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NANO PREYSSLER : AN EFFICIENT AND REUSABLE SOLID CATALYST FOR ESTERIFICATION OF AROMATIC ALCOHOLS

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ABSTRACT

The esterification of salicylic acid with benzylic alcohols, $RC_6H_4CH_2OH$(R=H, NO_2, OCH_3, Br,Cl,Me) was carried out in the presence of a new and green nano preyssler hetropoly acid both in thermal conditions and microwave irradiation. The effects of various parameters such as solvent type, molar ratio of substrate, catalyst loading, catalyst amount, temperature and reaction time were studied and the optimum conditions were obtained. This catalyst is recyclable, cost effective and environmental friendly and could be used in similar reactions.

KEYWORDS : *NanoPreyssler, Esterification , Catalyst, Heteropolyacid*

INTRODUCTION

Catalysis with Preyssler heteropolyacid (HPA) has been widely developed in a broad range of organic synthesis and environmentally benign catalysis during the past few years[1-3]. Good yields, high selectivity, economically convenience, ease of work up, high hydrolytic and thermal stability, and high catalytic activity of Preyssler have motivated increasing potential for nano catalysis in organic synthesis and environmentally benign catalysis [4,5]. Recently, we systematically investigated the catalytic behavior of Preyssler for many acid catalyzed reactions and found that this catalyst is more active than the other catalysts[6,7]. In order to perform a new contribution to the field of eco-friendly acid-catalyzed reactions coupled with nanatechnology, we report here on the results of esterification of salicylic acid with aromatic alcohols using nano-SiO_2 supported Preyssler , under thermal and microwave conditions.
The objective of this paper is to improve and modify of catalytic properties of Preyssler catalyst, with formula of H_{14} [Na P_5 W_{30} O_{110}], via nano form in esterification of benzylic alcohols.

EXPERIMENTAL

CHEMICALS AND INSTRUMENTS

H_{14} [$NaP_5W_{30}O_{110}$] was prepared according to our earlier work [1].Silica nano structures were obtained through a sol-gel method and were characterized by transmission electron microscopy and powder X-ray diffraction[8]. IR spectra were obtained with a Brucker 500 scientific spectrometer[8]. GLC analysis was performed on a Pu 4500 gas chromatograph with FID detector. The particle size and shape of nano structures of SiO_2 were observed by TEM (LEO 912 AB). The XRD profiles of the samples were obtained using a PW 3710-Philips powder diffractometer(Cu Kα irradiation).

GENERAL PROCEDURE

In a typical reaction benzylic alcohols , salicylic acid and nanocatalyst were refluxed in dichloroethan for 3 hr.At regular intervals,Karl fisher titration was performed for determination of produced water. The products were characterized by comparison of their spectroscopic data with those of authentic samples. Yields were determined by GC. Under MW irradiation a solution of salicylic acid, alcohol and nanocatalyst was irradiated for 3min .

RESULTS AND DISCUSSION

Nano-sized SiO_2 with different loading of Preyssler has been synthesized and the catalytic behavior of it has been studied in esterification of salicylic acid with different aromatic alcohols. The heteropolyacid in the SiO_2 nano particles was confirmed by infrared spectroscopy and confirmed that the heteropolyacid was successfully immobilized into the SiO_2 nano particles. The catalyst with 30wt.% loading showed good catalytic activity with a maximum conversion of salicylic acid as compared with other loadings(figure 1). Esterification reactions were found to occur faster with microwave irradiation than conventional heating. The results are shown in figure 2. As we can see this catalyst afforded excellent yields in very short times. A dramatic change in the way chemical synthesis can be achieved by microwave irradiation. Molar ratio of acid to alcohol, temperature, catalyst amount and reaction period influenced the ester yield during esterification.

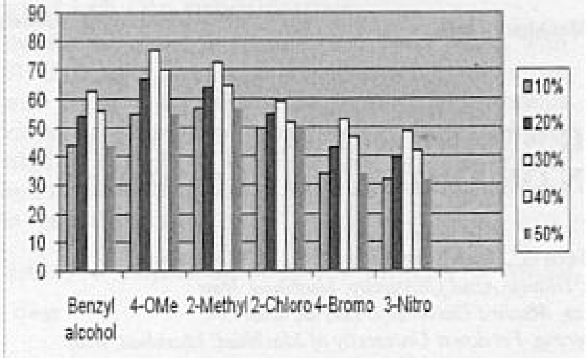

Figure.1 Esterification of aromatic alcohols with salicylic acid using preyssler supported on nano-SiO_2(reflux)

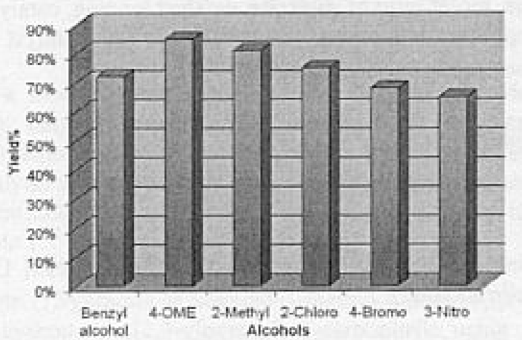

Figure.2 Esterification of aromatic alcohols with salicylic acid using preyssler supported on nano-SiO_2(microwave)

Reusability of the catalyst

In order to further evaluate performance of the catalyst, reuse experiments of the catalyst were carried out. The catalyst was reused for the next run under the same conditions. The results indicated that the activity of the catalyst was not affected even at the third run with the reused catalyst. This phenomenon implied that the catalyst can be efficiently recovered and recycled.

CONCLUSION

This research reports a new solid acid catalyst for the replacement of traditional liquid acids in important reactions and introduces a new catalyst for organic chemistry. This catalytic study may explore the wide application of preyssler solid acid catalyst in industry.

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