Solvent-free selective oxidation of benzyl alcohol by molecular oxygen over uranium oxide supported nano-gold catalyst for the production of chlorine-free benzaldehyde

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A detailed investigation on the production of chlorine-free benzaldehyde in the solvent-free oxidation of benzyl alcohol by O_2 over nano-gold supported on U_3O_8 has been carried out. Influence of different catalyst parameters (different methods of gold deposition on U_3O_8, gold loading and particle size, and catalyst calcination temperature) and reaction conditions (reaction period and temperature) on the process performance has been studied. The catalyst containing gold at higher concentration and with smaller gold particles showed the better process performance (higher benzyl alcohol conversion and benzaldehyde yield or selectivity). The benzyl alcohol conversion is largely increased but the selectivity for benzaldehyde is slightly decreased (while that of benzyl benzoate is increased) with increasing the reaction period or temperature. In the presence of solvent (*viz.* tolune, *p*-xylene, DMF or DMSO), the process performance was found to be inferior to that observed in the absence of any solvent. Substituted benzyl alcohols also can be oxidized by O_2 to corresponding aldehydes with high yield and/or selectivity, using the catalyst in the absence of any solvent.

1. Introduction

Unlike the gas phase oxidation of toluene, chlorine-free benzaldehyde can be produced by the liquid phase oxidation of benzyl alcohol without loss of carbon in the form of CO_2, a green house gas. A large amount of toxic waste is produced in the conventional preparation of benzaldehyde by reacting benzyl alcohol with stoichiometric or excess amounts of potassium or ammonium permanganate in aqueous acidic medium.[1] In order to avoid the use of organic solvent, a use of supercritical carbon dioxide as an effective reaction medium to perform the oxidation of primary and secondary aliphatic alcohols to corresponding carbonyl compounds with chromium trioxide supported silica has been reported.[2] In this case, the chromic oxide acts as an oxidizing agent. A use of environmentally clean oxidizing agent, such as H_2O_2 or more preferably O_2, but in the presence of organic solvent, has been reported earlier for the benzyl alcohol-to-benzaldehyde oxidation using different solid catalysts.[3–9] Solvent-free oxidation of benzyl alcohol to benzaldehyde by TBHP, using the easily separable/reusable MnO_4^- exchanged hydrotalcite or transition metal containing layered double hydroxide as a catalyst, has also been reported earlier.[10,11] The use of TBHP as the oxidizing agent, however, leads to the formation of tert-butanol as a by-product in the oxidation. To make the liquid phase benzyl alcohol-to-benzaldehyde oxidation process environmentally clean/green, it should be carried out in the absence of any solvent, using a clean oxidizing agent (*e.g.* O_2 or H_2O_2), preferably using molecular oxygen for favorable process economics.

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Recently, in our preliminary communication,[12] we have reported a totally green process for the solvent-free selective benzyl alcohol-to-benzaldehyde oxidation by molecular oxygen (at close to atmospheric pressure), using an easily separable/reusable nano-gold catalyst supported on different metal oxides (particularly the Au/MgO, Au/Al$_2$O$_3$, Au/ZrO$_2$ and Au/U$_3$O$_8$ catalysts), prepared by a homogeneous deposition precipitation (HDP) method for depositing nano-gold on the supports. Among the supported nano-gold catalysts, the Au/U$_3$O$_8$ showed the best performance in the process.[12] Later, Hutching and coworkers also reported the solvent-free oxidation of benzyl alcohol to benzaldehyde by O_2 using Au–Pd/TiO$_2$ catalyst.[13]

In this paper, we report our detailed investigation on the solvent-free selective oxidation of benzyl alcohol to benzaldehyde by O_2 over Au/U$_3$O$_8$ catalyst, which showed the best process performance (among the different supported nano-gold catalysts) in our preliminary work reported earlier.[11] Influence of the method of gold deposition, gold loading and calcination temperature of the catalyst on the benzyl alcohol conversion and benzaldehyde selectivity in the process has been investigated. The influence of the reaction conditions (*viz.* reaction time and temperature) on the process performance has also been studied. Use of the catalyst in the solvent-free oxidation of substituted benzyl alcohols by O_2 to corresponding aldehydes has also been investigated.

2. Experimental

2.1 Preparation and characterization of Au/U$_3$O$_8$ catalysts

The Au/U$_3$O$_8$ catalysts were prepared by different methods for depositing gold on U$_3$O$_8$ support by impregnation, deposition

precipitation, homogeneous deposition precipitation and co-precipitation methods, as follows [in all the four methods, the gold available for its deposition/incorporation in the catalyst was the same (8.0 wt% of the support)]:

(i) Deposition of gold on U_3O_8 by impregnation (IMP). The Au/U_3O_8 (IMP) catalyst was prepared by contacting the U_3O_8 (2.0 g) with concentrated aqueous solution of $HAuCl_4 \cdot 3H_2O$ (Thomas Baker Chem. Ltd., Mumbai, India), evaporating the extra liquid on water bath, drying at 100 °C for 12 h and finally calcining the solid in air at 400 °C for 2 h. The uranium oxide (U_3O_8) was obtained by hydrolyzing uranyl nitrate [$UO_2(NO_3)_2 \cdot 6H_2O$] (BDH, Mumbai) by aqueous ammonia (30%), washing the resulting precipitate, drying and then calcining at 500 °C for 4 h in air. The catalyst was denoted as Au/U_3O_8 (IMP).

(ii) Deposition of gold on U_3O_8 by deposition precipitation (DP). The Au/U_3O_8 (DP) catalyst was prepared by contacting the U_3O_8 under stirring with aqueous NaOH solution containing $HAuCl_4 \cdot 3H_2O$ at a pH of 7.0 and 70 °C for 1 h, aging the mixture at 30 °C for 1 h, filtering and thoroughly washing the solid with deionised water, drying and calcining the dried solid in air at 400 °C for 2 h. The catalyst was denoted as Au/U_3O_8 (DP). The deposition precipitation method was developed earlier by Haruta and coworkers[14] for depositing nano-gold on metal oxide support.

(iii) Deposition of gold on U_3O_8 by homogeneous deposition precipitation (HDP). The Au/U_3O_8 (HDP) catalyst was prepared by the HDP method described elsewhere.[15–17] The U_3O_8 (2.0 g) was contacted under stirring with aqueous solution of urea (5.19 g) containing $HAuCl_4 \cdot 3H_2O$ (0.32 g). The temperature of the reaction mixture was gradually increased up to 95 °C and maintained for 6 h. Thereafter, the mixture was aged at 30 °C for 12 h and then the solid was filtered, thoroughly washed with deionised water, dried at 90 °C for 12 h and finally calcined in air at 400 °C for 2 h. The catalyst was denoted as Au/U_3O_8 (HDP).

(iv) Preparation of Au/U_3O_8 by co-precipitation (CP). The appropriate quantities of uranyl nitrate, [$UO_2(NO_3)_2 \cdot 6H_2O$], and aqueous gold chloride solution were taken in a three-necked round bottom flask and diluted with 200 ml distilled water. This solution was then heated to 60 °C. The pH and temperature of the solution was monitored continuously. An aqueous solution of Na_2CO_3 (0.5 N) was added drop-wise to the heated solution until the pH of the solution reached 8.0. The stirring was continued further for 1 h at 60 °C. The reaction mixture was aged overnight at room temperature, filtered, washed thoroughly with distilled water (500 ml × 8 times), dried at 90 °C for 12 h and finally calcined in air at 400 °C for 2 h. The catalyst was denoted as Au/U_3O_8 (CP).

The U_3O_8 used in the above first three methods was prepared by hydrolyzing uranyl nitrate at a pH > 8.0, filtering, washing and drying the precipitate and then calcining in air at 400 °C for 2 h.

The catalysts were characterized for their Au content by ICP-OES (using a Perkin-Elmer analyzer) and also for their Au particle size by the XRD peak (at $2\theta = 38.2°$) broadening [using a Philips X-ray diffractometer (1730 series) and Cu Kα radiation]. The surface area of the Au/U_3O_8 catalysts was measured by the single point N_2 adsorption method (using a surface area analyzer, Quanta Chrome, USA).

2.2 Catalytic oxidation reaction

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 general reaction conditions: reaction mixture = 29 mmol benzyl alcohol (or substituted benzyl alcohol) + 0.1 g catalyst, temperature = 130 °C, pressure = 1.5 atm, and reaction time = 5 h. Unless otherwise mentioned, the reaction was carried out at the above general conditions. For studying the solvent effects, 5.0 ml of solvent (toluene, p-xylene, DMF or DMSO) were added to the reaction mixture. After the reaction, the reaction mixture was filtered, the solid catalyst was washed with hot toluene, and the reaction products and unconverted reactants from the filtrate were analyzed by gas chromatograph with flame ionisation detector, using a SE-30 column and N_2 as a carrier gas. Under the prevailing reaction conditions, no oxidation of solvent (toluene or xylene) was observed.

The conversion, product selectivity and product yield were calculated as follows: conversion (%) = [(moles of reactant converted) × 100] ÷ [(moles of reactant in feed], product selectivity (%) = [(moles of product formed) × 100] ÷ [(moles of reactant converted] and product yield (%) = (percentage of reactant converted to a particular product) or [conversion (%) × product selectivity (%) ÷ 100].

3. Results and discussion

Influence of the method of gold deposition, gold loading and calcination/pretreatment temperature of the catalyst (prepared by the HDP method), and also that of the reaction conditions (viz. absence or presence of different solvents, temperature and reaction period) have been studied on the conversion of benzyl alcohol and selectivities for benzaldehyde and benzyl benzoate in the benzyl alcohol oxidation over Au/U_3O_8 catalyst. The results are presented in Fig. 1–5 and Table 1. Influence of the catalyst preparation/pretreatment temperature on the surface properties (viz. surface area and gold particle size) and also on the turn-over-frequency (TOF), expressed as the rate of the reaction per unit mass of the catalyst or the deposited Au per unit time, is shown in Table 2. Results of the solvent-free oxidation of different substituted benzyl alcohols to their corresponding aldehydes are presented in Table 3.

3.1 Influence of the method of gold deposition

The results in Fig. 1 show a strong influence of the method of gold deposition on the catalyst performance in the solvent-free benzyl alcohol oxidation. The catalyst performance (benzaldehyde yield) observed for the different methods of gold deposition/catalyst preparation is in the following order: HDP > DP > CP > IMP.
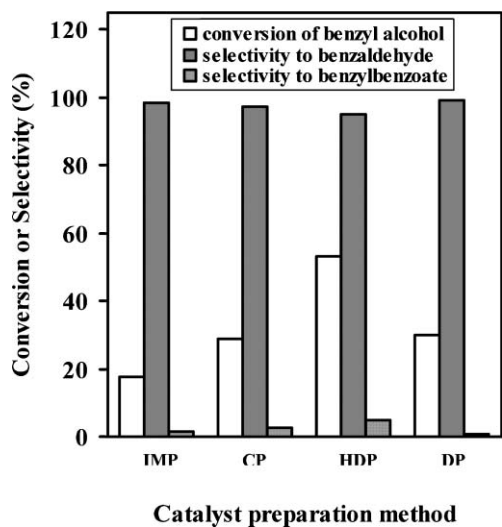
Fig. 1 Performance of the Au/U$_3$O$_8$ catalysts (calcined at 400 °C), prepared by the different gold deposition methods, in the solvent-free oxidation of benzyl alcohol (at 130 °C).

For the catalysts prepared by the different methods, the benzaldehyde selectivity was found to be more or less the same but they differ in their benzyl alcohol conversion activity, either because of the difference in their Au particle size or due to different gold loadings (Table 2).

The Au/U$_3$O$_8$ (HDP) showed the best performance. The lowest performance of the Au/U$_3$O$_8$ (IMP), having similar gold loading (8.0 wt%), is mostly attributed to its larger Au particle size, and consequently to its lower gold surface area. Whereas, the lower gold loading is responsible for the lower activity of the Au/U$_3$O$_8$ (CP) and Au/U$_3$O$_8$ (DP) catalysts containing smaller gold particles. When, the same amount of gold (8 wt% of U$_3$O$_8$) was available for its incorporation in the

Fig. 3 Influence of the calcination temperature of the Au(8 wt%)/U$_3$O$_8$ (HDP) catalyst on the solvent-free oxidation of benzyl alcohol (at 130 °C).

catalysts, the gold deposited by the DP and CP methods was appreciably lower than that of the HDP; in the later (HDP) method, the gold deposition is complete (*i.e.* 100% of the available gold).

In our earlier communication,[12] the Au/U$_3$O$_8$ (HDP) catalyst showed excellent reusability in the reaction (after the 1st, 3rd and 5th reuse of the catalyst, the benzaldehyde yields
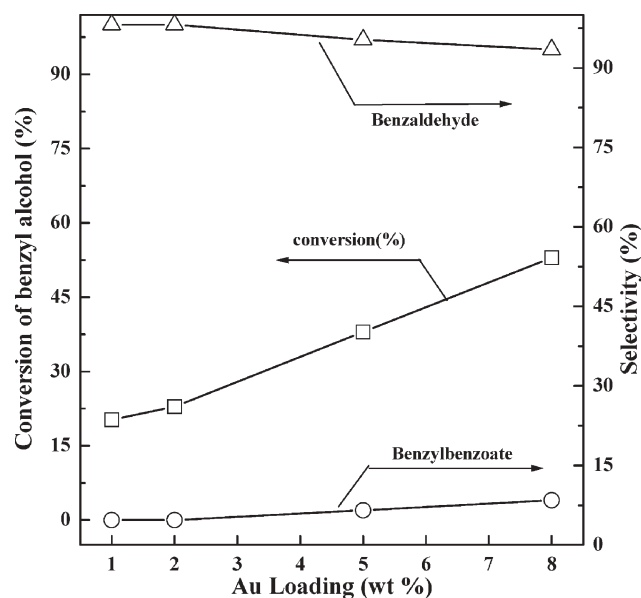

Fig. 2 Effect of the Au loading in the Au/U$_3$O$_8$ (HDP) catalyst (calcined at 400 °C) on the conversion and selectivity in the solvent-free oxidation of benzyl alcohol (at 130 °C).
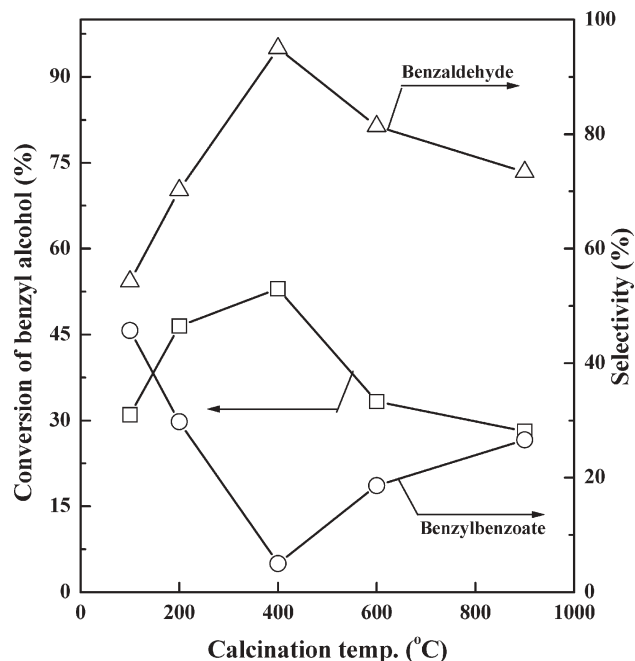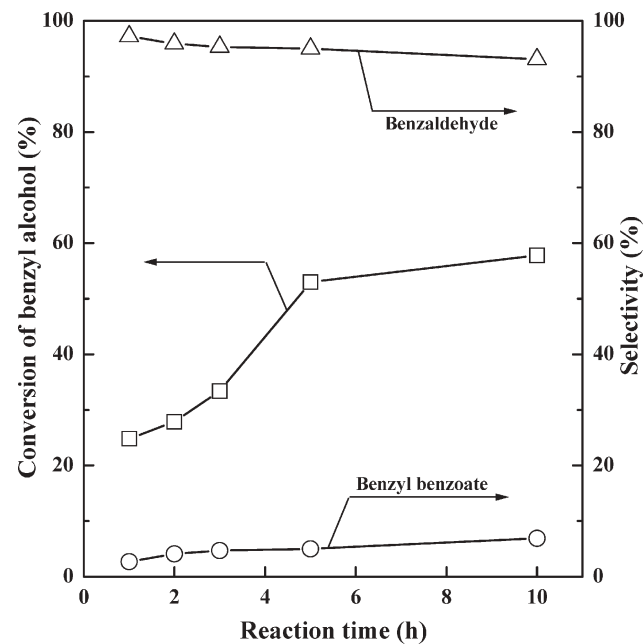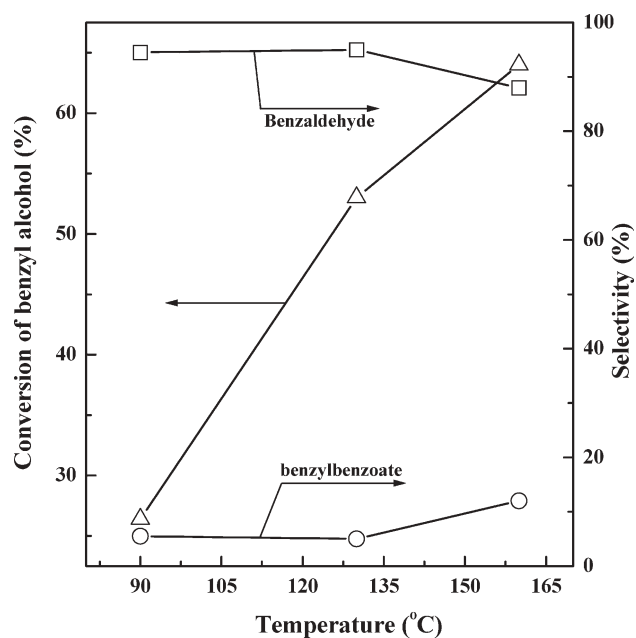

Fig. 4 Effect of the reaction time on the conversion and selectivity in the solvent-free oxidation of benzyl alcohol (at 130 °C) over the Au(8 wt%)/U$_3$O$_8$ (HDP) catalyst (calcined at 400 °C).

Fig. 5 Influence of the reaction temperature (reaction time = 5 h) on the conversion and selectivity in the solvent-free oxidation over the Au(8 wt%)/U_3O_8 (HDP) catalyst (calcined at 400 °C).

were 50, 50.3 and 49.8%, respectively) and the reaction was found to be essentially catalyzed by the heterogeneous supported gold catalyst (when the catalyst from the reaction mixture was removed after the initial reaction period of 30 min, there was no further appreciable increase in the conversion or yield).

All the further work was, therefore, carried out using the catalyst prepared by depositing gold on U_3O_8 by the HDP method.

3.2 Influence of gold loading

The results in Fig. 2 show that, with increasing the Au loading in Au/U_3O_8 (HDP) catalyst, its benzyl alcohol oxidation activity is increased markedly, almost linearly, while its selectivity for benzaldehyde is decreased due to the simultaneous formation of benzyl benzoate; the decrease in the benzaldehyde selectivity is, however, smaller.

It may be noted that the deposition of gold on the U_3O_8 support by the HDP method was quantitative; even no traces of gold was detected in the filtrate. This is most probably expected because of the strong adsorption of positively charged gold complexes under the basic conditions. Formation of $[Au(urea)_4]Cl_3 \cdot 2H_2O$ and/or $[Au_2(NH_2)_2Cl_2-(NCO)(OH)] \cdot H_2O$ complexes[18] has been observed earlier in the presence of urea at room temperature and 90 °C, respectively. Under the basic conditions of the HDP, the surface of U_3O_8 support becomes negatively charged [this is expected because of the fact that the pH corresponding to the isoelectric point of U_3O_8 (≈ 4.0) is much lower than the actual pH of the system]. The adsorption of positively charged Au complexes on the U_3O_8 support is, therefore, facilitated, leading to a complete deposition of gold from the solution.

The results (Fig. 2) also reveal that the selectivity of benzaldehyde is decreased with increasing the benzyl alcohol conversion. This is because of the fact that benzaldehyde is an intermediate product. The overall benzyl alcohol oxidation process involves the reaction pathway presented in Fig. 6. Since, no net formation of benzoic acid was observed over the Au/U_3O_8 catalysts and other metal oxide supported Au catalysts,[11] the benzoic acid reacts instantly with benzyl alcohol, which is available in much higher concentration, forming benzyl benzoate.

Table 1 Results for the oxidation of benzyl alcohol by molecular oxygen over the Au(8 wt%)/U_3O_8 (HDP) catalyst in the absence and presence of different solvents

Solvent used	Temp./°C	Conversion (%)	Selectivity (%)		Benzaldehyde yield (%)	TOF^a/mol g^{-1}$_{(Au)}$ h^{-1}
			Benzaldehyde	Benzylbenzoate		
Nil	130	53.0	95.0	5.0	50.4	0.37
Nil	110	40.5	96.5	3.5	39.1	0.29
Toluene	110	27.0	86.6	13.4	23.4	0.17
p-Xylene	110	45.0	82.5	17.5	37.1	0.27
DMF	135	49.6	72.0	28.1	35.7	0.26
DMSO	130	15.7	99.5	0.5	15.6	0.11

^{a} Rate of the formation of benzaldehyde per unit mass of the deposited gold per unit time.

Table 2 Surface area and Au particle size of the Au/U_3O_8 catalysts prepared by different methods (Au available for deposition on U_3O_8 = 8.0 wt%) and turn-over frequency (TOF) of the catalysts in the benzylalcohol-to-benzaldehyde oxidation

Method of catalyst preparation	Concentration of Au in the catalyst (wt%)	Calcination temp./°C	Surface area/m^2 g^{-1}	Particle size of Au/nm	TOF^a	
					/mol g^{-1}$_{(cat)}$ h^{-1}	/mol g^{-1}$_{(Au)}$ h^{-1}
Impregnation	8.0	400	6.2	34.6	0.010	0.13
Co-precipitation	4.7	400	5.2	12.2	0.016	0.35
DP	5.1	400	8.0	19.1	0.017	0.34
HDP	8.0	400	6.5	14.2	0.029	0.37
HDP	8.0	600	5.0	—	0.016	0.20
HDP	8.0	900	3.8	33.2	0.012	0.15

^{a} Rate of the formation of benzaldehyde per unit mass of the catalyst or deposited gold per unit time.

Table 3 Results for the solvent-free oxidation of different benzyl alcohols by molecular oxygen over the Au(8 wt%)/U_3O_8 (HDP) catalyst (calcined at 400 °C)

Substrate	Conversion (%)	Selectivity (%)		Aldehyde yield (%)	TOF[a]/mol g^{-1}$_{(Au)}$ h^{-1}
		Aldehyde	Ester		
3-NO$_2$PhCH$_2$OH	40.8	98.5	1.5	40.2	0.30
3-PhOPhCH$_2$OH	42.5	98.0	2.0	41.7	0.31
4-MeOPhCH$_2$OH	67.0	92.5	7.5	62.0	0.46
PhCH$_2$CH$_2$OH	42.1	43.0	57.0	18.0	0.13

[a] Rate of the formation of benzaldehyde per unit mass of the deposited gold per unit time.
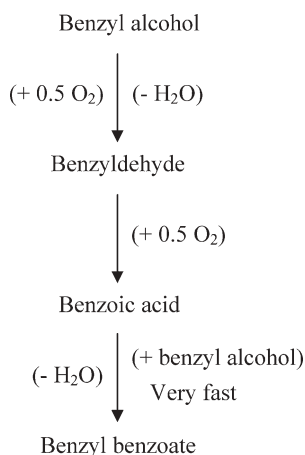
3.3 Influence of catalyst calcination temperature

The results in Fig. 3 show a strong influence of the temperature, at which the Au(8 wt%)/U_3O_8 (HDP) catalyst (after the gold deposition) was calcined, on the performance of the catalyst in the oxidation. With increasing calcination temperature, both the catalytic activity (benzyl alcohol conversion) and benzaldehyde selectivity pass through a maximum, while the selectivity for the benzyl benzoate formation is passed through a minimum, at the catalyst calcination temperature of 400 °C. This shows that the catalyst shows best performance when it is calcined at 400 °C. The lower performance of the catalyst at higher calcination temperatures (600 and 900 °C) is because of the increased gold particle size (Table 2) and consequently due to the decreased gold surface area. However, the lower catalyst performance at the lower calcination temperatures (100 and 200 °C) may be due to the presence of moisture in the catalyst.

3.4 Influence of reaction time

When the reaction period is increased from 1 to 10 h, the benzyl alcohol conversion and the selectivity for benzyl benzoate are increased but the selectivity for benzaldehyde is decreased (Fig. 4). The decrease in the benzaldehyde selectivity is attributed to the increase in the rate of benzyl benzoate formation due to the increase in the conversion of benzyl alcohol with increasing the reaction period. The benzaldehyde selectivity decrease is, however, quite small.

It is interesting to note that, at the lower reaction periods, the conversion is increased almost exponentially with the time,

Benzyl alcohol

(+ 0.5 O_2) | (- H_2O)

↓

Benzyldehyde

(+ 0.5 O_2)

↓

Benzoic acid

(- H_2O) | (+ benzyl alcohol)
Very fast

↓

Benzyl benzoate

Fig. 6 Reaction scheme for the benzyl alcohol-to-benzaldehyde oxidation over Au/U_3O_8 catalyst.

indicating autocatalytic conversion of benzyl alcohol. This is expected because of the fact that the benzoic acid formed in the oxidation reacts instantly with the reactant (benzyl alcohol), thereby increasing the benzyl alcohol conversion with the formation of benzyl benzoate.

3.5 Influence of reaction temperature

As expected, the influence of reaction temperature on the benzyl alcohol conversion is very strong (Fig. 5). However, the selectivity for benzaldehyde or benzyl benzoate is influenced appreciably only when the temperature is increased from 130 °C to 160 °C. Even at the higher temperature (160 °C), no net formation of benzoic acid was observed.

As observed in the earlier studies (Fig. 2 and Fig. 4), the benzaldehyde selectivity was decreased with increasing the benzyl alcohol conversion, further confirming benzaldehyde as an intermediate product as shown in the reaction scheme (Fig. 6).

3.6 Influence of the presence of solvent

The results in Table 1 clearly reveal that, the benzyl alcohol-to-benzaldehyde oxidation process shows the best performance in the absence of any solvent. Both the conversion and benzaldehyde selectivity in the oxidation in the presence of toluene, p-xylene, DMF (dimethylformamide) or DMSO (dimethylsulfoxide), as a solvent, are lower than that observed in the absence of any solvent.

The observed lower benzyl alcohol conversion activity of the catalyst in the presence of different solvents is mostly attributed to the competitive adsorption between the solvent and benzyl alcohol on the catalyst and thereby occupying part of the active sites of the catalyst by the adsorbed solvent molecules.

3.7 Oxidation of substituted benzyl alcohols

Results of the solvent-free oxidation of different substituted benzyl alcohols to corresponding aromatic aldehydes over the Au/U_3O_8 (HDP) are presented in Table 3.

The results reveal that, apart from benzyl alcohol, substituted benzyl alcohols can also be oxidized by molecular oxygen to their corresponding aldehydes with good to high selectivity and conversion in the absence of any solvent, using the environmentally-friendly, easily separable and reusable Au/U_3O_8 (HDP) catalyst. The catalytic activity in the oxidation, however, depends upon the substitutent group in the benzyl alcohols. For 4-methoxy benzyl alcohol, the catalyst

shows both high activity and high benzaldehyde selectivity. Whereas, for $PhCH_2CH_2OH$, the catalyst shows good activity but comparable selectivity for both aldehyde and benzyl benzoate. For 3-nitro- or 3-hydroxy-benzyl alcohol, the catalyst shows high aldehyde selectivity at a good conversion (Table 3).

4. Conclusions

Chlorine-free benzaldehyde can be produced by an environmentally-friendly solvent-free liquid phase oxidation of benzyl alcohol with molecular oxygen, even at low pressure (1.5 atm), using nano-gold supported U_3O_8, particularly prepared by the homogeneous deposition precipitation method. The Au/U_3O_8 (HDP) is a highly promising, easily separable and reusable catalyst for the solvent-free selective oxidation process. There is an optimum catalyst calcination temperature (400 °C) for achieving the highest benzyl alcohol conversion and benzaldehyde selectivity. The better process performance (i.e. higher benzaldehyde yield and selectivity) is achieved when the catalyst contains gold at higher concentration and also with smaller particle size.

With increasing reaction period or temperature, the benzyl alcohol conversion is increased markedly, but there is a small decrease in the selectivity for benzaldehyde and a small increase in the formation of benzyl benzoate. In the presence of commonly used solvent (toluene, p-xylene, dimethyl formamide or dimethyl sulfoxide), the process performance (both the benzaldehyde yield and selectivity) is found to be inferior to that observed in the absence of any solvent.

The Au/U_3O_8 (HDP) is also a highly promising catalyst for the solvent-free oxidation of substituted benzyl alcohols by O_2 to corresponding aldehydes and/or esters with their good selectivity and yields.

Acknowledgements

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