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Gas phase oxidation of alcohols to aldehydes or ketones catalysed by supported gold

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Primary and secondary aliphatic alcohols are smoothly oxidised by air to the corresponding carbonyl derivatives with high selectivity using 1% Au on silica.

Oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones plays a fundamental role in organic synthesis owing to the versatility of the carbonyl group as a building block.[1,2] Traditional methods based on the use of a stoichiometric amount of reagents, mainly heavy metal salts in high oxidation state, are useful tools for laboratory scale preparation,[3,4] but fail in industrial applications where serious problems related to the disposal of undesired by-products represent a strong drawback. Air, or pure oxygen, is a cheap and clean reagent suitable for bulk scale oxidation. Therefore, the aerobic oxidation of alcohols has, since the early experiments, long been investigated [5] by using different transition metals as catalysts, mainly belonging to the platinum group.[6] In practice, the oxidation of alcohols with air can be performed in the liquid phase or in the gas phase, depending mainly on the thermal stability and volatility of reagents and products. While many recent papers deal with studies on the aerobic oxidation in aqueous solution[6–8] or in other solvents,[9,10] less attention has been paid to the gas phase reaction and attempts at industrial application failed owing to selectivity problems.[11] Recently, gold catalysts have received a growing interest for various applications in organic and inorganic chemistry[12] mainly devoted to eco sustainable processes and, in particular, we and other research groups have investigated the oxidation of polyols[13–16] and aminoalcohols[17] to carboxylates, *o*-hydroxybenzyl alcohol to aldehyde[18] and the direct synthesis of hydrogen peroxide.[19]

An application of gold catalysts to the gas phase oxidation of ethanol has been reported in a preliminary study where an unusual high selectivity to acetaldehyde has been observed.[20]

We have now extended this research on gold catalysts and, in this paper, we show that several primary and secondary aliphatic alcohols can be easily oxidised to the corresponding carbonyl derivatives with high yields using air at atmospheric pressure, thus demonstrating that this cheap and clean methodology could be of general interest for organic synthesis.

Gold catalyst (1 wt%) supported on silica (Aerosil 200, Grace and Davison, surface area 200 m^2 g^{-1}, pore volume 1.7 ml g^{-1}) was prepared in the following manner: 8.5 ml of an aqueous solution of chloroauric acid containing 50 mg of Au were added

Table 1 Oxidation tests

Entry	Catalyst	Reagent	*T* (K)	Conversion (%)	Selectivity (%)
1	1% Au/SiO$_2$	1-Propanol	523	27	100[a]
			573	44	100[a]
2	1% Au/SiO$_2$	1-Butanol	523	51	100[a]
			573	63	94[a]
3	1% Au/SiO$_2$	1-Pentanol	523	23	100[a]
			573	29	100[a]
4	1% Au/SiO$_2$	Phenylcarbinol	523	50	100[a]
			553	75	98[a]
5	1% Au/SiO$_2$	Prop-2-en-1-ol	523	42	97[a]
6	1% Au/SiO$_2$	2-Propanol	373	69	100[a]
			423	100	100[a]
7	1% Au/SiO$_2$	2-Butanol	393	34	100[a]
			423	64	100[a]
8	1% Au/SiO$_2$	2-Pentanol	393	72	87[a]
			423	85	84[a]
9	1% Au/SiO$_2$	3-Pentanol	393	85	100[a]
			423	97	100[a]
10	1% Au/SiO$_2$	1-Propanal	523	14	4[b]
			573	16	3[b]
11	SiO$_2$	1-Propanol	523	20	4[a]
12	SiO$_2$	2-Propanol	413	4	0[a]

[a] To carbonyl derivates. [b] To propanoic acid.

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to 5 g of silica while mixing with a glass rod for 10 minutes. 8 ml of aqueous NH_3 (3%) was then added followed by 10 ml of an aqueous solution of $NaBH_4$ (60 mg per 10 ml), and the suspension stirred at 333 K for 10 min. The solid product was filtered, washed several times with water until the washings contained no chloride. The presence of metallic gold in the catalyst dried at 413 K for 5 h, was confirmed by XRPD analysis ($2\theta = 38.2$).

The oxidation of alcohols was carried out in a fixed bed vertical glass reactor fitted with a glass frit carrying the catalyst (0.2 g) and provided with an electronically controlled furnace. The air stream (1.2 mmol min^{-1}) was controlled by a mass flow instrument and the liquid reagent (0.5 mmol min^{-1}) was supplied through a syringe pump. Liquid vaporisation occurred on the reactor wall prior to the catalytic bed. The condensable reaction products were collected by bubbling the effluent into a cold trap (273 K) containing ethanol and an appropriate internal standard and analysed by GC (HP Plot Q 30 m silica fused capillary column) using helium as a carrier gas. The selectivity was calculated as mol of carbonyl product per mol of reacted alcohol and the carbon mass balance was close to 100% in the case of 100% selectivity. The estimated degree of confidence of the reported figures is ±3%.

Table 1 reports the results obtained in the experiments and shows a remarkable selectivity in the oxidation of aliphatic primary alcohols to aldehydes and secondary alcohols to ketones. The high chemoselectivity towards the alcoholic group presented by the gold catalyst minimizes the oxidation of the C–H and C–C–bonds and the further oxidation of the carbonyl group. In fact, the conversion of 1-propanal under similar experimental conditions is low and produces propanoic acid in very low yields (entry 10). Moreover, the carbon–carbon double bond in allyl alcohol was inactive to oxygen allowing its transformation into acrolein with high selectivity (entry 5).

Comparing the reactivity of primary and secondary alcohols it is evident that the activation of secondary alcohols occurs at lower temperature. Different conversion values obtained for homologous alcohols could be due to differences in the purity of the reagents, particularly in the case of the 98% pure 1-butanol where relatively low conversions have been observed.

In the case of primary alcohols, 1% gold on the support acts mainly as a surface modifier allowing a strong increment in the selectivity to aldehydes with respect to silica alone. In fact, the acidic centres of the support address the reaction to a deeper oxidation, as derived by the low yield and the excess of the formed water (entry 11). In the oxidation of secondary alcohols, gold acts also as a strong activator of the organic molecules because the support is almost inactive at low temperature (413 K) (entry 12).

During a prolonged oxidation test of 1-propanol at 573 K the catalyst was stable over 60 h. XRPD analysis of gold showed that the mean diameter of gold particles changed from 15 nm ($\omega_0 = 0.52$) to 25 nm ($\omega_0 = 0.32$) after 18 h and then remained stable after 60 h. It is worth noting that the catalytic behaviour here observed is due to relatively large gold particles.

In conclusion, 1% gold on silica represents an innovative catalyst suitable for the preparation of carbonyl compounds by clean oxidation of alcohols under mild conditions which could be relevant also for industrial application. The comparison between the gas phase oxidation reported here and the previously reported liquid phase oxidation of the alcoholic group[17] outlines the versatility of supported gold which offers the possibility of producing carbonyl derivatives in the first case, and carboxylates in the second case.

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