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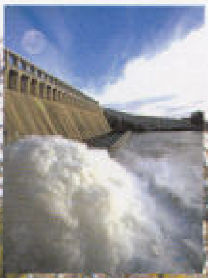

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SYNTHESIS OF ACETYL SALICYLIC ACID BY NANOPREYSSLER'S ANION AS GREEN, ECO-FRIENDLTY AND RECYCLABLE CATALYST

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ABSTRACT

Heteropolyacids (HPAs) have been used as catalysts for the reaction of salicylic acid with acetic anhydride. The performance of different forms of heteropoly acids in the presence of acetic anhydride as acetylating agent for acetylation of salicylic acid was compared. The best conditions were observed using Preyssler and NanoPreyssler as catalysts. The catalyst is recyclable and reusable.

Keywords: Heteropolyacid; Aspirin; NanoPreyssler; Catalyst

INFLUENCE OF GEOMETRICAL VARIABLES OF DARRIEUS WIND ROTOR ON ITS PERFORMANCE

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ABSTRACT

Darrieus wind turbines offer a number of advantages such as simplicity of design of structure, generator, and any control system. With the roto being the direct means of extracting kinetic energy from the wind, its particular geometry must undoubtedly have a great effect on the overall performance of the turbine. The rotor geometrical parameters investigated in this study were: number of blades, chord to radius ratio, solidity, height to radius ratio. Moreover, the effects of Reynolds number were also included. The analysis was based on the use of a multiple streamtube model and NACA0012 rotor-blade profile. Results are presented in the form of power and torque coefficients as functions of tip-speed ratio.

Keywords: Darrieus wind Turbine, Multiple streamtube Model

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INTRODUCTION

In the last two decades the broad utility of HPAs as acid and oxidation catalysis has been demonstrated in a wide variety of synthetically useful selective transformations of organic substrates [1,2]. Heteropolyacids, presently being used in several industrial processes, are important for the so-called clean technologies since many of the environmental pollution and corrosion problems of the traditional technologies are avoided [3]. HPAs are more active catalysts than conventional inorganic and organic acids for various reactions in solution [4]. They are used as industrial catalysts for several liquid-phase reactions [5,6], such as alcohol dehydration [7], alkylation [8], or esterification [9]. They are not corrosive and environmentally benign, presenting fewer disposal problems.

Solid heteropoly acids have attracted much attention in organic synthesis owing to easy workup procedures, easy filtration, and minimization of cost and waste generation due to reuse and recycling of the catalysts [10]. Among the HPAs, Preyssler catalyst is green with respect to corrosiveness, safety, quantity of waste, and separability. This heteropoly acid with fourteen acidic protons is an efficient "supper acid" solid catalyst with unique hydrolytic stability (pH=0-12) [11].

Acetylation of salicylic acid produces acetyl salicylic acid or aspirin. Since 1899, when Dreser introduced the clinical use of aspirin, it has become one of the most extensively and widely used drugs. As a consequence, it has also been studied in greater depth. Even after so many years, new properties of aspirin are still being discovered today.

Aspirin is an important drug worldwide and conventionally is prepared by an acid-catalyzed process. The most widely employed catalysts for this reaction are concentrated sulfuric and phosphoric acids [12]. Both acids are strongly corrosive and must be handled with care.

Keggin-type HPAs and other derivatives have also been reported to be efficient catalysts for the esterification reactions[13].

In the present research, we have described the direct acetylation of salicylic acid to aspirin. The major goal is the development of nanocatalyst application (nanoPreyssler) in organic synthesis. We now report the application of nanoPreyssler catalyst, with exclusive properties surpassing the Keggin heteropolyacids, for highly selective and rapid liquid-phase O-acetylation of salicylic acid in order to synthesize aspirin.

MATERIALS AND METHODS

Materials. Acetic anhydride, salicylic acid, sodium tungstate dihydrate, molybdotungstate dihydrate, orthophosphoric acid, sulfuric acid and keggin were obtained from Merck.

Catalyst Preparation. Keggin type HPAs were acquired from commercial sources. Potassium salt of Preyssler's anion was prepared according to the procedure developed in our laboratory [14]. Preyssler heteropolyanion, H14_P5, was prepared as follows: 33 g $Na_2WO_4.2H_2O$ were dissolved in 45 mL of water and mixed at 45°C for 30 min. Then this solution was cooled to room temperature, and 25 mL of concentrated phosphoric acid was added. The resulting yellow solution was refluxed for 5 h. The solution was brought to room temperature, diluted with water and then during stirring, 10 g of KCl was added. The mixture was stirred and then heated up to dryness.

The product was dissolved in warm water and then upon cooling to room temperature, white crystals were formed. The free acid was prepared by passing a solution of potassium salt in water through a column of resin and evaporating the elute to dryness under vacuum [14]. Silica-supported Preyssler nanoparticles were prepared according to our previous work [15].

General Procedure. The homogeneous process was performed by adding acetic anhydride (5 mL) to a solution of Preyssler (0.2 g) and salicylic acid (2 g) at room temperature with stirring. At the end of reaction, the mixture was diluted with 50mL of water, and the crude product was precipitated in an ice bath. The crude product was removed and after the usual work up, the resulting solid was washed with cold water and recrystallized in ethanol. The product was characterized by comparison of its spectroscopic IR data, and melting point with that of an authentic sample. The product yield was determined quantitatively.

Recycling of the catalyst. At the end of the reaction, the catalyst was recovered by water, and re-used in another reaction. IR spectrum of the recovered solid catalyst indicated that the catalyst can be recovered without structural degradation. The recycled catalyst was used for many reactions without observation of appreciable lost in its catalytic activity.

RESULTS AND DISCUSSION

Highly selective acetylation of salicylic acid with acetic anhydride at room temperature is carried out for the first time by an inexpensive, recyclable nanoPreyssler's anion. The result shows that nanoPreyssler has higher activity and performance in esterification reactions compared with the other heteropoly acids such as Preyssler and Keggin as well as normal method using H_2SO_4. The yields of O-acetylation of salicylic acid into aspirin with various heteropoly acids are given in Table 1.

Compared with Keggin and Dawson, NanoPreyssler (H_{14}_P_5) is more active and show higher selectivity and minimizing side reactions. Fig. 1 gives the yield of aspirin in esterification reaction obtained using Nano H_{14}_P_5 ,Keggin and Dawson under the same conditions. It can be seen from the figure that the activity of H_{14}–P_5 nano form is higher than other heteropoly acids.

Table 1: Yields Of Aspirin In *O*-Acetylation Of Salicylic Acid with Various Heteropoly Acid Catalysts at Room Temperature.

Catalyst	Yield (%)	Time (min)
NanoPreyssler($H_{14}[NaP_5W_{30}O_{110}]$)	87	30
Preyssler ($H_{14}[NaP_5W_{30}O_{110}]$)	82	30
Keggin ($H_3[PW_{12}O_{40}]$)	70	30
Dawson ($H_6[P_2 W_{18}O_{62}]$)	76	30

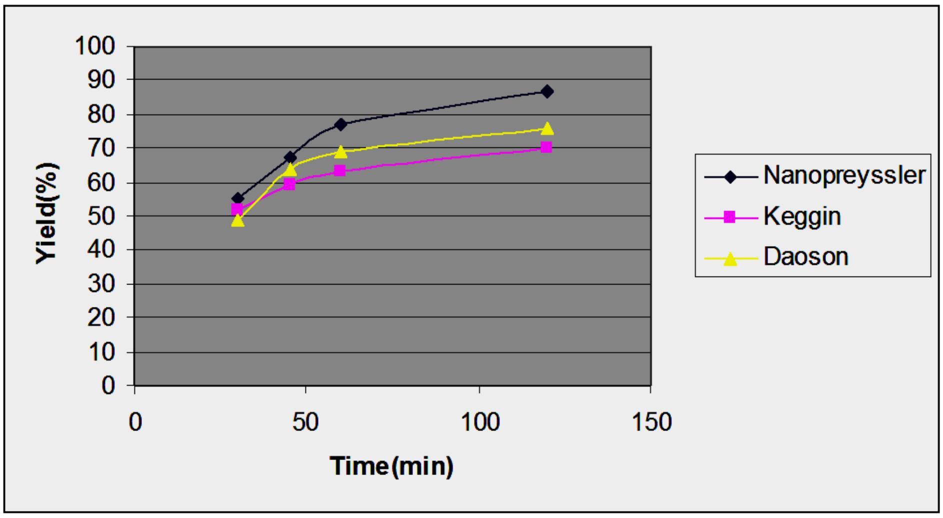

Figure 1: Yield of Aspirin as A Function of Time in The Presence of Nanopreyssler, Keggin and Dawson Heteropoly Acids.

CONCLUSIONS

This study demonstrates that Preyssler is an effective solid acid catalyst for aspirin synthesis. Among various forms of HPA catalysts used, NanoPreyssler shows higher activity compared to the other forms such as Preyssler, Keggin and Dawson. This method demonstrates the applicability of Preyssler's anion for those reactions that require solid catalysts with strong acidic properties, high thermal stability and functionality over a wide range of pH. In addition, simple experimental setup and procedure makes this method a useful addition to the present methodologies.

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REFERENCES

[1] Misono, M., Selective catalytic reactions and separations: Oiso, *Catal. Rev. Sci. Eng.*, Vol. 29, 1987, 269.
(b) Misono, M., New Catalytic Aspects of Heteropolyacids and Related Compounds - to the Molecular Design of Practical Catalysts, *Catal. Rev. Sci. Eng.*, Vol. 30, 1988, 339.

[2] Firouzabadi, H. and A.A. Jafari, Design and one-pot synthesis of α-aminophosphonates and bis(α-aminophosphonates) by iron (III) chloride and cytotoxic activity, *J. Iran. Chem. Soc.*, Vol. 2, 2005, 85.

[3] Kozhevnikov, V., Heterogeneous acid catalysis by heteropoly acids: Approaches to catalyst deactivation , *J. Molecular Catalysis A: Chemical*, Vol. 305, No 1-2, 2009, pp 104-111.

[4] Heravi, M.M., F.K., Behbahani and F.F. Bamoharram, $H_{14}[NaP_5W_{30}O_{110}]$: A heteropoly acid catalyzed acetylation of alcohols and phenols in acetic anhydride, *J. Molecular Catalysis*, No. 253, 2006, pp16–19.

[5] Izumi, Y., K. Urabe and A. Onaka, Zeolite, Clay and Heteropolyacids in Organic Chemistry, *VCH, Weinheim*, Kodansha, Tokyo, 1992, p. 99.

[6] Kozhevnikov, I.V., Esterification of 2,6-pyridinedicarboxylic acid with n-butanol catalyzed by heteropoly acid $H_3PW_{12}O_{40}$ or its Ce(III) salt, *Catal. Rev. Sci. Eng.* Vol. 102, 1995, pp 73-77.

[7] Wong, S., M. Appleberg, C.M. Ward and D.R. Lewis, Aspirin Resistance in Cardiovascular Disease: A Review, *European Journal of Vascular and Endovascular Surgery*, Vol. 27, No. 5, 2004, pp 456-465.

[8] Izumi, Y., R. Hasebe, H. Kondoh and K. Urabe, Reductive carbonylation of nitrobenzene catalyzed by heteropolyanion-modified palladium, *J. Catal.*, Vol. 72, 1992, pp 37-46.

[9] Soeda, H., T. Okuhara and M. Misono, Catalysis by Heteropoly Compounds , *Chem. Lett.*, Vol.64 , 1994, 909.

[10] Schwegler, M.A., H. van Bekkum and N. Munck, Mo/W interchange of heteropoly anions as a measure of stability: a P NMR study, *Appl. Catal.*, Vol. 63, 1990, pp 343-351.

[11] Heravi, M.M., F.K. Behbahani and F.F. Bamoharram, Acetylation of alcohols, phenols and salicylic acid by heteropoly acids in acetic anhydride: a green and eco-friendly protocol for synthesis of acetyl salicylic acid (Aspirin), *ARKIVOC*, 2007, pp 123-131.

[12] (a) Pavia, D.L., G.M. Lampman and G.S. Kriz, Introduction to Organic Laboratory Techniques: A Contemporary Approach, Philadelphia, 1976, p. 27.
(b) Miller, J.A. and E.F. Neuzil, Modern Experimental Organic Chemistry, Heath Lexington, 1982, p. 192.

[13] Hu, C., M. Hashimoto, T. Okuhara and M. Misono, Novel Catalysis of Cesium Salt of Heteropoly Acid and its Characterization by Solid-state NMR, *J. Catal.*, Vol. 143, 1993, 437.

[14] Heravi, M.M., M. Khorasani, F. Derikvand, H.A. Oskooie and F.F. Bamoharram, Highly efficient synthesis of coumarin derivatives in the presence of H14[NaP5W30O110] as a green and reusable catalyst, *Catalysis Communications*, Vol. 8, 2007, pp 1886–1890.

[15] Heravi, M.M., S. Sajadi, H.A. Oskooie, R. Hekmat Shoar and F.F. Bamoharram, Supported Preyssler Nanoparticles in Synthesis of 1,3-Diaryl-5-spirohexahydropyrimidines, S. *Afr. J. Chem.*, Vol. 62, 2009, pp 246-250.