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Green and reusable heteropolyacid catalyzed oxidation of benzylic, allylic and aliphatic alcohols to carbonyl compounds

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Abstract

Benzylic, allylic and aliphatic alcohols were transformed into the corresponding carbonyl compounds by catalytic oxidation of preyssler type heteropolyacid supported onto silica gel, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$, in a heterogeneous system. The catalyst can be recovered and reused.

Keywords: Oxidation; Alcohols; Carbonyl compounds; Heteropolyacid; Preyssler; $H_{14}[NaP_5W_{30}O_{110}]$

1. Introduction

Aldehydes and ketones represent an important class of products and intermediates in the fine chemicals and specialities [1]. The oxidation of alcohols to carbonyl compounds is an important transformation of organic synthesis, and several methods have been explored to accomplish such a conversion [2–10]. These methods involve the use of expensive reagents, long reaction times, strongly acidic condition and tedious work-up procedure leading to the generation of a large amount of toxic waste. Considering these facts, there is still a need to introduce new catalysts for this conversion.

Instead of conventional waste-producing oxidation procedures such as the stoichiometric application of environmentally benign oxidants has gained the preference in the past years [11–18].

Heteroplyacids, HPAs, have many advantages that make them economical and environmentally attractive in both academic and industrial signification; they are useful acids and oxidation catalysts in various reactions since its catalytic features can be varied at a molecular level [19–21]. Among them, the Keggin-type [22] HPAs have long been known to be good catalysts for oxidation reactions [23,24]. They exhibit great advantages: for example, their catalytic properties can be tuned by changing the identity of charge-compensating counter cations, heteroatoms and framework metal atoms [19].

Although Keggin type polyoxoanions and their derivatives have been widely studied and much attention has been devoted to the catalytic behavior of the Keggin's and their derivatives [25–30], the catalytic reactions and the application of Preyssler's anion has been largely overlooked [31].

Preyssler type heteropolyacid, $H_{14}[NaP_5W_{30}O_{110}]$, is remarkable owing to its exclusive physicochemical properties. They include strong Brönsted acidity, reversible transformations, solubility in polar and non-polar solvents, high hydrolytic stability and high thermal stability, that are very important in catalytic processes.

The structure of Preyssler's anion, $[NaP_5W_{30}O_{110}]^{14-}$, are shown in Fig. 1. The anion has an approximate D_{5h}

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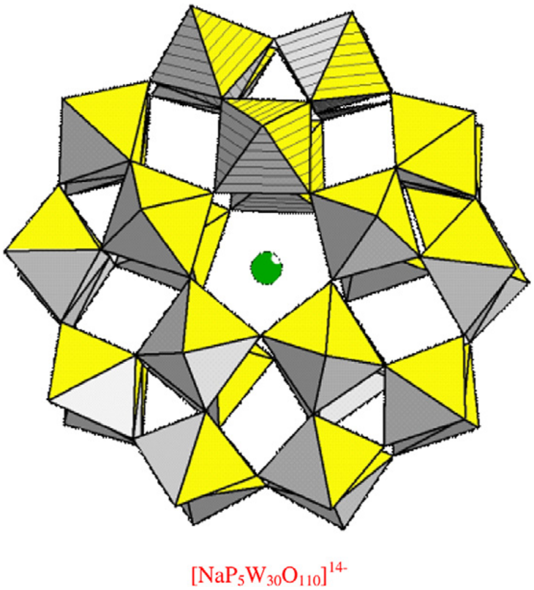


Fig. 1. Preyssler's anion structure.

symmetry and consists of a cyclic assembly of five PW_6O_{22} units; each derived from the Keggin anion, $[PW_{12}O_{40}]^{3-}$, by the removal of two sets of three corner–shared WO_6 octahedra. A sodium ion is located within the polyanion on the fivefold axis and 1.25 Å above the pseudo mirror plane that contains the five phosphorus atoms [32]. Preyssler polyanion as a large anion can provide many "sites" on the oval-shaped molecule that are likely to render the catalyst effective. Recently, we have reported on catalytic behavior of Preyssler's anion [33,34]. Armed with these experiences and in continuation of our works on the oxidation of alcohols, the application of heteropoly anions in organic synthesis [35], and development of applications for Preyssler's anion and due to the importance of carbonyl compound in the perfumery, pharmaceutical, dyestuff and agrochemical industries [36] herein we wish to report the catalytic ability of this catalyst in oxidation of various alcohols.

2. Experimental

All the chemicals were purchased from Merck Company. All products were known compounds and identified by comparison of their spectra and physical data on the literature description [37].

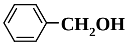
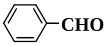
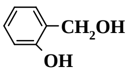
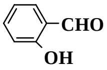
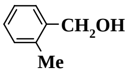
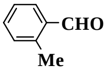
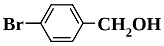
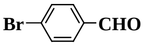
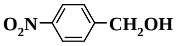
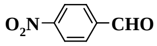
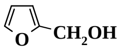
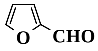
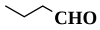
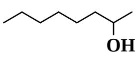
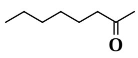
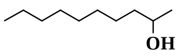
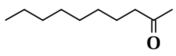
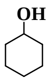
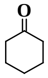
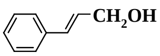
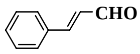
Preyssler type heteropolyacid, H_{14}-P_5 (i.e. $H_{14}[NaP_5W_{30}O_{110}]$), was prepared by passage of a solution of the potassium salt in water through a column (50 cm × 1 cm) of Dowex 50 W × 8 in the H^+ form and evaporation of the elute to dryness under vaccum.

Supported heteropolyacid catalyst was synthesized according to our previous report [33] using impregnating a support in the form of powder (SiO_2) with an aqueous solution of the H_{14}-P_5 (50% equivalent weight). After stirring the mixture, the solvent was evaporated, dried at 120 °C and was calcinated at 250 °C in a furnace prior to use.

2.1. Oxidation of alcohols to carbonyl compounds using H_{14}-P_5 supported onto silica gel: general procedure

A mixture of benzyl alcohol (1 mmol) and catalyst (0.03 g) in acetic acid (5 mL) was refluxed at boiling point of acetic acid for indicated time (Table 1). The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was filtered. To the filtrate diethyl ether (15 mL) was added. The mixture then washed with

Table 1
Oxidation of alcohols using H_{14}-P_5 supported onto silica gel

Entry	Alcohol	Product	Time (min)	Yield (%)[a]
1			13	99
2			10	98
3			12	99
4			14	99
5			15	98
6			30	97
7			18	96
8			18	96
9			20	98
10			21	97
11			20	99
12			20	98

[a] Yields analyzed by GC.