3rd International Congress on Nanoscience and Nanotechnology (ICNN 2010)

9 - 11 November 2010 / Shiraz University, Shiraz, Iran

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EFFICIENT SYNTHESIS OF ASPIRIN USING NANO SILICA-SUPPORTED PREYSSLER AS A GREEN AND RECYCLABLE CATALYST

as poster/oral presentation.

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ICNN 2010
International Congress on Nanoscience and Nanotechnology
9-11 November 2010 Shiraz - Iran

EFFICIENT SYNTHESIS OF ASPIRIN USING NANO SILICA-SUPPORTED PREYSSLER AS A GREEN AND RECYCLABLE CATALYST

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KEYWORDS
Aspirin, Recyclable catalysts, Heteropolyacids, nanoSiO$_2$

ABSTRACT
Synthesis of aspirin at room temperature *via* O-acetylation of salicylic acid in the presence of a nanosilica-supported preyssler as a recyclable and green catalyst is reported. The reaction was carried out by $H_{14}P_5$/nanoSiO$_2$ with different loadings. The performance of nanosilica-supported preyssler with various loadings was compared with sulfuric acid method. The heteropolyacids show higher activity compared with H_2SO_4.

INTRODUCTION

Heteropolyacids (HPAs) are strong Bronsted acids composed of heteropolyanions and protons as the countercations and are used to replace environmentally harmful liquid acid catalysts[1]. Heteropolyacids due to their unique physicochemical properties are widely used as homogeneous and heterogeneous acid and also oxidation catalysts. In many cases HPA-based catalysts have higher activity than known traditional catalysts [2]. 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 [3].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 [4]. In heterogeneous as well as homogeneous conditions, HPAs are more effective than conventional catalysts [2].

We now report the application of a green and recyclable solid acid catalyst, nanosilica-supported preyssler, 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.

EXPERIMENTAL SECTION

Materials

Acetic anhydride, salicylic acid, sodium tungstate dihydrate, molybdotungstate dihydrate, orthophosphoric acid, sulfuric acid, ethanol, potassium chloride and nanosilica 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[5]. 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 220°C 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 10-50%H_{14}–P_5/nanoSiO$_2$ at room temperature with intense stirring for 1 hour time that we obtained as an optimum 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 with that of an authentic sample. The product yield was determined quantitatively.

RESULTS AND DISCUSSIONS

The performance of nanosilica-supported preyssler in different loadings was compared with H_2SO_4. The heteropolyacids show higher activity compared with H_2SO_4. The reaction was carried out by $H_{14}P_5$/nanoSiO_2 with different loadings. Catalyst loading was varied from 10% to 50%. As illustrated in Table 1, the yield of aspirin increased with an increase in catalyst loading from 10% to 50%. Fig.1showes the yield of aspirin as a function of time in the presence of $H_{14}P_5$/nanoSiO_2(50wt%) and H_2SO_4. It can be seen from the figure that the activity of $H_{14}P_5$/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	$H_{14}[NaP_5W_{30}O_{110}]$/nano$SiO_2$(10wt%)	27
2	$H_{14}[NaP_5W_{30}O_{110}]$/nano$SiO_2$(20wt%)	34
3	$H_{14}[NaP_5W_{30}O_{110}]$/nano$SiO_2$(30wt%)	65
4	$H_{14}[NaP_5W_{30}O_{110}]$/nano$SiO_2$(40wt%)	72
5	$H_{14}[NaP_5W_{30}O_{110}]$/nano$SiO_2$(50wt%)	85
6	$H_{14}[NaP_5W_{30}O_{110}]/SiO_2$(50wt%)	78
7	H_2SO_4	53

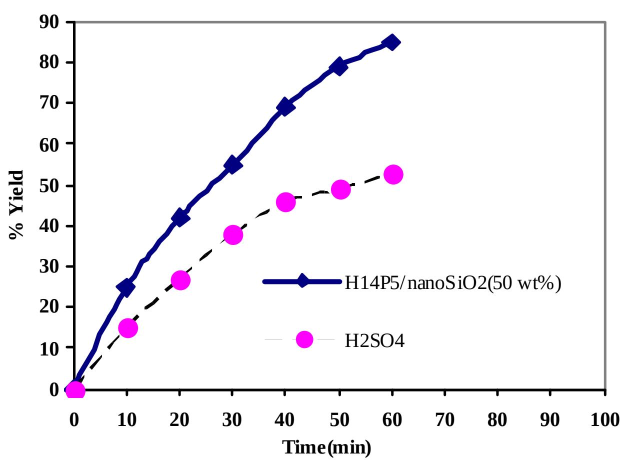

Fig.1. Yield of aspirin as a function of time with two different catalysts.

CONCLUSIONS

Nanosilica-supported preyssler catalyst is an effective solid acid catalyst for preparation of aspirin.

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