



Melamine-Schiff base/manganese complex with dendritic structure: An efficient catalyst for oxidation of alcohols and one-pot synthesis of nitriles

Milad Kazemnejadi^{a,b,*}, Mahsa Nikookar^b, Mohammad Mohammadi^b, Alireza Shakeri^c, Mohsen Esmaeilpour^{a,*}

^a Department of Chemistry, College of Science, Shiraz University, Shiraz 7194684795 Iran

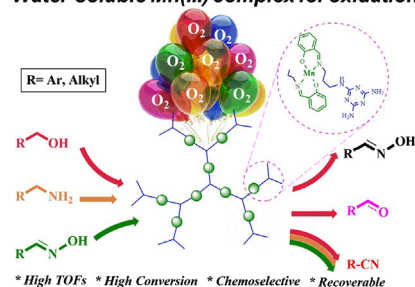
^b Department of Chemistry, College of Science, Golestan University, Gorgan 491774979, Iran

^c Faculty of Chemistry, College of Science, University of Tehran, Tehran 1417466191, Iran

GRAPHICAL ABSTRACT

Efficient and selective oxidation of alcohol to the corresponding carbonyl and/or nitrile and oxidation of amine to the corresponding nitrile can be carried out by a new recoverable water-soluble dendritic melamine-based Mn(III) complex in the presence of 2,4,6-trichloro-1,3,5-triazine (TCT) and O₂ at room temperature.

Water-soluble Mn(III) complex for oxidation



ARTICLE INFO

Article history:

Received 23 December 2017

Revised 16 May 2018

Accepted 16 May 2018

Available online 18 May 2018

Keywords:

Mn(III) complex
Water-soluble catalyst
Reusable
Nitriles
Alcohol oxidation
Amine oxidation

ABSTRACT

Efficient and selective oxidation of alcohol to the corresponding carbonyl and/or nitrile was carried out by a new water-soluble melamine-based dendritic Mn(III) complex (Melamine-Mn(III)-Schiff base complex) in the presence of 2,4,6-trichloro-1,3,5-triazine (TCT) and O₂ at room temperature. Also, the oxidation of amine to the corresponding nitrile with high selectivity and conversion was performed at room temperature using the current method and high amounts of turnover frequencies (TOFs) were obtained for reactions. This system was also applicable for direct preparation of oxime through oxidation of alcohol. The catalyst was characterized by Fourier-transform infrared (FTIR), ultraviolet-visible (UV-Vis), thermogravimetric analysis (TGA), energy-dispersive X-ray (EDX), X-ray photoelectron spectroscopy (XPS), CHN and inductively coupled plasma (ICP) analyses. Also, oxidation/reduction behavior of the catalyst was studied by cyclic voltammetry (CV). Moreover, chemoselectivity of the catalyst was discussed with various combinations. The water-soluble catalyst could be recycled from the reaction mixture and reused for several times with a very low losing in efficiency. The recovered catalyst was also investigated with various analyses. Finally, gram scale preparation of nitrile was evaluated by present method.

© 2018 Elsevier Inc. All rights reserved.

* Corresponding authors at: Department of Chemistry, College of Science, Shiraz University, Shiraz 7194684795 Iran (M. Kazemnejadi).

E-mail addresses: miladkazemnejad@yahoo.com (M. Kazemnejadi), mohsen.esmaeilpour1250@gmail.com (M. Esmaeilpour).

1. Introduction

Nitriles, as a key constituents in various natural products, are present in HIV protease inhibitors, 5-lipoxygenase inhibitors and many other biologically important molecules [1]. Also, they can be applied in the preparation of various valuable compounds such as polymers, agrochemicals, pharmaceuticals, and dyes [2]. They are widely used as important intermediates for conversion to heterocyclic compounds such as tetrazoles [3], thiazoles [4], oxazoles [5] and 2-oxazolines [6]. Moreover, nitriles can be readily transformed into amides, amines, esters, carboxylic acids, etc. [7]. Nitriles can be prepared from aldehydes [8], oxime ethers [9], thioamides [10], carboxylic acids and their esters [11], aldoximes [12], amides [13] and primary aliphatic nitro compounds [14]. An attractive approach to the synthesis of nitriles is the direct oxidation of alcohols, which are cheap and commercially available starting materials [15]. Some methods have been reported for the one-pot conversion of alcohols to nitriles including the treatment of H_5IO_6/KI [16], $NaIO_4/KI$ [17], $Ni^{2+}/S_2O_8^{2-}/OH^-$ [18], $MnO_2/MgSO_4$ [19], 1,3-diiodo-5,5-dimethylhydantoin or I_2 [20], KI or I_2 /tert-butyl hydroperoxide (TBHP) [21], $Ru(OH)_x/Al_2O_3/air$ [22], trichloroisocyanuric acid [23], copper salts/(2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO)/ O_2 [15], I_2 or $t-BuOCl/TEMPO$ [24] with ammonia as a nitrogen source.

Oxidative conversion of primary amines into the corresponding nitriles has also been studied well using $Mn_xCe_{1-x}O_s$ [25], $Pb(OAc)_4$ [26], AgO [27], cobalt peroxide [28], Co_3O_4 -based catalysts [29], $Cu/N,N'$ -dimethylethylenediamine (DMEDA)/TEMPO [30], $Cu(I)$ or $Cu(II)$ with oxygen [31], $RuCl_3$ and related Ru reagents [32], $Ru/activated\ carbon$ [33] and trichloroisocyanuric acid with TEMPO [7]. However, most of applied catalysts for the oxidation of benzylamines suffer from lack of selectivity due to various oxidation products (Scheme 1a). Oxidation of benzyl amine gives five [30] plausible products and as a result, it is not suitable for a reaction with no selectivity toward nitrile products. High temperature, pressure, toxic reagents, and wastes or their combinations are often employed to promote efficient nitrile formation.

Dehydration of aldoximes is another route for the preparation of nitriles that has been developed by some reagents such as TCT [12], SeO_2 [34], TCT/DMF complex [35], phosphonitrilic chloride [36], clay [37], etc. (Scheme 2). Among them, using DMF/TCT solution gave milder conditions and more efficient yields than others.

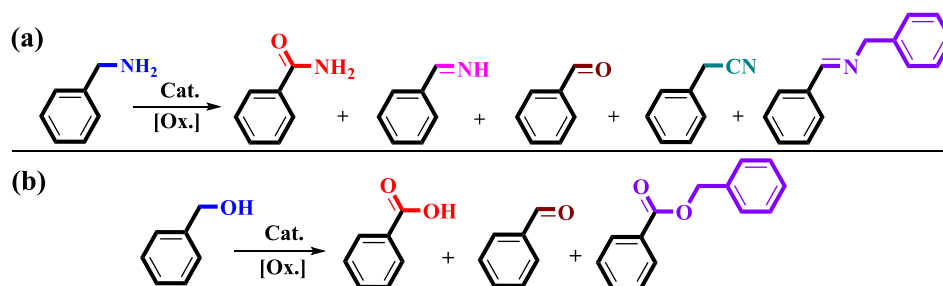
Carbonyl compounds are also useful intermediates in organic synthesis and can serve as valuable building blocks for the manufacturing of pharmaceuticals and agrochemicals [38]. These compounds can be readily prepared from alcohol oxidation. Various methods for the oxidation of primary alcohols to aldehydes have been developed in the literature [39]. However, there is a continuous demand to develop synthetic methods for discriminating efficiently various functional groups. In this point of view, chemoselective methods allow the oxidation of primary alcohols without the exhorting of competitive secondary alcohols.

Oxidation of benzyl alcohol gives three plausible products that is not suitable for a reaction with no selectivity toward aldehyde and/or nitrile target [40] (Scheme 1b). Relatively few methods allow this type of selectivity [41] and often the limitations that are associated with some of them, that make them highly desirable novel, mild, and selective procedures.

Due to lower toxicity as well as low cost of Mn complexes than other transition metal complex systems, they attracted great deal of attentions in case of oxidation programs [38]. Various approaches have been reported for Mn(III) and Mn(II) salts as well as their complexes for the oxidation of alcohols [10,38]. In this study, one-pot transformation of alcohol to nitrile was firstly performed by alcohol oxidation using a recoverable water-soluble melamine-Mn(III)-Schiff base complex in the presence of molecular oxygen, as a green and readily available oxygen source followed by a method which has been previously reported by De Luca et al. [35] in which TCT/DMF complex was considered for transformation of oxime to nitrile in mild conditions. Next, we will show the capability of this methodology for the oxidation of various benzyl amines, benzyl alcohols, aliphatic amines and aliphatic alcohols to corresponding nitriles as well as chemoselective oxidation of benzyl alcohols and aliphatic alcohols to aldehydes. Chemoselectivity behavior, mechanism studies, scalability, recoverability and kinetic of the process were also investigated in this study.

2. Experimental

All chemicals were purchased from Sigma and Fluka and used without any further purification. All solvents were distilled and dried before use. The progress of reactions were followed by thin layer chromatography (TLC) on silica gel or gas chromatography (GC) using a Shimadzu-14B gas chromatography equipped with HP-1 capillary column and N_2 as a carrier gas. Anisole was used as an internal standard. FTIR spectra were obtained using a BRUKER EQUINOX 55 FTIR spectrophotometer using KBr pellet. Nuclear magnetic resonance (NMR) spectra (1H and ^{13}C) were recorded in $CDCl_3$ and $DMSO-d_6$ using 300 MHz instrument. Cyclic voltammetry (CV) was performed using a BAS CV-27 voltammograph. The sample cell consisted of a double-walled glass crucible with an inner volume of 15 mL, which was fitted with a Teflon lid incorporating a three-electrode system and argon bubbler. The cell temperature was maintained at 25.0 ± 0.1 °C by means of a HAAKE D8 recirculating bath. BAS 2013 Pt electrodes (1.6 mm diameter) were used as the working and counter electrodes. Elemental analyses (C, H, N) were done using a Perkin Elmer-2004 instrument, and UV-Vis analyses were carried out on UV Spectrolab BEL photonic. X-ray photoelectron spectroscopy (XPS) measurements were performed using an XR3E2 (VG Microtech) twin anode X-ray source with $AlK\alpha = 1486.6$ eV. The elements in the samples were probed by energy-dispersive X-ray (EDX) spectroscopy accessory to the Philips scanning electron microscopy (SEM). Thermal



Scheme 1. Possible products from oxidation of (a) benzyl amine and (b) benzyl alcohol.

Download English Version:

<https://daneshyari.com/en/article/6990170>

Download Persian Version:

<https://daneshyari.com/article/6990170>

[Daneshyari.com](https://daneshyari.com)