



Comparison of Catalysts Preyssler and Silica-Supported Nano Preyssler in the Synthesis of Acetyl Salicylic Acid

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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. Heteropoly acids 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 Silica-supported Preyssler Nanoparticles as catalysts. The catalyst is recyclable and reusable.

Keywords: Heteropolyacid, 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. These materials can replace the corrosive liquid acids currently used in many industries. A variety of materials have been used as solid acid catalysts such as clays, zeolites, sulfated metal oxides, heteropoly acids (HPAs), *etc.* Each of these materials offers unique properties that can influence the catalytic activity. Among these solid acids, heteropoly acids have unique properties such as strong Brønsted acidity, structure alterability, high proton mobility and environmental friendliness. They show very strong Brønsted acidity values, approaching the

super acid region. Due to their stronger acidity, they generally exhibit higher catalytic activities than conventional catalysts, such as mineral acids, ion-exchange resins, zeolites, etc. They are widely used in both heterogeneous and homogeneous systems¹⁻⁵.

Heteropoly acids, 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^{1,2,6}.

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 solid "super acid" catalyst with unique hydrolytic stability (pH=0-12)^{7,8}.

Over the last decade, due to the unique properties of nanoparticles along with their novel properties and potential applications in different fields, synthesis and characterization of catalysts with lower dimensions have become the most interesting topic of research⁹. As the particle size decreases, the relative number of surface atoms and hence the activity increases. Moreover, due to quantum size effects, nanometer-sized particles may exhibit unique properties for a wide range of applications¹⁰.

Recently, most considerations raised the interest for synthesis of Keggin nano catalysts¹¹, but the synthesis and catalytic activity of Preyssler nano-catalyst has been largely overlooked. 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 characterization¹². The exceptional properties of nano particles encouraged us to immobilize $H_{14}[NaP_5W_{30}O_{110}]$ into the SiO_2 nano particles and investigate the catalytic behavior of this new catalyst.

Organic esters represent an important class of intermediates widely used in fine chemicals, drugs, plasticizers, food preservatives, pharmaceuticals, solvents, perfumes, cosmetics and chiral auxiliaries¹³. Acetyl salicylic acid is commonly known by its trade name aspirin. Aspirin is a registered trademark of Bayer AG in Germany and more than 80 other countries. Aspirin is an effective non-steroidal analgesic, antipyretic and anti-inflammatory drug and is one of the most widely used medicine around the world¹⁴⁻¹⁸.

The synthesis of aspirin is classified as an esterification reaction. Salicylic acid is treated with acetic anhydride, an acid derivative, causing a chemical reaction that turns salicylic acid's hydroxyl group into an acetyl group. Small amounts of sulfuric acid (and occasionally phosphoric acid) are almost always used as a catalyst. This method is commonly employed in undergraduate teaching labs^{19,20}. Both acids are strongly corrosive and must be handled with care. In the present study, esterification of salicylic acid with acetic anhydride was carried out with Preyssler and Silica-Supported NanoPreyssler.

Experimental

Acetic anhydride, salicylic acid, sodium tungstate dihydrate, potassium chloride, orthophosphoric acid, sulfuric acid and other chemicals were obtained from Merck Company and used as received.

Catalyst preparation

Potassium salt of Preyssler's anion was prepared according to the procedure developed in our laboratory⁷. Preyssler HPAs, $H_{14}P_5$, was prepared as follows: 33 g $Na_2WO_4 \cdot 2H_2O$ 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 upon cooling to room

temperature white crystals was 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 vacuum⁷.

Silica-supported Preyssler nano particles were prepared according to our previous work²¹. For synthesis of supported catalyst, a solution of surfactant in cyclohexane (0.2 M) was added to a solution of Preyssler acid in a specified amount of water. The molar ratio of water to surfactant was selected as 3, 5 and 7. Then, tetraethoxysilan was added into the microemulsion phase. After mixing for various times (8, 12, 18, 25 and 30 h) at room temperature, dispersed Preyssler acid/SiO₂ nano structures were centrifuged (1500 rpm) and the particles were rinsed with acetone (4 times) and dried in a vacuum oven. The optimum ratio of water to surfactant was 3:1 and the optimum time²¹ was 30 h. Although micro emulsion procedure has been used by some authors, this method has never been reported for the synthesis of Preyssler nanostructures with different morphologies.

General procedure for aspirin synthesis

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 50 mL 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.

Catalyst recycling

At the end of the reaction, the catalyst was recovered by water and re-used in the same reaction. The recycled catalyst was used without observation of appreciable lost in its catalytic activity.

Results and Discussion

Silica-supported Preyssler nanostructures were obtained through a microemulsion method. The presence of heteropolyacid (H₁₄[NaP₅W₃₀O₁₁₀]) on the SiO₂ nano particles was confirmed by infrared (IR) spectroscopy (Figure 1). It could therefore be confirmed that the heteropolyacid (H₁₄[NaP₅-W₃₀O₁₁₀]) was successfully immobilized onto the SiO₂ nano particles. IR study showed that the HPA stayed intact on the nano particles after it was recycled two times in the reaction²¹.

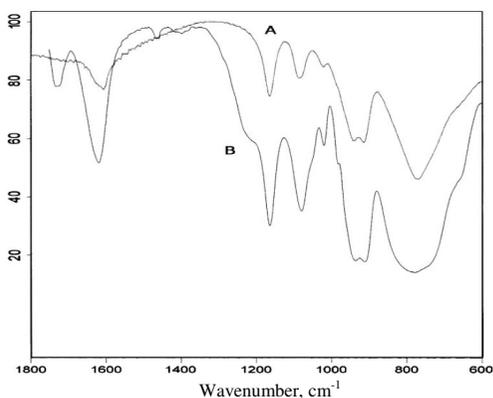


Figure 1. IR spectroscopy of Preyssler heteropolyacid in nano form (A) and bulk form (B)²²

The results of acetylation of salicylic acid with acetic anhydride using two Preyssler form as catalysts at room temperature (20 °C) are shown in Table 1.

Table 1. Yields of aspirin in acetylation of salicylic acid with two different heteropolyacid catalysts at room temperature

Entry	Time, min	Catalyst	Yield, %
1	30	NanoPreyssler ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$)	72
2	30	Preyssler ($H_{14}[NaP_5W_{30}O_{110}]$)	66
4	45	NanoPreyssler ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$)	76.5
5	45	Preyssler ($H_{14}[NaP_5W_{30}O_{110}]$)	71.5
7	60	NanoPreyssler ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$)	79
8	60	Preyssler ($H_{14}[NaP_5W_{30}O_{110}]$)	74.75
10	90	NanoPreyssler ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$)	82.5
11	90	Preyssler ($H_{14}[NaP_5W_{30}O_{110}]$)	75
13	120	NanoPreyssler ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$)	85
14	120	Preyssler ($H_{14}[NaP_5W_{30}O_{110}]$)	76.5

The experiment was carried out for the first time by an inexpensive, recyclable Nano Preyssler's anion. The results show that Nano Preyssler has higher activity and performance in esterification reactions compared to Preyssler.

The best yield of aspirin (85%) with 100% selectivity was attained with Nano Preyssler at almost 2 h of reaction at room temperature. Preyssler has also lower activity than the supported Nano Preyssler. It leads to 76.5% aspirin with 100% selectivity after 2 h (Entry 10).

It is clear from these reactions that the efficiency of ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) is higher than these of Preyssler. The reason is due to higher surface area available and also preservation of HPA structure in the silica-supported form of Preyssler. Also, as a matter of fact, if the particle size of nanomaterial decreases, the relative number of surface atoms will be increased and thus the catalyst activity will be enhanced.

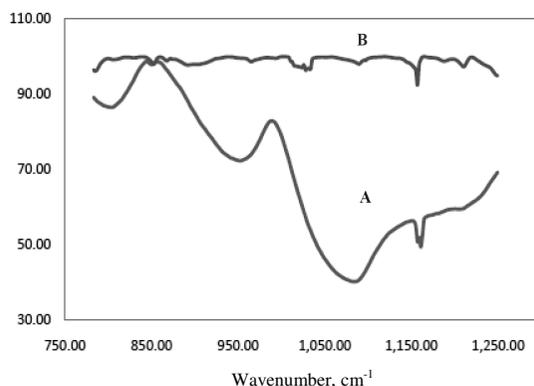


Figure 2. IR spectroscopy of recovered Preyssler heteropolyacid in nano form (A) and bulk form (B)

The reusability of the catalyst was also investigated. At the end of the reaction, the catalyst was recovered by a simple filtration. The recycled catalyst was washed with water and subjected to a second run of the reaction process. IR spectrum of the recovered solid catalyst (Figure 2) indicated that the catalyst can be recovered without structural degradation.

Conclusion

The present study demonstrates that Preyssler is an effective solid acid catalyst for the preparation of aspirin. Among different forms of Preyssler catalysts used, SiO₂ supported Nano Preyssler shows higher activity compared to the Preyssler. This method demonstrates the applicability of Preyssler's anion for those reactions that require solid catalysts with strong acidic properties. In addition, simple experimental setup and procedure makes this method a useful addition to the present methodologies.

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