A green process for chlorine-free benzaldehyde from the solvent-free oxidation of benzyl alcohol with molecular oxygen over a supported nano-size gold catalyst

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Benzyl alcohol is oxidized selectively to benzaldehyde with high yield, with a little formation of benzylbenzoate, by molecular oxygen over a reusable nano-size gold catalyst supported on U_3O_8, MgO, Al_2O_3 or ZrO_2 in the absence of any solvent.

Liquid phase oxidation of benzyl alcohol is an important preferred reaction practically for the production of chlorine-free benzaldehyde, without loss of carbon in the form of CO_2 (a geenhouse gas). The preparation of benzaldehyde by reacting benzyl alcohol with stoichiometric or excess amounts of potassium or ammonium permanganate in aqueous acidic medium[1] is not environmentally benign at all, because of the formation of a large amount of toxic waste. A few studies on the benzyl alcohol-to-benzaldehyde oxidation by H_2O_2 or O_2 in the presence of organic solvent, using different solid catalysts, such as Pd/C,[2] Pd(II) hydrotalcite,[3] Pd-Ag/pumice,[4] Ru-Co-Al hydrotalcite,[5] Ni-containing hydrotalcite[6,7] and nano-size NiO_2,[8] have been reported. However, because of the use of organic solvent, the benzaldehyde production in these cases is not environmentally benign, even though an environmentally clean oxidant (O_2 or H_2O_2) is used. Recently, Choudhary *et al.*[9,10] have reported the solvent-free oxidation of benzyl alcohol to benzaldehyde over MnO_4^--exchanged hydrotalcite[9] and transition metal containing layered double hydroxides and/or mixed hydroxides,[10] using *tert*-butylhydroperoxide (TBHP) as the oxidant; after consumption TBHP leaves *tert*-butanol as a co-product and hence it is not a clean oxidizing agent. To be a cost effective and environmentally-friendly (or green) process, the benzyl alcohol-to-benzaldehyde oxidation with high selectivity and yield must be accomplished under solvent-free conditions, using molecular oxygen (which is not only a clean agent but also the cheapest oxidizing agent) as the oxidant and also using a highly active solid catalyst (which is easily separable and also reusable) in the process. This has been achieved in the present investigation. We report in this Communication a totally green process for the liquid phase selective oxidation of benzyl alcohol to benzaldehyde, with high selectivity and yield, by molecular oxygen using easily separable and reusable supported nano-size gold catalysts (*viz*. Au supported on U_3O_8, MgO, Al_2O_3 or ZrO_2) in the absence of any solvent.

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Results showing the solvent-free liquid phase oxidation of benzyl alcohol to benzaldehyde by molecular oxygen over nano-size gold supported over different metal oxides are presented in Table 1. In the absence of any catalyst, the benzyl alcohol conversion was 4% with 96% and 5% selectivity for benzaldehyde and benzylbenzoate, respectively. The preparation (by homogeneous deposition precipitation of gold on support) and characterisation of the supported nano-size gold catalysts are given earlier.[11] The liquid phase oxidation of benzyl alcohol over the supported Au catalysts, was carried out in a magnetically stirred reactor (capacity: 10 cm^3), provided with a mercury thermometer for measuring the reaction temperature and reflux condenser, at the following reaction conditions: reaction mixture = 29 mmol benzyl alcohol + 0.1 g catalyst, temperature = 130 °C, pressure = 1.5 atm, and reaction time = 5 h. After the reaction, the catalyst was removed from the reaction mixture by filtration and the reaction products and unconverted reactants were analysed by gas chromatography with a flame ionisation detector, using a SE-30 column and N_2 as carrier gas.

From the results in Table 1 the following important observations can be made:

• Among the gold catalysts, the Au/U_3O_8 catalyst showed the best performance [both high activity (53% conversion) and selectivity (95%)] in the oxidation of benzyl alcohol to benzaldehyde. The other supported gold catalysts, particularly Au/MgO, Au/Al_2O_3 and Au/ZrO_2 also showed good activity in the benzyl alcohol-to-benzaldehyde oxidation.

• The highest activity (benzyl alcohol conversion of 68.9%) was shown by the Au/Al_2O_3 catalyst. However, this catalyst showed somewhat lower benzaldehyde selectivity (65%).

• The Au/Fe_2O_3 catalyst showed very high selectivity (100%) for benzaldehyde but low activity (16.2% conversion) in the oxidation.

• The order of the catalysts for the benzaldehyde formation (benzaldehyde yield) is Au/U_3O_8 (50.4%) > Au/Al_2O_3 (44.8%) > Au/ZrO_2 (44.1%) > Au/MgO (43.9%) > Au/ZnO (37.6%), Au/BaO or Au/La_2O_3 (35.5%) > Au/MnO_2 (34.5%) > Au/Sm_2O_3 (33.3%) > Au/Eu_2O_3 (32.4%) > Au/CaO (30.4%) > Au/CoO (26.7%) > Au/NiO (25.0%) > Au/CuO (18.6%) > Au/Fe_2O_3 (16.2%).

The results reveal a strong influence of metal oxide support on the catalytic performance (both the benzyl alcohol conversion activity and product selectivity in the oxidation of benzyl alcohol to benzaldehyde) of the supported gold catalysts. However, since the supported gold catalysts do not have the same gold loading, their comparison may not be valid. It is, however, interesting to note that the Au/ZrO_2 catalyst shows

Table 1 Results of the oxidation of benzyl alcohol-to-benzaldehyde by O_2 over different metal oxide supported nano-size gold catalysts in the absence of any solvent

Nano-gold catalyst	Conc. of gold (wt.%)	Gold particle size/nm	Conversion of benzyl alcohol (%)	Selectivity (%)		Benzaldehyde yield (%)	TOF[a]/mol g(Au)$^{-1}$ h^{-1}
				Benzaldehyde	Benzylbenzoate		
Au/MgO	7.5	8.9 ± 0.7	51.0	86.0	14.0	43.9	0.34
Au/CaO	4.7	9.6 ± 1.2	33.3	91.3	8.6	30.4	0.38
Au/BaO	5.3	7.1[a]	43.5	81.5	18.5	35.5	0.39
Au/Al_2O_3	6.4	3.6 ± 1.1	68.9	65.0	35.0	44.8	0.41
Au/ZrO_2	3.0	4.5 ± 1.20	50.7	87.0	13.0	44.1	0.85
Au/La_2O_3	6.5	n.d.	51.6	68.8	31.3	35.5	0.32
Au/Sm_2O_3	4.2	7.9 ± 0.5	44.4	75.0	25.0	33.3	0.46
Au/Eu_2O_3	6.6	n.d.	37.5	87.5	12.5	32.4	0.29
Au/U_3O_8	8.0	9.4 ± 3.2	53.0	95.0	5.0	50.4	0.37
Au/MnO_2	4.1	6.1 ± 1.7	39.7	88.8	11.1	34.5	0.49
Au/Fe_2O_3	6.1	5.8 ± 0.3	16.2	100	—	16.2	0.15
Au/CoO	7.1	5.7 ± 1.3	28.3	95.2	4.8	26.7	0.22
Au/NiO	6.2	23.1 ± 3.7	32.0	78.0	22.0	25.0	0.23
Au/CuO	6.8	11.7 ± 2.6	27.0	69.0	31.0	18.6	0.16
Au/ZnO	6.6	5.9[a]	40.5	92.8	7.2	37.6	0.33

[a] Rate of the formation of benzaldehyde per unit mass of the deposited gold per unit time.

high activity (much higher than many of the supported Au catalysts) inspite of the fact that its Au loading is the lowest. This may be because of the lower Au particle size of the Au/ZrO_2. A comparison of the data also indicates that there is no direct relationship between the Au loading and the performance (in the benzyl alcohol-to-benzaldehyde oxidation) of the supported Au catalysts.

When the supported Au catalysts were compared for their turn-over-frequency (TOF), measured in terms of the rate of benzaldehyde formation per unit mass of gold deposited on the different metal oxide support, the supported Au catalysts show the following order: Au/ZrO_2 > Au/MnO_2 > Au/Sm_2O_3 > Au/Al_2O_3 > Au/BaO > Au/CaO > Au/U_3O_8 > Au/MgO > Au/ZnO > Au/ La_2O_3 > Au/Eu_2O_3 > Au/NiO > Au/CoO > Au/CuO > Au/Fe_2O_3. The interaction between the supported gold and the support is expected to play an important role in deciding both the gold particle size and catalytic performance of the supported gold catalysts.

When the promising supported nano-size gold catalysts, Au/U_3O_8, Au/MgO, Au/Al_2O_3 and Au/ZrO_2, were reused in the benzyl alcohol-to-benzaldehyde oxidation, the variation in the benzaldehyde yield and selectivity was within 3–5%, indicating an excellent reusability of the catalysts. For the Au/U_3O_8 catalyst, the benzaldehyde yield after 1st, 3rd and 5th reuse was 50.1, 50.3 and 49.8%, respectively. The supports (*viz*. MgO, Al_2O_3, ZrO_2 and U_3O_8) alone showed negligible small activity for the oxidation of benzyl alcohol. Also, when the catalysts from the reaction mixture were removed after the initial reaction period of 30 min, there was no further appreciable increase in the conversion or yield, indicating that the reaction is essentially catalyzed by the heterogeneous supported gold. Use of supported gold catalysts has also been reported earlier for the selective oxidation by molecular oxygen of glycerol to glyceric acid,[12] polyhydroxylated aliphatics to monocarboxylates[13] and aliphatic/aromatic aldehydes to carboxylic acids.[14]

It is interesting to note that benzyl benzoate is the only other product formed apart from benzaldehyde and the formation of benzoic acid was not at all detected in GC and/or in GC-MS analysis. The reactions involved in the oxidation process are as follows:

$$C_6H_5CH_2OH + 0.5\ O_2 \rightarrow C_6H_5CHO + H_2O \quad (1)$$

$$C_6H_5CHO + 0.5\ O_2 \rightarrow C_6H_5COOH \quad (2)$$

$$C_6H_5COOH + C_6H_5CH_2OH \rightarrow C_6H_5COOCH_2C_6H_5 \quad (3)$$

The absence of benzoic acid in the GC and GC-MS analysis indicates that, as soon as benzoic acid is formed (reaction (2)), it reacts immediately with benzyl alcohol, which is available in much higher concentration, forming benzyl benzoate (reaction (3)).

The organic solvent-free preparation of chlorine-free benzaldehyde from the selective oxidation of benzyl alcohol by molecular oxygen using the supported nano-size gold catalyst, particularly nano-size gold supported on U_3O_8, MgO, Al_2O_3 or ZrO_2, is a totally clean process. Also, no operational problems are foreseen for use of this green process in the large scale production of benzaldehyde. The process may be carried out at higher oxygen pressure (>1.5 atm) to increase both the conversion and product yield or to reduce the reaction time.

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