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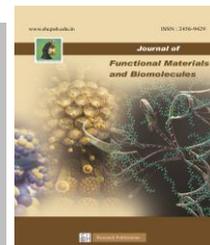
Oxidation of Benzyl alcohol to Benzaldehyde catalysed by 9-Molybdomanganate

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Abstract

Polyoxometalates (POMs) are structurally interesting class of compounds with widespread applications in several fields of science, especially with the advent of nanomaterials that are being utilized for various novel applications. A catalyst $(NH_4)_6[Mn^{IV}Mo_9O_{32}]$ was prepared and the catalytic activity of the synthesized Waugh type POM was studied and found that the oxidation of benzyl alcohol to benzaldehyde by H_2O_2 catalyzed by the POM was found to be efficient.

Keywords: polyoxometalate, catalysis.

1 Introduction

Polyoxometalates (POMs) which are otherwise called as "inorganic metal oxygen clusters" comprises a vast variety of inorganic compounds which show molecular, electronic, structural versatility, reactivity that makes these compounds interesting and useful in many applications. Right from their discovery until recently their existing implication in various branches of science are noteworthy since these compounds produce a class of remarkably novel structures with surprising applications [1]. Polyoxometalates (POMs) has numerous applications in various fields and the prominent among them is catalysis. It has been noted that at present, more than 80% of the applications for patents in POMs is related to catalysis [2]. The use of POMs as catalysts can be found as early as the beginning of the twentieth century [3]. In 1970s, the systematic investigations of the catalytic activities of POMs began when potential applications of POMs in catalysis was identified and a rapid development is being made till date and is bound to move further in the days to come. The multifunctionality and structural features make the heteropoly compounds have an edge over other catalysts. HPAs have strong Bronsted acidity [4] and has been used as an efficient oxidant. They exhibit a reversible multielectron transfer reaction which is the key behind reactions like the oxidation of benzyl alcohol to benzaldehyde.

Many heteropoly compounds were found to be soluble in polar solvents and are also thermally stable. This feature of POMs is another important aspect useful [5] in the catalysis reactions performed in both heterogeneous and homogeneous media [6]. There are many reactions that are catalyzed by POMs, for example, the reaction of oxidation of methacrolein to methacrylic acid [7], hydration reaction of isobutene [8], polymerization reaction of tetrahydrofuran to a polymeric diol [9], formation of n-butanol from butane [10] and other such processes. Moreover, the direct oxidation reaction of ethylene to acid was industrialized by Showa Denko [11] and the production of ethyl acetate using a heteropoly acid catalyst was developed by BP Amoco. These prove the industrial viability of POMs as efficient catalysts.

2 Experimental

Chemicals required for this work viz, ammonium molybdate, manganese sulphate, hydrogen peroxide and acetonitrile were analytical grade and purchased from E-Merck-India Ltd and they were used without any further purification. UV spectra is recorded using VARIAN CARY50 - UV – visible spectrophotometer. FT-IR spectra were recorded using Perkin-Elmer spectrum two spectrophotometer between the wave region 400 cm^{-1} - 4000 cm^{-1} using a pellet made using substance diluted with KBr. The yield of the product in the oxidation of benzyl alcohol to benzaldehyde was identified by Shimadzu - gas chromatograph using FID detector.

2.1. Preparation of the catalyst $(NH_4)_6[MnMo_9O_{32}]$

The ammonium salt of manganomolybdate as in the title has been prepared according to literature [12], with slight modification. In a typical reaction setup 5.0g of ammonium molybdate was dissolved in 40ml of boiling water. To this hot solution, 2ml of hydrogen peroxide was added slowly with vigorous stirring. The resulting yellow colour solution was further boiled for 5min with stirring. To the yellow colour solution, 5ml of hot manganese sulphate solution was added slowly with stirring, the solution turned into deep orange colour. The deep orange colour solution was boiled for 10min and left for cooling. On cooling the orange colour compound was crystalised. The crystals are filtered, washed with water/ethanol and recrystallized with hot water.

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2.2. Oxidation of benzyl alcohol

The oxidation reaction was carried out by taking benzyl alcohol (2.2 mmol) and H_2O_2 (4.5 mmol) in a round bottomed flask which was fitted with a reflux condenser. The contents are dissolved in a 50: 50 % aqueous acetonitrile solution. The Catalyst $(NH_4)_6[MnMo_9O_{32}]$ (0.1g) was added with constant stirring at 50°C for 2-3 hrs. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was carefully extracted using diethyl ether, in which the product benzaldehyde in the organic phase was concentrated to obtain the crude sample. The same procedure was repeated for different catalytic concentrations such as 0.2g, 0.3g, 0.4g and 0.5g.

3 Results and Discussion
3.1. UV – Visible Spectrum of $(NH_4)_6[MnMo_9O_{32}]$

UV-Visible spectroscopy is a one of the tools for characterizing materials. The UV spectrum corresponding to the electronic excitation of Mn^{IV} in the synthesised POM is given in Fig 1. The spectrum shows a maximum absorption at 340nm which is the characteristic excitation shown by Mn^{4+} ions [13]. This confirms the presence of Mn in higher oxidation state in the synthesised POM.
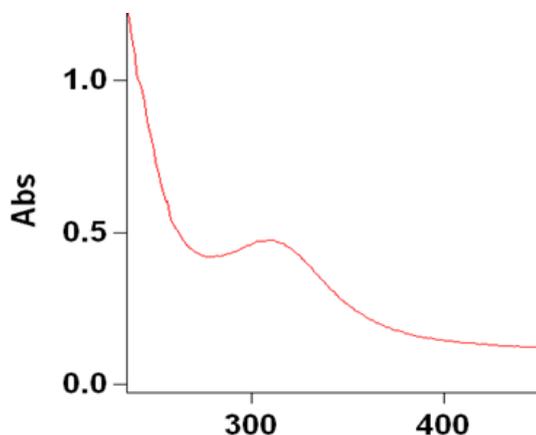

Fig 1. The ultra violet spectrum of $(NH_4)_6[Mn^{IV}Mo_9O_{32}]$

3.2. Infrared Spectral study of $(NH_4)_6[Mn^{IV}Mo_9O_{32}]$

Infrared spectroscopy is another analytical tool to identify and characterize the materials. This spectroscopy measures the vibrational excitations in the molecule. Each signal in an IR spectrum is associated with a vibrational mode in the molecule. The frequency of absorption depends on the reduced mass of atoms in that particular vibrational mode and the force constant involved in the vibration. The infrared spectroscopy is the simple and rapid method which is often used due to its reliability in assigning a compound to its class. It can also provide other useful information on structure, symmetry, purity, isomers and hydrogen bonding.

The infrared spectra for the compound $(NH_4)_6[MnMo_9O_{32}]$ synthesised is shown in Fig 2. The peak at 3485cm^{-1} is assigned to stretching vibration of $\nu_{(N-H)}$ in NH_4^+ group. the peak located at 1401cm^{-1} is due to bending vibration of $\delta_{(H-N-H)}$ in NH_4^+ group. These two vibrations confirm the presence of NH_4^+ group both in micro

and macro scale samples. The characteristic peaks of the core Waugh type POM cluster were found at 934, 900, 694, 595 and 542 cm^{-1}. The strong and medium sharp doublets at 934, 900cm^{-1} were due to stretching vibrations of $\nu(Mo-O)$ terminal oxygen. The peaks corresponding to the (Mo–O–Mo) bending vibrations on the oxygen bridge were at 694, 595 and 542 cm^{-1}. The characteristic (Mo–O–Mo) asymmetric stretching vibration was seen at 496cm^{-1} [14]. This IR analysis confirms the formation of the Waugh type of ammonium salt of molybdomanganate.
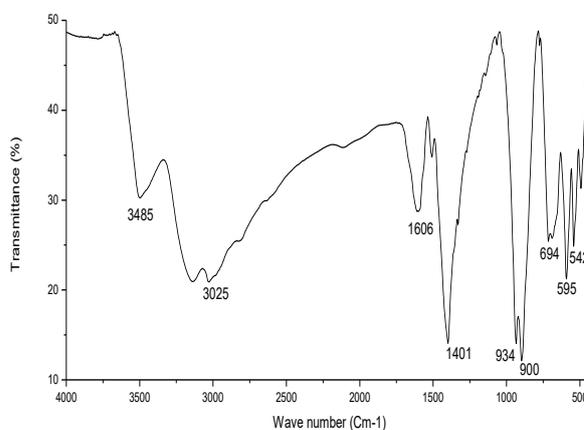

Fig 2. FTIR Spectra of $(NH_4)_6[MnMo_9O_{32}]$

3.3. Product analysis

The progress of the reaction is monitored by TLC and the yield of the product was identified by Gas liquid chromatography using FID as detector. The chromatogram of the product obtained after the completion of the catalytic reaction with the catalyst load of 0.1g is shown in Fig 3.
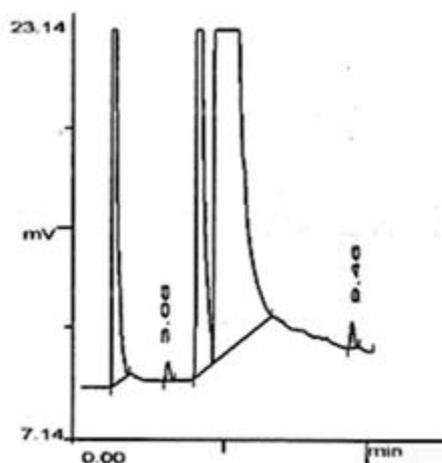

Fig 3. The chromatogram of the product obtained after the oxidation reaction by 0.1g of the catalyst

During the oxidation of benzyl alcohol to benzaldehyde, the effect of catalyst was studied by varying the catalytic load from 0.1g to 0.5g keeping the concentration of hydrogen peroxide constant at 4.5mol. A maximum yield was obtained with the catalytic load 0.5g. The percentage composition of all the components in the reaction mixture are

measured from the area of peaks in the chromatogram and tabulated in Table 1 for the catalyst load of 0.1g.

The main product benzaldehyde is detected at the retention time around 5.00 and the results of the yield of the benzaldehyde for the catalytic load 0.1g, 0.2g, 0.3g, 0.4g, and 0.5g are given in table 2. The result shows an increasing trend with the increase in the catalytic load. However, there is only a slight increase in yield was observed from 4.0g to 0.5g where it reached the maximum conversion of the product.

It was also observed that, the reaction did not proceed when either the catalyst or the hydrogen peroxide was absent. Generally during oxidation of the primary alcohols to aldehyde, an acid was produced as an additional product but in this reaction catalysed by molybdomanganate (IV),

the formation of acid was not observed. Additionally, the present method is very advantageous because it does not require any activator like Na_2HPO_4 (or) phase transfer reagent like tetra alkyl pyridinium ion etc. for the reaction. Therefore, the present method was very efficient since there was good yield in reasonable time.

The oxidation of benzyl alcohol to benzaldehyde by H_2O_2 catalyzed by the POMs which has Mn(IV), and this Mn(IV) converts the alcohol into carbonyl derivatives as the final product during which the Mn(IV) of the POM catalyst is converted into Mn(III) which again is converted back to the original Mn(IV) by the action of H_2O_2. The following mechanism is suggested for the conversion of alcohol into aldehyde.

$$[Mn^{IV}Mo_9O_{32}]^{5-}+R_1R_2CHOH\rightarrow[Mn^{III}Mo_9O_{32}]^{6-}+R_1R_2C=O+ H_2O$$
$$[Mn^{III}Mo_9O_{32}]^{6-}+H_2O_2\rightarrow[Mn^{IV}Mo_9O_{32}]^{5-}+H_2O$$

Table 1 The data extracted from the chromatogram for the product obtained for the catalyst load 0.1mmol

R.T	Height	Area	Height%	Area%
1.11	236270	15988874	27.1638	12.1018
3.06	341	77196	0.0392	0.0584
4.10	22086	25099149	25.3905	18.9972
4.81	411850	90855360	47.3501	68.7671
9.46	490	99742	0.0563	0.0755

Table 2 Effect of catalyst load on the yield

Catalyst Load (g)	H_2O_2 (mmol)	Yield (%)
0.1	4.5	68.76
0.2	4.5	72.21
0.3	4.5	79.99
0.4	4.5	92.10
0.5	4.5	99.55

4 Conclusions

The catalyst $(NH_4)_6[Mn^{IV}Mo_9O_{32}]$ was prepared and characterized using UV and IR spectroscopy and the catalytic activity of the synthesized Waugh type POMs was studied and found that the oxidation of benzyl alcohol to benzaldehyde by H_2O_2 catalyzed by the POM is efficient and very minimum quantity of the catalyst was sufficient for the catalytic reaction.

Conflict of Interest

The authors whose names are listed immediately below certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or nonfinancial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

References

[1] M. T Pope, A. Muller, Angew. Chem. Int. Ed. 30, (1991), 34.

[2] D.E. Katasoulis, Chem. Rev. 98, (1998) 359.

[3] M. Misono, N.Nojiri, Appl. Catal. 64, (1990) 1.

[4] M.N. Timofeeva, Applied Catalysis A, 256, (2004) 19.

[5] E. Rafiee, S. Eavani, RSC Adv. 6, (2016), 46433.

[6] Sa-Sa Wang, Guo-Yu Yang, Langmuir, 37, (2021), 1925.

[7] Harald Böhnke, Johann Gaube, and Jochen Petzoldt, Ind. Eng. Chem. Res., 45, (2006), 8794

[8] Shuai Wang Enrique Iglesia ACS Catal., 6, (2016), 7664

[9] M. Bernhard Stadler, Christoph Wulf, Thomas Werner, Sergey Tin, G. Johannes de Vries, ACS Catal. 9, (2019), 8012

[10] B. Kolesinska, J. Fraczyk, M. Binczarski, Materials, 12, (2019), 350.

[11] K.K. Showa Denko, Jpn. Kokai Tokkyo Koho, 9, (1997), 48744.

[12] L.C.W. Baker, T.J.R. Weakley, J. Inorg. Nucl. Chem. 28, (1966), 447.

[13] L.P. Kazanskii, Doctoral (Chem.) Dissertation, Moscow: Inst Phys. Chem. of the USSR Acad. Sci., 1970.

[14] Haiyan Cheng, Yuanhang Ren, Shuxia Liu, and Linhua Xie, Z. Anorg. Allg. Chem., 634, (2008), 977.