# A comparative study of alcohol oxidation over nanoporous gold in gas and liquid phase

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## ARTICLE INFO

## ABSTRACT

The aerobic oxidation of methanol and ethanol in liquid phase is investigated using unsupported nanoporous gold (npAu) catalysts and compared to gas phase experiments. We pursue the question if this material is still suited as a type of model catalyst even under much more complex conditions in liquid phase. Indeed, npAu is an active catalyst for both liquid and gas phase oxidation of methanol and ethanol with $O_2$ under mild conditions (starting at 40 °C). While in case of methanol solely the self coupling product (methyl formate) is detected, the more facile formation of the acetaldehyde in case of ethanol results in the formation of the free aldehyde (acetaldehyde) and the coupling product (ethyl acetate) in similar amounts. To further probe the surface chemistry, cross coupling reactions between both alcohols, as well as the acetaldehyde are performed. As observed also in gas phase experiments, the formation of the surface bonded aldehyde by β-H elimination of the alcoxy species is rate determining.

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## 1. Introduction

For the production of fine and specialty chemicals, development of new efficient solid catalysts is one of the most important topics in academic research [1]. Catalytic reactions have to proceed with increasing atom-economy to minimize cost and waste under environmentally benign "green" conditions [2,3]. One of the cornerstones in catalysis is the selective oxidation of alcohols, in particular methanol, for the production of e.g. plastics, detergents, paints, cosmetics, food additives and drug intermediates [4,5]. Traditional catalysts are noble metals (Au, Ag, Cu, Pt, Pd etc.) in the form of nanoparticles dispersed on suitable supports [1,4,6–12]. Unfortunately, the complexity of the catalytic systems under reaction conditions renders a straight forward prediction of reactivity and selectivity often impossible. Model studies on well-defined surfaces under ultrahigh vacuum conditions can guide the design of catalysts as they provide insights into the fundamental reactivity of catalytic surfaces. Studies on pre-oxidized Au single crystalline surfaces already provide a framework of reactivity for the

oxidation of alcohols, aldehydes, and amines [13–16]. However, in gas phase oxidation reactions using gold nanoparticle catalysts, the interface between the particle and the reducible oxidic support material was observed to provide active centers, e.g., for oxygen activation [17,18]. This scenario, indeed, is not easily reflected by model reactions on pre-oxidized gold surfaces. This so called pressure and material gap was recently overcome for gas phase reactions by a bulk-nanostructured gold material, the nanoporous gold (npAu) [19–21]. The sponge-like network of about 30 nm large ligaments provides an extended almost pure and strongly curved gold surface. This material could, hence, be used to bridge the gap between the model studies and more complex traditional supported catalysts, in sense of a scale up. Since its first discovery as an active catalyst for CO oxidation in 2006 [22] a number of studies revealed that with respect to the activation of molecular oxygen from the gas phase traces of Ag [23,24] and a large fraction of low coordinated surface sites similar to 5 nm large particles [25] are critical.

Gas phase catalytic studies on the oxidation of primary alcohols over npAu provided a pattern of reactivity and a mechanistic understanding on the molecular level [19,20,26–28]. Key to the reactivity of the gold surface is surface bonded oxygen which reacts as a Brønstedt base and abstracts the alcoholic proton. The

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resulting surface bonded alcoxy species can undergo further hydrogen elimination yielding the surface bonded aldehyde. This step was found to be rate limiting and determines the selectivity of the reaction.

So far, there is no comparative study on the reactivity for this type of reaction in the condensed, i.e., liquid phase using npAu. Not only that the application range in liquid phase is much broader, the vast majority of studies on supported gold catalysts for alcohol oxidation are performed in liquid phase [6,30]. As compared to gas phase catalysis physicochemical parameters, such as the solubility of oxygen, slower diffusion and adsorption due to solvation typically lead to a very different activity. Also, the chemical reactivity of the solid/liquid interface can be quite different than the solid/gas interface [31,32]. In this study we investigate the oxidation of methanol and ethanol over nanoporous gold catalysts with the emphasis on the liquid phase. Because of their relatively high vapor pressure, both alcohols can be investigated under "mild" conditions, i.e., at temperatures well below 100 °C for vapor and liquid phase reactions, making a comparison under both conditions possible. Studies by Hutchings et al. demonstrated that operating at low temperatures (<110 °C) is essential for high product selectivity in case of methanol oxidation [29]. Using a continuously stirred batch reactor and a plug flow reactor we investigate the activity and selectivity of the self and cross coupling of these alcohols under various conditions (temperature and oxygen concentration), trying to establish a pattern of reactivity and deduce a molecular mechanism of transformation. High resolution transmission electron microscopy (HRTEM) before and after catalytic experiments is used to gain information on the surface roughness, number of low coordinated sites and the structure (ligament size) of the npAu catalysts.

## 2. Materials and methods

### 2.1. Synthesis of nanoporous gold (npAu)

Ingots of the master alloy, with nominal composition of $Au_{25}$-$Ag_{75}$ (numbers denoting atomic percent), were prepared by arc melting the constituents (Au 99.995 %, Ag 99.999 %). The ingots were sealed in evacuated quartz tubes and homogenized at 920 °C for 120 h. Sheets were then formed by cold-rolling to a thickness off 0.125 mm, followed by a recovery anneal at 620 °C for 3 h in air. Laser cutting into circular discs, 5 mm in diameter, completed the master alloy preparation. NpAu catalysts were obtained by corrosion of such master alloy discs. For potentiostatic dealloying (potentiostat BioLogic SP-200), a typical three electrode system consisting of a gold wire formed as a basket to hold the $Au_{25}Ag_{75}$ alloy discs was employed as working electrode, as well as a platinum auxiliary electrode and a platinum quasi reference electrode. This method avoids any potential contamination over time by, e.g., chloride as was observed for standard reference electrodes such as a Ag/AgCl electrode. The etching process was performed at 60 mV in 5 M nitric acid (HNO₃, Sigma-Aldrich, ≥65 %) at room temperature. The potential was applied till the anodic current became negligibly small (24 h) corresponding to removal of over 99 at.% Ag (calculation based on the measured charge, see also Fig. S1).

### 2.2. Characterization of npAu

For quantitative analysis of residual Ag content in npAu, Atomic Absorption Spectroscopy (AAS 5 FL, Jena Analytik) was carried out as described in previous publications [33]. The homogenous distribution of residual Ag through the npAu disc was checked by Energy Dispersive X-ray spectroscopy (EDX, Bruker XFlash 6 | 30). For

determination of the specific microscopic surface area of npAu with Eq. (1), cyclic voltammograms of npAu samples in 0.5 M sulfuric acid (H₂SO₄, VWR Chemicals, 95 %) between −0.4 V and 1.7 V were recorded using a scan rate of 10 to 1 mV s⁻¹ (potentiostat BioLogic SP-200), a gold wire with fixed npAu as working electrode, a platinum counter electrode and a commercial Ag/AgCl (in 3 M KCl) reference electrode.

$$A_m = \frac{IE}{v * Q_{ref} * m(npAu)} \qquad (1)$$

IE: integrated area of Au-reduction peak in AV
v: sweep velocity (1–10 V s⁻¹)
$Q_{ref}$: gold oxide monolayer charge is 400 μC cm⁻² [34]
m(npAu): weight of npAu (10–15 mg)

Structural characterization of npAu samples was carried out by scanning electron miscroscopy (SEM, Zeiss Supra 40). From these images sizes of ligaments and pores were determined by measuring 400 diameters each. For structural characterization of the npAu by transmission electron microscopy (TEM), thin, electron transparent lamellas were cut from the npAu discs with a Focused Ion Beam (FIB) using a FEI Nova 200 FIB. Subsequent TEM measurements have been performed in the bright field mode using parallel illumination on a FEI Titan 80/300 (S)TEM microscope equipped with a Cs-corrector for the objective lens. Micrographs were taken to compare npAu before and after catalytic experiments with respect to size distribution, atomic distances between surface steps, crystallinity and contaminations.

### 2.3. Catalytic oxidation of primary alcohols on npAu in liquid phase

Liquid phase oxidation reactions were carried out in a batch reactor (AmAr Equipments PVT. Ltd., Mumbai; reaction volume of 60–450 mL, see Scheme 1). The temperature of the reactor and pressure of gas phase were controlled by installed thermocouple and pressure gauges. To ensure an optimal gas-liquid contact, a self-gassing hollow shaft stirrer was used. In this way the gas was continuously dispersed in the liquid to ensure fast equilibration of dissolved oxygen. The reactor was filled with 60 mL of an alcohol (methanol MeOH, VWR Chemicals, 99.8 %; ethanol EtOH, VWR Chemicals, 100 %) or alcohol diluted with high purity water, another alcohol or acetaldehyde (AcH, Sigma-Aldrich, ≥99.5 %). The npAu discs (10–15 mg) were mounted in a metallic net basket inside the reactor to avoid catalyst mechanical damage during catalytic experiments. After loading and sealing the reactor was purged with nitrogen (Linde 5.0) and oxygen (Linde 5.0) twice, and subsequently pressurized and heated to the designated
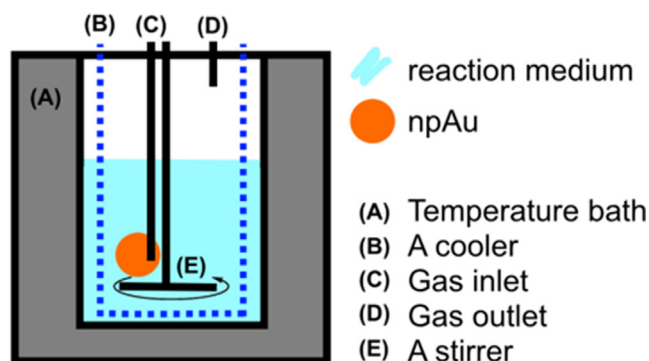


**Scheme 1.** Schematics of the catalytic reactor; various temperatures (A/B), gas partial pressures (C) and stirring speeds (E) can be applied. The catalyst is mounted in a net basket direct next to the gas inlet to avoid any mechanical damage via stirring and to ensure oxygen adsorption on the catalyst.