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PREPARATION OF SILICA-SUPPORTED PREYSSLER NANOPARTICLES AND ITS CATALYTIC PERFORMANCE IN ESTERIFICATION OF ACETYLSALICYLIC ACID WITH ACETIC ANHYDRIDE

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ABSTRACT

The extensive demand for cleaner environment is forcing chemical industry to use less hazardous materials. In this regard, heteropolyacids attracted considerable amount of interest due to the less toxic behavior in addition of possessing higher acidity. Heteropolyacids have been used as catalysts for the reaction of salicylic acid with acetic anhydride. The performance of different forms of Preyssler in the presence of acetic anhydride as acetylating agent for acetylation of salicylic acid was compared. The best conditions were observed using silica-supported Preyssler nanoparticles as catalysts. The catalyst is recyclable and reusable.

KEYWORDS : *Heteropolyacid, Aspirin, Acetylsalicylic acid, Silica-supported Preyssler Nanoparticles, Catalyst.*

INTRODUCTION

The drive to develop green processes has led to the development of solid acid catalysts to a significant increase in research activities both in academic and industrial sections. A variety of materials have been used as solid acid catalysts such as clays, zeolites, sulfated metal oxides, heteropolyacids, etc. Each of these materials offers unique properties that can influence the catalytic activity. Among these solid acids, Heteropolyacids (HPAs) have unique properties such as strong Bronsted acidity, structure alterability, high proton mobility and environmental friendliness. Due to their stronger acidity, they generally exhibit higher catalytic activities than conventional catalysts, such as mineral acids, zeolites, etc. They are widely used in both heterogeneous and homogeneous systems [1-5].

In our attempt to use HPAs as catalysts in organic reactions, we reported that Preyssler type of HPAs, $H_{14}[NaP_5W_{30}O_{110}]$, shows strong catalytic behavior[6]. Due to the unique properties of nano particles along with their novel properties and potential applications in different fields [7], we decided to investigate the catalytic behavior of silica-supported Preyssler nanoparticles.

EXPERIMENTAL

CATALYST PREPARATION

Potassium salt of Preyssler's anion was prepared according to the procedure developed in our laboratory. Preyssler heteropolyanion, H_{14} - P_5, was prepared as follow: Na_2WO_4 .$2H_2O$ was dissolved in water and mixed at 45 °C for 30 min. Then this solution was cooled to room temperature, and 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, KCl was added. The mixture was stirred and then heated up to dryness. The product was dissolved in warm water and upon cooling to room temperature white crystals formed. 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 [8].

Silica-supported Preyssler nano particles were prepared according to our previous work [9].

GENERAL PROCEDUR

The homogeneous process was performed by adding acetic anhydride to a solution of nano Preyssler and salicylic acid 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.

RECYCELING OF THE CATALYST

At the end of the reaction, the catalyst was recovered by water, 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

The heteropolyacid ($H_{14}[NaP_5W_{30}O_{110}]$) on the SiO_2 nano particles was confirmed by infrared (IR) spectroscopy(Fig.1). IR spectroscopy demonstrates that ($H_{14}[NaP_5W_{30}O_{110}]$) is preserved in the HPA/SiO_2 nano particles. It could therefore be confirmed that the heteropolyacid ($H_{14}[NaP_5W_{30}O_{110}]$) was successfully immobilized onto the SiO_2 particles [9]. The results of

the acetylation of salicylic acid with acetic anhydride at room temperature are shown in Table 1.

Table 1: Yields of aspirin in acetylation of salicylic acid at room temperature.

ENTRY	TIME (MIN)	CATALYST	YIELD (%)
1	30	Nano Preyssler	72
2	30	Preyssler	66
3	30	H_2SO_4	41
4	45	Nano Preyssler	76.5
5	45	Preyssler	71.5
6	45	H_2SO_4	43.5
7	60	Nano Preyssler	79
8	60	Preyssler	74.75
9	60	H_2SO_4	45
10	90	Nano Preyssler	82.5
11	90	Preyssler	75
12	90	H_2SO_4	49
13	120	Nano Preyssler	85
14	120	Preyssler	76.5
15	120	H_2SO_4	52

The results show that nanoPreyssler has higher activity and performance in esterification reactions compared preyssler and sulfuric acid. The best yield of aspirin (85%) with 100% selectivity was attained with nanopreyssler at almost 2 hours of reaction at room temperature. Shorter and longer times gave somewhat lower yields (entry 13). Preyssler has lower activity than nanopreyssler. It leads to 76.5% aspirin with 100% selectivity after 2 hour (entry 14).

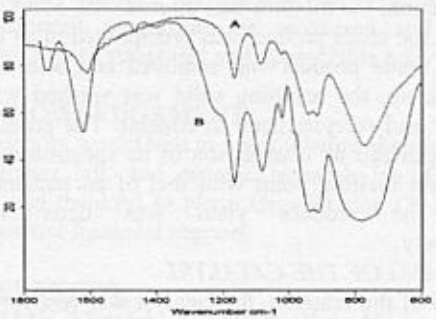

Fig .1 Infrared spectroscopy of Preyssler heteropolyacid in nano form (A) and bulk form (B) [10].

In Fig .2 a comparison of the efficiency of this catalyst in the synthesis of acetylsalicylic acid after recycling two times is reported. As shown in Fig .2 the yields of the reaction after using this catalyst two times show 2-5% reduction.

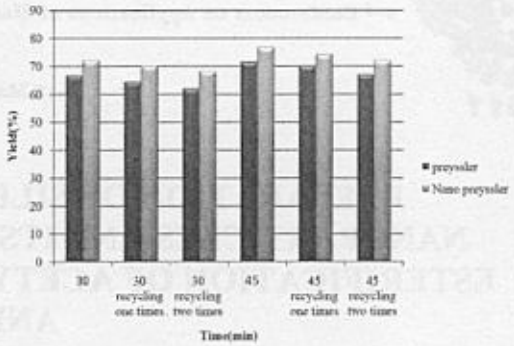

Fig .2 Efficiency of catalysts in the synthesis of acetylsalicylic acid after recycling one and two times

CONCLUSION

This study demonstrates that nano Preyssler catalyst is an effective solid acid catalyst for preparation of aspirin. Among various forms of Preyssler catalysts used, nano Preyssler shows higher activity compared to the Preyssler. This method demonstrates the applicability of nano Preyssler for those reactions that require solid catalysts with strong acidic properties, high thermal stability and functionality over a wide range of pH.

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