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Solvent-free oxidation of primary alcohols to aldehydes using supported gold catalysts

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Supported Au catalysts are investigated for the oxidation of primary alcohols under solvent-free conditions in the absence of base. Three representative primary alcohols have been investigated: benzyl alcohol, octan-1-ol and geraniol using a range of supports for gold nanocrystals prepared using coprecipitation, deposition precipitation and impregnation. For benzyl alcohol and octan-1-ol selective oxidation to the corresponding aldehydes is observed, particularly with Au/CeO_2, whereas for more acidic supports, e.g. Fe_2O_3, subsequent oxidation of the aldehydes to the corresponding acids, forming an ester (benzyl benzoate, octyl octanoate, respectively) by reaction with the alcohol, by a standard acid-catalysed mechanism. Alternatively, the mechanism of ester generation could involve hemiacetal formation between the aldehyde and residual alcohol, followed by direct oxidation to the observed ester. The reaction of geraniol is much more complex and the reaction is carried out in the presence and absence of acids to gain a full understanding of the interplay between oxidation and isomerisation reactions. Comparison with other active catalysts reveals that using Au catalysts in solvent free conditions gives very high turnover frequencies for the synthesis of the aldehydes with 100% selectivity (150 h^{-1} and 26 h^{-1} for benzyl alcohol and octan-1-ol, respectively), which are comparable to the best reported to date for these reactions.

KEY WORDS: solvent free oxidation; supppported gold catalysts.

1. Introduction

It is now 20 years since it was predicted that gold would be the most active catalyst for the selective hydrochlorination of acetylene [1]. This prediction was subsequently confirmed, and in particular this was the first time that cationic gold was shown to be an active heterogeneous catalyst [2,3]. Prior to this observation, gold was largely considered to be inactive as a heterogeneous catalyst for redox reactions and only a few studies had examined its potential as a catalyst. However, the observation that gold was the best catalyst for triggering this hydrochlorination demonstrated that it could no longer be ignored as an active component of heterogeneous catalysts. The seminal work of Haruta [4,5] has, undoubtedly, led the way by demonstrating that supported gold catalysts are exceptionally active for the oxidation of CO at low temperatures.

In recent years, there has been intense interest in the use of supported gold catalysts for a broad range of hydrogenation and oxidation reactions [6–25] and in the last few years several hundred papers and patents have been published [25]. Most of this research has focussed on aspects of the preparation of active catalysts for the low temperature oxidation of CO and, to a lesser extent, the mechanism by which this fascinating reaction occurs [11,14,15,17,22]. There has also been a significant recent interest in the application of gold catalysts to the low temperature water gas shift reaction [18,26–31], since the CO oxidation step is often considered as a half reaction of this process [32]. Surprisingly, much less attention has been given to selective oxidation using gold catalysts. Notably, Haruta, Delgass and Moulijn have shown that propene can be oxidised to propene oxide as long as H_2 is added as a sacrificial reductant [33–37]. Recently, the oxidation of cyclohexane to cyclohexanol and cyclohexanone has been shown to be feasible using supported Au catalysts with molecular oxygen, under mild conditions [38,39]. Most recently, we have shown that H_2 can be selectively oxidised to hydrogen peroxide using molecular oxygen as oxidant and supported Au–Pd alloys. This reaction is widely recognised as being one of the most demanding oxidations [40,41]. Hence, it is clear that supported gold catalysts have significant potential for selective oxidation.

Rossi and Prati and co-workers [42–45] were the first to demonstrate that alcohols, in particular diols and sugars, can be oxidised selectively to various monoacids, as long as base is present. Subsequently, we demonstrated that Au/C catalysts could give 100% selectivity for the oxidation of glycerol to glycerate [46,47]. Most recently, the oxidation of sorbitol has been studied with supported Au–Pd alloys [48]. All these previous studies have involved alcohols that are water miscible and the oxidation reactions have been carried out using aqueous base as the medium. In the absence of base, no activity has yet been reported with supported Au catalysts, yet supported Pd and Pt catalysts are very active under such conditions [49].

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The oxidation of primary alcohols to aldehydes is a fundamental laboratory and commercial procedure. The process is of immense industrial synthetic interest as aldehydes are both valuable intermediates as well as being high value components for the perfumery industry. At present, many oxidations of this type are carried out using stoichiometric oxygen donors, e.g. chromate or permanganate, that are both expensive to operate and have toxicity issues [50]. Consequently, there has been significant interest in the development of catalytic approaches to this problem, and in particular, in the design of suitable heterogeneous catalysts, many of which use H_2O_2 as the oxidant. Pd catalysts have been used but, until recently, these catalysts have shown relatively low activity. Kaneda and co-workers [51] have, however, shown that hydroxyapatite-supported Pd nanoclusters are highly effective and give very high turnover frequencies in the oxidation of benzyl alcohol but show very limited activity for octan-1-ol. Against this background, we decided to study the oxidation of primary alcohols using supported Au catalysts under solvent free conditions and in the absence of base. We have selected a number of catalyst formulations for this initial proof of concept investigation and in this paper, we present our initial observations showing that supported gold catalysts have significant potential for the selective oxidation of primary alcohols to aldehydes. Furthermore, the turnover frequencies we observe in these initial studies, using non-optimised catalysts and conditions, are amongst the highest reported to date [51].

2. Experimental

2.1. Catalyst preparation

2.1.1. Coprecipitation

Au/SiO_2, Au/CeO_2 and Au/Fe_2O_3 catalysts were prepared using a coprecipitation procedure as follows. For the Au/SiO_2 catalyst an aqueous solution comprising (37 mL of a solution of $HAuCl_4.3H_2O$ – 5 g (Johnson Matthey), dissolved in water (250 mL)) mixed with tetraethyl orthosilicate (162 mL Aldrich), in water (200 mL) was stirred and aqueous ammonia (35%) was added dropwise until pH = 10.1 was achieved (about 25 mL). The solid formed was recovered by filtration and dried in air (150 °C, 3 h) and analysed using atomic absorption spectroscopy and found to be 0.7 wt% $Au–SiO_2$.

A 2 wt% Au/CeO_2 catalyst was prepared using the same procedure using either aqueous solutions of cerium nitrate (70 mL of a solution of $Ce(NO_3)_3·6H_2O$ (100 g) in water (200 mL)) in place of the tetraethyl orthosilicate.

A 5 wt% Au/Fe_2O_3 catalyst was prepared in a similar manner but using sodium carbonate as the precipitating agent. An aqueous solution comprising (25 mL, $HAuCl_4$ (Johnson Matthey) 5 g dissolved in water 250 mL) mixed with $Fe(NO_3)_3·9H_2O$ (25.25 g, Aldrich) in water (500 mL) was stirred at 80 °C and aqueous sodium carbonate (Aldrich, 0.25 mol/L was added dropwise until pH = 8.3 was achieved. The material was recovered by filtration, washed with hot water and dried in air (80 °C, 16 h).

2.1.2. Impregnation

About 2 wt% Au/TiO_2 and 2 wt% Au/C catalyst were prepared by impregnation as follows. TiO_2 (Degussa, P25, 9.8 g) was mixed with an aqueous solution of chloroauric acid (17.26 mL, $HAuCl_4·3H_2O$ (5 g) dissolved in water 250 mL) and the mixture dried on a rotavapor and then dried in flowing air (200 °C, 3 h). Carbon (Johnson-Matthey, 9.8 g) was mixed with an aqueous solution of chloroauric acid (17.26 mL, $HAuCl_4·3H_2O$ (5 g) dissolved in water 250 mL). The suspension was stirred for 30 min then filtered. The resulting solid was dried at 80 °C, then placed in a furnace and calcined in air at 400 °C for 3 h.

3. Alcohol oxidation

The oxidation reactions were carried out in a stirred reactor (100 mL, Autoclave Engineers Inline MagneDrive III). The vessel was charged with alcohol (40 mL) and catalyst (0.2 g). The autoclave was then purged 5 times with oxygen leaving the vessel at 2 bar guage. The stirrer was set at 1500 r.p.m. and the reaction mixture was raised to the required temperature. Samples from the reactor were taken periodically, via a sampling system, ensuring that the volume purged before sampling was higher than the tube volume, and analysed by gas chromatography. The identification of the products was made using combined gas chromatography and mass spectrometry.

4. Ammonia TPD characterisation

The TPD analysis was performed using a Micromeritics Autochem 2910 apparatus. The sample (0.1 g) was first degassed in an argon flow at 200 °C for 1 h, using a heating ramp from room temperature of 10 °C/min. They were then cooled to room temperature, then ammonia gas was flowed over the sample for 5 min (20 mL/min). Following this, argon was flowed over the sample (50 mL/min) and the temperature was kept constant for 1 h. Before starting the desorption analysis, the baseline was checked for stability. The analysis was then started using a temperature ramp of 5 °C/min.

5. Results and discussion

5.1. Benzyl alcohol oxidation

Our initial studies focussed on the oxidation of benzyl alcohol as this reaction is often employed as a model reaction for alcohol oxidation. Furthermore, this molecule was chosen because of its relatively high reactivity and because the main product is a non-enolisable aldehyde, reducing in this way the number of possible side products. The oxidation was investigated at 100 °C with O_2 as oxidant in the absence of solvent and using the supported gold catalysts; the results are shown in table 1 and figure 1. In the absence of catalyst or when using the support in the absence of gold no oxidation was observed, confirming that the presence of gold was essential to obtain catalytic oxidation.

With the SiO_2, CeO_2 and TiO_2 supports, selective oxidation to benzaldehyde took place and over the course of the 3 h experiment no by-products were observed. The best results were observed using Au/CeO_2. For the SiO_2-supported catalyst, we investigated the effect of increasing the amount of catalyst and the O_2 pressure, and in both cases the conversion increased but now the ester, benzyl benzoate, was observed (table 1, figure 1) and traces of acetal.

In contrast to the SiO_2-, TiO_2- and CeO_2-supported catalysts, Au/Fe_2O_3 and Au/C catalysts were much more active for the formation of the ester, after reaction for 3 h (table 1, figure 1). Comparison of the data at the same conversion (table 1) reveals that the Au/Fe_2O_3 and Au/C catalysts are not totally selective for the formation of the aldehyde and the selectivities with these catalysts are always lower than the SiO_2-, TiO_2- and CeO_2-supported catalysts. We considered that by-product formation was mainly linked to the presence of acid sites on the support materials used. Addition of a small amount of hydrochloric acid (5 μL) to the reaction mixture using the SiO_2-supported catalyst provided supporting evidence for this proposal since acid addition increased the conversion but also led to ester formation (table 1).

Table 1
Oxidation of benzyl alcohol using gold catalysts[a]

Catalyst	3 h reaction data		$S_{0.5}$[b]	$S_{1.0}$	$S_{1.5}$	[Au] %[c]
	Conv (%)	Sel (%)[b]				
Au/SiO_2	1.9	100	100	100	100	0.12
Au/SiO_2[d]	4.6	87.6	89.6	90.4	91.9	0
Au/SiO_2[e]	4.7	92.2	87.4	92.6	93.3	0.09
Au/SiO_2[f]	2.4	94.3	94.9	95.0	95.2	0
Au/CeO_2	3.4	100	100	100	100	0.05
Au/TiO_2	0.65	100	100	–	–	0
Au/Fe_2O_3	7.1	87.6	87.3	87.5	87.4	0.02
Au/C	2.3	90.4	88.6	88.9	88.7	0

[a] Reaction conditions: alcohol (40 mL), catalyst (0.2 g), 1500 rpm, 100 °C, P_{O_2} 2 bar.
[b] Selectivity to the aldehydes, the ester being the only other observed product, S_x selectivity to the aldehyde at x% benzyl alcohol conversion.
[c] % gold leached from the catalyst.
[d] Catalyst (0.4 g).
[e] P_{O_2} 6 bar.
[f] HCl (5 μL, 37%) added.

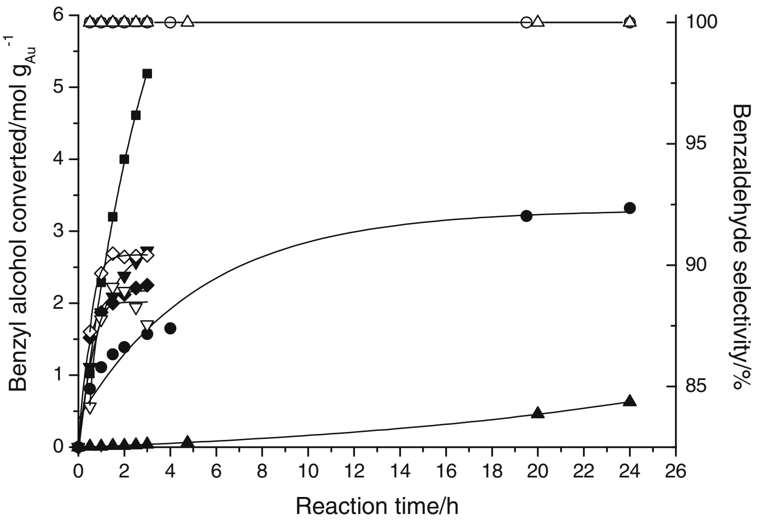


Figure 1. Oxidation of benzyl alcohol in the absence of solvents using gold catalysts as a function of reaction time; conversion – solid symbols, selectivity – open symbols; (■) Au/SiO_2; (●) Au/CeO_2; (▲) Au/TiO_2; (▼) Au/Fe_2O_3; (◆) Au/C.

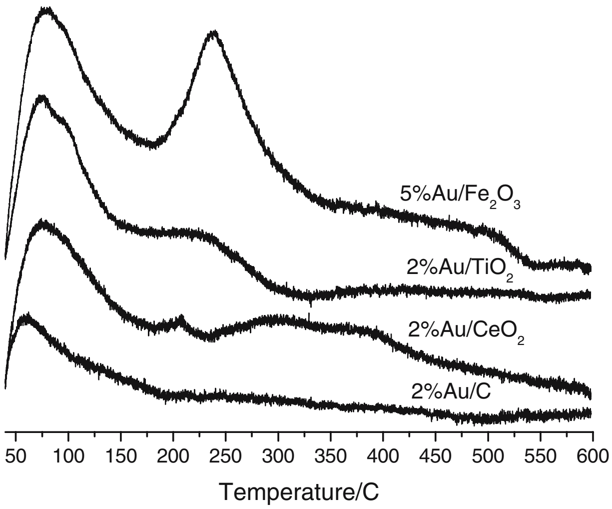


Figure 2. Diagrams of ammonia TPD of some of the catalysts used in the study.

Table 2
Oxidation of octanol using gold catalysts[a]

Catalyst	3 h reaction data		$S_{0.5}$[b]	$S_{1.0}$	$S_{1.5}$	[Au] %[c]
	Conv (%)	Sel (%)				
Au/SiO$_2$	0	–	–	–	–	–
Au/TiO$_2$	0	–	–	–	–	–
Au/CeO$_2$	0.57	100	100	–	–	0
Au/C	0	–	–	–	–	0
Au/Fe$_2$O$_3$	1.5	55.9	100	80.4	55.9	0.04
Au/Fe$_2$O$_3$[d]	2.1	49.4	67.5	60.7	55.0	0

[a] Reaction conditions: alcohol (40 mL), catalyst (0.2 g), 1500 rpm, 100 °C, P_{O_2} 2 bar.

[b] Selectivity to the aldehydes, the ester being the only other observed product, S_x selectivity to the aldehyde at x% octanol conversion.

[c] % gold leached from the catalyst.

[d] P_{O_2} 6 bar.

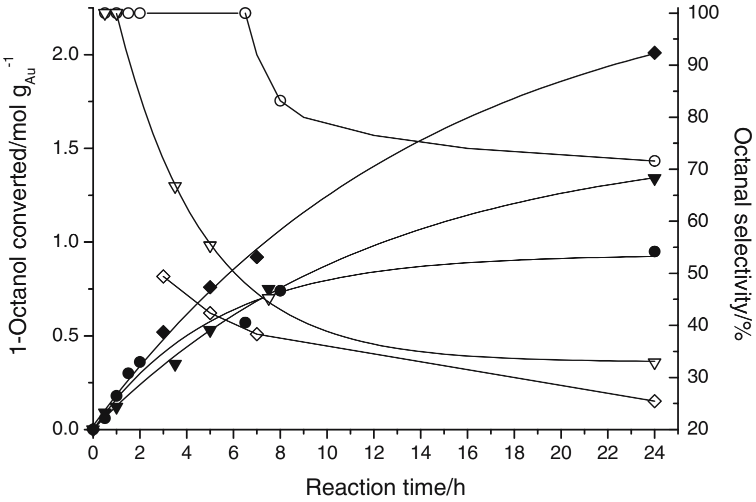


Figure 3. Oxidation of octanol in the absence of solvents using gold catalysts as a function of reaction time; conversion – solid symbols, selectivity – open symbols; (●) Au/CeO$_2$ at 2 bar O$_2$; (▼) Au/Fe$_2$O$_3$ at 2 bar O$_2$; (◆) Au/Fe$_2$O$_3$ at 6 bar O$_2$.

The hypothesis that the catalyst acidity was responsible for the by-product formation was confirmed by ammonia TPD analysis of these catalysts (figure 2). All these catalysts present a desorption peak at about 100 °C, which is ascribed to physisorbed ammonia. However, 5%Au/Fe_2O_3 shows a large ammonia desorption peak at 250 °C, corresponding to strongly acidic sites.

One of the key factors that must be considered for heterogeneous catalysts operating in three phase systems is the possibility that active components can leach into the reaction mixture, thereby leading to catalyst deactivation or, in the worst case, to the formation of an active homogeneous catalyst. The final reaction solutions were filtered to remove the particles of catalyst and analysed by atomic absorption spectroscopy to determine the amount of Au leached; the results are shown in table 1. With these catalysts, no significant gold was found in the filtered reaction mixtures, so the reactions are heterogeneously catalysed by the supported gold catalysts.

5.2. *Octan-1-ol oxidation*

The oxidation of octan-1-ol was investigated at 100 °C again with O_2 as oxidant in the absence of solvent, using the supported gold catalysts; the results are shown in table 2 and figure 3. Octan-1-ol was selected as it is much more resistant with respect to oxidation compared with benzyl alcohol [51] and consequently is a much more demanding substrate. In the absence of catalyst or when using the support in the absence of

Table 3
Oxidation of geraniol using gold catalysts[a]

Catalyst	3 h reaction data					$S_{1.0}$	S_{10}	[Au] %[c]
	Conv (%)	Sel (%)						
		L	*t*-C	*c*-C	N			
Au/SiO_2	0.21	0	30.5	58.2	5.9	82.6	48.0	0
Au/SiO_2[d]	2.1	2.6	23.0	0	6.4	41.4	24.1	0
Au/CeO_2	46.7	0	4.8	23.8	2.3	51.5	46.9	0.05
Au/C	17.5	0	12.1	65.3	6.2	96.5	82.4	0
Au/TiO_2	11.6	0.8	18.6	48.1	8.0	95.5	70.1	0
Au/Fe_2O_3	12.6	0	11.2	66.9	6.0	81.7	72.3	0

[a] Reaction conditions: alcohol (40 mL), catalyst (0.2 g), 1500 rpm, 100 °C, P_{O_2} 2 bar.
[b] Selectivity to L-linalool, *t*-C *trans* citral, *c*-C *cis*-citral, N nerol, S_x selectivity to citral (cis + trans) at x% geraniol conversion.
[c] % gold leached from the catalyst.
[d] P_{O_2} 6 bar.

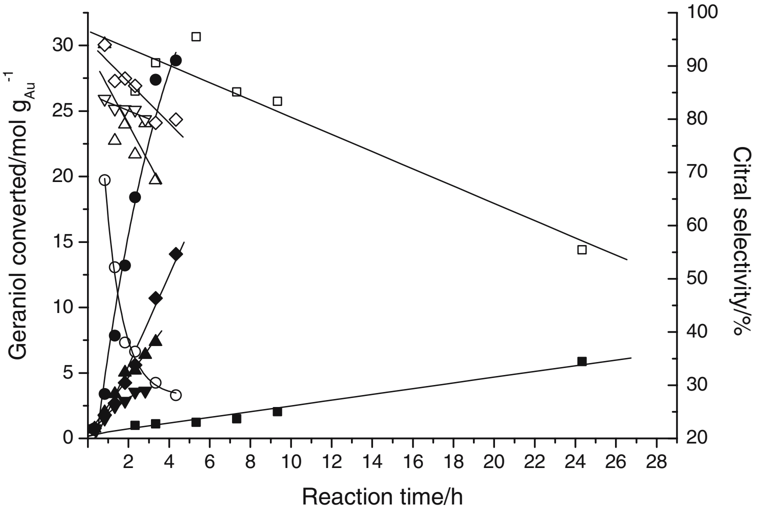


Figure 4. Oxidation of geraniol in the absence of solvents using gold catalysts as a function of reaction time; conversion – solid symbols, selectivity – open symbols; (■) Au/SiO_2; (●) Au/CeO_2; (▲) Au/TiO_2; (▼) Au/Fe_2O_3; (◆) Au/C.

gold, as in the case of benzyl alcohol, no oxidation was observed, confirming that the presence of gold was essential to obtain catalytic oxidation. However, no oxidation was observed with Au/SiO_2, Au/TiO_2 or Au/C catalysts. Au/CeO_2 did show some activity and only octanal was observed as product. In contrast, Au/Fe_2O_3 was much more active but gave very high selectivities for the formation of the ester, octyl octanoate, after reaction for 3 h (table 2, figure 3). Comparison of the data at the same conversion (table 2) reveals that the Au/Fe_2O_3 catalyst was not very selective to the aldehyde, even at lower conversions. The final solutions recovered after reaction were again filtered to remove the catalyst particles and analysed by atomic absorption spectroscopy to determine the amount of Au leached. The data are shown in table 2, and clearly demonstrate that with these catalysts, no loss of gold was observed using the solvent-free conditions employed in this study.

6. Geraniol oxidation

Heartened by the observation of selective oxidation of the two model alcohol substrates using supported gold catalysts, we investigated the oxidation of geraniol as an example of a terpene alcohol containing a number of functional groups that could be oxidised, or react in other ways. The oxidation was investigated at 100 °C using O_2 as oxidant in the absence of solvent using the supported gold catalysts and the results are shown in table 3 and figure 4. In the absence of catalyst or when using the support in the absence of gold, no oxidation was observed, confirming that the presence of gold was essential to achieve catalytic oxidation.

Au/CeO_2 Au/C, Au/Fe_2O_3 and Au/TiO_2 were all found to be very active for the conversion of geraniol. However, a very broad product range was observed. At low conversion, cis- and trans-citral were the main products, but at higher conversions, we identified many products such as β-pinene, limonene, γ-terpinene, linalool, nerol and some traces of geranic acid. For high conversions some condensation products with $M = 2\times M_{\mathrm{Geraniol}} - 18$ were detected. These products were likely formed by acid-catalysed isomerisation and this will be discussed subsequently. The Au/SiO_2 catalyst was much less active for this reaction but still gave mainly cis- and trans-citral. Only a limited amount of oxidation of the hydroxyl group to form citral was observed under these conditions (table 3).

After reaction, the solutions were filtered to remove the particles of catalyst and analysed by atomic absorption spectroscopy to determine the amount of Au leached and the sdata are shown in table 3. Hence, with

Table 4

Oxidation of geraniol using gold catalysts in the presence of solvents[a] using Au/SiO_2 catalyst

Catalyst	3 h reaction data					$S_{1.0}$	S_{10}
	Conv (%)	Sel (%)					
		L	*t*-C	*c*-C	N		
CCl_4 (ACS-Aldrich – 99.9%)	72.5	17.3	1.9	2.3	2.8	77.5	35.1
CCl_4 (HPLC-Aldrich – 99.9%+)	0.6	87.6	0	12.4	0	4.8	–
$CHCl_3$ (Aldrich – 99%+)	1.1	0	15.0	85.0	0	100	–
CH_2Cl_2 (Aldrich – 99.8%)	0.6	0	0	57.9	0	39.4	–

[a] Reaction conditions: alcohol (30 mL), solvent (10 mL), catalyst (0.2 g), 1500 rpm, 100 °C, P_{O_2} 2 bar.

[b] Selectivity to L-linalool, *t*-C *trans* citral, *c*-C *cis*-citral, N nerol, S_x selectivity to citral at x% geraniol conversion.

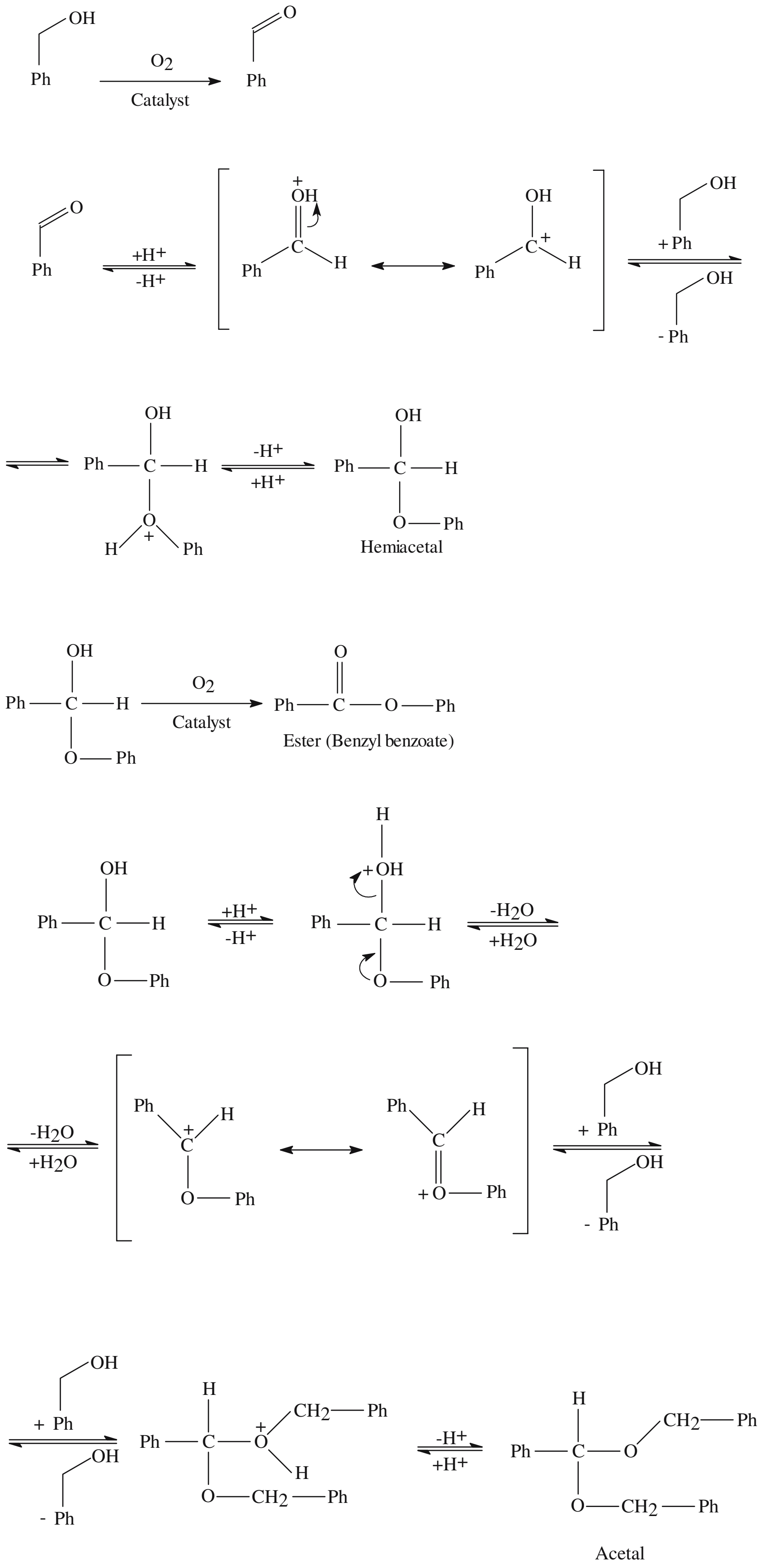
Table 5

Oxidation of geraniol using Au/SiO_2 in the presence of acids and base[a]

Acid/base	3 h reaction data					$S_{1.0}$	S_{10}
	Conv (%)	Sel (%)					
		L	*t*-C	*c*-C	N		
None	0.21	0	30.5	58.2	5.9	82.6	48.0
p-Toluenesulfonic acid	9.3	0	24.4	33.8	12.1	91.7	55.4
Triflic acid	26.3	3.8	10.6	45.1	4.6	84.3	45.2
Nitric acid	13.8	0	14.8	67.3	4.4	94.1	85.8
Hydrochoric acid	12.5	0	7.4	57.9	9.8	86.4	66.7
Ammonium hydroxide	10.8	0	11.0	74.9	9.9	92.9	86.3

[a] Reaction conditions: alcohol (40 mL), catalyst (0.2 g), 1500 rpm, 100 °C, P_{O_2} 2 bar, 1.5 mmol acid/base added.

[b] Selectivity to L-linalool, *t*-C *trans* citral, *c*-C *cis*-citral, N nerol, S_x selectivity to citral at x% geraniol conversion.


O2
Catalyst
+H+
-H+
Hemiacetal
Ester (Benzyl benzoate)
-H2O
+H2O
Acetal

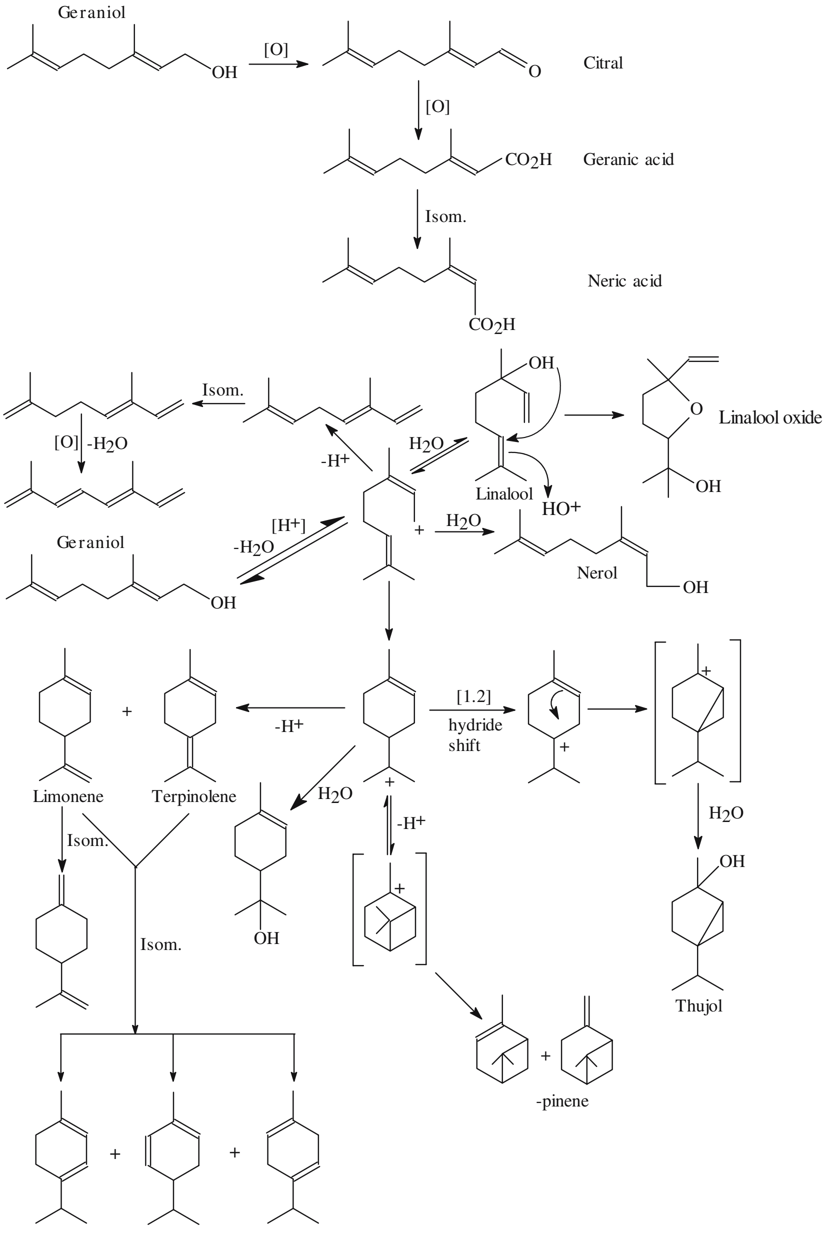
Scheme 1.

these catalysts, no loss of gold was observed using the solvent free conditions employed in this study.

In an attempt to control the product selectivity observed with geraniol, the oxidation was investigated in the presence of solvents (table 4). We investigated the use of chlorinated solvents and found that the use of CCl_4 (Aldrich ACS grade) led to a dramatic increase in conversion. However, this increase in activity led to decreased selectivity in cis- and trans-citral. We found this to be due to the presence of traces of HCl in this solvent. Use of HCl-free CCl_4, led to a much lower conversion being observed. The key observation is that use of these solvents led to a decrease in the amount of oxidation products as compared with the products of isomerisation reactions. To demonstrate the role of acidity and basicity in the reactions of geraniol, a set of experiments was carried out in which trace amounts of acid or base (1.5 mmol) were added under solvent free conditions to the Au/SiO_2 catalyst, which displayed very low activity in the absence of acid or base. The results (table 5) show that the conversion of geraniol was significantly enhanced under these conditions and the selectivity to cis-citral was enhanced.

7. Comments on the reaction mechanism of by-product formation

It is of interest to comment on the formation of the by-products observed with benzyl alcohol oxidation (Scheme 1). The initial reaction is the selective formation



Scheme 2.

of the aldehyde. However, under acidic conditions, catalysed by Brønsted acid sites on the surface of the support, the aldehyde reacts with the alcohol, which is present in great excess under our solvent-free conditions, and this forms the hemiacetal, which on oxidation yields the ester. In addition, the hemiacetal can react to form the acetal. We consider that the alternative pathway *via* oxidation to benzoic acid does not occur under our conditions, as none of the latter was observed. Similar reaction pathways are available for the reactions of octan-1-ol and geraniol. However, the reactions of geraniol are dominated by acid- or base-catalysed isomerisation reactions (Scheme 2).

8. Comparison of the activity of supported Au catalysts with supported Pd and Ru catalysts

Comparison of the turnover frequency of Au/CeO_2 for benzyl alcohol and octan-1-ol oxidation shows that this catalyst has an activity comparable with the highest yet reported. Further, this is achieved using a catalyst that is prepared using a relatively facile procedure, and subsequently employed under conditions, which have yet to be optimised. The Au/CeO_2 catalyst gives a TOF of 150 mol(aldehyde) mol(Au)$^{-1}$ h^{-1} for the oxidation of benzyl alcohol. In comparison, the hydroxyapatite-supported Pd catalyst reported by Kaneda and coworkers, acknowledged to be one of the most active heterogeneous catalyst developed to date for the oxidation of alcohols to the corresponding carbonyl compounds, exhibits a TOF of 500 h^{-1} under comparable experimental conditions. The results also compare favourably for the oxidation of similar substrates catalysed by Ru/Al_2O_3(TOF 300 h^{-1}) [52]. However, there is a marked difference in activity for octanol oxidation to octanal, which is acknowledged to be a poor substrate with hydroxyapatite-supported Pd catalysts [51]. The Au/CeO_2 catalyst gives a TOF of 26 h^{-1} whereas the hydroxyapatite-supported Pd catalyst exhibits a TOF of only 0.2 h^{-1} under comparable conditions. Hence, with this substrate, the unoptimised Au catalyst gives a TOF over two orders of magnitude higher than previous heterogeneous catalysts.

9. Conclusions

In this study, we have shown that supported Au catalysts, prepared by relatively simple co-precipitation and impregnation procedures are very effective catalysts for the selective oxidation of primary alcohols, under solvent free conditions. The TOFs observed for both reactions are amongst the highest yet reported for both reactions to date. It should be noted that these are only preliminary results using non-optimised catalysts, although the catalysts we have selected are considered representative of supported gold catalysts used in the study of redox reaction previously [7,8]. It is also important to note that the reaction conditions and, in particular, the reactor configuration have yet to be optimised and improvements can be expected when using a flow reactor. However, these results point to the clear potential offered by supported gold catalysts for selective oxidation reactions using solvent free condition.

Acknowledgments

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