



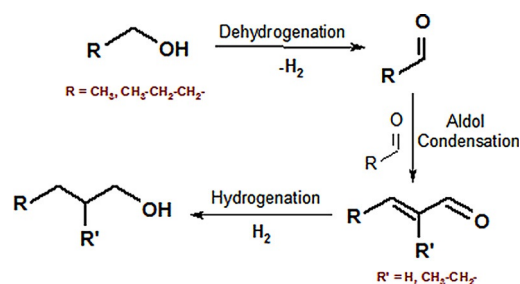
Non-Oxidative Dehydrogenation Pathways for the Conversion of C₂–C₄ Alcohols to Carbonyl Compounds

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Gold nanoparticles (NPs) supported on hydrotalcite (Au/HT) are highly active and selective catalysts for the continuous, gas-phase, non-oxidative dehydrogenation of bioderived C₂–C₄ alcohols. A sharp increase in turn over frequency (TOF) is noted when the size of Au NPs is less than 5 nm relating to the strong synergy between metallic Au NPs and the acid-base groups on the support surface. It is shown that catalytic activity depends critically on Au NP size, support composition, and support pretreatments. A reaction pathway elucidated from kinetic isotope effects suggests that the abstraction of β-H by Au NPs (C–H activation) is the rate-determining step in the dehydrogenation of bioderived C₂–C₄ alcohols.

The formation of aldehydes and ketones from biomass-derived compounds such as glycerol and C₂–C₄ alcohols is a subject of considerable interest, as these products can be used to form carbon–carbon bonds in compounds needed for chemical intermediates and transportation fuels.^[1,2] For example, acetaldehyde obtained from bioethanol offers a very promising green alternative to the conventional ethylene route. Transition-metal-catalyzed oxidation of alcohols to carbonyl compounds (aldehyde and ketones) using environmentally friendly oxidants (e.g., oxygen and hydrogen peroxide) was recently utilized as an alternative to stoichiometric oxidation using toxic and expensive oxidants or sulfoxides (Swern oxidation).^[3] Alternatively, carbonyl-containing compounds can be produced selectively from alcohols by transfer hydrogenation to hydrogen acceptors.^[4] However, transfer hydrogenation is not atom-economical and consumes hydrogen and forms alkanes as byproducts. Consequently, oxidant-free, acceptor-less dehydrogenation of alcohols to aldehydes and ketones is a particularly attractive route offering advantages such as: (a) prevention of water formation, which can lead to catalyst deactivation; (b) production of hydrogen, an attractive feed stock; and (c) suppression of carboxylic acid formation owing to over oxi-

dation of product aldehydes.^[5] Thus from an atom efficiency and safety perspective, oxidant-free dehydrogenation of alcohols to carbonyl-containing compounds and molecular hydrogen is an attractive reaction (Scheme 1).



Scheme 1. Upgrading reaction of C₂–C₄ alcohols to carbonyl compounds and higher alcohols through a Guerbet pathway.

Following the first reports of the high catalytic activity of supported Au nanoparticles (NPs) for low-temperature CO oxidation, considerable interest developed in exploiting Au NPs as catalysts for a wide variety of chemical transformations.^[6] Remarkably, Au NPs were recently reported to exhibit catalytic activities similar to or higher than group VIII metals for selective aerobic oxidations.^[7] As Au nanoparticles are often implicated in redox reactions,^[8,9] we chose to investigate the activity of Au deposited on hydrotalcite (HT) for the dehydrogenation of C₂–C₄ alcohols. While previous work has shown that Pd and Cu supported on HT can be used for the liquid phase, non-oxidative dehydrogenation of aliphatic and aromatic alcohols,^[10] these catalysts are less selective than Au/HT for the dehydrogenation of aliphatic alcohols.

Herein, we demonstrate that Au NPs deposited on HT are effective heterogeneous catalysts for the continuous gas-phase, non-oxidative dehydrogenation of primary and secondary alcohols to aldehydes and ketones, respectively. We also show that the catalytic activity and selectivity of such catalysts depends on the temperature at which the support is pre-treated and the size of the Au NPs. To the best of our knowledge, this is the first report showing the catalytic activity of Au/HT catalysts for the gas-phase, non-oxidative dehydrogenation of C₂–C₄ alcohols.

Au NPs were produced on acidic, basic, and amphoteric supports by deposition–precipitation (DP) using urea as the precipitating agent. The activity of these materials for *n*-butanol dehydrogenation is very sensitive to support composition.

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Under identical reaction conditions, Au NPs (3–5 nm in diameter as determined from TEM images) supported on silica-alumina (Si-Al) are particularly active and the activity (butanol conversion) decreases in the order Si-Al (95%) \gg TiO₂ (50%) $>$ γ -Al₂O₃ (42%) $>$ MgO (35%) $>$ HT (32%) $>$ HAP (18%) (Figure S1 in the Supporting Information). Aldehyde selectivity also depends on the support composition. Supports that are weakly acidic and basic, such as HT and hydroxyapatite (HAP), are more selective towards *n*-butanol dehydrogenation to *n*-butanal, whereas more strongly acidic supports, such as Si-Al or γ -Al₂O₃, catalyze the formation of butenes and *n*-butyl ether (Figure 1). TiO₂, though selective to C₈₊ alcohols, showed sig-

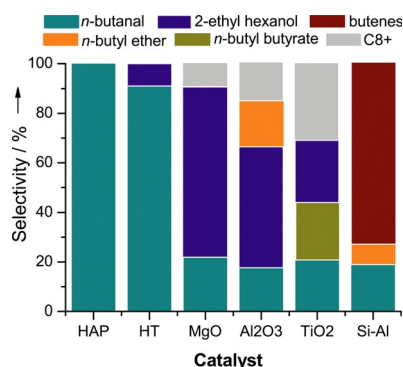


Figure 1. Selectivity patterns of various supported Au catalysts in *n*-butanol dehydrogenation reactions. Reaction conditions: $T = 473$ K, partial pressure of *n*-butanol $P_{n\text{-butanol}} \approx 2$ kPa, mass of catalyst $M_{\text{cat}} = 0.05\text{--}0.1$ g (3 wt % Au), total gas flow rate (Q_{tot}) adjusted to maintain the butanol conversion at ca. 30–35%.

nificant selectivity to esters. Purely basic supports, such as MgO, produced significant yields of Guerbet products, such as ethyl-2-hexanol, suggesting that the aldehydes undergo aldol condensation and hydrogenation on this support (Scheme 1). Thus, amphoteric supports, containing weakly acidic and basic groups, such as HT and HAP, exhibit the most promising properties for non-oxidative dehydrogenation of aliphatic alcohols.

Comparison in synthesis procedures using similar weight loadings of Au showed that the DP method leads to better activity than catalysts prepared by impregnation of the support with an Au precursor. However, changing the precipitating agent from urea to NaOH has a negligible effect on the catalytic activity (Figure S2). Control reactions demonstrated that HT and Au/SiO₂ are inactive for *n*-butanol dehydrogenation at 473 K. However, a physical mixture of Au/SiO₂ and HT showed an intermediate level of conversion, albeit significantly lower than that obtained from the Au/HT (Figure S2). These results illustrate the necessity of having the metal and basic sites in close proximity to realize co-operative catalytic enhancement and suggest that the Au–HT interface plays a crucial role in enhancing the catalytic activity.

Particle size and particle size distribution are often critical characteristics for tuning the activity/selectivity of metal supported catalysts.^[11] The size of Au NPs on the HT support was altered by either regulating the concentration of Au precursor

or by varying the aging time used during the DP synthesis procedure (Figure S3–S4). HAuCl₄ was used as the Au precursor. Improved Au NP dispersion was possible when the point of zero charge (PZC) of the support material was higher than five.^[12] HTs have a PZC of ~ 10 , suggesting that a good dispersion of Au NPs can be achieved on the surfaces of HT.^[13] Figure 2 shows the effect of average particle size on the turn-

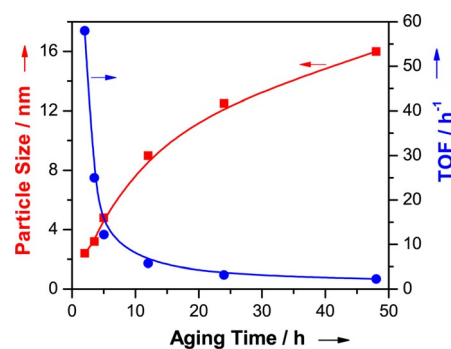


Figure 2. Dependence of TOF and mean particle size of Au/HT in *n*-butanol dehydrogenation reactions. Reaction conditions: $T = 423$ K, $P_{n\text{-butanol}} \approx 2$ kPa, $M_{\text{cat}} = 0.1$ g, $Q_{\text{tot}} = 150$ cm³ min⁻¹.

over frequency (TOF) for *n*-butanol dehydrogenation. As can be seen, the activity per surface Au atom, the TOF, decreases strongly with increasing particle size, confirming that alcohol dehydrogenation is structure sensitive.^[14] Previous experimental and theoretical studies show that the surface of Au NPs is composed of planar sites, perimeter sites, and low coordinated edge and corner sites.^[15] As particle size increases, the ratio of low-coordinated sites to high coordinated sites decreases. This suggests that the dehydrogenation of *n*-butanol occurs preferentially on coordinatively unsaturated sites (CUS). Consistent with this reasoning, calculations of the TOF based solely on the corner/edge sites (Figure S5) leads to a single value (~ 145 h⁻¹) for the reaction conditions reported in Figure 2, independent of the Au NP size.

For comparison, Cu/HT and Pd/HT catalysts having similar metal loadings to that of Au/HT were prepared by the DP method. The results presented in Figure 3 demonstrate that while Pd/HT is more active than Au/HT for *n*-butanol dehydrogenation, it is much less selective for aldehyde formation and exhibits significant selectivity towards aldehyde decarbonylation to form propene. Cu/HT is slightly more active than Au/HT, but tends to form esters (see Figure 3). Both Pd/HT and Cu/HT deactivated with time on stream (Figure S6). In the case of Pd/HT, CO produced by aldehyde decarbonylation poisons the surface of Pd, whereas in the case of Cu/HT, butanoic acid produced by hydrolysis of the ester possibly poisons the basic sites on HT. By contrast, Au/HT was stable under the reaction conditions for 5 h and TEM images taken before and after reaction showed no evidence for an increase in Au particle size (Figure S7). The absence of sintering is attributed to the interaction of Au NPs with Al present on the support surfaces, in agreement with previous studies showing that Al provides strong anchoring sites for stabilization of Au NPs.^[12] This inter-

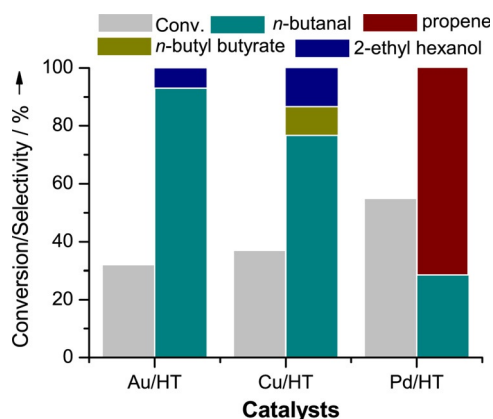


Figure 3. Conversion and product selectivity observed for *n*-butanol dehydrogenation over HT-supported Au, Cu, and Pd. Reaction conditions: $T = 473$ K, $P_{n\text{-butanol}} \approx 2$ kPa, $M_{\text{cat}} = 0.1$ g (3 wt% metal), $Q_{\text{tot}} = 150$ cm³ min⁻¹.

pretation is supported by elemental mapping studies, which show that Au NPs are mainly located on the edge of the HT crystallites where aluminum is concentrated preferentially (Figure S8). These results demonstrate that HT not only enhances the activity and selectivity to aldehyde, but also the stability of the supported Au NPs for gas-phase, non-oxidative dehydrogenation of alcohols.

Rate measurements carried out under differential conditions suggest that, irrespective of the metal dispersed on HT, the reaction is first order in *n*-butanol. The apparent activation energies for Pd/HT, Cu/HT, and Au/HT are 44, 49, and 55 kJ mol⁻¹ respectively, over the temperature interval of 423–473 K (Figure S9–S10).

Support pretreatment affects the catalytic activity and selectivity of Au/HT. Increasing the HT calcination temperature from 473 to 873 K, before deposition of Au, increased the *n*-butanol conversion three-fold, decreased the selectivity to aldehyde and the consecutive formation of ethyl-2-hexanol. IR studies of adsorbed CO₂ suggest that the increase in conversion and selectivity towards higher alcohols relates to the formation of stronger basic sites with increasing pretreatment temperature (Figure S11). However, time-on-stream data showed that HT pretreated at high temperatures is not as stable and deactivates much more rapidly than when the support is calcined at lower temperatures (473–623 K). This pattern may possibly be a result of the greater sensitivity of high-temperature pretreated HT to water produced during ethyl-2-hexanol formation (Scheme 1).^[13]

The reaction temperature also has a significant effect on the activity and selectivity of Au/HT. As shown in Figure 4, the catalyst activity for *n*-butanol dehydrogenation is almost ten-fold higher at 573 than at 423 K, whereas the selectivity to *n*-butanal remains above 82% up to 573 K. The slightly decreased selectivity to aldehydes at high temperature is a result of the formation of Guerbet alcohols. Thus, reaction at 423–493 K leads to a high rate of alcohol consumption and a high selectivity to *n*-butanal.

The suitability of Au/HT for dehydrogenation of primary and secondary alcohols was examined for alcohols containing two

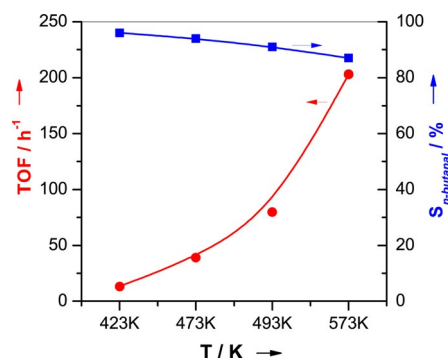


Figure 4. Temperature dependence in TOF and selectivity to aldehyde over Au/HT catalysts in *n*-butanol dehydrogenation reactions. Reaction conditions: $T = 423$ – 573 K, $P_{n\text{-butanol}} \approx 2$ kPa, $M_{\text{cat}} = 0.1$ g (3 wt% Au), $Q_{\text{tot}} = 150$ cm³ min⁻¹.

to four carbon atoms. The activity of Au/HT dehydrogenation increases monotonically in the order ethanol < propanol < isopropanol < butanol (Figure S12–S13). In all instances, the selectivity to the primary product of alcohol dehydrogenation was greater than 80%.

A reaction mechanism for the dehydrogenation of alcohols over the Au/HT can be proposed. It is widely accepted that alcohol dehydrogenation proceeds through initial cleavage of the alcohol hydroxyl O–H bond to form an adsorbed alkoxide.^[12] A key question is whether the alkoxide forms on the basic HT or on the Au NPs, as reported for Pd/HAP.^[10] It is known that atomic oxygen bound to coinage metals promotes Brønsted acid–base reactions with protons present on the reactant molecule.^[16] Dehydrogenation is, therefore, known to occur in the absence of a metal oxide support as long as atomic oxygen is present on Au NPs. In the absence of adsorbed oxygen, the composition of the support plays a critical role in defining the catalytic activity and selectivity towards the desired products. Davis and co-workers reported that the activation energy for the formation of alkoxides by dissociative adsorption of alcohol on bare Au surface is much higher than in presence of a base.^[17] Thus the initial activation of alcohols on metal alone is unlikely and more likely occurs on the surface of the basic support. It should be emphasized here that silica-supported Au nanoparticles are inactive for alcohol dehydrogenation as the basicity of hydroxyl groups on silica is too weak to abstract protons from alcohols to form alkoxides.^[18] To confirm the role of basic sites in the dehydrogenation of *n*-butanol over Au/HT, poisoning experiments were conducted by co-feeding butanoic acid together with *n*-butanol. The presence of butanoic acid resulted in a complete suppression of catalytic activity, demonstrating that basic sites on HT play an important role in enhancing the catalytic activity of the Au/HT.

It is, therefore, proposed that the initial deprotonation of alcohols to form an alkoxide intermediate occurs on the surface of the basic support and that coordinatively unsaturated sites on nearby Au NPs abstract the α -H of the resulting alkoxide to form the aldehyde, as shown in the Supporting Information. This hypothesis was tested by determining the kinetic isotope effects for the dehydrogenation of ethanol. The kinetic isotope

effect, k_H/k_D , for dehydrogenation of C_2H_5OH versus C_2D_5OD was 2.2 at 473 K, whereas only a small kinetic isotope effect (1.0–1.2) was observed for the reaction of C_2H_5OH versus C_2H_5OD (Figure S14). These observations indicate that the rate-determining step involves the cleavage of an α -C–H bond of an alkoxide species by CUS edge or corner atoms on the Au NPs. This finding is consistent with the observation of a decrease in the TOF for *n*-butanol dehydrogenation with increasing Au NP size (Figure 2).

In conclusion, we showed that the non-oxidative dehydrogenation reaction of *n*-butanol to *n*-butanal can be carried out with high selectivity over Au deposited on calcined hydrotalcite (HT). More basic supports, such as MgO, promote the aldol condensation of *n*-butanal to ethyl-2-hexanol, whereas strongly acidic sites promote the etherification of the alcohol to form an ether, and/or dehydration of the alcohol to form an alkene. Studies of Au/HT show that the rate of C_2 – C_4 alcohol dehydrogenation is most rapid on small rather than large Au nanoparticles (NPs) owing to the higher fraction of coordinatively unsaturated sites (CUS) sites on small NPs. H/D isotopic tracer studies reveal that the rate-limiting step in the reaction is abstraction of α -H from an alkoxide formed by alcohol adsorption on basic sites of the support located in close proximity to CUS sites on Au NPs.

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