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NANO SILICA-SUPPORTED PREYSSLER AS A GREEN AND ECO-FRIENDLY CATALYST FOR EFFICIENT SYNTHESIS OF ASPIRIN

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ABSTRACT

Heteropolyacids due to their unique physicochemical properties are widely used as homogeneous and heterogeneous acid and oxidation catalysts. In many cases HPA-based catalysts have higher activity than known traditional catalysts. Heteropolyacids (HPAs) are strong Bronsted acids composed of heteropolyanions and protons as the counterions and are used to replace environmentally harmful liquid acid 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 these acids. In comparison with 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. In the present investigation, we have applied a green and recyclable solid acid catalyst, nanosilica-supported preyssler ($H_{14}[NaP_5W_{30}O_{110}]$) for highly selective and rapid liquid-phase O-acetylation of salicylic acid in order to synthesize aspirin at room temperature. The usual catalysts in aspirin synthesis are toxic liquid acids such as HNO_3 and H_2SO_4 , which would cause serious corrosive and other environmental problems. 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. To our knowledge, no attempt has been made to use nanosilica-supported preyssler catalysts for the mentioned reaction. The reaction was carried out by using $H_4P_5/nanoSiO_2$ with different loadings. Catalyst loading was varied from 10 to 50wt%. The performance of nanosilica-supported preyssler in various loadings was compared with those of H_2SO_4 . The yield of aspirin was increased from 27% to 85% with an increase in catalyst loading from 10 to 50wt%. The yield is 53% in sulfuric acid method.

Keywords: Aspirin; Recyclable Catalysts; Heteropolyacids; NanoSiO₂

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Heteropolyacids due to their unique physicochemical properties are widely used as homogeneous and heterogeneous acid and oxidation catalysts. In many cases HPA-based catalysts have higher activity than known traditional catalysts. Heteropolyacids (HPAs) are strong Bronsted acids composed of heteropolyanions and protons as the counterions and are used to replace environmentally harmful liquid acid 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 these acids. In comparison with 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. In the present investigation, we have applied a green and recyclable solid acid catalyst, nanosilica-supported preyssler ($H_{14}[NaP_5W_{30}O_{110}]$) for highly selective and rapid liquid-phase O-acetylation of salicylic acid in order to synthesize aspirin at room temperature. The usual catalysts in aspirin synthesis are toxic liquid acids such as HNO_3 and H_2SO_4 , which would cause serious corrosive and other environmental problems. 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. To our knowledge, no attempt has been made to use nanosilica-supported preyssler catalysts for the mentioned reaction. The reaction was carried out by using $H_{14}P_5/nanoSiO_2$ with different loadings. Catalyst loading was varied from 10 to 50wt%. The performance of nanosilica-supported preyssler in various loadings was compared with those of H_2SO_4 . The yield of aspirin was increased from 27% to 85% with an increase in catalyst loading from 10 to 50wt%. The yield is 53% in sulfuric acid method.

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INTRODUCTION

Heteropolyacid (HPA) based catalysts are interesting class of compounds exhibiting superacidity ($H_0 = -13$). 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, H₂SO₄, HNO₃, HBr) and even strong acids such as HClO₄ and CF₃SO₃H [4].

The HPA with Keggin type anions such as PW₁₂O₄₀ are most suitable for acid catalysis. These are referred to as tungstophosphoric acid (TPA). The unique characteristics of HPAs like the soft basicity of the polyanion, the pseudo liquid phase (in some cases) and their tunable acidity can be exploited for various reactions [5]. The application of Preyssler catalyst is mostly limited and only a few demonstrations of catalytic activity have been reported. 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 [6]. The structure of this catalyst is shown in Fig. 1. On the other hand, Keggin structure involves 4 three-fold M₃O₁₃ 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 [6].

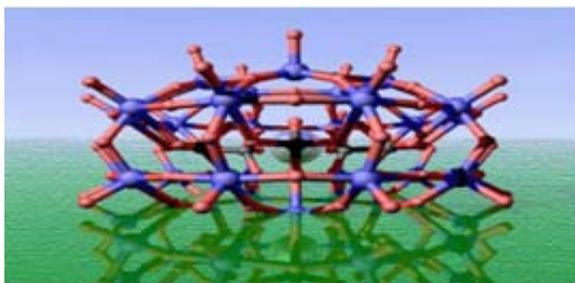


Figure 1: Preyssler structure [7].

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 [8]. In the near 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 these acids [9]. 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 [10].

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 H₁₄[NaP₅W₃₀O₁₁₀]/SiO₂ is an eco-friendly catalyst for the synthesis of *aspirin* [6].

Aspirin 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, aspirin 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, nanosilica-supported preyssler and Keggin, for highly selective and rapid liquid-phase O-acetylation of salicylic acid in order to synthesize aspirin at room temperature. The usual catalyst in the synthesis of aspirin is toxic liquid acids such as HNO_3 and H_2SO_4 , which would cause serious corrosive and other environmental problems. To our knowledge, no attempt to use nanosilica-supported preyssler catalysts for the latter reaction has been made so far.

MATERIALS AND METHODS

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

Catalyst Preparation. Heteropolyacid preyssler was prepared according to the procedure reported before [11]. 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 0.2g of 10-50wt% $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]/\text{nanoSiO}_2$, $\text{H}_{14}\text{P}_5/\text{SiO}_2$ and $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]/\text{SiO}_2$ 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.

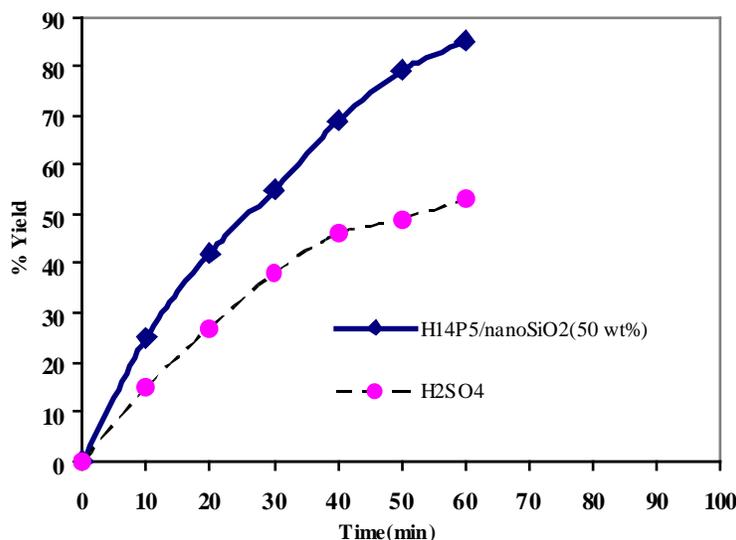
RESULTS AND DISCUSSION

The performance of $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]/\text{nanoSiO}_2$, $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]/\text{SiO}_2$ and $[\text{H}_3\text{PW}_{12}\text{O}_{40}]/\text{SiO}_2$ at different loadings was compared with H_2SO_4 . The heteropolyacids show higher activity compared with H_2SO_4 . Among heteropolyacids, nano-supported preyssler was the effective one. 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 aspirin was increased with an increase in catalyst loading from 10 wt% to 50 wt%. It can be seen from the figure that the activity of $\text{H}_{14}\text{P}_5/\text{SiO}_2$ (50wt%) is higher than sulfuric acid.

Effect of the Reaction Time. Fig.2 gives the yield of aspirin as a function of time under the same conditions in the presence of $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]/\text{nanoSiO}_2$ (50wt%) and H_2SO_4 . It can be seen from this figure that the activity $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]/\text{nanoSiO}_2$ (50wt%) is higher than that of sulfuric acid.

Table 1. Comparison of aspirin yields in two different processes at room temperature after 60 min.

Entry	Catalyst	Yield (□□%)
1	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]/nanoSiO ₂ (10wt%)	27
2	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]/nanoSiO ₂ (20wt%)	34
3	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]/nanoSiO ₂ (30wt%)	65
4	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]/nanoSiO ₂ (40wt%)	72
5	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]/nanoSiO ₂ (50wt%)	85
6	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]/SiO ₂ (10wt%)	20
7	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]/SiO ₂ (20wt%)	35
8	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]/SiO ₂ (30wt%)	62
9	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]/SiO ₂ (40wt%)	68
10	H ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]/SiO ₂ (50wt%)	78
11	H ₄ [PW ₁₂ O ₄₀]/SiO ₂ (20wt%)	30
12	H ₄ [PW ₁₂ O ₄₀]/SiO ₂ (30wt%)	55
13	H ₄ [PW ₁₂ O ₄₀]/SiO ₂ (40wt%)	63
14	H ₄ [PW ₁₂ O ₄₀]/SiO ₂ (50wt%)	69
15	H ₂ SO ₄	53

**Figure 2: Yield of aspirin as a function of time with two different catalysts.**

CONCLUSIONS

Nano silica-supported preyssler catalyst was an effective solid acid catalyst for the preparation of aspirin. The results also indicate that the reaction time was an important factor. H₁₄[NaP₅W₃₀O₁₁₀] and H₃[PW₁₂O₄₀] catalysts in heterogonous phase can be recovered and reused without loss of structures and appreciable activity.

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