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Research Note

# Highly selective oxidation of benzyl alcohol to benzaldehyde catalyzed by bimetallic gold–copper catalyst

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ABSTRACT

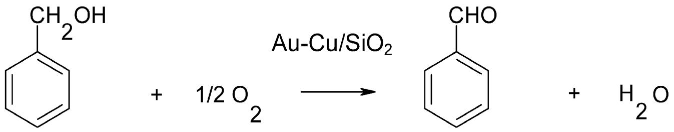
The present study focuses on the smooth oxidation of benzyl alcohol by air in a vapor phase process affording benzaldehyde with high selectivity and yield, using mono- and bimetallic gold–copper on silica catalyst. Particularly efficient was the catalyst 1% Au–Cu/$SiO_2$ with the weight ratio Au/Cu = 4, leading to perfume-grade, acid-free benzaldehyde in over 98% yield.

Selective oxidation of alcohols to the corresponding aldehydes and ketones has involved many efforts from both academic and industrial research owing to the versatile role of the carbonylic group as a building block [1–3]. In this context, catalytic methods leading to high quality grade benzaldehyde are particularly attractive for application in perfumery and food industries. By quantity, benzaldehyde (bitter-almond odor) is the second most important aromatic molecule (after vanillin) used in the cosmetics and flavor industries. Since 1863, benzaldehyde was for long time synthesized by the hydrolysis of benzalchloride derived from toluene chlorination. Today, synthetic benzaldehyde is still commercially produced by this way, along with the toluene oxidation route, where the aldehyde is the by-product of benzoic acid industry [4]. However, organic chlorine or benzoic acid contamination are limiting factors in high demanding uses of benzaldehyde. Moreover, growing ecological restrictions are pushing the progressive shut down of polluting processes based on stoichiometric oxidants, whereas selective oxidation using the eco-friendly air or molecular oxygen in the presence of heterogeneous catalyst is earning a general praise [5–8]. Both liquid and gas phase oxidation of alcohols, mainly depending on thermal stability and volatility of the reagents, have been for long time investigated [1]. Recently, supported gold nanoparticles have been shown to be a versatile catalyst for alcohol oxidation addressing the selectivity toward carboxylates in the presence of aqueous alkali [9–12].

Concerning the benzyl alcohol oxidation to benzaldehyde in the absence of alkali, early reports deal principally with liquid phase reactions which rarely reach the total conversion and show a selectivity in the range of 90–100% in spite of a quite low TOF [2, 13–16].

On the other hand, the gas phase oxidation of volatile alcohols on supported gold resulted to be effective for achieving the corresponding aldehydes and ketones [17–19]. In particular, reacting with air benzyl alcohol in the presence of gold on silica catalyst, a quite high selectivity (>99.5%) could be obtained only in a restricted range of conversion (50–75%) [19]. The need to produce benzaldehyde in high yield for avoiding expensive and polluting purification techniques prompted us to extend this research. As a strategy, in order to stabilize the almost total selectivity of gold under conditions ensuring the complete conversion of the reagent, a series of mono- and bimetallic catalysts were investigated; among them, the gold–copper combination supported on silica resulted to be particularly effective (Scheme 1).

Gold supported on silica catalyst (1 wt% Au nominal loading, $SiO_2$ aerosil from Grace, $A_s = 200\ m^2/g$, $V_p = 1.7\ ml/g$) was prepared using an incipient wetness technique followed by $NaBH_4$



**Scheme 1.** Aerobic oxidation of benzyl alcohol to benzaldehyde with gold–copper based catalysts.

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**Table 1**

| Catalyst | Cu/Au (w/w) | $T_{ext}$ (°C) | $T_{bed}$ (°C) | Conversion (%) | Selectivity (%) | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | 0/1 | 280 | 326 | 75 | 98 | 74 |
| 2 | 1/0 | 290 | 327 | 51 | 78 | 40 |
| 3 | 4/1 | 270 | 317 | 89 | 94 | 84 |
| 4 | 3/2 | 270 | 319 | 91 | 92 | 84 |
| 5 | 1/1 | 270 | 304 | 73 | 98 | 72 |
| 6 | 1/4 | 260 | 313 | 98 | >99 | 98 |

Catalyst = 0.2 g; benzyl alcohol = 0.36 mmol/min; air = 20 ml/min; $T_{ext}$ is the set-up temperature and $T_{bed}$ is the observed temperature of the catalyst bed.

reduction [19]: 8.5 ml of an aqueous solution of $HAuCl_4$ or $CuCl_2$, containing 50 mg of Au or Cu, were impregnated onto 5 g of silica, while mixing with a glass rod for 10 min. The chloroauric acid solution was prepared dissolving metallic gold sponge in *aqua regia* and diluted to the appropriate volume, while the cupric chloride solution was obtained by dissolving $CuCl_2 \cdot 2H_2O$ in the proper $H_2O$ amount. The resulting powder was then contacted with 8 ml of aqueous $NH_3$ (3%), 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. Owing to the reported detrimental effect of chloride to obtaining small gold particles size and good catalytic activity [20], the solid product was washed several times with water until washings contained no chloride.

Bimetallic catalysts of different Au–Cu ratios were prepared as above. Mixtures of $HAuCl_4$ and $CuCl_2$ were used as metal precursors of the catalysts with a nominal total metal loading of 1% on silica. The series of mono- and bimetallic catalysts is listed in Table 1.

Before the oxidation tests, each catalyst has been submitted to a thermal treatment in air flow (20 ml/min) at 250 °C for 2 h.

ICP analyses, performed on the fresh samples $Au{:}Cu/SiO_2$ (1:1) and $Au{:}Cu/SiO_2$ (4:1), showed Au/Cu ratios slightly superior to the expected ones. In particular, the first catalyst has revealed a ratio of 1.1, the second one of 4.5, while the total metal loading was close to 1%.

The XRPD spectra of the catalysts are reported in Supporting Information. Whereas gold alone exhibited sharper peaks at $2\Theta$ 38.2°, 44.3°, 64.3°, 77.4°, corresponding to Au metal, copper alone produced broad peaks, assignable to CuO at $2\Theta$ 35.5° and 38.5°.

The 4:1 and 1:1 Au/Cu (w/w) bimetallic catalyst showed broad peaks at $2\Theta$ values close to the elemental gold, whereas no peaks assignable to oxidic copper derivatives or metallic copper appeared. Also in the used bimetallic catalysts no peak corresponding to copper species could be detected.

According to the reported XRD data (MDI Jade 5.0) the peaks of the $Au_3Cu$ alloy (Bogdanovite) overlap all the metal gold peaks (see WMF images in Supporting Information).

XPS spectra of the silica supported bimetallic 1:1 and 4:1 Au/Cu catalysts showed the presence of signals due to metal Au (4f) at 84.0 eV, as well as silicon and oxygen. No signals related to copper species were detected while the surface ratio Au/Si resulted to be 0.001 for the first catalyst and 0.003 for the second one. Note that the signals due to $Au_3Cu$ alloy can hardly been distinguished from elemental gold [21].

Poorly resolved TEM images of the bimetallic catalysts were obtained (see MDI images in Supporting Information). Transmission EELS analysis showed the presence of gold at 2206.0 eV in Au–$SiO_2$. A slightly broader signal always at 2206.0 eV was present in the 1:1 and 4:1 Au/Cu catalysts. A positive response to copper was obtained by analyzing the Cu–$SiO_2$ catalyst at 938.0 eV while in the bimetallic catalyst copper was not detectable at this last energy, whereas a new broad peak at ca. 2218.0 eV resulted to be not assignable to any copper species.

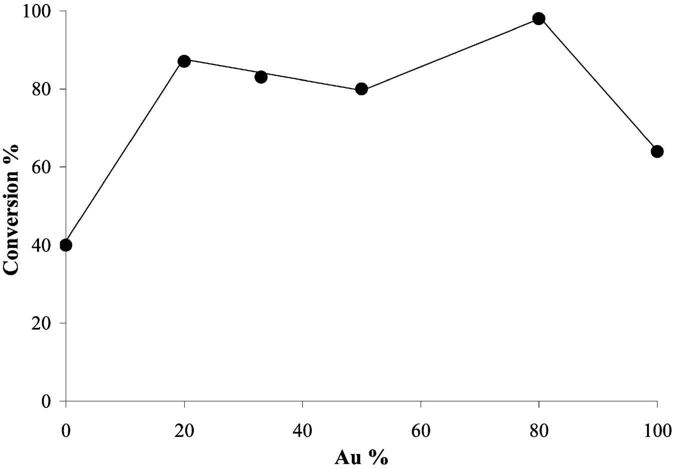

**Fig. 1.** Extrapolated conversion at $T_{bed} = 313\,°C$ for different Au–Cu weight compositions.

The oxidation of benzyl alcohol was carried out in a fixed bed vertical glass reactor ($h = 250$ mm, $d = 12$ mm), fitted with a glass frit carrying the catalyst (0.2 g) and provided with an electronically controlled furnace. The air stream (20 $N\,ml\,min^{-1}$) was controlled by a mass flow instrument and the liquid reagent (0.36 $mmol\,min^{-1}$, oxygen/alcohol molar ratio = 0.5) was supplied through a syringe pump. Liquid vaporisation occurred on the reactor wall prior to the catalytic bed. The tests were performed at different temperatures in the range 250–350 °C: below 250 °C no benzyl alcohol oxidation occurred and over 350 °C the product underwent degradation with coking. The condensable reaction products were collected by bubbling the effluent into a cold trap (273 K) containing ethanol as the solvent and 1-butanol as an internal standard and analyzed by GC (HP Plot Q 30 m silica fused capillary column) using helium as a carrier gas. The selectivity was calculated as mol of produced benzaldehyde per mol of reacted benzyl alcohol and the carbon mass balance was close to 100% in the case of selectivity near 99%.

The results related to the catalytic tests are summarized in Table 1 and plotted in Fig. S1 (Supporting Information).

The analytical data show that the selectivity to benzaldehyde at high conversion can be tuned using Cu–Au bimetallic catalysts and controlling the Cu/Au ratio. In this manner, the key-role of gold in determining the selectivity and the synergistic effect of copper in stabilizing the selectivity at high conversion can be emphasized. In fact, gold alone allowed 98% selectivity at moderate conversion (75% at 326 °C, Table 1, Fig. S1A in Supporting Information) but its performance sharply decreased on growing the conversion with the temperature. On the other hand, copper produced the worst performance owing to its low selectivity (78% at 327 °C, Table 1, Fig. S1B in Supporting Information). Differently, the combination Cu–Au led to high conversion at lower temperatures, a requirement for stabilizing the high selectivity conditions. By careful optimization of the two-metal catalyst, 100% selectivity at almost total conversion (98%) could be obtained using the catalyst with a Cu/Au = 0.25 weight ratio at 313 °C (Table 1, Fig. S1F in Supporting Information). As a general consideration, the higher the Au loading with respect to Cu, the better the catalytic activity, except for the ratio Cu/Au = 1, which did not follow this trend. Selectivity is strongly dependent on temperature, which favors the oxidation to benzoic acid but also coking for values above 330 °C.

Moreover, we have observed that the higher Au loading in the bimetallic catalyst favors the benzyl alcohol oxidation as shown in Fig. 1, where the conversion at the fixed bed temperature (313 °C), derived from Fig. S1, is plotted vs. the %Au in the metal composition.

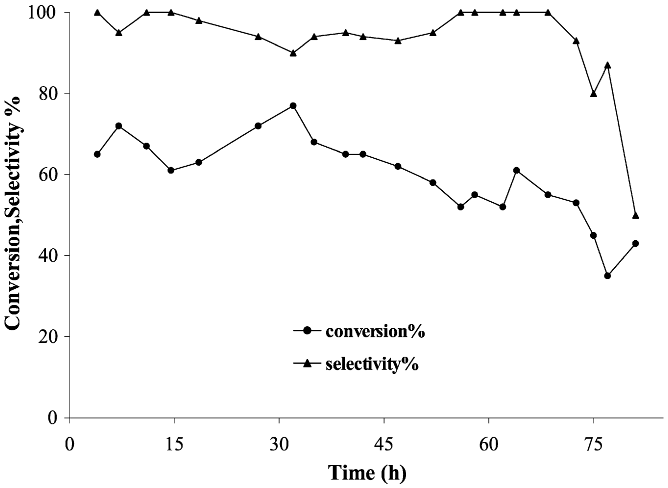

**Fig. 2.** Life-time test of the 1% $Au/SiO_2$ catalyst at 315 °C.

The discontinuous catalytic behavior of the pure metals and various bimetallic compositions is evidenced, in particular, by the remarkable peak at 80% Au composition.

From GC analysis it was possible to identify water beside benzaldehyde as a condensable reaction product. Traces of benzoic acid were present only in the experiments above 330 °C. In no case benzylbenzoate was detected. Tars on the catalyst were also deposited above 330 °C.

In order to estimate the catalyst life-time, an 80 h test on 1% $Au/SiO_2$ was carried out at 280 °C (reactor temperature) meanwhile sampling for analysis was done every 3–4 h. The single metal catalyst was chosen on the basis of the easy determination of the particle size by XRD (no peaks overlapping).

The plot conversion and selectivity vs. time (Fig. 2) showed a general good trend: selectivity, in particular, maintained a steady value around 90–100% for 70 h, then it rapidly dropped to 50% while conversion fluctuated in a wider range (50–75%) and then dropped below 40%. The decay of the catalytic behavior is probably ascribed to the formation of a pitch-dark covering deposited on the catalyst. No attempts were done for restoring the catalyst activity.

X-ray diffraction analysis of gold ($2\Theta = 38.2^\circ$) using the Scherrer equation [22] demonstrated that the mean diameter of gold particles changed during the test from 15.5 to 27.8 nm after 47 h (Fig. S2, Supporting Information).

It is worth noting that gold particles rapidly doubled their average diameter and they remained stable until the end of the test. The use of different techniques (ICP, XRPD, XPS, TEM-EELS) did not allow a clear characterization of the bimetallic Au–Cu system. According to XRPD, $Cu/SiO_2$ catalyst contains oxidic copper (CuO), whereas no copper species were evidenced in the bimetallic catalysts by other techniques. As hypotheses, either the presence of undetectable CuO nanoparticles or alloyed copper, as $Au_3Cu$, could be supposed as active species beside metallic gold.

In conclusion, the present study on gold–copper catalysts applied to the gas-phase oxidation of benzyl alcohol has emphasized the key-role of gold highlighted by a synergistic effect with copper. Although gold alone led to interesting values of selectivity and conversion, the most promising achievements have been obtained with a mixed $Cu–Au/SiO_2$ catalyst producing over 99% selectivity at 98% conversion. We believe that this result could be exploited to assess a clean catalytic process for perfumery grade benzaldehyde (>99%), where chlorinated products and benzoic acid must be avoided.

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## Supporting Information

The online version of this article contains additional supplementary material.

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