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Solvent free oxidation of benzyl alcohol and its derivatives into corresponding aldehydes on nano structured ZnO as catalyst

Sorror Sadeghi* and Fariba Maleki
Islamic Azad University of Kermanshah, Department of Chemistry, Kermanshah 6718997551, Iran.

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Abstract: In this article a simple and convenient method is reported for the effective conversion of benzyl alcohol and its derivatives to their corresponding aldehydes in the presence of nano structured ZnO as the catalyst. According to the results, this method has high reaction rates, high yields of the products, and the best advantage of this oxidation is solvent-free condition.

Keywords: Nano catalyst, ZnO, Oxidation, Potassium permanganate, Benzyl alcohol.

Introduction

Carbonyl compounds in the chemicals industry are precursors with wide applications. The oxidation of alcohols to carbonyl products is an important conversion in organic chemistry. Aromatic aldehydes have attracted a great deal of attention as important materials for the production of other chemicals.

Several methods are known for selective oxidation of alcohols to the corresponding carbonyl compounds. However, they are not free from some disadvantages.

Oxidation of benzoins are efficiently performed with zeolite A, without any oxidizing agent under solvent-free conditions and microwave irradiation; the method is clean, fast, facile, efficient, low-cost and environmentally benign and operates selectively only on benzoins [1].

At the other research a new highly selective heterogeneous catalyst is developed from phosphomolybdic acid for the oxidation of alcohols by supporting poly oxomolybdate anions on vanadium–aluminum mixed oxide. The Keggin anion was found to be stable on the surface of vanadium–aluminum mixed oxide unlike alumina [2]. A TEMPO-catalyzed selective oxidation of alcohols to the corresponding aldehydes and ketones using $NaIO_4$ as the terminal oxidant has been reported [3]. An efficient and selective aerobic oxidation of alcohols to the corresponding aldehydes or ketones in the ionic liquid [bmim][PF_6] using CuCl/TEMPO/base catalytic system has been developed [4].

N-tert-Butylbenzene sulfenamide (1)-catalyzed oxidation of various primary and secondary alcohols to the corresponding aldehydes and ketones was efficiently carried out by using *N*-chlorosuccinimide (NCS) in the coexistence of potassium carbonate and molecular sieves 4 Å at easy-to-control the range of temperatures [5]. A new trimetallic Co-Ce-Ru compound acted as a highly efficient heterogeneous catalyst for the oxidation of various alcohols into the corresponding carbonyls, including less-reactive primary alcohols, in the presence of molecular oxygen under mild reaction conditions [6].

For oxidation of organic materials, one turns often to high-valent metal oxides or their mineral salts like potassium permanganate ($KMnO_4$). In this article a simple and convenient method is reported for the effective conversion of benzyl alcohol and its derivatives to their corresponding aldehydes in the presence of Nano structured ZnO as the catalyst [7].

A selective oxidation of alcohols to corresponding carbonyl compounds in room temperature ionic liquid [bmim]BF_4 was achieved by using sodium hypochlorite as the oxygen source [8].

*Corresponding author. Tel: +98 831 7243181; Fax: +98 831 7252218; E-mail: Soroor.sadeghi@yahoo.com

Keggin-type heteropoly acids revealed high catalytic activity for swift and selective oxidation of various hydroxy functionalities to the corresponding carbonyl groups using ferric nitrate as an oxidant under mild solvent-free conditions [9].

A selective oxidation of benzylic alcohols to the corresponding aldehydes in room temperature ionic liquid was achieved by using TEMPO/HBr/H_2O_2 system, and both ether-insoluble acetamido-TEMPO and ionic liquid [bmim]PF_6 can be successfully recovered and reused for the oxidation of the same or different substrate [10].

Alumina or silica gel are used as catalysts for a solvent-free oxidation of benzoins to the corresponding benzils. These catalysts are easily recovered after completion of the reactions, which are carried out either by heating in sand bath or using microwave irradiation. The main advantages of these reactions are: (1) easy recovery of the alumina or the silica gel upon completion of the reactions; (2) yields are high and the products contain minimum by-products; (3) no environmental pollution; (4) low cost as no reaction solvents are required.

The supported ruthenium hydroxide (Ru(OH)x) catalysts prepared with three different TiO_2 supports and an Al_2O_3 support showed the high catalytic activity for the oxidation of alcohols with molecular oxygen. In the presence of the most active catalyst, various kinds of alcohols could be converted into the corresponding carbonyl compounds in high yields [11].

Surface complex formed by the adsorption of a benzyl alcoholic compound. This absorption is due to the surface complex between nano ZnO and benzyl alcohol, and is assigned to the charge transfer from benzyl alcohol to nano ZnO on the surface complex [12].

Results and discussion

The effect of nano catalyst quantity carried out using different amounts of it.

The results show that increasing the amount of nano catalyst in solvent free condition and at 30 minutes will increase the reaction yield. The optimum concentration of nano catalyst was 0.5 mmol and after that has no more increasing in yield of the reaction. The free-nano ZnO oxidation reaction has also been checked.

Table 1: Oxidation of benzyl alcohol (1 mmol) by $KMnO_4$ (0.5 mmol) in the presence of various amount of nano catalyst in solvent free condition

Entry	substrate	nano ZnO(mmol)	time(min)	yield (%)
1	benzyl alcohol	0	30	65
2	benzyl alcohol	0.25	30	80
3	benzyl alcohol	0.5	30	90
4	benzyl alcohol	0.75	30	90

Effect of solvents, carried out by using several solvents as mentioned before, the obtained results showed the optimum oxidation at solvent free condition (90 % at 30 minutes). We have conducted the oxidation of structurally different derivatives of this alcohol with this oxidation system under solvent- free conditions using only 0.5 mmol of the ZnO nanocatalyst.

Table 2. Oxidation of benzyl alcohol (1 mmol) by $KMnO_4$ (0.5 mmol),in various organic solvents

Entry	Solvent	nano ZnO (mmol)	Time (min)	Yield (%)
1	dichloromethane	0.5	30	50
			60	60
2	n-hexane	0.5	30	40
			60	50
3	ethyl acetate	0.5	30	70
			60	80
4	acetonitrile	0.5	30	80
			60	30
5	solvent free	0.5	30	90

Oxidations of benzyl alcohol and its derivatives performed on nano ZnO as catalyst. Oxidation of benzyl alcohol and its derivatives, such as 4-methoxybenzyl alcohol, 2-methoxybenzyl 3-methoxybenzyl 2-chlorobenzyl alcohol 4-chlorobenzyl alcohol, 3-chloro benzyl alcohol, 4-bromobenzyl alcohol 2-bromobenzyl alcohol, 2-methylbenzyl alcohol, 3-methylbenzyl alcohol, 4-fluoro benzyl alcohol, into corresponding aldehydes proceeded at high conversion (99% in some cases) in lower than 30 minutes, and selectivity on the ZnO nano catalyst. All products are known and purified by column chromatography or TLC on silica gel, when necessary.

Table 3: Oxidation of benzyl alcohol derivatives (1 mmol) by $KMnO_4$ (0.5 mmol) in solvent free condition.

No.	substrate	Nano ZnO(mmol)	Time (min)	yield (%)
1	2-methoxy benzyl alohol	0.5	30	99
2	3- methoxy benzyl alcohol	0.5	30	99
3	4-methoxy benzyl alcohol	0.5	30	99
4	2- chloro benzyl alcohol	0.5	40	99
5	3- chloro benzyl alcohol	0.5	40	99
6	4- chloro benzyl alcohol	0.5	40	99
7	2- bromo benzyl alcohol	0.5	45	95
8	4- bromo benzyl alcohol	0.5	45	95
9	4-fluoro benzyl alcohol	0.5	30	99
10	2- methyl benzyl alcohol	0.5	30	95
11	3- methyl benzyl alcohol	0.5	30	95

Conclusion

According to the results, this method is suitable for the oxidation of benzyl alcohol and its derivatives to their aldehydes in up yields without over-oxidation to the carboxylic acids. Over-oxidation did not occur using this method.

The advantages of this method are high reaction rates, high yields of the products, and solvent-free condition.

Experimental

The mixture of nano ZnO (0.5 mmol,0.04 g) and potassium permanganate(0.5 mmol,0.079g) as an oxidant agent , stirred for 5 to 10 minutes both in the presence of solvents such as dichloro methane ,n-hexane, ethyl acetate, acetonitrile (2 mmol) or solvent free conditions, benzyl alcohol(1 mmol,1.03 ml,0.108 g) added to the mixture and stirred for 30 minutes.

The nano ZnO used as catalyst has Purity of: 99.5%, APS: 20 nm,SSA: 50 m^2/g, Morphology: nearly spherical, density: 5.606 g/cm.

The heterogeneous mixture filtered and the solvent removed, before the oxidation yield checked by TLC.

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