

[A0018]

Catalytic Oxidation of Alcohols, Phenols using Vanadium Substituted Keggin Heteropolyacids and Preyssler catalysts in Green conditions

Ali Gharib^{1,2*}, Manouchehr Jahangir¹, Mina Roshani¹

¹*Department of Chemistry, Islamic Azad University, Mashhad, IRAN*

²*Agricultural Researches and Services Center, Mashhad, IRAN*

*Author to whom correspondence should be addressed: aligharib5@yahoo.com

Abstract: The oxidation of Alcohols, Phenols were catalyzed using Vanadium Substituted Keggin Heteropolyacids and Preyssler catalysts in green conditions and mild.

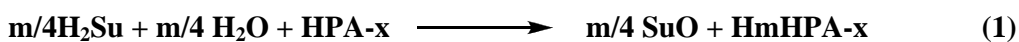
Keywords: Oxidation, vanadium, heteropolyacid, catalyst, alcohol

1. Introduction

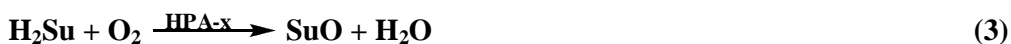
Heteropolyacids (HPAs) catalyze a wide variety of reactions in homogeneous or heterogeneous (liquid-solid, gas-solid or liquid-liquid biphasic) systems, offering strong options for more efficient and cleaner processing compared to conventional mineral acids [1]. Being stronger acids, heteropoly acids will have significantly higher catalytic activity than conventional catalysts such as mineral acids, mixed-oxides, zeolites etc. In particular, in organic media the molar catalytic activity of heteropoly acid is often 100-1000 times higher than that of H₂SO₄ [2]. The Keggin-type HPAs typically represented by the formula H_{8-x}[XM₁₂O₄₀], when X is the heteroatom (most frequently P⁺⁵ or Si⁺⁴), x is the oxidation state, and M is the addenda atom (usually W⁺⁶ or Mo⁺⁶), are the most important for catalysis [3]. They have been widely used as acid and oxidation catalysts for organic synthesis and found several industrial applications. The catalytic function of heteropolyacids (HPAs) and related polyoxometalate compounds have attracted much attention particularly in the last two decades [4]. Polyoxametalates (POMs) are a class of molecularly define organic metal-oxide clusters, posses intriguing structure and diverse properties [5,6]. These compounds exhibiting high activity in acid base type of catalytic reactions, hence they are used in many catalytic areas as homogeneous and heterogeneous catalysts [7]. The important advantages of this heteropolyacid such as: strong Bronsted acidity with 14 acidic protons, high thermal stability, high hydrolytic stability (pH=0–12), reusability, safety, quantity of waste, separability, corrosiveness, high oxidation potential and greenness along with exclusive structure have attracted much attention on this catalyst. We now wish to report an efficient

use of the heteropolyacids of the series $H_{3+n}PMo_{12-n}V_nO_{40}$ (HPA- n , $n > 1$) in the oxidation of alcohols to corresponding aldehydes under mild experimental conditions.

Aldehydes and ketones represent an important class of products and intermediates in the fine chemicals and specialties [8]. Some of compounds are for oxidation such as, Classical reagents of this type are manganese dioxide (MnO_2), potassium permanganate ($KMnO_4$), chromium trioxide (CrO_3), potassium chromate (K_2CrO_4), and potassium dichromate ($K_2Cr_2O_7$) [8]. These are all frequently-used reagents, either in the laboratory or in industry, and yet they are beset with multiple liability. The other drawbacks against such oxidants and their use in multistage organic synthesis, in spite of their power are also their lack of selectivity, strong protic and aqueous conditions, low yields of the products, and tedious work-up [9]. As an example, the oxidation of primary alcohols to aldehydes by a chromium(VI) salt in sulfuric acid is often accompanied by the formation of a hemiacetal between the resulting aldehyde and the alcohol substrate, following by the ready oxidation of this intermediate to an ester [10]. Therefore, we wish to report our reseaches with a new method about oxidation of alcohols using some of heteropolyacids (HPAs) types. The Solutions of Mo–V phosphoric heteropoly acids of composition $H_{3+x}PMo_{12-x}V_xO_{40}$ (HPA- x , where x is the number of vanadium atoms in a molecule that is equal to (3–4)) are applied as selective catalysts of partial oxidation of various organic compounds by oxygen [11]. Reactions in the presence of HPA- x generally are performed as a two-stage process:



Overall reaction:



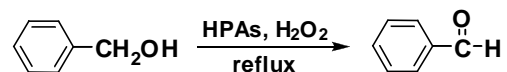
In these processes, HPA- x plays the part of a reversible oxidizer. The oxidation of alcohols to carbonyl compounds is an important transformation of organic synthesis, and several methods have been explored to accomplish such a conversion [12]. These methods involve the use of expensive reagents, long 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 [13]. Heteropolyacids (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 [14]. Among them, the Keggin-type [15]. HPAs have long been known to be

good catalysts for oxidation reactions [16]. 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 [17]. 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 [18], the catalytic reactions and the application of Preyssler's anion has been largely overlooked [19]. Preyssler type heteropolyacid, $H_{14}[NaP_5W_{30}O_{110}]$, is remarkable owing to its exclusive physicochemical properties. They include strong Bronsted acidity, reversible transformations, solubility in polar and non-polar solvents, high hydrolytic stability and high thermal stability, that are very important in catalytic processes.

2. Results and discussion

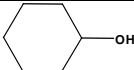
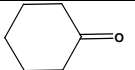
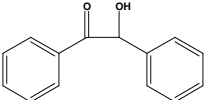
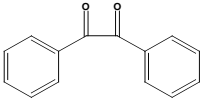
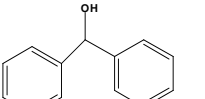
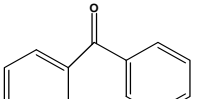
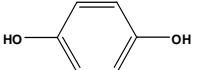
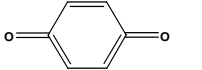
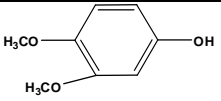
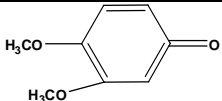
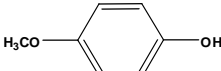
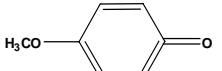

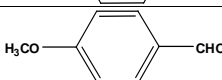
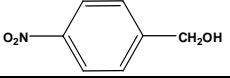

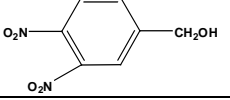
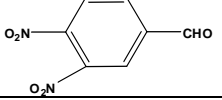
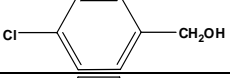

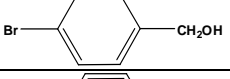
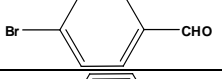
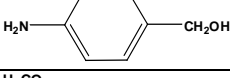
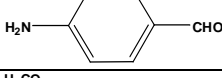
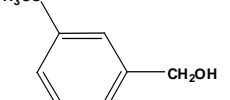
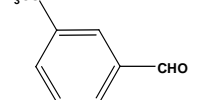
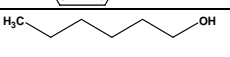
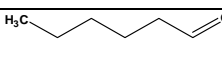
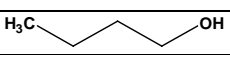
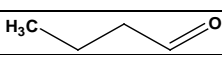
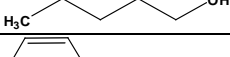
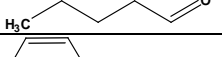
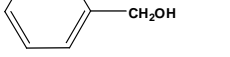
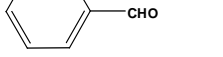
The heterogeneous catalytic oxidation of a variety of alcohols, by substituted vanadium heteropolyacids types and preyssler type heteropolyacid are being reported (Scheme 1).



Alcohols are converted to the corresponding aldehydes. The yields of the products were very high in the presence of mixed addenda types of preyssler with Mo atom and substituted vanadium heteropolyacids types. We investigate the reusability of the catalyst. For this purpose, we first carried out the oxidation of alcohols in the presence of the catalyst. After completing of the reaction, the catalyst was removed and washed with chloroform and subjected to a second run of the oxidation process with the same substrate. The results of the first experiment and subsequent experiments were almost consistent in yields (97% and 94%), and catalysts no loss its catalytic activity (Table 1, entry 5). It is noteworthy to mention that after oxidation of one alcohol, the catalyst could be reused for the oxidation of another alcohol. We examined the oxidation of benzyl alcohol, recovered the catalyst and used it for the oxidation of 1-Hexanol and found no difference regarding the yield and time of reaction (Table 1, entries 14, 17). The results of Preyssler supported catalysts with different loadings in this oxidation were showed in Table 2.

The strong interactions with surface silanol groups and interaction between hydroxyl silanol groups and acidic protons were caused lower yield than bulk state of preyssler catalyst (equation 4), [20].

Table 1. Oxidation of alcohols using Preyssler catalysts types in presence 30% hydrogen peroxide as oxidant agent and chloroform as solvent in reflux conditions

Entry	Substrate	Product	^a Y(%)	^a Y(%)	^a Y(%)	^a Y(%)	^a Y(%)	Time (min)
			H ₁₄ -P ₅	H ₁₄ -P ₅ Mo	H ₁₄ P ₅ (50%)	H ₁₄ P ₅ (40%)	H ₁₄ P ₅ (30%)	
1			96	98	90	82	74	25
2			77	81	69	60	53.5	90
3			76	82	67	61.5	52.5	90
4			95	98	91	80	73	30
5			97.5 (97,97)	98.5	94 (94,93) ^b	83.5	76	35
6			96	97	93	80	72.5	35
7			91.5	96	84 (84,83) ^b	76.5	65	60
8			88.5	90	80	72	58.5	60
9			86	87.5	77	64	52	60
10			87	91	80.5	71	59	60
11			82	85	73	62	51.5	60
12			89	95.5	84.5	73	61	60
13			89	94.5	83	75	63	60
14			87	91	79	70.5	62	60
15			89	92	81	72	64	60
16			85	90	76	67	58.5	60
17			91 (91,90) ^b	93.5	83 (83,82) ^b	74	60.5	60

^aisolated yield. ^bIn parentheses, yields obtained in the first and second reuse of the catalyst. Y= Yield

The yields for oxidation of alcohols using silica supported Preyssler with different loadings and molybdenum substituted Preyssler were showed in Table 1.

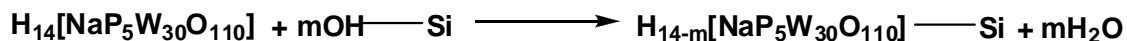
Table 2. Oxidation of alcohols using Vanadium substituted keggin heteropolyacids catalysts types in presence 30% hydrogen peroxide as oxidant agent and chloroform as solvent in reflux conditions

Entry	^a Yield(%) H ₄ [PMo ₁₁ VO ₄₀]	^a Yield(%) H ₅ [PMo ₁₀ V ₂ O ₄₀]	^a Yield(%) H ₆ [PMo ₉ V ₃ O ₄₀]	^a Y(%) H ₇ [PMo ₈ V ₄ O ₄₀]	Time (min)
1	85	90	93	98	25
2	72	78.5	82	86	90
3	73.5	82	83	85	90
4	90	93.5	96	99	30
5	88	92	95	99	35
6	83.5	89	94.5	98	35
7	85	87	93	97	60
8	82	85.5	88	93	60
9	75	81.5	86	90	60
10	81.5	85	91	94.5	60
11	77	82.5	86	90	60
12	85	90	93.5	97	60
13	87	91	94	96.5	60
14	83	88.5	92.5	94	60
15	85	90.5	94	96	60
16	87.5	91	95.5	97	60
17	78.5	81	84.5	88	60

^aisolated yield.

The oxidation reactions of alcohol in presence of the vanadium substituted keggin heteropolyacids have high yields. Because, the reduction potentials of heteropolyanions containing Mo and V are high as these ions are easily reduced and also, it seems symmetry is decreased by replacing of the molybdenum with vanadium in heteropolyacids catalysts. Oxidative ability decreases generally in the order: **V- > Mo- > W-** containing heteropolyanions, which means that the vanadium-containing heteropoly compounds are the strongest oxidants (Table 2) [21].

The presence of an electron-donating on group on the aromatic ring of alcohols structure were caused the corresponding aldehydes or ketones high yields , (Table 1, 2 entries 5-7, 13).



Equation 4. Form of interaction acidic protons of HPAs with hydroxyl silanol groups



3. Conclusion

In summary, the oxidation of various alcohols to carbonyl compounds in the presence of an inexpensive reusable, easy to handle, non-corrosive, high hydrolytic and thermal stability, eco-friendly and environmentally benign solid acid catalyst have been studied. Using this catalyst offers advantages including simplicity of operation due to the heterogeneous nature of the reaction, easy work-up, high yields of products, high selectivity and the recyclability of the catalyst. It is noteworthy to mention that the catalyst is recyclable and could be reused without significant loss of the catalytic activity. It could be recovered by filtration, washing with chloroform, and subjected to a second or even another reaction. Even after three runs for the oxidation reaction, the catalytic activity of the catalyst was almost the same as that of the freshly used catalyst. Also, in this reaction H_2O_2 is oxidant agent, and its product is water in the oxidation reaction final. This oxidant agent is environmentally friendly. Generally, This is a green chemistry method for the oxidation of alcohols and its similar compounds.

4. Experimental

4.1. Instruments

^1H NMR spectra were recorded on an FT-NMR Bruker 100 MHz Aspect 3000. IR spectra were recorded on a Buck 500 Scientific Spectrometer (KBr Pellets). The mass spectra were scanned on a Varian Mat. CH-7 at 70 eV. GLC analysis was performed on a Pu 4500 gas chromatograph with FID detector. The purity determination of the products was accomplished by GC analysis.

4.1. Materials and Methods

Alcohols, chloroform, hydrogen peroxide was obtained from Merck Company and was standardized by well-known methods (Hydrogen Peroxide Product Information Manual, Analytical Procedure) and Keggin vanadium substituted heteropolyacids were commercially available chemicals. $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$, ($\text{H}_{14}\text{-P}_5$) and $\text{H}_{14}[\text{NaP}_5\text{W}_{29}\text{MoO}_{110}]$, ($\text{H}_{14}\text{-P}_5\text{Mo}$) were prepared in according to the literature [22]. The oxidation products were characterized by comparison of their spectral (IR, ^1H NMR), TLC and physical data with the authentic samples. For the preparation of supported Preyssler ($\text{H}_{14}\text{-P}_5$)/ SiO_2 [22]. After stirring the heterogeneous solution-support mixture, the solvent was evaporated, samples were dried at 120°C and the catalysts were calcined at 250°C in a furnace prior to use. Some

of the heteropolyacids (HPAs) catalysts: $H_4[PMo_{11}VO_{40}]$, $H_5[PMo_{10}V_2O_{40}]$, $H_6[PMo_9V_3O_{40}]$ and $H_7[PMo_8V_4O_{40}]$, were prepared in according to Brégeault method [23-25].

4.2. General procedure

Oxidation of alcohols to corresponding aldehydes or ketones a typical Procedure:

A mixture of aldehyde (2.0 mmol), heteropolyacid catalyst (0.05 mmol), hydrogen peroxide 30% (0.03 mol) as oxidant agent and chloroform (10 mL) in d (5 mL) was stirred at reflux temperature for 35 minutes. The progress of reaction was monitored by TLC. After the completion of the reaction, the mixture was filtered to separate the catalyst, and washed with 5% aqueous solution of $NaHCO_3$ (3 x10 mL). Anhydrous $MgSO_4$ (4 g) was added to the solution and filtered after 20 minutes. Chloroform was removed. The solid was crystallized from chloroform. The aldehydes or ketones were obtained in good yield (Table 1).

References:

- [1] Y. Izumi, K. Urabe, M. Onaka, Zeolite Clay and heteropoly acid in organic Reactions, Kodansha/VCH, Tokyo, (1992).
- [2] I. V. Kozhevnikov, Catalysts for fine chemicals, in: Catalysis by Polyoxometalates, vol 2, Wiley, Chichester, (2002).
- [3] M. Misono, M. Unique acid catalysis of heteropoly compounds (heteropolyoxometalates) in the solid state. Chem. Commun. (2001) 1141.
- [4] I.V. Kozhevnikov, Russ. Chem. Rev. 56 (1987) 811.
- [5] M. T. Pope, A. Muller, Polyoxometalates: From Platonic Solid to Anti-Retroviral Activity, Kluwer, Academic Publishing, Dordrecht, (1994).
- [6] C. L. Hill, Chem. Rev. 98 (1998).
- [7] M. T. Pope, A. Muller, Angew. Chem Int. Ed. Engl. 30 (1991) 34.
- [8] B. M. Trost, Comprehensive Organic Synthesis (Oxidation), Pergamon press, New York, Vol. 7 (1991).
- [9] E. W. Warnhoff, D. G. Martin, W. S. Johnson, Org. Syn. 4 (1963) 162.
- [10] H. O. House, Modern Synthetic Reactions, 2nd ed. W. A. Benjamin: Menlo Park, CA, 1972, pp. 257-291.
- [11] T. Okuhara, N. Mizuno, M. Misono, Appl. Catal. A: General, 222 (2001) 63.
- [12] S. Zhang, L. Xu, M.L. Trudell, Synthesis 11 (2005) 1757.
- [13] R. A. Sheldon, I.W.C.E. Arends, A. Dijkman, Catal. Today 57 (2000) 157.
- [14] T. Okuhara, M. Misono, Adv. Catal. 41 (1996) 113.



- [15] J. F. Keggin, *Nature* 131 (1933) 908.
- [16] M. Misono, *Catal. Rev. Sci. Eng.* 29 (1987) 269.
- [17] J. N. Moorthy, N. Singhal, P. Venkatakrishnan, *Tetrahedron Lett.* 45 (2004) 5419.
- [18] Y. Izumi, M. Ono, M. Ogawa, K. Urabe, *Chem. Lett.* 825 (1993).
- [19] M.K. Harrup, C. Hill, L.J. Cardona, *Inorg. Chem.* 33 (1993).
- [20] K. Bruckman, M. Che, J. Haber, J. M. Tatibouet, *J. M. Catal. Lett.* 25 (1994) 225.
- [21] I.V. Kozhevnikov, K. I. Matveev, “Homogeneous Catalysts Based on Heteropoly Acids (Review)”, *Applied Catalysis.* 5 (1983) 135.
- [22] F. F. Bamoharram, M. M. Heravi, M. Roshani, M. Jahangir, A. Gharib, *Appl. Catal.* 302 (2006) 42-47.
- [23] G.A. Tsigdinos, C.J. Hallada, *Inorg. Chem.* 7 (1968) 437.
- [24] P. Courtin, *Rev. Chim. Min.* 8 (1971) 75.
- [25] A. Atlamsani, M. Ziyad, J.M. Bregeault, *J. Chim. Phys.* 92 (1995) 1344.

