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Using Supported Heteropoly Acids as a Eco-Friendly and Recyclable Catalyst for Efficient Synthesis of Acetylsalicylic Acid

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Abstract
Catalytic performance of supported Preyssler and Keggin heteropolyacids on silica, H$_{14}$[NaP$_5$W$_{30}$O$_{110}$]/SiO$_2$ and H$_3$[PW$_{12}$O$_{40}$]/SiO$_2$, have been studied at room temperature for highly selective and rapid liquid-phase O-acetylation of salicylic acid in order to synthesize acetylsalicylic acid which is well-known century-old chemical pharmaceutical. The usual catalysts in acetylsalicylic acid synthesis are toxic liquid acids such as HNO$_3$ and H$_2$SO$_4$, which would cause serious corrosive and other environmental problems. The performance of silica-supported preyssler and Keggin with various loadings is compared with sulfuric acid method. The heteropolyacids show almost 25% more activity compared with H$_2$SO$_4$.

Keywords: Acetylsalicylic acid, Green catalysts, Supported Heteropolyacids, SiO$_2$

Introduction
The catalytic function of heteropolyacids (HPAs) and related polyoxometalate compounds have attracted much attention particularly in the last two decades [1]. HPAs has attracted much interest because of its potential of great economic rewards and green benefits [2]. They also have excellent activity and can be easily recovered from reaction mixtures and reused. Acidic or neutral substances, such as SiO$_2$, active carbon, acidic ion-exchange resin, etc., are all suitable supports, but SiO$_2$, which is relatively inert towards HPAs, is the one most often used [3]. They are also of great interest as model systems for studying fundamental problems of catalysis [4]. Using HPA-based catalysts, it is frequently possible to obtain higher selectivity and successfully solve ecological problems [4]. HPAs are well-known to be strong Bronsted acids. All the HPAs are stronger than the usual inorganic acids (HCl, H$_2$SO$_4$, HNO$_3$, HBr) and even such strong acids as HClO$_4$ and CF$_3$SO$_3$H [4].

The application of Preyssler catalyst is mostly limited and only a few demonstrations of catalytic activity have been reported [12]. The important advantages of this heteropolyacid such as: strong Bronsted acidity with 14 acidic protons, high thermal stability, high hydrolytic stability (pH 0–12), reusability, safety, quantity of waste, separability, corrosiveness, high oxidation potential and greenness along with exclusive structure have attracted much attention on this catalyst [5]. The structure of this catalyst is shown in Fig. 1. On the other hand, Keggin
structure involves 4 three-fold\(\text{M}_3\text{O}_{13}\) groups. The total assemblage contains 40 close-packed oxygen atoms and has a tetrahedron pocket in its center for the heteroatom. The Keggin anions offer a limited hydrolytic and thermal stability compared to the Preyssler structure [5].

![Fig.1. Preyssler structure [6]](image)

The application of clean catalytic technologies, especially those with the use of heterogeneous catalysts, is becoming increasingly important for the development of environmentally benign chemical processes [7]. In the future, the number of such processes will undoubtedly increase because HPA-based catalysts have higher activity than known traditional catalysts. In view of green chemistry, the substitution of harmful liquid acids by solid reusable HPAs as catalyst in organic synthesis is the most promising application of this acids [8]. In comparison with the liquid mineral acids, solid acids could be easily separated from the reaction mixture by simple filtration with high recovery. This advantage directly leads to a decrease in equipment cauterization and environment pollution [9]. The effect of various parameters such as catalyst type, loading, temperature, and reaction time on the yield of products were studied and compared with those obtained, using traditional acids. It is found that \(\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}] /\text{SiO}_2\) is an eco-friendly catalyst for synthesis of acetylsalicylic acid [5].

Acetylsalicylic acid is both an organic ester and an organic acid. It is used extensively in medicine as a pain killer (analgesic) and as a fever-reducing drug (antipyretic). When ingested, acetylsalicylic acid remains intact in the acidic stomach, but in the basic medium of the upper intestinal tract, it hydrolyzes forming the salicylate and acetate ions. However, its additional physiological effects and biochemical reactions are still not thoroughly understood. It is now reported the application of a green and recyclable solid acid catalyst, silica-supported preyssler and Keggin, for highly selective and rapid liquid-phase O-acetylation of salicylic acid in order to synthesize acetylsalicylic acid at room temperature. The usual catalyst in the synthesis of acetylsalicylic acid is toxic liquid acids such as \(\text{HNO}_3\) and \(\text{H}_2\text{SO}_4\), which would cause serious corrosive and other environmental problems.

**Experimental**

**Materials**

Acetic anhydride, salicylic acid, sodium tungstate dihydrate, molybdotungstate dihydrate, orthophosphoric acid, Tungstophosphoric acid, sulfuric acid, ethanol, potassium chloride and silica gel. All the chemicals were obtained from Merck Company and used as received.

**Catalyst Preparation**

Heteropolyacid preyssler was prepared according to the procedure reported before [10]. Supported heteropolyacid catalysts were prepared by impregnating a support in the form of
powder (SiO$_2$) with an aqueous solution of the heteropolyacid with different concentrations. Samples were dried at 120-140°C, and the catalysts were calcined at 220°C for preyssler and 300°C for Keggin in a furnace prior to use.

**General Procedure**

The reactions were performed by mixing 2 g salicylic acid, 5 mL acetic anhydride with 0.05 g of 10-50Wt% H$_{14}$P$_5$/SiO$_2$ and H$_4$[SiW$_{12}$O$_{40}$]/SiO$_2$ at room temperature with intense stirring for the mentioned time. At the end of reaction, the mixture was diluted with 50 mL of water, and then the crude product was precipitated in an ice bath. The crude product was removed and 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 (using an Electro thermal IA 9100 Digital Melting Point apparatus) with those of an authentic sample. The product yield was determined quantitatively.

**Results and Discussion**

The performance of H$_{14}$[NaP$_5$W$_{30}$O$_{110}$]/SiO$_2$ and H$_4$[PW$_{12}$O$_{40}$]/SiO$_2$ in different loadings was compared with H$_2$SO$_4$. The heteropolyacids show higher activity compared with H$_2$SO$_4$. The reaction was carried out with different loadings. Catalyst loading was varied from 10 wt% to 50 wt%. As illustrated in Table 1, the yield of acetylsalicylic acid increased with an increase in catalyst loading from 10 wt% to 50 wt%. It can be seen from the figure that the activity of H$_{14}$P$_5$/SiO$_2$ (50wt%) is higher than sulfuric acid.

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<tr>
<td>1</td>
<td>H$<em>{14}$[NaP$<em>5$W$</em>{30}$O$</em>{110}$]/SiO$_2$(10wt%)</td>
<td>20</td>
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<td>2</td>
<td>H$<em>{14}$[NaP$<em>5$W$</em>{30}$O$</em>{110}$]/SiO$_2$(20wt%)</td>
<td>35</td>
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<td>3</td>
<td>H$<em>{14}$[NaP$<em>5$W$</em>{30}$O$</em>{110}$]/SiO$_2$(30wt%)</td>
<td>62</td>
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<td>4</td>
<td>H$<em>{14}$[NaP$<em>5$W$</em>{30}$O$</em>{110}$]/SiO$_2$(40wt%)</td>
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<td>5</td>
<td>H$<em>{14}$[NaP$<em>5$W$</em>{30}$O$</em>{110}$]/SiO$_2$(50wt%)</td>
<td>78</td>
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<tr>
<td>6</td>
<td>H$<em>4$[PW$</em>{12}$O$_{40}$]/SiO$_2$(20wt%)</td>
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<tr>
<td>7</td>
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<tr>
<td>8</td>
<td>H$<em>4$[PW$</em>{12}$O$_{40}$]/SiO$_2$(40wt%)</td>
<td>63</td>
</tr>
<tr>
<td>9</td>
<td>H$<em>4$[PW$</em>{12}$O$_{40}$]/SiO$_2$(50wt%)</td>
<td>69</td>
</tr>
<tr>
<td>10</td>
<td>H$_2$SO$_4$</td>
<td>53</td>
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</table>

**Effect of the reaction time**

Fig.2 gives the yield of acetylsalicylic acid as a function of time under the same conditions in the presence of H$_{14}$P$_5$/SiO$_2$(50wt%) and H$_2$SO$_4$. It can be seen from the Figure that the activity of H$_{14}$P$_5$/SiO$_2$(50wt%) is higher than that of sulfuric acid.
Conclusions

Silica-supported preyssler catalyst is an effective solid acid catalyst for preparation of acetylsalicylic acid. The results also indicate that the reaction time was an important factor. $\text{H}_{14}\text{[NaP}_{5}\text{W}_{30}\text{O}_{110}]$, $\text{H}_{3}\text{[PW}_{12}\text{O}_{40}]$ catalyst in heterogenous phase can be recovered and reused without loss of structures and appreciable activity.

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References


ستن استیل سالسیلیک اسید با استفاده از هتروپلی اسیدهای نهش یافته به عنوان کاتالیست های دوستدار محیط زیست و قابل بازیابی تارک اسلامی*، علی احمدی‌بزرگی‌فر، مجید هروی، حسین نظری

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چکیده

ستن استیل سالسیلیک اسید در دمای اتفاق از طریق استیلاپلیاسن سالسیلیک اسید توسط استیک ایندنوزی در حضور پرایسر و کی شیمیایی بر روی سیلیکات‌کلر که از انواع هتروپلی اسیدهای است برای کمک گردید به داشتن تکنولوژی تمیز که نیاز اساسی جامعه می‌باشد مورد بررسی قرار گرفته است. کاتالیست های مورد استفاده در این چا همگی قابل استفاده مجدد می‌باشند. استیل سالسیلیک اسید که دارای مهم‌ترین کاربرد در فیلم‌سازی کاتالیستی‌های فسفور و سیلیکون‌پوشی‌های غلظت هر چه درد دیگر، این کاتالیست‌ها به‌عنوان کاتالیست‌های نهش‌پذیر در بارگذاری های مختلف از اسید سولفوریک می‌باشند. شده است. هتروپلی اسیدها فعالیت بالایی در مقایسه با اسید سولفوریک از خود نشان دادند.

واژه‌های کلیدی: استیل سالسیلیک اسید، کاتالیست سیز، هتروپلی اسید های نهش‌پذیر، SiO2

*دانشجوی کارشناسی ارشد رشته مهندسی شیمی

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