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Bulk Gold Catalyzes Hydride Transfer in the Cannizzaro and Related Reactions

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ABSTRACT

Bulk gold was found to catalyze the Cannizzaro reaction of benzaldehyde and related disproportionation reactions in superheated water. At 200°C and 1.5 MPa for ~48 hours, benzaldehyde conversions increased linearly with added gold at low loadings, but this trend reversed at the higher gold loadings. Ratios of the primary products benzoic acid and benzyl alcohol exceeded unity, increasing with increasing amounts of gold. These observations are attributed to the reactivity of benzyl alcohol in the presence of gold, which is proposed to react via cross-disproportionation with benzaldehyde to yield toluene and benzoic acid, transitioning to benzyl alcohol disproportionation that forms toluene and reforms benzaldehyde at higher gold loadings. Turnover frequencies for both benzaldehyde (0.00013 s^{-1}) and benzyl alcohol (0.0011 s^{-1}) were quite low and experiments of varied duration demonstrated that very few turnovers occurred under the reaction conditions. Proposed mechanisms for the catalyzed reactions include hydride transfer from gold-bonded alkoxides to surface gold atoms. These observations expand the known catalytic capabilities of bulk gold to include hydride transfer, a fundamental process in organic chemistry and biochemistry. The simple, environmentally benign reaction conditions

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are reminiscent of organic geochemical processes, with implications for both geomimicry and green chemistry approaches to chemical challenges.

KEYWORDS: alkoxide, benzaldehyde, benzyl alcohol, disproportionation, geomimicry, hydrothermal

INTRODUCTION

Hydride transfer is one of the most fundamental processes in organic chemistry[1–5] and biochemistry[6–8] and is one of the simplest reduction/oxidation reactions.[9] It is an important aspect of processes as diverse as organic synthesis,[10] fuel storage,[11] fuel cells,[12] and the biochemical reactions of cellular respiration[13] and photosynthesis.[14] In organic chemistry, hydride transfer is a critical component of many hydrogenation, hydroformylation, and hydrosilation reactions.[10] Almost all elements form bonds to hydrogen that are, in principle, capable of being involved in hydride transfer, and a wide array of reducing agents based on hydride transfer from boron and aluminum have been described.[9] Additionally, reactions involving transfer of hydride from carbon are also known,[10] with important examples from the chemical industry including acid-catalyzed petroleum cracking[15] and acid-catalyzed dimerization of isobutylene to form larger hydrocarbons.[16] There is also current interest in using hydride transfer for the activation of simple hydrocarbons by co-conversion of more reactive functional groups such as alcohols.[17]

Importantly, organic hydride donors are of current interest in the context of carbon dioxide reduction,[18] which is challenging because “free” hydride cannot be used, as the presence of Brønsted acids would lead to the formation of molecular hydrogen rather than reduction. Direct hydride transfer from one carbon atom to another avoids formation of hydride anions and occurs in several well-known organic reactions, including the Meerwein-Pondorff-Verley reduction,[19] the Oppenauer oxidation,[20] and the Cannizzaro reaction.[21] These reactions are slow in the absence of catalysts, yet disproportionation reactions of aldehydes reminiscent of the Cannizzaro reaction occur without catalysts in superheated or supercritical H_2O, which have been investigated with benzaldehyde,[22–25] acetaldehyde,[26–29] and formaldehyde.[30–33] Though reports of heterogeneous catalysis of the Cannizzaro reaction are limited,[34–36] here we report that bulk metallic gold is capable of catalyzing hydride transfer in the disproportionation of benzaldehyde and related reactions at comparatively modest hydrothermal conditions.

Although historically considered to be a rather inactive catalyst for organic reactions,[37–39] interest in gold as a catalyst was stimulated by several landmark papers demonstrating useful catalytic activity,[40–42] to the extent that metallic gold has now been described as the best available catalyst for some reactions.[43] Most of the reports of heterogeneous gold catalysis involve supported nanoparticles,[44,45] while bulk gold is usually much less active as a catalyst.[37,38,46–48] Nevertheless, catalytic activity for bulk gold has been demonstrated for several reactions, including oxidation of CO,[49,50] oxidative additions to isocyanides,[51–53] oxidations of amines[54–56] and alcohols,[50,56,57] and reactions of carbenes generated from diazoalkanes.[58] In contrast to bulk metals, the electronic properties of other metal catalysts including metal clusters, supported nanoparticles, and supported dispersed single atoms are strongly affected by the chemical nature of the support, the presence and identity of ligands or other metals, and the coordination (saturation) of the metal atoms.[59,60] Thus, bulk metal materials offer the opportunity to probe the fundamental catalytic capabilities of noble metals.

Hydrogenation on supported gold nanoparticles using organic hydride donors in what are formally cross-disproportionation reactions have been reported,[61–64] though hydride transfer usually requires a heterogeneous catalyst with Brønsted acidic sites,[65] such as those found in zeolites.[65,66] Gold-catalyzed bimolecular organic reactions also usually require additional reagents that act as oxidants or nucleophiles.[49–58] In contrast, the reactions described herein occur on simple bulk metallic gold as the catalyst and require no additional reagents. The reactions take place in H_2O as the solvent under hydrothermal conditions that mimic those of many geochemical reactions,[67,68] thus they may be appropriate for green chemistry applications.[69]

EXPERIMENTAL

Solutions of benzaldehyde or benzyl alcohol in water, typically at a concentration of 100 millimolal, were sealed in fused silica tubes and heated in a temperature-controlled oven for fixed time periods, typically ~48 hours, analogous to previous work.[25,67,70–72] The reaction temperature was 200°C and under the conditions of the experiments the pressure inside the tubes was determined by the saturated vapor pressure of water, which is 1.5 MPa at this temperature.[73] The reactants have aqueous solubilities at lower temperatures that are comparable to or exceed their experimental concentrations,[74–76] indicating they are fully dissolved at the experimental temperature. Experiments were performed in the presence of varying quantities of one of several metallic gold powders from two commercial sources. The first was a large particle size bulk powder with particles ranging from ~1 to 1000 microns produced by precipitation from a gold chloride solution in the presence of oxalic acid (Salt Lake Metals, Salt Lake City, UT, USA). The other two powders were a small particle size (0.5-0.8 micron) powder, which allowed comparison with a previous study,[50] and a medium particle size (5.5-9.0 micron) powder, both of which were obtained from Alfa Aesar (Ward Hill, MA, USA). Organics in each experiment were extracted with dichloromethane and quantified using a gas chromatograph with flame ionization detection. Detailed descriptions of the materials and methods are given in the Electronic Supplementary Information.

RESULTS & DISCUSSION

Gold-Catalyzed Hydrothermal Reactions of Benzaldehyde

Compared to water alone, the conversion of benzaldehyde at a fixed reaction duration was significantly enhanced by the presence of gold powder (Figure 1, data reported in Table S1). At 200°C, 1.5 MPa, and a fixed reaction duration of 2902 minutes (~48 hours), the conversion of 100 millimolal benzaldehyde in water alone was only ~1%. This result is not surprising, as the Cannizzaro reaction is traditionally understood to require strong base,[77] and the reaction of benzaldehyde under hydrothermal conditions in the absence of base is quite slow at temperatures below ~300°C.[25,78] In the presence of gold powder, the conversion increased approximately linearly with the quantity of gold powder added to the reaction tube, up to ~56% conversion with ~0.5 g of the large particle size gold. A similar trend was observed using the small particle size 0.5-0.8 micron gold, where conversions of ~13% were reached with ~0.2 g of gold. This approximately linear dependence on gold loading suggests that gold is acting as a catalyst under conditions where the reaction is under kinetic control; see further below. At higher gold loadings (more than 0.5 g, Figure 1), a linear trend was no longer observed, and the net conversion of benzaldehyde decreased with further increasing quantities of gold.

The major reaction products, both in the presence and absence of gold, were benzyl alcohol and benzoic acid, which are those expected for the Cannizzaro reaction (**Scheme 1**, Reaction **1**). The hydrogen balance always exceeded 100% (Table S1), consistent with the addition of hydrogen derived from H_2O to the organic products, as in the Cannizzaro reaction, and suggesting that the formation of H_2 was not a dominant pathway. However, the ratios of acid-to-alcohol exceeded unity, particularly at higher gold loadings (Figure 2), and other products were observed, including benzene and toluene (Figure S4). The yield of benzene increased with

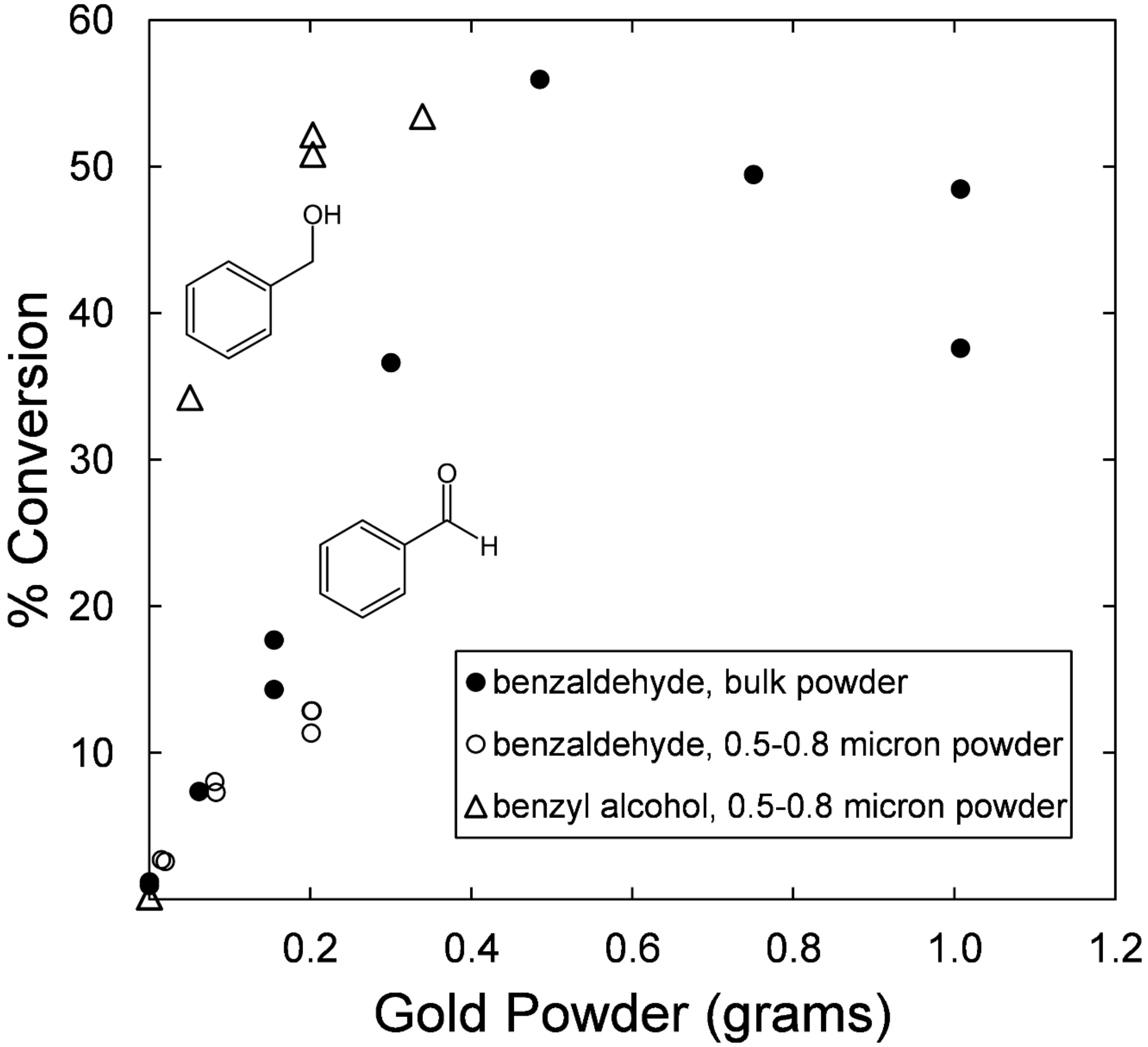
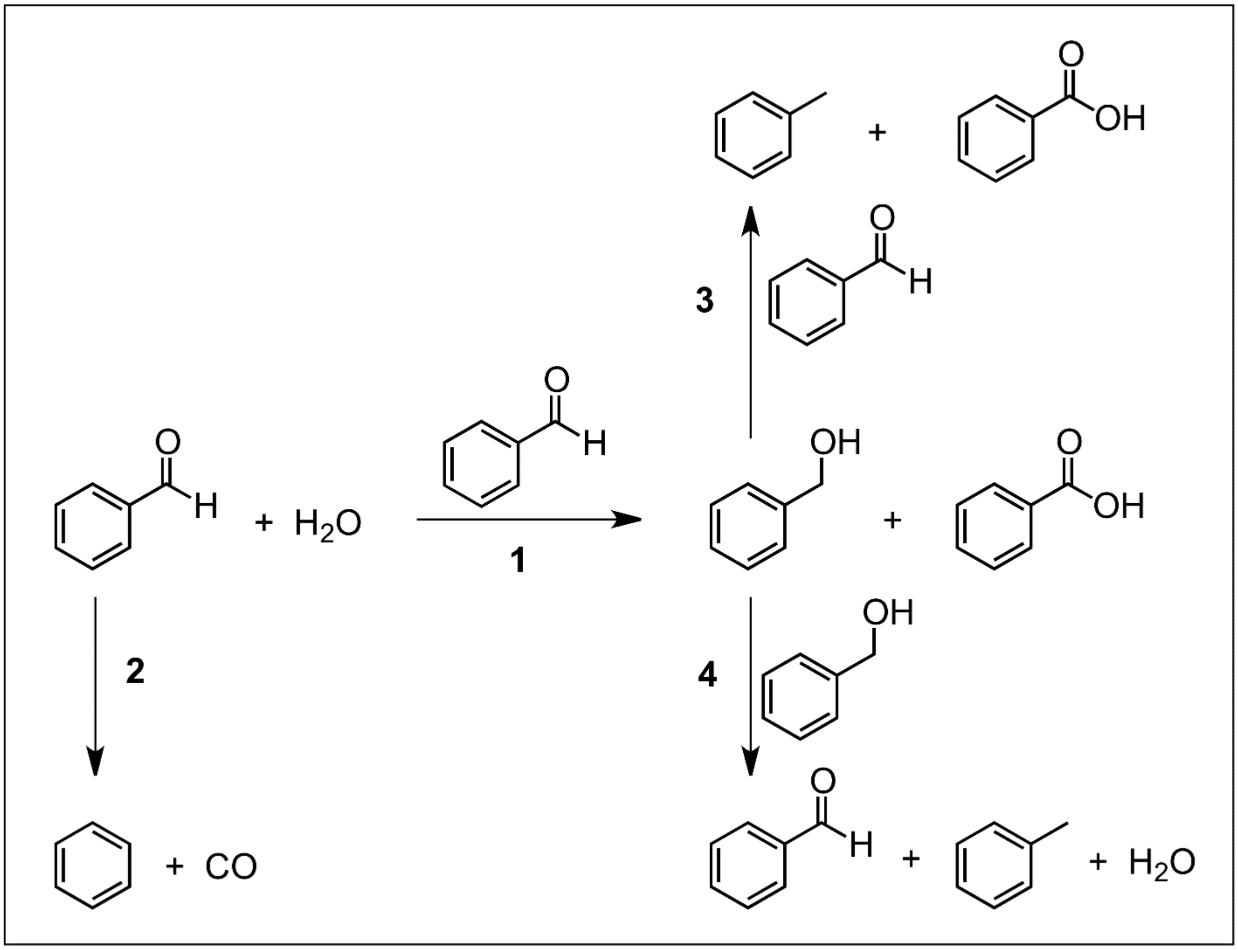


Figure 1. Conversion of benzaldehyde (circles) and benzyl alcohol (triangles) as functions of added gold powder (data from Table S1). All experiments were conducted at 200°C and 1.5 MPa for a constant duration of 2902 minutes with 100 millimolal concentration of organic reactant. The open circles and the open triangles indicate experiments using the small particle size 0.5-0.8 micron gold powder; the filled symbols indicate experiments using the large particle size gold powder.

Scheme 1. Bulk Gold-Catalyzed Reactions of Aqueous Benzaldehyde and Benzyl Alcohol Solutions (200°C, 1.5 MPa)



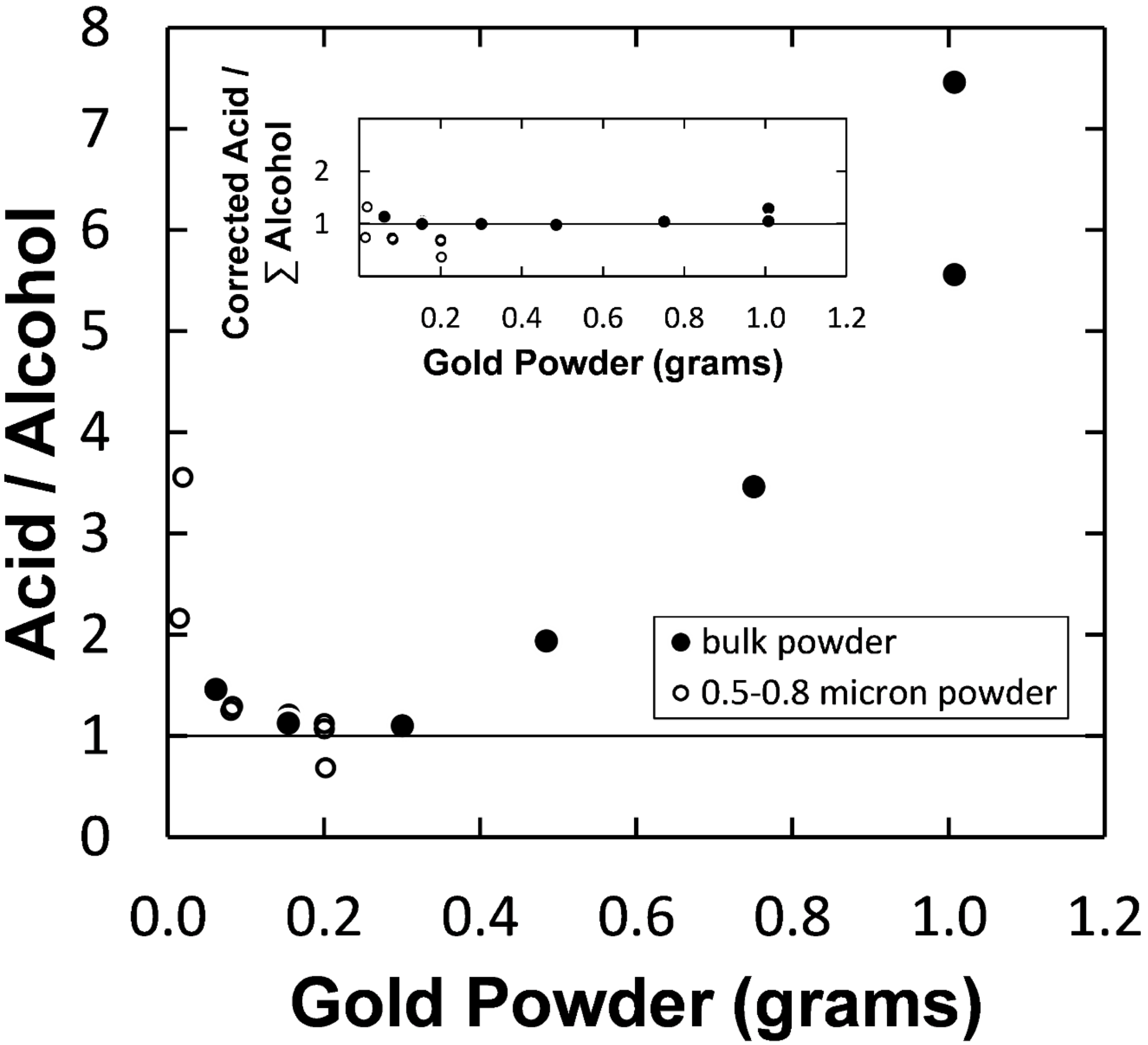


Figure 2. The ratio of the yield of benzoic acid to the yield of benzyl alcohol, as a function of the quantity of large particle (filled circles) and small 0.5-0.8 micron particle (open circles) gold powder, for reactions of 100 millimolal benzaldehyde at 200°C and 1.5 MPa for a constant duration of 2902 minutes. The inset shows the same ratios corrected to account for cross-disproportionation of the alcohol and uncatalyzed reactions.

increasing gold loading and correlated closely with benzaldehyde conversion. Therefore, benzene formation can be attributed to a gold-catalyzed primary decarbonylation reaction of the benzaldehyde starting material (**Scheme 1**, Reaction **2**). Decarboxylation of benzoic acid could also be a source of benzene, but this reaction is only weakly gold-catalyzed,[79] and is so slow at temperatures much higher than 200°C that it cannot be an important reaction pathway.[78] Unlike benzene, the yield of toluene did not correlate with benzaldehyde conversion. Instead, the toluene yield was relatively low at low gold loadings (*i.e.*, at low benzaldehyde conversions) and was significantly higher at higher gold loadings (*i.e.*, at higher benzaldehyde conversions). As discussed further below, toluene formation is proposed to result from a gold-catalyzed secondary reaction of the primary benzyl alcohol product (**Scheme 1**, Reaction **3**). A slight enhancement in the yields of the primary products benzyl alcohol, benzoic acid, and benzene was observed upon a doubling of the starting concentration of benzaldehyde in the presence of ~0.2 g of the small particle size 0.5-0.8 micron gold powder (Figure S5). The enhancement was far less than would be expected for a bimolecular reaction occurring in solution, implying that the disproportionation products did not form in solution via the standard homogenous catalysis mechanism.

The Acid-to-Alcohol Ratio: Support for a Gold-Catalyzed Cannizzaro Reaction.

The observed acid-to-alcohol ratios could be consistent with the Cannizzaro reaction if benzyl alcohol was being depleted in secondary reactions, such as in the formation of toluene. At lower conversions of benzaldehyde, *i.e.*, when the concentration of benzyl alcohol is relatively low and the concentration of benzaldehyde relatively high, the most likely source of toluene is a cross-disproportionation reaction to form toluene and benzoic acid (**Scheme 1**, Reaction **3**). This reaction pathway has been proposed previously in studies of hydrothermal reactions of benzaldehyde (in the absence of gold) and a viable mechanism in solution can be proposed that includes a hemiacetal intermediate.[22,25] To assess this hypothesis, the yield of toluene plus the yield of alcohol were compared with the yield of benzoic acid accounted for by the Cannizzaro reaction.

For the cross-disproportionation reaction (**Scheme 1**, Reaction **3**), the quantity of toluene formed is stoichiometrically equal to the quantity of benzoic acid formed via this pathway, and also the quantity of benzyl alcohol lost via this pathway. Thus, the yields of benzoic acid (corrected for minor competing uncatalyzed reactions, as described in the Electronic Supplementary Information) were adjusted by subtracting the yield of toluene in the same experiment to obtain the yield of benzoic acid attributed to the Cannizzaro reaction. Furthermore, total yields of benzyl alcohol were obtained by adding the observed quantities of benzyl alcohol and toluene for each experiment. For experiments starting with benzaldehyde, the ratios of corrected benzoic acid yields derived from the Cannizzaro reaction to total benzyl alcohol yields are close to unity for all quantities of gold and benzaldehyde conversion, as shown in the inset in Figure 2. On this basis, it is concluded that the primary gold-catalyzed reaction of benzaldehyde is indeed the Cannizzaro disproportionation reaction.

Gold-Catalyzed Hydrothermal Reactions of Benzyl Alcohol

The secondary cross-disproportionation reaction of benzyl alcohol and benzaldehyde is the major reason for the yields of benzyl alcohol and benzoic acid being unequal and is almost certainly a factor contributing to the deviation from linear behavior of benzaldehyde conversion at higher loadings of gold (Figure 1). However, cross-disproportionation is unable to account for the net *decrease* in benzaldehyde conversion at the highest gold loadings. An additional reaction pathway where benzaldehyde is a *product* is presumably operating at these higher gold loadings. To explore other possible reaction pathways, experiments were performed with benzyl alcohol as the starting reactant. Benzyl alcohol was found to be even more reactive in the presence of gold powder than benzaldehyde (Figure 1, data reported in Table S2).

Experiments at 200°C, 1.5 MPa, and a fixed duration of 2902 minutes resulted in an almost linear dependence of alcohol conversion on the quantity of gold loaded into the reaction tubes (Figure 1). Similar to benzaldehyde, the conversion of benzyl alcohol in the absence of gold was very low, ~0.2%. Toluene and benzaldehyde were the major products in the presence of gold, consistent with benzyl alcohol self-disproportionation (**Scheme 1**, Reaction **4**), which has also been observed on gold nanoparticles supported on silica, titania, and other supports.[80–83] The hydrogen balance values for these experiments were less than 100% (Table S1), consistent with a loss of hydrogen from the organic reactants to H_2O. Analogous to the benzaldehyde experiments, the ratio of the disproportionation products benzaldehyde and toluene deviated from the expected value of unity due to secondary and side reactions, as detailed in the Electronic Supporting Information. The most significant contributor to this deviation is the reactivity of benzaldehyde in the presence of gold. Assuming the cross-disproportionation reaction is the dominant mechanism for consuming benzaldehyde at low gold loadings, the total benzaldehyde was compared to the toluene derived from benzyl alcohol disproportionation, with the yield of benzoic acid being stoichiometrically equal to the amount of toluene produced via cross-disproportionation, as described in the Electronic Supplementary Information. The ratios of the total benzaldehyde yields to the corrected toluene yields are close to unity, except at the lowest gold loadings (Figure S6). Thus, the major reaction in experiments starting with benzyl alcohol in the presence of gold is self-disproportionation.

Benzyl alcohol disproportionation provides a mechanism for reformation of benzaldehyde, which is the reason for the decrease in net conversion of benzaldehyde at the highest gold loadings (Figure 1). In the case of experiments starting with benzaldehyde, as the amount of gold is increased and the benzyl alcohol concentration begins to exceed that of the starting benzaldehyde, the system transitions from cross-disproportionation of benzyl alcohol and benzaldehyde (**Scheme 1**, Reaction **2**) to alcohol self-disproportionation (**Scheme 1**, Reaction **4**) as the dominant secondary reaction. Either reaction can account for deviations of the benzoic acid to benzyl alcohol ratios from those commensurate with the Cannizzaro reaction (Figure S7), but it is not possible to directly quantify the contribution of each reaction.

Turnover Frequency of Gold-Catalyzed Reactions

The surface area of the small 0.5-0.8 micron gold powder was determined via Brunauer-Emmett-Teller (BET) adsorption of nitrogen to be 0.73 m^2/g, which agrees well with the 0.75 m^2/g reported for this powder by Ketchie and colleagues.[50] Using this measurement, the total surface area of gold in each experiment was calculated and converted to the number of surface gold atoms using 0.0875 nm^2 as an estimate of the surface area of a gold atom.[50,84] Using these data, the powder has a dispersion of 0.27% surface gold atoms relative to the total number of gold atoms. Turnover was then calculated from linear regression of the equivalents converted versus the number of surface gold atoms for the experiments with lower quantities of gold where secondary reactions are minimized (Figure 3), resulting in minimum turnover frequencies (TOFs) of 0.00013 s^{-1} and 0.0011 s^{-1} for benzaldehyde and benzyl alcohol, respectively. The TOF for benzyl alcohol is about three orders of magnitude smaller than the TOF for aqueous glycerol oxidation using the same powder[50] or for benzyl alcohol oxidation using supported nanoparticles in organic solvent.[83] Benzyl alcohol oxidation in the absence of O_2 on supported gold has a TOF that is also over an order of magnitude larger than the TOF observed in this study.[83]

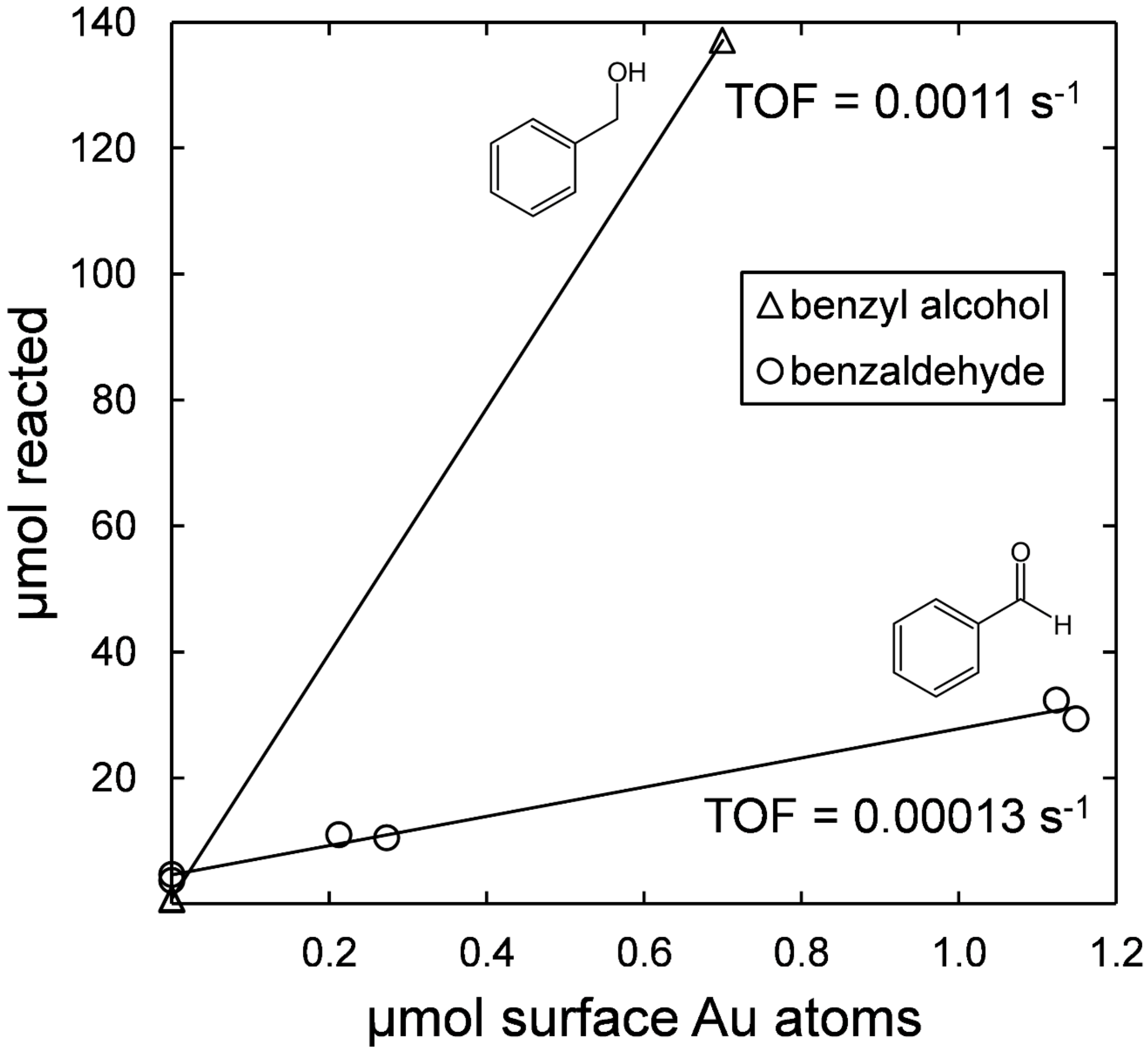


Figure 3. Total benzaldehyde (circles) or benzyl alcohol (triangles) consumed versus the number of surface gold atoms in experiments at 200°C and 1.5 MPa with 100 millimolal reactant concentration and the small particle size 0.5-0.8 micron gold powder. Only experiments with gold loadings of less than 0.1 g are included, as these experiments have the lowest conversions and the smallest contributions from secondary reactions. Regression leads to turnover frequencies (TOFs) calculated using the total reaction duration (2902 minutes).

While gold-catalyzed benzaldehyde and benzyl alcohol disproportionations may be inherently slower than oxidations, the low observed TOFs could be attributed to a decrease in catalytic activity of the gold powder over the experimental duration. Scanning electron microscopy (SEM) images of the small 0.5-0.8 micron gold powder prior to use showed some particles smaller than 0.5 microns, though there was no strong evidence for particles in excess of ~1 micron (Figure 4A). Prior to each experiment, the vessels were vortexed to create a suspension, but at the end of the experiment the gold had formed a cohesive sheet. This aggregated gold could be broken up in the extraction process, but SEM images of this used powder showed particles that were much larger in size than 0.8 microns (Figure 4B). It appears that the original particles had fused (*i.e.*, undergone sintering); indeed, this used powder was reminiscent of the large particle size bulk powder (see Electronic Supplementary Information). Aggregation was not reported when the small 0.5-0.8 micron particle size gold powder was used at 60°C in the presence of water[50] so it is likely a consequence, at least in part, of the higher temperature used in this study. Aggregation of the small 0.5-0.8 micron particle size gold decreases the surface area available for catalysis and the surface areas indicated by the BET measurements would only be available during the earliest stages of the experiment. To investigate this hypothesis, several experiments were performed with benzaldehyde for half the normal duration, *i.e.*, 1451 minutes, with the small 0.5-0.8 micron particle size gold. Most of these experiments exhibited benzaldehyde conversions similar to those observed in experiments conducted for the normal duration (2902 minutes) with the same gold loading, indicating that nearly all the conversion occurs in the first half of the experiment (Figure 5). The conversion of one such half-duration experiment greatly exceeded that of other experiments, even those conducted for the usual 2902 minutes. The origin of this

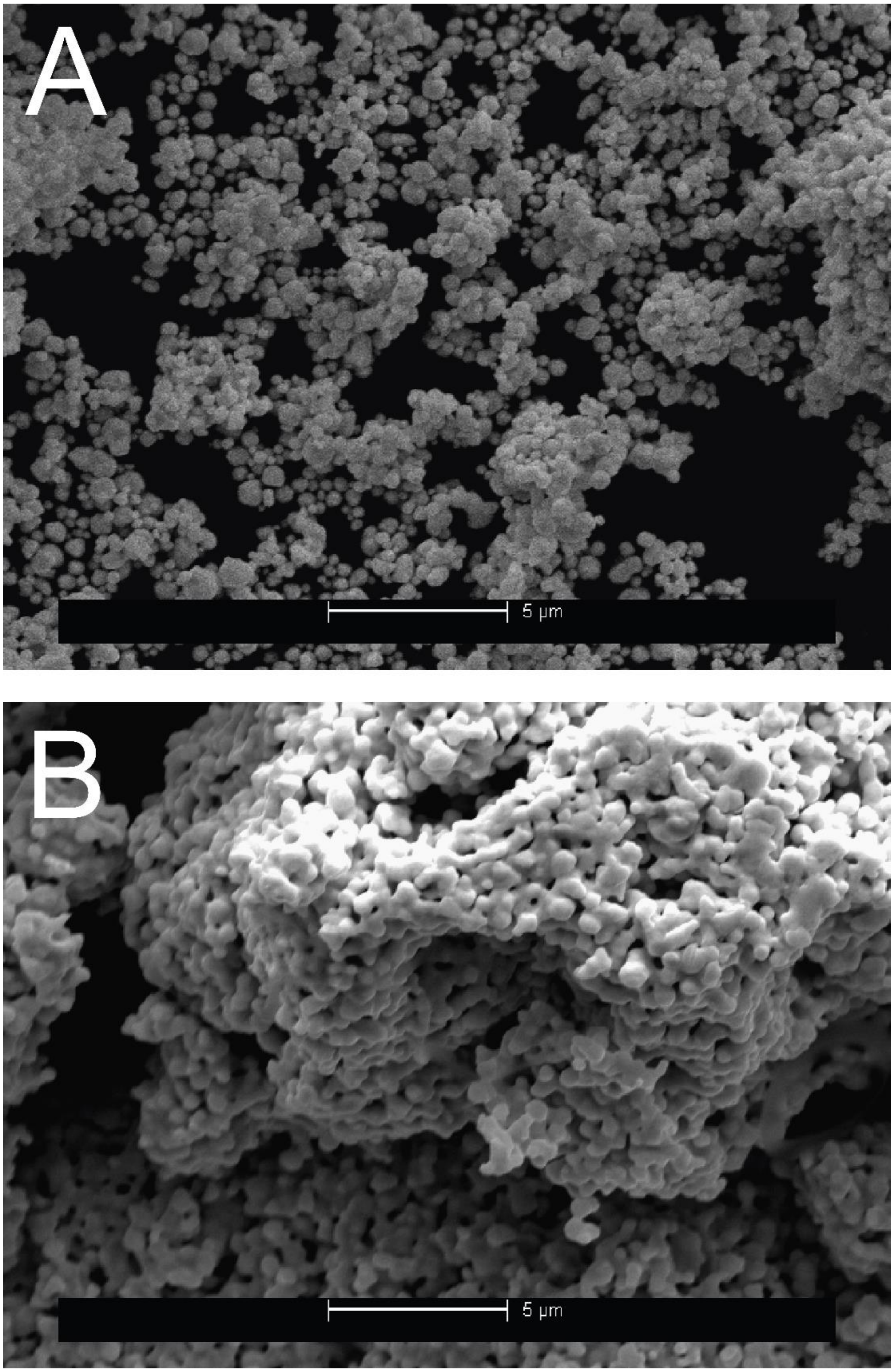


Figure 4. A) SEM image of the small particle size 0.5-0.8 micron gold powder after processing but prior to use in an experiment. B) SEM image of the small particle size 0.5-0.8 micron powder recovered from an experiment after reaction with benzaldehyde (200 °C, 1.5 MPa, 2902 minutes).

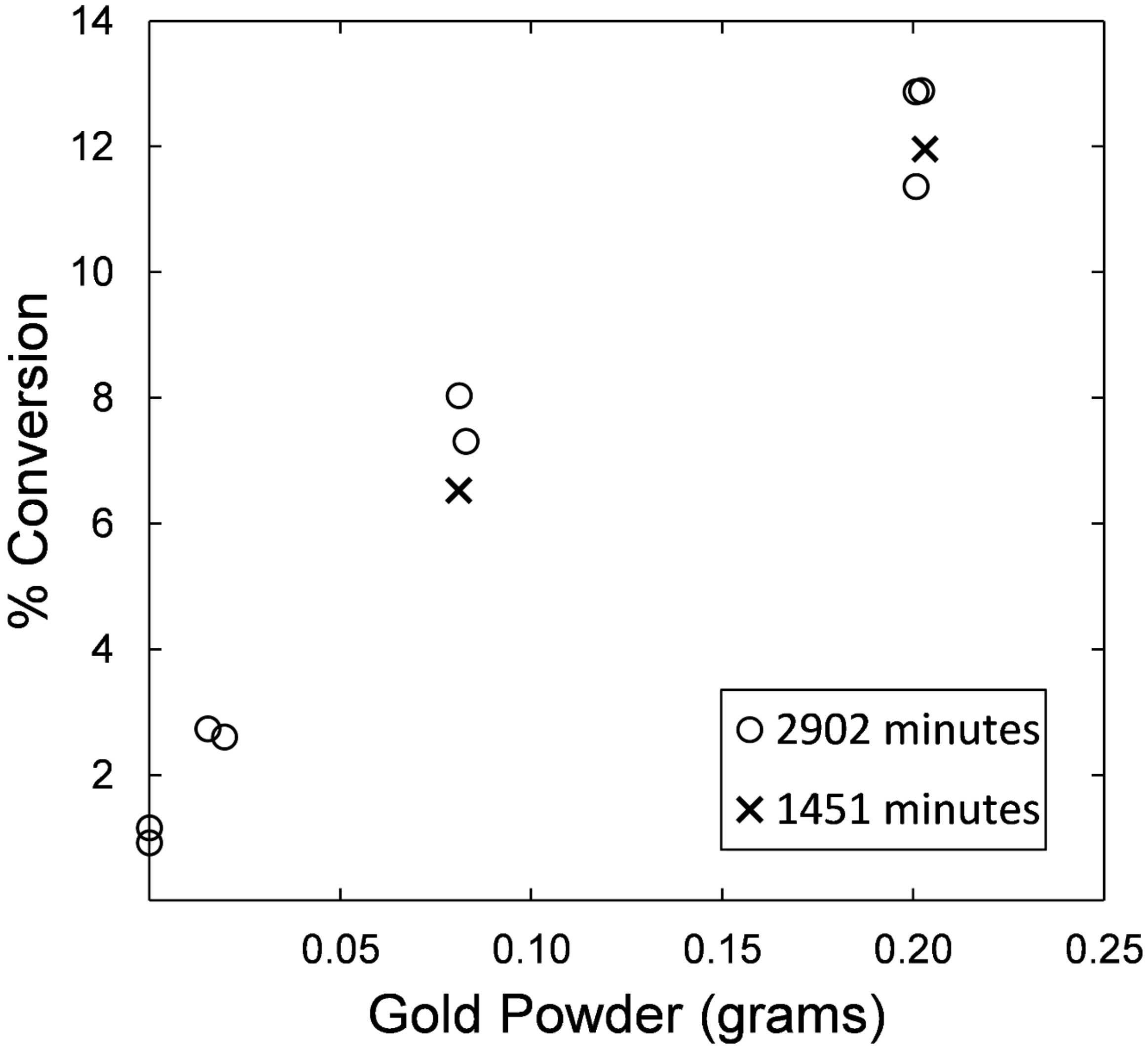


Figure 5. Conversion of 100 millimolal benzaldehyde in experiments with small particle size 0.5-0.8 micron gold powder conducted for 2902 minutes (circles) and 1451 minutes (crosses) at 200 °C and 1.5 MPa. One experiment conducted for 1451 minutes had a higher conversion (27%) and is not shown.

anomalous result is unknown, as the gold in this experiment macroscopically appeared aggregated like the others.

Presumably due to its larger particle size and heterogeneous morphology, the large particle size gold powder did not aggregate, and no obvious differences were observed in SEM images of used and unused powders (see Electronic Supplementary Information). Indeed, the bulk powder was recovered, washed, and reused for some experiments, though reuse of this gold more than once resulted in a noticeable yet irreproducible decrease in catalytic ability (results not shown). The reason for this loss of catalytic performance is unclear, though disproportionate loss of the smallest particles from the bulk gold powder would decrease its specific surface area, leading to decreased conversions for a given mass of gold.

Aggregation of the small particle size 0.5-0.8 micron gold powder could explain the unexpected observation that the small particle size and large particle size powders are similarly effective at catalysis of benzaldehyde conversion (Figure 1). If this is the case, an intermediately sized powder that does not aggregate could afford higher conversions than either the small particle size or large particle size powders, and unlike the small particle size powder, exhibit different conversions at different experiment durations. This hypothesis was assessed by conducting a series of benzaldehyde experiments employing a fixed amount (0.5 g) of medium particle size 5.5-9.0 micron gold powder for varied durations (Table S3). The BET surface area of this powder is 0.047 m^2/g, corresponding to a dispersion of only 0.018%, which are each over an order of magnitude smaller than those of the small 0.5-0.8 micron powder. Although SEM images of this powder suggest that it did not aggregate under the experimental conditions (see Electronic Supplementary Information), overall conversions of benzaldehyde with this powder were comparatively low and did not appear to depend on experiment duration. An estimate of the TOF for this powder, using the longest-duration experiments, is 0.0003 ± 0.0002 s^{-1}, which is the same as that determined for the small 0.5-0.8 micron powder. These observations show that both the small and medium particle size powders act as catalysts for only short durations at the beginning of the experiment and suggest that aggregation of the small 0.5-0.8 micron powder is a moot issue. Instead, changes in surface morphology at the atomic scale not readily observable via SEM or the formation of polymers or strongly adsorbed organics could account for the decrease in activity over the duration of the experiment. For instance, it has been suggested that benzoic acid is capable of poisoning gold-based catalysts.[85–87]

The TOFs determined in this study correspond to only 10s of turnovers in each experiment, under the assumption that all surface atoms are equally effective catalytic sites. Thus, not only do the small and medium particle size powders become inactivated, it may be that only surface gold atoms in specific configurations are capable of catalysis, which has been suggested for catalysis with gold nanoparticles.[81,83] These results suggest that the large particle size bulk powder, in spite of its low specific surface area, possesses comparatively more catalytically active gold atoms than the smaller powders, which is perhaps related to the irregular and variable particle shape of the large particle size bulk powder (see Electronic Supplementary Information). It is also possible that gold clusters or nanoparticles are formed from the bulk metal powders under hydrothermal conditions and that these are the actual catalysts, with the large particle size powder having a greater propensity toward the production of such smaller particles. Thus, although the turnover frequencies measured here are low, these are minimum values. The turnover frequencies could potentially be drastically improved by dispersing gold on an inert support in an effort to mitigate deactivation, which would also offer a substantial improvement in atom economy relative to bulk gold. With properly optimized catalysts, reasonable reaction rates could be obtained at temperatures lower than those employed here, though development and characterization of improved catalysts are beyond the scope of the present study.

Mechanisms of the Gold-Catalyzed Reactions

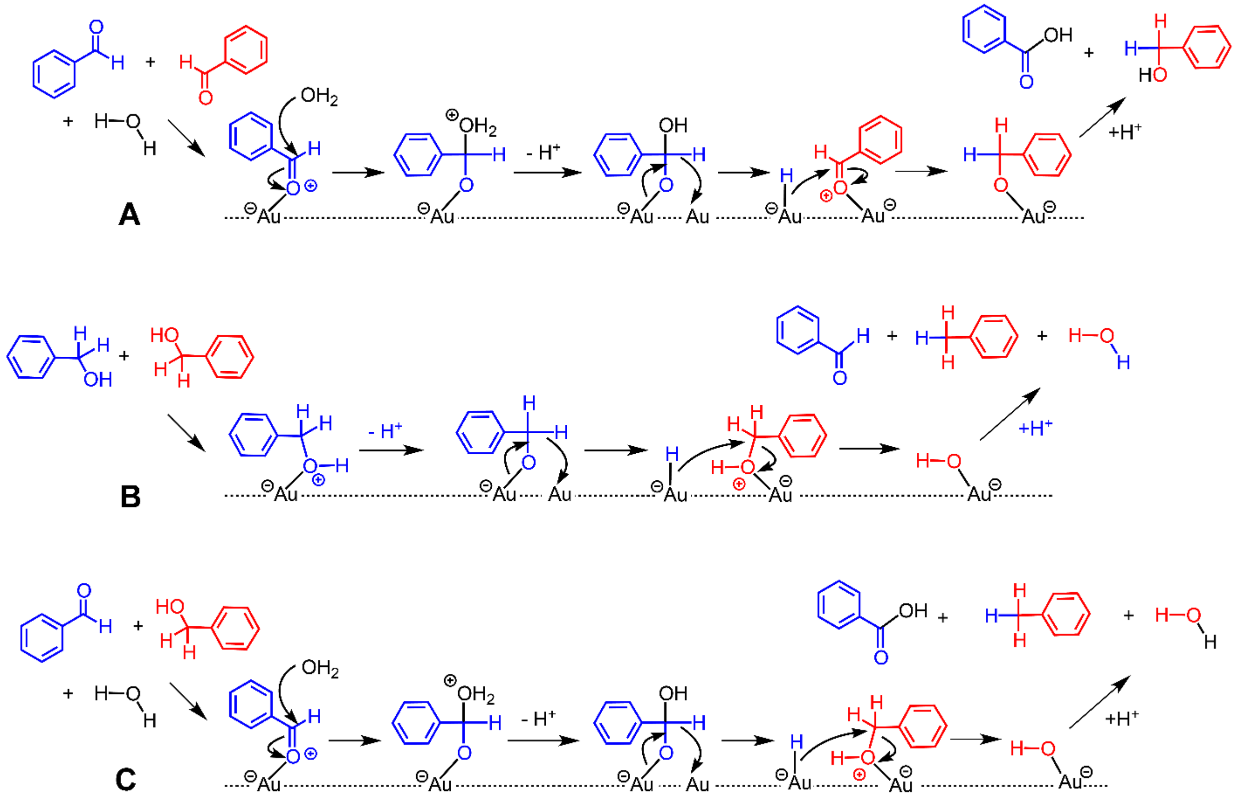
The data discussed above provide strong evidence for bulk gold catalysis of disproportionation reactions involving benzaldehyde and benzyl alcohol. The experimental design places limits on the ability to gain a detailed mechanistic understanding of these processes; nevertheless, some important insights can be obtained. The traditional method for determining whether heterogeneously catalyzed reactions are in the diffusion or kinetically (intrinsically) controlled domain is to determine the dependence of the reaction rate on the rate of stirring.[88] However, stirring is not possible with the present experimental design; instead, other probes of reaction domain were used. First, the total number of organic reactant molecules is much greater than the number of gold surface atoms. The BET measurements give a nitrogen-accessible surface area of 0.73 m^2/g for the small particle size gold. At the largest loading of this gold (0.3391 g), the estimated number of gold surface atoms is 2.8×10^{18}. The number of organic reactant molecules used in a typical (~100 millimolal) experiment is 2.4×10^{20}. Thus, the number of reactant molecules exceeds the number of gold surface atoms by nearly two orders of magnitude, suggesting that the reaction rate is not appreciably limited by diffusion of the organics to the surface. Second, experiments in which the concentration of benzaldehyde was doubled resulted in only a slight increase in conversion to products (Figure S5), also arguing against the reaction rate being controlled by diffusion to the surface. Third, the rate of the reaction was found to vary almost linearly with the mass (and thus, surface area) of the gold, at least until secondary follow-up reactions became important (Figure 1). This observation provides strong support for reaction in the kinetic (intrinsic) limit.[88] Finally, the rates of the reactions of benzaldehyde and benzyl alcohol were found to be quite different under the same conditions and loadings of gold, in ways that cannot be accounted for by differences in diffusion coefficients of these molecules. Specifically, benzyl alcohol reacts roughly an order of magnitude faster than benzaldehyde but its diffusion coefficient in hot water (121°C) is actually slightly smaller than that of benzaldehyde.[89] Taken together, these data strongly suggest that the reactions occur in the kinetic or intrinsic domain, and that the relative rates reflect relative reactivities on the gold surface.

Observations of disproportionations of both benzaldehyde and benzyl alcohol, as well as a cross-disproportionation involving both of these reactants, suggest gold is capable of catalyzing hydride transfer, which is putatively a central elementary step in these reactions. Indeed, substituent effects for gold-catalyzed benzyl alcohol oxidation indicate a positively charged transition state at the α-carbon[83,85,90,91] and abstraction of hydride from this carbon is invoked as rate-determining.[85,92–95] Direct evidence for bonding of hydrogen to gold was obtained via spin-trapping with electron paramagnetic resonance spectroscopy,[92] direct detection of a hydride anion bonded to a gold surface has been reported using infrared spectroscopy[96,97] and inelastic neutron scattering,[97] and calculations suggest that bonding of hydrogen on pure gold is feasible.[93] Supported gold nanoparticles have also been observed to catalyze hydrogen transfer from isopropanol to benzaldehyde,[61–63] and a recent computational study of this process invoked a gold-hydride complex as a possible intermediate.[64] In bonding with hydride, gold acts as a Lewis acid, resulting in a favorable soft acid-soft base interaction.[98]

For gold-catalyzed oxidation of benzyl alcohol in the presence of molecular oxygen, typically conducted with supported catalysts,[99] O_2 serves to regenerate the active gold surface by oxidizing gold-bound hydride[60,85,91–93,100] and is also thought to participate in the regeneration of gold-affiliated hydroxide when base is present,[93,101,102] which facilitates formation of alkoxide intermediates.[93,103,104] Oxidation of benzyl alcohol via dehydrogenation in the absence of molecular oxygen has also been studied on gold catalysts with basic supports, such as hydrotalcite.[81,83,94,105,106] Though mechanistically unclear, in this reaction gold-bound hydride must be protonated in some fashion in order to be released as H_2 and regenerate the catalytic surface. In the case of hydrotalcite, one possibility is that the acidic functionality of hydrotalcite (*i.e.*, $AlO\text{-}H^{\delta+}$) serves as a Brønsted acid for this purpose.[81] In contrast, gold catalysts supported on silica[81,83] or titania[80,82] caused disproportionation of benzyl alcohol in the absence of molecular oxygen rather than dehydrogenation, and disproportionation is thought to occur to some extent even in the presence of oxygen.[107] Since these previously reported reactions were performed in an aprotic solvent[81,83] or in the absence of solvent,[80,82] silica and titania could not offer Brønsted acidity as they must be hydrated to behave in this manner. In the present work, the bulk gold catalysts also lack Brønsted acidity. Thus, one possible conclusion from a preponderance of these prior observations is that in the absence of oxygen or a Brønsted acid, the apparent fate of gold-bound hydride is its reaction with a suitable organic hydride acceptor, resulting in disproportionation.

Proposed mechanisms for the disproportionation reactions described in this work consistent with formation of gold-bound hydride are summarized in **Scheme 2**. In **Scheme 2A**, two benzaldehyde molecules and one water molecule form benzoic acid and benzyl alcohol, which is analogous to the classical Cannizzaro reaction (**Scheme 1**, Reaction **1**). Benzaldehyde interacts with a surface gold atom via its carbonyl oxygen, giving this oxygen a positive charge. This charge decreases electron density at the carbonyl carbon, making it more amenable toward nucleophilic attack by H_2O, which results in formation of a gold-bonded hydrate upon deprotonation. Alternatively, the hydrate could form in solution and itself bond to the gold

Scheme 2. Proposed Mechanisms for Gold-Catalyzed Reactions.



surface, as hydrates have been suggested to interact with gold in a manner similar to other alcohols.[93,101] In either case, the surface-bound hydrate transfers hydride to another gold atom, leading to the formation of benzoic acid. In the next step, hydride is transferred to another benzaldehyde molecule, likely bonded to the gold surface as in the first step. Protonation of the resulting gold-bonded alkoxide yields a benzyl alcohol molecule. In this mechanism, proton transfer is assumed to occur via H_2O derived from the solvent, though the autoionization of water at high temperatures is characterized by a larger K_w compared to ambient,[108,109] which increases the concentrations of hydroxide and hydronium ions that can participate in proton transfer, as well as possibly hydrate formation.

The proposed mechanism for benzyl alcohol disproportionation depicted in **Scheme 2B** is analogous to that for benzaldehyde disproportionation described above. Overall, two benzyl alcohol molecules react to form benzaldehyde and toluene with the liberation of a H_2O molecule (**Scheme 1**, Reaction **4**). Benzyl alcohol bonds to a surface gold atom via its hydroxyl oxygen, which can lead to a gold-bonded alkoxide upon deprotonation. This alkoxide then donates hydride to another gold atom, a step that is consistent with proposed mechanisms for benzyl alcohol oxidation on gold,[81,83,85,92,95,100] liberating a benzaldehyde molecule. Hydride is then transferred from gold to another gold-bonded benzyl alcohol molecule, resulting in the liberation of a toluene molecule, which is facilitated by the positive charge on the hydroxyl oxygen, making it a good leaving group. A H_2O molecule is subsequently formed upon protonation of the gold-bonded hydroxide. The mechanism for the cross-disproportionation reaction (**Scheme 1**, Reaction **3**) is depicted in **Scheme 2C** and is simply a summation of elementary steps from the mechanisms for the other two reactions.

The key transient intermediates in these proposed mechanisms are adsorbed to the surface of the catalyst via a gold-oxygen bond. Support for their intermediacy is provided by extensive experimental and computational studies on crystal gold substrates by the Friend research group.[110–113] Transient gold-oxygen bonded intermediates have been identified in gold catalyzed alcohol oxidation, in addition to surface bound hydroxyl groups derived from H_2O. Importantly, the surface-bound hydroxyl groups were found to be stabilized by the presence of water.

Clearly, further work would be required to provide firmer evidence for these proposed mechanisms, though they are consistent with the major observations and explain how gold is able to catalyze the reactions. Specifically, the mechanisms account for the observation that benzyl alcohol reacts faster and has a larger TOF than benzaldehyde, because unlike benzaldehyde, benzyl alcohol does not need to form a hydrate prior to hydride transfer to gold. In the case of aldehyde disproportionation, gold essentially increases the lifetime of the reactive tetrahedral intermediate by trapping it on the surface of the gold, since hydrates generally become less stable with increasing temperature, as has been observed for acetaldehyde.[114–117] In the case of alcohol disproportionation, gold facilitates initial cleavage of the O-H bond, analogously increasing the lifetime of the reactive alkoxide. It is also possible that the gold surface could facilitate direct hydride transfer, without formation of a gold-bound hydride intermediate, as the local concentration of organic reactants at the surface is likely higher than in solution, though it is unknown to what extent this occurs. Moreover, radical mechanisms cannot be ruled out completely, which might be consistent with observations of small quantities of bibenzyl (Table S2) that could arise via coupling of benzyl radicals. The involvement of radicals, at least to some extent, would be consistent with the suggestion of a radical component of the mechanism for the homogenously catalyzed Cannizzaro reaction.[118,119] However, reactions that require breaking of

O-H bonds in H_2O are much more likely to proceed via heterolytic cleavage than via homolytic cleavage, pointing toward ionic mechanisms. Finally, the proposed mechanisms offer no insight into the mechanism of the gold-catalyzed decarbonylation of benzaldehyde, which has been observed both here and on other gold catalysts involved in benzyl alcohol disproportionation.[81,83]

CONCLUSIONS

Bulk gold was found to catalyze a series of related disproportionation reactions under hydrothermal conditions that require cleavage of C-H, O-H, and C-O bonds, specifically involving the formal transfer of hydride from a carbon donor atom to a carbon acceptor atom, proposed to occur via what is formally a gold-bound alkoxide anion. Importantly, the tentative mechanisms proposed here attempt to reconcile proposed mechanisms in the literature for benzyl alcohol oxidation in the absence of oxygen, considering that some catalysts including bulk gold result in benzyl alcohol disproportionation rather than dehydrogenation. The observed reactions represent an important expansion of the scope of catalysis by metallic gold at the water interface,[120–122] as most of the previously studied gold-catalyzed reactions are also subject to catalysis by other metals.[123–125] It is quite possible other metals may act as catalysts for these disproportionation reactions, a topic worthy of future investigation.

In the conventional Cannizzaro reaction, a high concentration of base is required to initiate hydride transfer in solution. Under hydrothermal conditions, gold catalyzes hydride transfer in the absence of added base and catalyzes reactions for which there are no homogeneous base catalysis equivalents. The reaction conditions are minimalist in that they require only water as the solvent and bulk metallic gold as a reusable catalyst. The use of hydrothermal water provides many advantages. First, water is ubiquitous and is the ultimate green solvent. Second, the reactants and products are soluble in water at high temperature, but when cooled to room temperature many organic compounds will spontaneously separate from the solvent, facilitating product isolation. Third, the higher thermal energy of hydrothermal water is advantageous in overcoming reaction barriers. Lastly, the larger autodissociation constants of H_2O at high temperatures[108,109] facilitate proton transfer. Though expensive and rare compared to some other metals, more effective and efficient gold catalysts could be employed in future studies of these reactions. Interestingly, metallic gold is formed via deposition from hydrothermal solutions that are often associated with hydrocarbons in the major gold deposits of the world, such as Witswatersrand in South Africa[126,127] and the Carlin-type deposits in Nevada,[128] thus it is conceivable that gold could catalyze transformations of organic compounds dissolved in the parent hydrothermal fluid in these geologic environments. The reactions described here therefore adhere to the tenets of the emerging field of geomimicry,[67–69] where useful chemical processes are conducted in a manner inspired by those occurring in active geologic environments and consistent with many green chemistry principles.

CONFLICTS OF INTEREST

There are no conflicts to declare.

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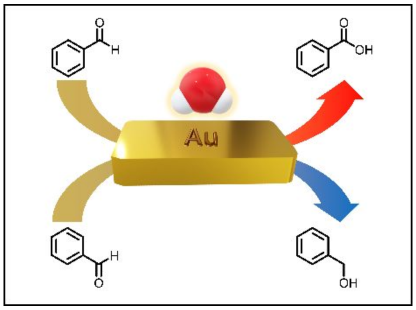

Disproportionation reactions of benzaldehyde and benzyl alcohol are catalyzed by bulk gold with hot water as the only other reagent