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NANOPREYSSLER'S ANION AS HETEROGENEOUS AND RECYCLABLE CATALYSTS FOR THE SYNTHESIS OF ACETYL SALICYLIC ACID

as poster/oral presentation.

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NANOPREYSSLER'S ANION AS HETEROGENEOUS AND RECYCLABLE CATALYSTS FOR THE SYNTHESIS OF ACETYL SALICYLIC ACID

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ABSTRACT

Synthesis of aspirin via O-acetylation of salicylic acid in the presence of heteropoly acids has been investigated in order to contribute toward clean technology, which is the most important need of the society. 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.

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. Heteropolyacids (HPAs), 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. Among the HPAs, Keggin family appeared as interesting candidates for strong acid-demanding reactions. 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) [1].

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.

Acetylation of salicylic acid by various heteropoly acids has been reported before [2,3]. In the present research, we have described the direct acetylation of salicylic acid to aspirin by using nanopreyssler. The results were also compared with the previous studies using other HPAs. The major goal was the development of application of heteropoly acids in industry.

EXPERIMENTAL SECTION

Materials

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

Catalyst Preparation

Keggin type heteropolyacids were acquired from commercial sources. Potassium salt of Preyssler's anion was prepared according to the procedure developed in our laboratory. The free acid was prepared by passage of a solution of the potassium salt in water through a column of resin and evaporation of the elute to dryness under vacuum [4].

General Procedure

The homogeneous process was performed by adding acetic anhydride (5 mL) to a solution of $H_{14}\_P_5$ (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, H-NMR, Mass) 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 sublimation process, and re-used in another reaction. 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.

Table 1. Yields of aspirin in *O*-acetylation of salicylic acid with various heteropolyacid catalysts at room temperature.

Entry	Time (min)	Catalyst	Yield (%)
1	30	NanoPreyssle ($H_{14}[NaP_5W_{30}O_{110}]$)	**87**
2	30	Preyssler ($H_{14}[NaP_5W_{30}O_{110}]$)	**82**
3	30	Keggin ($H_3[PW_{12}O_{40}]$)	**76**
4	30	Dawson ($H_6[P_2W_{18}O_{62}]$)	**69**

Compared with mineral acids such as H_2SO_4, Preyssler ($H_{14}\_P_5$) and Nano $H_{14}\_P_5$ are more active and show higher selectivities and minimizing side reactions. Fig. 1 gives the yield of aspirin in esterification reaction obtained using $H_{14}\_P_5$, Nano $H_{14}\_P_5$ and H_2SO_4 under the same conditions. It can be seen from the Figure that the activity of H_{14}–P_5 and its nano form is higher than that of sulfuric acid.

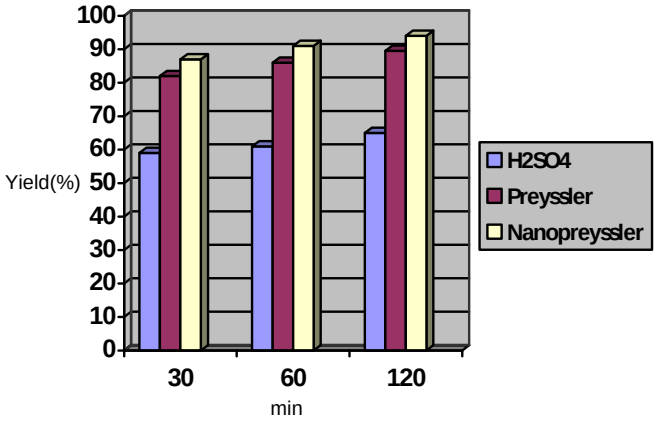

Fig. 1. Yield of aspirin as a function of time in the presence of $H_{14}[NaP_5W_{30}O_{110}]$, Nano form and H_2SO_4.

CONCLUSIONS

Preyssler catalyst is an effective solid acid catalyst for preparation of aspirin. Among various forms of Preyssler catalysts used, NanoPreyssler shows higher activity compared to the other forms of HPACs such as Preyssler and Keggin types. 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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