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Catalysis Communications



Short Communication

Solvent-free selective oxidation of primary alcohols-to-aldehydes and aldehydes-to-carboxylic acids by molecular oxygen over MgO-supported nano-gold catalyst

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ARTICLE INFO

Article history: Received 13 May 2011 Received in revised form 1 July 2011 Accepted 1 July 2011 Available online 8 July 2011

Keywords: Alcohols Aldehydes Au/MgO Molecular oxygen Solvent-free oxidation

ABSTRACT

Magnesium oxide supported nano-gold catalyst (prepared by the homogeneous deposition precipitation technique) showed high activity/selectivity and excellent reusability in the oxidation of different primary alcohols and aldehydes to corresponding aldehydes and carboxylic acids, respectively, by molecular oxygen (under atmospheric pressure) in the absence of any solvent. Influence of the catalyst calcination temperature (400–900 °C), reaction temperature (50–120 °C) and use of different solvents (viz. toluene, p-xylene, DMF or DMSO) on the oxidation reaction has also been studied.

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1. Introduction

Liquid phase primary alcohols-to-aldehydes and aldehydes-tocarboxylic acid oxidations are important organic transformation reactions. Particularly, the benzyl alcohol-to-benzaldehyde oxidation is commercially important for the production of chlorine-free benzaldehyde, required for perfumery and pharmaceutical industries. To be a cost effective and environmentally-friendly (or green) process, the alcohol or aldehyde oxidation with high product selectivity and yield must be accomplished under solvent-free condition, using molecular oxygen (which is not only a clean but also the cheapest oxidizing agent) as an oxidant and also using a highly active solid catalyst (which is easily separable and also reusable) in the process.

A few studies have been reported earlier for the benzyl alcohol-tobenzaldehyde oxidation by clean oxidizing agents (hydrogen peroxide or oxygen) but in the presence of organic solvent, using solid catalysts, such as Pd/C [1], Pd-hydrotalcite [2], Pd-Ag/pumice [3], Ru-Co-Al-hydrotalcite [4], Ni-hydrotalcite [5,6] and NiO₂ [7]. Solvent-free oxidation of benzyl alcohol-to-benzaldehyde by *tert*-butyl hydroperoxide (which leaves *tert*-butanol as a co product and hence it is not a clean oxidizing agent) has also been reported making use of solid catalysts, such as MnO_4^{-1} -exchanged hydrotalcite [8], transition metal containing LDH (Layered Double Hydroxides) and/or mixed hydrotalcite [9], Au/TiO₂ [10], Au/MgO [11] and Au/U₃O₈ [12]. Use of a few noble metal (Pd or Ru) containing solid catalysts for the alcohol oxidation has also been reported [13–20].

Aldehydes can be oxidized to carboxylic acids by atmospheric oxygen but with very low product yield [21]. Several other oxidizing reagents have been reported for obtaining good product yields in the oxidation of aldehydes. However, the commonly used oxidants like chromic acid, potassium permanganate (in acidic, basic and neutral solution), bromine and nitric acid are not suitable for the aldehvde-tocarboxylic acid oxidation because of the formation of hazardous waste. A few studies have been reported on the oxidation of aldehvde using homogeneous or heterogeneous catalysts/reagents, such as Cotype ion-exchange membrane [22], transition metal ions [23] and silica gel supported potassium permanganate [24] in stoichiometric amounts. The stoichiometric reactions have severe limitations, such as the formation of large amounts of liquid and solid wastes and the corrosive nature of the reaction medium. Recently, we have observed that MnO_4^{-1} -exchanged hydrotalcite shows high activity for the oxidation of benzaldehyde to benzoic acid by tert-butyl hydroperoxide [8]. A use of Ni-acetate catalyst in ionic liquid for the aromatic aldehyde oxidation has also been reported [25]. Our earlier preliminary studies on the solvent-free oxidation of benzyl alcohol to benzaldehyde by molecular oxygen over a number of supported nanogold catalysts revealed that the Au/MgO catalyst, prepared by the homogeneous deposition precipitation method, shows very good activity and high selectivity in the alcohol oxidation [26]. In this paper, we report our investigation on the solvent-free selective oxidation of different primary alcohols and aldehydes to corresponding aldehydes



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^{1566-7367/\$ -} see front matter © 2011 Published by Elsevier B.V. doi:10.1016/j.catcom.2011.07.001

Table 1

Performance of the Au/MgO catalyst in the oxidation of different primary alcohols by molecular oxygen (reaction conditions: alcohol = 30 mmol, pressure = 0.95 atm, catalyst = 0.1 g, bath temperature = 120 °C and reaction time = 5 h).

Entry	Alcohol	Product	Conversion of alcohol (%)	Selectivity (%)	
				aldehyde	ester
1	2	3	4	5	6
1	Ph-CH ₂ OH	Ph-CHO	55.5	95.0	5.0
2	3NO2-Ph-CH2OH	3NO ₂ -Ph-CHO	47.5	98.5	1.5
3	30Ph-Ph-CH ₂ OH	30Ph-Ph-CHO	48.5	98.0	2.0
4	3MeO-Ph-CH ₂ OH	3MeO-Ph-CHO	52.0	90.0	10.0
5	2MeO-Ph-CH ₂ OH	2MeO-Ph-CHO	53.0	90.5	9.4
6	4MeO-Ph-CH ₂ OH	4MeO-Ph-CHO	68.0	95.0	5.0
7	Ph-CH ₂ -CH ₂ OH	Ph-CH ₂ -CHO	46.0	60.5	39.5
8	Ph-CH ₂ -CH ₂ - CH ₂ OH	Ph-CH ₂ -CH ₂ -	42.0	85.5	14.4
9	4MeO-Ph-CH ₂ - CH ₂ -CH ₂ OH	4MeO-Ph-CH ₂ - CH ₂ -CHO	30.2	78.5	21.4
10	4 <i>t</i> -(CH ₃) ₃ -Ph- CH ₂ OH	4 <i>t</i> -(CH ₃) ₃ -Ph- CHO	60.0	88.0	12.0

and carboxylic acids, respectively, by molecular O_2 (at atmospheric pressure) over the Au/MgO catalyst. Influence of the catalyst calcination temperature, reaction temperature and use of different solvents on the process performance has also been studied. The catalyst showed high activity/selectivity and excellent reusability in both oxidation processes.

2. Experimental

2.1. Catalyst preparation and characterization

The preparation and characterization of Au/MgO catalyst (Au loading = 0.38 mmol/g, surface area = $47 \text{ m}^2/\text{g}$ and Au particle size = 9.0 nm) have been described elsewhere [11,27]. The gold on MgO was deposited by the homogeneous deposition–precipitation technique [28,29]. For studying the influence of catalyst calcination temperature on the process performance, the Au/MgO catalyst after its preparation was calcined in muffle furnace at different temperatures (200 °C, 400 °C, 700 °C or 900 °C) for a period of 2 h. Unless otherwise mentioned, the catalyst calcination temperature was 400 °C.

2.2. Catalytic reactions

The oxidation of alcohols or aldehyde by molecular O_2 over the MgO supported gold catalyst was carried out in a magnetically stirred round bottom flask (capacity: 25 cm^3), provided with a mercury thermometer and a reflux condenser connected to O_2 filled rubber balloon, under near atmospheric pressure. Unless otherwise mentioned, the oxidation was carried out in the absence of solvent at the following reaction conditions: reaction mixture = 30 mmol alcohol or 10 mmol aldehyde, catalyst = 0.1 g, pressure = 0.95 atm., bath temperature = 120 °C, reaction time = 5 h. In case of alcohol oxidation, after the completion of reaction, the catalyst was removed from the reaction mixture by filtration. The reaction products and unconverted

reactant were analyzed by gas chromatograph with a flame ionization detector, using a SE-30 column and N_2 as a carrier gas. While in case of aldehyde oxidation, after the completion of reaction, the reaction mixture was treated with ethyl acetate (30 ml). The catalyst was separated by filtration and washed with ethyl acetate. The filtrate was then treated with water and the organic layer was separated. The product from the organic layer was purified by column chromatography using silica gel with petroleum ether/ethyl acetate as eluent. The catalyst was further washed with acetone, dried and reused. The reaction product isolated by column chromatography, was confirmed by NMR and IR spectroscopy.

3. Results and discussion

3.1. Oxidation of alcohols and aldehydes over Au/MgO

Results of the oxidation of different primary alcohols by molecular O_2 over the Au/MgO catalyst at near atmospheric pressure are presented in Table 1. From the results following important observations can be made:

- In the oxidation of primary alcohols, the products observed are only the corresponding aldehyde and ester. A corresponding carboxylic acid is not detected in the products. The formation of significant amount of ester, however, indicates that a corresponding acid is formed in a significant amount in the alcohol oxidation but, as soon as formed, it is reacted with the alcohol, leading to the ester formation. The consecutive reactions involved in the alcohol oxidation are given in Scheme 1. The reaction step 3 (i.e. esterification) is expected to be much faster than the reaction steps 1 and 2.
- − The catalyst showed very good activity in the oxidation of all the alcohols, depending upon the nature of substituent group (R') and/or the length of alkyl chain [(CH₂)n] in the alcohol. It shows highest activity for the oxidation of 4-methoxy benzyl alcohol (entry 6) and lowest activity for the oxidation of 4-MeO-(C₆H₄)-(CH₂)-CH₂OH (entry 9). In most cases, the aldehyde selectivity was quite high (90–98%), A lower aldehyde selectivity (consequently higher ester selectivity) was observed for the oxidation of alcohols with longer alkyl chain (CH₂)n- with n≥0 (entry 7 to 9).
- For the different isomers of methoxy benzyl alcohol, the catalyst showed the highest activity and selectivity in the oxidation of 4methoxy benzylalcohol (entry 6). Its performance for the oxidation of other two isomers was comparable (entries 4 and 5).

Result showing the catalyst performance in the oxidation of different aldehydes [represented by a general formula: $R-(CH_2)n-CHO$ where R = alkyl or aryl (with or without substitution) and n = 0 or 1] to corresponding carboxylic acids by molecular O_2 at near atmospheric pressure are presented in Table 2. Important observations made from the result are as follows:

The catalyst showed a very good activity for the oxidation of benzaldehyde with high benzoic acid yield of 95% (entry 1). However, the product yield in the oxidation of substituted benzaldehydes is significantly lower (69–89%) than that observed for the benzaldehyde oxidation (entry 2–8). Also, the product yields for the oxidation of aliphatic aldehyde (75%) is also lower (entry 10). Nevertheless, the catalyst showed good activity even for the oxidation of substituted

$$\mathbf{R}\text{-}\mathbf{CH}_{2}\text{-}\mathbf{OH} \xrightarrow{(1)} \mathbf{R}\text{-}\mathbf{CHO} \xrightarrow{(2)} \mathbf{R}\text{-}\mathbf{COOH} \xrightarrow{(3)} \mathbf{RCOOCH}_{2}\mathbf{R}$$

$$\xrightarrow{(+O) (-H_{2}O)} (+O) \xrightarrow{(+O)} (+O$$

 $[R = R'-(C_6H_4)-(CH_2)n, where R' = H, OCH_3, OPh, NO_2 or t-butyl and n = 0,1 or 2]$

Table 2

Performance of the Au/MgO catalyst in the oxidation of different aldehydes by molecular oxygen (reaction conditions: aldehyde = 10 mmol, catalyst = 0.1 g, pressure = 0.95 atm, bath temperature = 120 °C, reaction time = 5 h).

Entry	Aldehyde	Product	Isolated yield (%)
1	Ph-CHO	Ph-COOH	95
2	3-MeO-Ph-CHO	3-MeO-Ph-COOH	83
3	4-MeO-Ph-CHO	4-MeO-Ph-COOH	89
4	Ph-CH ₂ -CHO	Ph-CH ₂ -COOH	80
5	4t-(CH ₃) ₃ -Ph-CHO	$4t-(CH_3)_3-Ph-COOH$	75
6	2-Br-Ph-CHO	2-Br-Ph-COOH	85
7	4Me-Ph-CHO	4Me-Ph-COOH	82
8	3Me-Ph-CHO	3Me-Ph-COOH	69
9	(2-NC ₅ H ₄)-CHO	$(2-NC_5H_4)-COOH$	83
10	CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -	CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -	75
	CH ₂ -CHO	СООН	
11	CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -	CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -	93 ^a
	CH ₂ -CHO	CH ₂ -COOH	
12	3Me-Ph-CHO	3Me-Ph-COOH	90 ^a

^a Reaction time was 9 h

benzaldehydes and aliphatic aldehydes to corresponding carboxylic acids. It also showed good activity for the oxidation of pyridine-2-carboxaldehyde to pyridine-2-carboxylic acid (entry 9). Higher carboxylic acid yield could be obtained by increasing the reaction period (entries 11 and 12).

In both the oxidation reactions, the catalyst can be reused several times. In the 4-methoxy benzyl alcohol-to-4methoxy benzyldehyde oxidation, the alcohol conversion in the 5th reuse of the catalyst was 67.5% with the aldehyde selectivity of 95%. Also, in the benzaldehyde oxidation, the isolated yield of benzoic acid in the 4th reuse of the catalyst was 95%.

Influence of the reaction temperature, catalyst calcination temperature and use of different solvents in the 4-methoxy benzyl alcohol-to-4-methoxy benzaldehyde and benzaldehyde-to-benzoic acid oxidations over the catalyst have also been studied.

3.2. Influence of reaction temperature

Results showing the influence of reaction temperature on the conversion and selectivity or product yield in the solvent-free 4-methoxy benzyl alcohol-to-4-methoxy benzaldehyde and benzaldehyde-tobenzoic acid oxidation reactions over the catalyst are presented in Fig.1.

Up to the temperature of 80 °C, there was almost no reaction. With increasing the temperature above 80 °C, the conversion in the alcohol oxidation and the isolated product yield in the benzaldehyde oxidation are increased exponentially. In the alcohol oxidation, the selectivity for aldehyde is decreased while that for ester is increased with increasing the temperature.

3.3. Influence of catalyst calcination temperature

Results showing the influence of calcination temperature of the Au/MgO catalyst on its performance in the 4-methoxy benzyl alcoholto-4-methoxy benzaldehyde and benzaldehyde-to-benzoic acid oxidation reactions under solvent-free conditions are presented in Fig.2.

In both oxidation reactions, the catalyst showed best performance when it was calcined at 400 °C; the product yield in both cases passes through a maximum at the catalyst calcinations temperature of 400 °C. A similar observation was made earlier for the benzyl alcoholto-benzaldehyde oxidation by tert-butyl hydroperoxide over the same catalyst [11]. The poor performance of the catalyst calcined at 200 °C may be due to incomplete decomposition of the catalyst precursor and/or because of the presence of moisture in the catalyst. The decrease in the catalyst performance with increasing the calcinations temperature above 400 $^\circ C$ (i.e. at 700 $^\circ C$ and 900 $^\circ C)$ is expected mostly because of the sintering of gold particles in the catalyst. The Au particle size of the catalyst is increased from 9 nm to 36 nm with increasing the temperature from 400 °C to 900 °C [27,30]. The increased Au particle size has, however, no significant effect on the aldehyde selectivity in the alcohol oxidation. The role of MgO in the catalyst is to separate gold particles from each other and thereby to avoid their growth through Au particles – MgO (support) interactions. The high



Fig. 1. Influence of reaction temperature on the solvent-free a) 4-methoxy benzyl alcohol-to-4-methoxy benzaldehyde oxidation and b) benzaldehyde-to-benzoic acid oxidation.



Fig. 2. Influence of catalyst calcination temperature on the solvent-free a) 4-methoxy benzyl alcohol-to-4-methoxy benzaldehyde oxidation and b) benzaldehyde-to-benzoic acid oxidation.

specificity of the oxidation reactions is attributed to the nano gold particles – MgO (support) interactions.

3.4. Influence of the presence of solvent

Results showing the influence of the use of different solvents in the oxidation of 4-methoxy benzyl alcohol to 4-methoxy benzaldehyde on the catalyst performance in the alcohol oxidation reaction are presented in Table 3.

The results clearly reveal that the catalyst shows best performance in the alcohol-to-aldehyde oxidation process in the absence of any solvent. The alcohol conversion was the highest in the absence of solvent. The selectivity for aldehyde was also the highest in the absence of solvent, except in the case of DMSO as the solvent. The observed much lower aldehyde yield in the presence of solvent may be a consequence of a competitive adsorption of solvent molecules on the catalyst surface preventing ready access to the active sites of the catalyst.

Table 3

Performance of the Au/MgO catalyst in the oxidation of 4-methoxy benzyl alcohol by molecular oxygen in the presence of different solvents (bath temperature 120 0 C and reaction time = 5 h) (DMF = dimethylformamide, DMSO = dimethylsulfoxide).

Entry	Solvent	Conversion of 4-methoxy alcohol (%)	Selectivity (%)	
			Aldehyde	Ester
1	Toluene	25.0	80.0	20.0
2	p-Xylene	39.2	79.5	20.4
3	DMF	46.0	72.0	28.0
4	DMSO	20.5	95.5	4.4
5	Nil	68.0	95.0	5.0

4. Conclusions

Nano-gold supported on MgO (prepared by homogeneous deposition precipitation method) shows very good catalytic activity/selectivity in the primary alcohols-to-aldehydes and aldehydes-to-carboxylic acid oxidations by molecular oxygen at near atmospheric pressure under solvent-free condition. Both the oxidation protocols are green/ environmentally friendly. In both cases, the catalyst can be easily removed from the reaction mixture and reused several times without a significant loss of its catalytic activity. The catalyst shows inferior performance in the presence of different solvents and its activity in both the processes is strongly influenced by its calcination temperature and also by the reaction temperature. The catalyst shows its optimum performance in both processes when it is calcined at 400 °C.

Acknowledgments

VRC and DKD are grateful to the National Academy of Sciences, India, for the NASI Senior Scientist Platinum Jubilee Fellowship and Project Assistantship, respectively.

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