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SILICA-SUPPORTED KEGGIN NANO PARTICLES AS A CATALYST FOR THE SYNTHESIS OF ACETYL SALICYLIC ACID

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ABSTRACT

Keggin as an eco-friendly solid acid catalyst has been used as catalyst for acetylation of salicylic acid with acetic anhydride. The reaction was carried out by keggin/nanoSiO_2 with different loadings. The performance of heteropoly acid in the presence of acetic anhydride as acetylating agent for acetylation of salicylic acid was compared.The heteropolyacid shows higher activity compared with H_2SO_4.

KEYWORDS : *Nanoparticles, Acetyl salicylic acid, Heteropolyacid, Silica*

INTRODUCTION

Acetylsalicylic acid, also known by trade name Aspirin or ASA, is an acetyl derivative of salicylic acid that is a white, crystalline, weakly acidic substance, with melting point 137°C. It is useful in the relief of headache and muscle and joint aches.

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 [1]. HPAs have 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]. The HPA with Keggin type anions such as $H_4[SiW_{12}O_{40}]$ are most suitable for acid catalysis. 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 [4].

In the present investigation, we have applied a green and recyclable solid acid catalyst, nanosilica-supported Keggin ($H_4[SiW_{12}O_{40}]$/nanoSiO_2) 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.

EXPERIMENTAL SECTION

Materials

Acetic anhydride, salicylic acid, sulfuric acid, tungsto(VI) silicic acid, ethanol, and silica gel were obtained from Merck Company and used as received.

Catalyst Preparation

Supported heteropolyacid catalysts were prepared by impregnating a support in the form of powder (nanoSiO_2) with an aqueous solution of the heteropolyacid with different concentrations. Samples were dried at 120-140°C, and the catalysts were calcined at 300°C in a furnace prior to use.

General Procedure

The reactions were performed by mixing salicylic acid, acetic anhydride with 20-50% $H_4[SiW_{12}O_{40}]$ /nanoSiO_2 at room temperature with intense stirring. At the end of reaction, the mixture was diluted with 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 with that of an authentic sample. The product yield was determined quantitatively.

RESULTS AND DISCUSSIONS

The reaction was carried out by $H_4[SiW_{12}O_{40}]$ /nanoSiO_2 with different loadings. Catalyst loading was varied from 20% to 50%. The performance of nanosilica-supported keggin in different loadings was compared with H_2SO_4. The heteropolyacids show higher activity compared with H_2SO_4. As illustrated in Table 1, the yield of aspirin increased with an increase in catalyst loading from 20% to 50%. Fig.1 shows the

yield of aspirin as a function of time in the presence of $H_4[SiW_{12}O_{40}]$ /nanoSiO_2(50wt%) and H_2SO_4. It can be seen from the figure that the activity of $H_4[SiW_{12}O_{40}]$ /nanoSiO_2 (50wt%) is higher than sulfuric acid.

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

Entry	Catalyst	Yield (%)
1	$H_4[SiW_{12}O_{40}]$/nanoSiO_2(20wt%)	32
2	$H_4[SiW_{12}O_{40}]$/nanoSiO_2(30wt%)	55
3	$H_4[SiW_{12}O_{40}]$/nanoSiO_2(40wt%)	62
4	$H_4[SiW_{12}O_{40}]$/nanoSiO_2(50wt%)	71
5	H_2SO_4	53

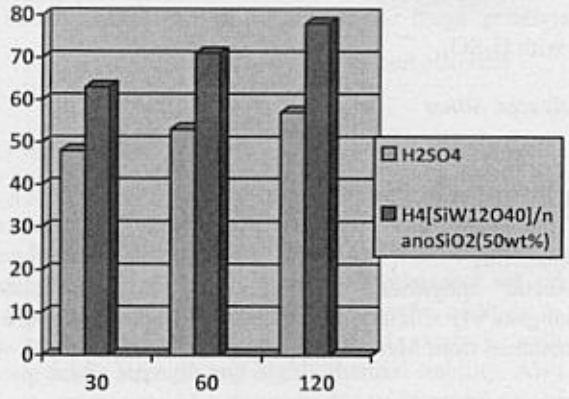

Fig. 1 Yield of aspirin as a function of time in the presence of $H_4[SiW_{12}O_{40}]$/nanoSiO_2(50wt%) and H_2SO_4.

CONCLUSIONS

Nano silica-supported keggin catalyst is an effective solid acid catalyst for preparation of aspirin. The results also indicate that the reaction time was an important factor. $H_4[SiW_{12}O_{40}]$ catalyst in heterogonous phase can be recovered and reused without loss of structures and appreciable activity.

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