Available online at www.sciencedirect.com

ScienceDirect

Catalysis Communications 8 (2007) 205–210

CATALYSIS COMMUNICATIONS

www.elsevier.com/locate/catcom

Solvent-free selective oximation of aldehydes using facile and reusable heterogenous polyoxometalate

Razieh Fazaeli [a], Shahram Tangestaninejad [a,*], Hamid Aliyan [b]

[a] *Department of Chemistry, Isfahan University, Isfahan, 81746-73441, Iran*
[b] *Department of Chemistry, Islamic Azad University, Shahreza branch, 86145-311, Shahreza, Isfahan, Iran*

Received 10 August 2005; accepted 29 May 2006
Available online 16 June 2006

Abstract

The efficiency of various heteropoly compounds as well-known solid acids was investigated and a new procedure was developed for synthesis of *Z*-isomers of aldoximes. This method consistently has the advantage of excellent yields and short reaction times. Furthermore, the catalyst could be easily recovered after completion of the reaction and reused without a considerable loss of its activity.

Keywords: *E*- and *Z*-isomers of oximes; Aldoxime; Hydroxylamine hydrochloride; Heteropolyacid; Polyoxometalate; Supported catalyst; Heterogeneous

---

1. Introduction

A considerable attention has been recently paid to the solvent-free reactions [1,2]. These reactions are of interest from ecological point of view and offer advantages in terms of yield, selectivity and simplicity of the procedure [3]. Oximes are useful intermediates in organic chemistry and are utilized for purification and characterization of aldehydes and ketones [4]. Addition of hydroxylamine hydrochloride to carbonyls to yield oximes is one of the best examples of nonenzymatic addition–elimination reaction in organic synthesis [5]. These reactions usually produce both isomeric aldoximes (*Z* and *E*) (Scheme 1), which have biological activities. These isomers can be separated using chromatography or recrystallization techniques [6–9].

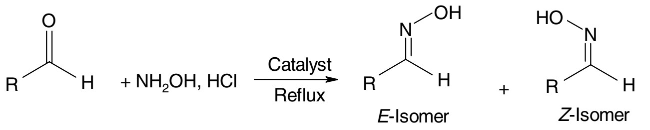
The reagents used for oximation of aldehydes and ketones can also catalyze the interconvertion of *Z*- and *E*- isomers. Since the reaction rate and equilibrium constant for a mixture of *Z* and *E* isomers is temperature dependent [10,11], therefore, is critical to control the temperature during the reaction.

Until now, very few improved procedures have been reported for the synthesis of *Z*-isomers of oximes using catalyst such as K_2CO_3 [12]. The development of efficient and versatile catalytic systems for selective conversion of aldehydes to oximes is an active ongoing research area and thus, further improvement for better yields and milder reaction conditions is needed. In view of this, we utilized polyoxometalates (POMs), as efficient Bronsted acid catalysts for controlling the stereochemistry of the reaction of hydroxylamine hydrochloride with aldehydes in solid state. The majority of POMs have structures composed of molybdenum and tungsten polyhedrons. Other elements occur in small amounts in these structures [13,14]. Dozens of structural types of polyoxometalates are known to date. The best known is the Keggin structure that is adopted by many polyoxometalates. The Keggin heteropoly anions are typically represented by the formula $[XM_{12}O_{40}]^{n-}$. They are composed of a central tetrahedron XO_4 surrounded by 12 edge- and corner-sharing metal-oxygen octahedral MO_6 (Fig. 1) [13].

---

[*] Corresponding author. Tel.: +98 311 7932705; fax: +98 311 6689732.
E-mail address: stanges@sci.ui.ac.ir (S. Tangestaninejad).

1566-7367/$ - see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.catcom.2006.05.055



Scheme 1.

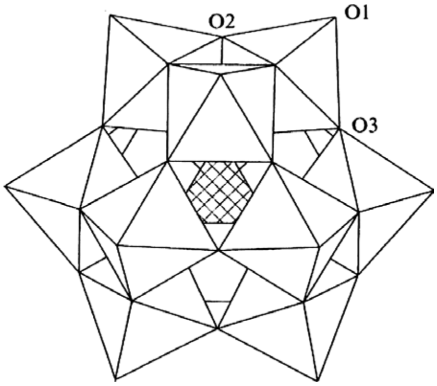


Fig. 1. The Keggin structure of the heteropoly anion $[XM_{12}O_{40}]^{n-}$: terminal (O1), edge-bridging (O2), corner-bridging (O3) oxygen atoms. Many polyoxometalate catalysts adopt this structure, for example, $H_3[PW_{12}O_{40}]$ and $H_3[PMo_{12}O_{40}]$.

Many results have been previously reported on the acidic properties of the dodecamolybdo(tungsto)phosphoric acids, $H_3PMo_{12}O_{40}$ or $H_3PW_{12}O_{40}$, and many promising reactions have been reported including: dehydration, alkylation, isomerization, oxy-dehydrogenation [15–17], oxydehydrogenation of alkanes [18], oxidation of alkylarenes [19], thioacetalization and transthioacetalization reactions [20], oxidation of amines and sulfides [21], epoxidation of allylic alcohols [22], cyclization of (+)-citronellal to (−)-isopulegol [23], Friedel–Crafts acylation [24], acylation reactions of anisole [25], Fries rearrangement of aryl esters [26], mesostructured aluminosilicate alkylation [27], decomposition of nonafluoropentanoic acid [28], gas phase synthesis of methyl *tert*-butyl ether [29], and esterification of acrylic acid by butanol [30].

Herein, we wish to report a suitable method for the use of metal oxides (KSF montmorillonite clay, Al_2O_3, Carbosil–SiO_2, TiO_2 and ZrO_2) as inorganic supports and poly(4-acetyrilmethyl)pyridinium chloride (or PMP) [31] and activated carbon as organic supports with Keggin-type polyoxometalates, $H_3PW_{12}O_{40}$ (denoted as HTP hereafter), and $H_3PMo_{12}O_{40}$ (denoted as HMP hereafter). These are cheap, reusable, and easily available for preparation of heterogeneous catalysts.

2. Experimental

Tungstophosphoric acid and molybdophosphoric acid (HTP and HMP) were purchased from Merck and were purified by extraction with Et_2O from aqueous solution of the acid. After treating at 150–300 °C for 1–2 h under reduced pressure, pure HTP and HMP were obtained [32]. All solvents were reagent grade. All reaction mixtures were monitored by GC or TLC (using 0.25 mm E-Merck silica gel 60 F_{254} precoated glass plates). Melting points were recorded on a Barnstead Elentrothermal 9200 apparatus, and are uncorrected. IR spectra were recorded on a Perkin–Elmer FT/IR-Impact 400D spectrophotometer. ^1H NMR spectra were recorded on a Bruker AW 500 MHz spectrometer.

2.1. General procedure for synthesis of the supported polyoxometalates

The supported HTP and HMP catalysts were prepared by method of incipient wetness. In a typical process, a 400 mg portion of HTP or HMP were dissolved in deionized water and impregnated dropwise onto 1600 mg poly(4-acetyrilmethyl)pyridinium chloride (or PMP), SiO_2 (Cabosil 20), activated carbon, Al_2O_3 (Merk), TiO_2 (Degussa), ZrO_2 and KSF-montmorilonite supports, under constant agitation. The resulting pastes were dried for 4 h at 110 °C and then calcined for 4 h at 250 °C (for all supports, except PMP) [32–35]. To obtain further information on the structure of the catalysts, we analyzed PMP–POM by infrared spectroscopy. The infrared spectrum of PMP–HTP exhibited strong vibrations at 1080 (P=O), 973 (W=O), 900 and 819 cm^{-1}, while that of HTP, they were observed at 1080, 982, 893 and 808 cm^{-1}, respectively. The results suggest that the structure of the phosphotungstic acid of unit PMP–POM was similar to that of HTP.

2.2. General procedure for preparation of Z-isomer of oximes in the presence of supported-POM

Hydroxylamine hydrochloride (1.5 mmol), supported-POM, (0.4 g) and aldehydes (1 mmol) were ground together in a mortar and pestle at room temperature for several minutes. The progress of reaction was monitored by GC and TLC. After complete disappearance of the starting material, the reaction mixture was cooled, washed with cold diethyl ether and filtered to remove the supported-POM. Then the mixture was poured into ice-water and extracted with cold diethyl ether (25 mL). The organic solution was dried over Na_2SO_4 to give the crude *Z*-aldoximes.

3. Results and discussion

The reaction of aldehyde with hydroxylamine hydrochloride in the presence of catalytic amounts of organic and inorganic supported-polyoxometalates (HTP or HMP) resulted in formation of aldoximes.

Various types of aromatic aldehydes, with electron donating (Table 1, entries 5 and 6) and withdrawing (Table 1, entries 1–4) groups, were rapidly condensed with hydroxylamine hydrochloride, and afforded the corresponding *Z*-isomers of oximes (OH cis to aryl) in excellent