for coupling of higher alcohols. Residual Ag did not seem to play a role for this reaction, either.

6. Reactions in liquid phase

As NPG showed excellent catalytic activity for simple alcohols and even for some higher alcohols in the gas phase using molecular oxygen as an oxidant as discussed in the previous section, it is natural to apply NPG catalyst for more complicated reactions in the liquid phase. There are a large number of reviews and monographs regarding reactions in the liquid phase using gold nanoparticle catalyst [5, 43–45]. Most of them used gold nanoparticles dispersed on metal oxides, but a recent review dealt with NPG as the catalyst [46]. Asao et al. reported oxidation of alcohols in the liquid phase using molecular oxygen as an oxidant on NPG [47]. Oxidation of 1-phenylbutanol was successful with methanol as the solvent under O₂ atmosphere (**Figure 11**). After a 10-h reaction at 60°C, the yield of the corresponding ketone product was 96%. For comparison, they also tested the reaction on simple gold film and undealloyed Au₃₀Ag₇₀ film as catalyst but the reaction did not proceed. This study showed that additives (bases, stabilizers, ligands, etc.) and cumbersome work-up procedures (filtration, centrifugation, etc.) for aerobic oxidation of alcohols in the liquid phase were not required on NPG.

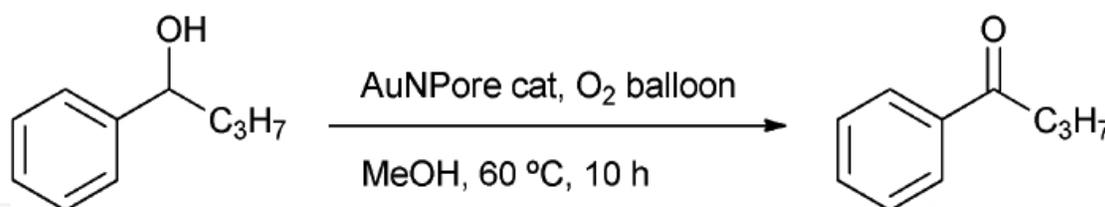


Figure 11. Chemical formula for the oxidation of 1-phenylbutanol on NPG with methanol as solvent under O₂ atmosphere. Reprinted with permission from Ref. [47]. Copyright 2012 the Royal Society of Chemistry.

They continued to report more complicated reactions such as the direct synthesis of amides and amines through the selective oxidation of alcohols, which is very challenging with conventional transition-metal catalysts [48]. Amides are one of the most important functional groups in biological systems and they are the basis of synthetic polymers and modern pharmaceutical molecules. The direct amidation of an alcohol would be ideal and the most economic pathway [49]. By conducting selective aerobic oxidation of methanol in the coexistence of amines on NPG, they synthesized formamide products directly (**Figure 12**). It was noteworthy because formamide products were obtained from cheap and abundant materials (methanol, oxygen molecules) and without toxic CO gas and under mild conditions (ambient pressure, neutral pH). For the reaction, residual Ag was essential.

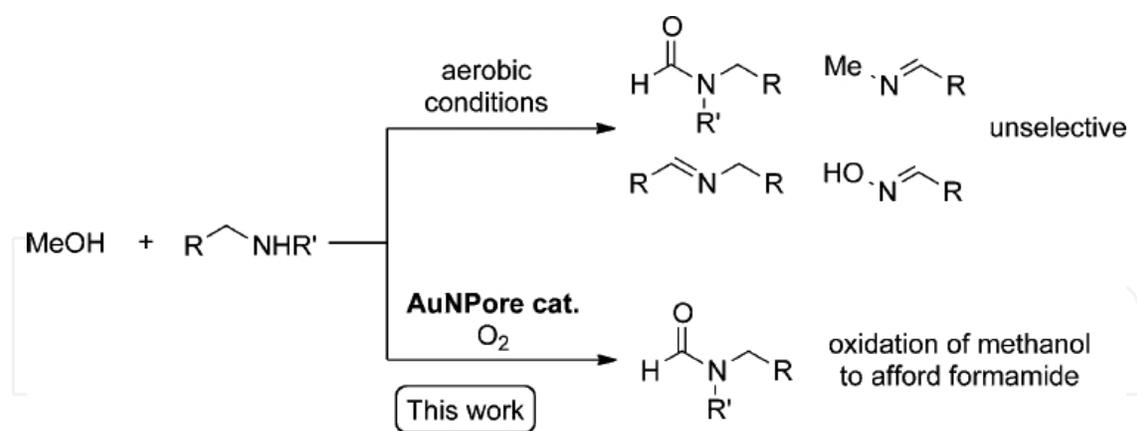


Figure 12. Scheme of aerobic oxidation of the mixture of methanol and alkylamine. High selectivity is achieved on NPG to form formamide (bottom line). Reprinted with permission from Ref. [48]. Copyright 2013 Wiley-VCH Verlag GmbH.

Wichmann et al. also reported direct coupling of primary alcohols and amines to corresponding amides using NPG in the liquid phase [49]. They showed that reaction of methanol and dimethylamine produced industrially relevant dimethylformamide at 40°C. In this reaction, the activation of molecular oxygen was also the key reaction. The reaction was facilitated by doping NPG with an admetal such as Ru and Ag.

Most liquid-phase reactions using NPG were oxidation. Reduction reaction or hydrogenation is more difficult because H-H dissociation is not easy on gold. But recently, some studies were reported. Yamamoto have provided a more detailed review on the reduction reaction along with some reactions of C—C bonding formation on NPG [46].

7. Stability and activation of NPG catalyst

Due to the robust three-dimensional (3D) network structure composed of ligaments, NPG films show much higher durability compared to the gold nanoparticles dispersed on metal oxide particles. The supported Au nanoparticles are in powder form and easy to lose. Gold nanoparticles are also prone to agglomeration upon heating and easily deactivated. However, NPG structure is of nanometer size and it is also prone to coarsening upon heating. Researchers tried to enhance the thermal stability by coating the structure with metal oxide [50] or ozone [51]. Wichmann et al. compared the thermal stability of pristine NPG and NPG coated with titania. They also compared the changes in catalytic activity at an elevated temperature [7]. They found that titania-covered NPG maintained its structure up to 600°C, and the loss of activity was only 4% for CO oxidation at 250°C and under high CO concentrations for more than 72 h (**Figure 13**). They explained this enhanced stability with the pinning of surface gold atoms, especially at step edges by deposited titania [51]. Coating NPG with metal oxide generally increases the catalytic activity of uncoated NPG as boundaries of metal oxide particles deposited on NPG surface are presumed to be active sites for the dissociation of the reactant molecules [12].

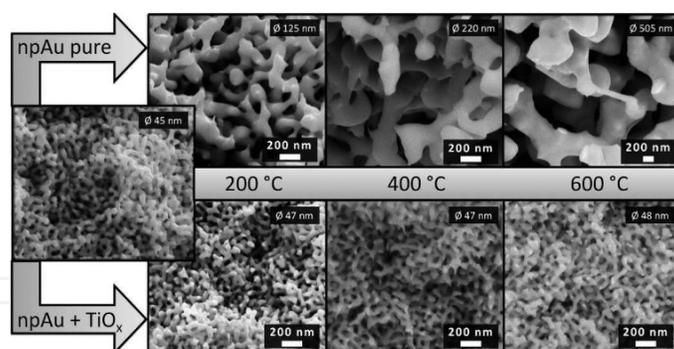


Figure 13. Scanning Electron Microscopy images of bare NPG and titania deposited NPG structures. Annealing comparison shows structural stability of titania-deposited NPG structures. Reprinted with permission from Ref. [7]. Copyright 2013 Wiley-VCH Verlag GmbH.

Depending on the preparation method, NPG is sometimes not catalytically active or the catalytic activity is not reproducible. It is believed to be caused by contaminants during the preparation. Therefore, finding a way to reliably activate NPG as the catalyst has been recognized as one of the important issues for applying NPG in real applications. Therefore, finding a reliable way to activate NPG films for catalytic activation is drawing more and more attention. Activation is usually done by flowing reactant gases at an elevated temperature for some time until NPG becomes catalytically active [14, 15, 39]. However, this process is often not reproducible and inconsistent [52]. Recently, Friend et al. reported a reliable way to activate NPG for the catalytic partial oxidation of alcohol using ozone at atmospheric pressure [53]. After preparing NPG films from $\text{Ag}_{70}\text{Au}_{30}$ ingot by conventional dealloying in nitric acid, they inserted the NPG films in a flow reactor and raised temperature from 30 to 150°C in a flow of 30 g/Nm³ of ozone in a 50% O_2 /He gas mixture. The temperature was held at 150°C for 1 h and lowered to 50°C. Then, again the temperature was raised to 150°C in a flow of 10% methanol and 20% O_2 . They tested the catalytic activity of ozone-activated NPG with the oxidation of

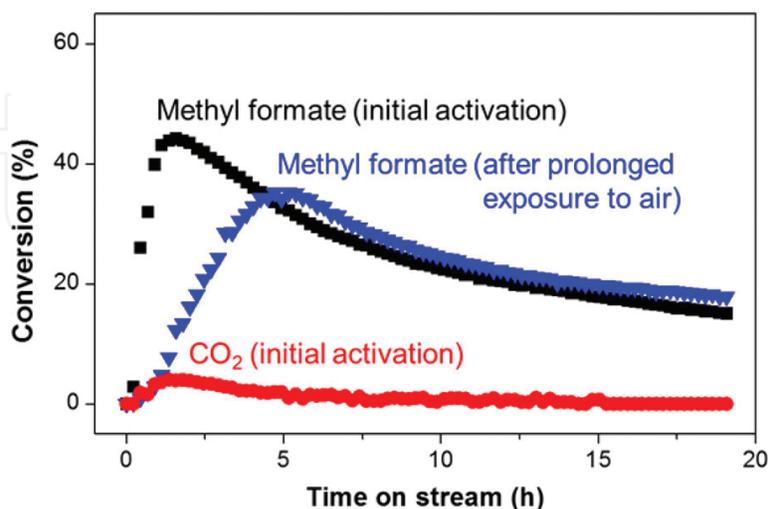


Figure 14. Comparison of conversion to methyl formate (black squares) with that to CO_2 (red circles) vs. time after ozone treatment of NPG. The catalytic activity is maintained for 4 months after exposure to air (blue triangles). Reprinted with permission from Ref. [53]. Copyright 2015 American Chemical Society.

methanol to methyl formate, as this reaction is already studied on NPG in detail [39]. The ozone-activated NPG films showed good catalytic activity for the reaction and more importantly, they maintained stable catalytic activity for at least 1 week (**Figure 14**). But, their catalytic activity for other reactions was different from that of O₂- or CO-activated NPG [14, 15, 39]. For example, the ozone-activated NPG films were not active for CO oxidation.

8. Conclusion

In this chapter, we surveyed the studies on nanoporous gold (NPG) as a catalyst. First, we discussed various preparation methods of NPG and its structures. NPG catalysts are initially applied to CO oxidation and found to be very effective at temperatures as low as -30°C. Since then, CO oxidation was the most studied reaction using NPG catalyst. Studies on the reaction mechanism and related DFT calculations were also reviewed. The model reaction as well as the practical aspects of removing CO residue in hydrogen stream were also discussed. As dissociation of hydrogen molecule is difficult on gold surface, few studies reported reactions regarding hydrogen. However, we also discussed those few reported hydrogen oxidation and generation studies. Beyond those simple reactions, researchers have great interest for applying NPG to more complicated reactions such as alcohol oxidation. Initially, aerobic oxidations of gas-phase alcohols were reported. Liquid-phase reactions with more complex molecules were also reported. For those reactions, numerous studies already reported that gold nanoparticles supported on metal oxide supports have good reactivity and selectivity. However, those catalysts are in powder form and have problems of loss and recovery. Gold nanoparticles are also prone to agglomeration during reaction, losing catalytic activity. NPG can be a potential solution for those problems as it is an extended body of porous structure and metal oxide particles can be deposited on them and used as an inverse catalyst. Moreover, as it does not need any support, there is no problem of particle agglomeration. Besides, NPG has a potential application in green chemistry and controlling selectivity because molecular oxygen can be used as an oxidant and it maintains a delicate balance between oxidation power and interaction with intermediate products. Therefore, the scope of reactions is expected to grow using NPG as a catalyst to more and more complex reactions in organic synthesis beyond those simple and gas-phase reactions. Especially, studies on complex catalyst systems of NPG with deposited metal oxide particles will grow as the interface between NPG surface and metal oxide particles can provide additional important controls over reactivity and selectivity.

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