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Tin exchanged Tungstophosphoric acid supported on K-10 as catalyst for synthesis of n-Butyl levulinate from Furfuryl alcohol

Jennifer S. Dicks, Manishkumar S. Tiwari, Vivek V. Ranade and Haresh G. Manyar*
School of Chemistry and Chemical Engineering, Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast, BT9 5AG, Northern Ireland, UK
**corresponding author: h.manyar@qub.ac.uk*

Introduction

Recently, the development of lignocellulose derived biofuels and fuel-additives has taken center stage to address the threefold challenge of increasing energy demand, dwindling crude oil resource and tightening emission controls. The first generation biofuels such as ethanol and biodiesel are associated with compatibility and lower energy density issues. However lignocellulosic biomass, which is an abundant resource, can easily be hydrogenated to furfuryl alcohol (FA). The conversion of FA to levulinic esters such as butyl levulinate (BL) becomes a potential route to next generation biofuels and fuel-additives. BL has high oxygen content, high octane number, low water solubility and similar physical properties to diesel fuel [1]. Apart from being potential fuel-additive with unique properties such as stable flashpoint, high lubricity, nontoxic nature and better flow properties under cold conditions, BL is also a value-added chemical with applications in plasticizers, flavors, fragrance, drug intermediates and as a solvent. The process for synthesis of BL from FA involves alcoholysis using an acid catalyst through formation of a series of reaction intermediates. The process also forms various oligomeric/polymeric side products. Further studies are required for developing more selective process with high yield of BL and lower formation of polyfurfuryl alcohol products. In present study, we have evaluated the use of tin exchanged heteropoly acids supported on K10 as solid acid catalysts for alcoholysis of FA. Tungstophosphoric acid (TPA) is most widely used HPA because of its better thermal stability and higher acidity [2]. The current work aims at synthesis of tin exchanged tungstophshphoric acid supported on K-10 with different amount of tin and its activity toward synthesis of BL from FA and 1-butanol. The catalyst was thoroughly characterized using different techniques such as FT-IR, XRD, UV-Vis, pyridine-IR, SEM and TEM; and the reaction conditions were optimized for high selectivity to BL.

Materials and Methods

Tin exchanged tungstophosphoric acid supported on K-10 catalysts (20%w/w Sn_x-TPA/K-10) with different amount of Sn were prepared by sequential incipient wetness technique using $Sn(II)Cl_2$ and TPA solutions in methanol as precursors. The as prepared materials were dried at 120°C, followed by calcination at 300°C for 3h in tubular furnace under flowing air. Different amounts of Sn (x varying from 0 to 1.5) were used to replace proton of TPA represented as 20%(w/w) Sn_x-TPA/K-10.

All the reactions were performed in 20 ml glass reactor equipped with magnetic stirrer at 110 °C for 5 h and periodically taken samples were analysed using gas chromatography (Agilent Technologies 7820A) equipped with FID detector and HP-5 capillary column. The products were identified by GC-MS.

Results and Discussion

Effect of various catalysts

Synthesis of BL from FA is a two-step reaction with formation of two intermediates as shown in Scheme 1. Different catalysts such as tin exchanged TPA supported on K-10, TPA supported on K-10, bentonite clay and K-10 were screened for butanolysis of FA (Figure 1).

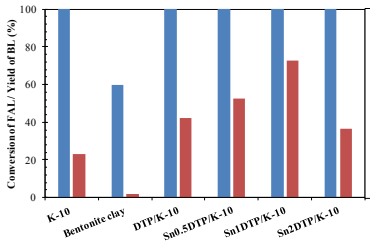
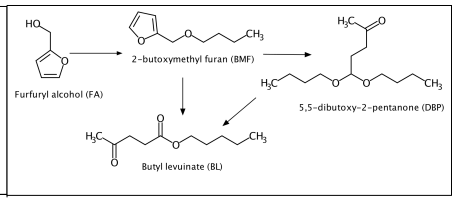


Figure 1. Comparison of various catalysts for alcoholysis of furfuryl alcohol to butyl levulinate Reaction conditions: FA:butanol 1:20, catalyst wt. 0.3 g, temperature 110 °C, (■) Conversion of FA,(■) Yield of BL.



Scheme 1. Reaction network for alcoholysis of furfuryl alcohol to butyl levulinate.

For catalyst screening, reactions were carried out at 110°C with 1:20 mole ratio of FA and 1-butanol and with 0.3g of catalyst for 150 min. Two different clays were first screened to compare their activity for reaction. K-10 gave 100% FA conversion and yield of BL as 23.2% in 150 min while bentonite gave 60% FA conversion with 1.2% yield of BL. The higher activity of K-10 clay is due to higher acidity of K-10 as compared to bentonite. Based on above results K-10 was chosen as support for the TPA and tin exchanged TPA.

The activity for different TPA supported catalyst was compared on basis of yield of BL as the FA conversion was found to be 100% in all cases. Yield of BL was calculated at the end of 150 min. Supporting only TPA on K-10 have given 42.4% yield of BL which is higher than K-10. Replacing H^+ ion in TPA with Sn has resulted in better activity, as with $Sn_{0.5}$TPA/K-10 100% conversion of FA with 52.6% yield of BL was achieved. Further replacement of proton with Sn i.e. Sn_1TPA/K-10 resulted in the increased activity with 72.6% yield of BL and 100% conversion of FA. Upon further increase in Sn amount resulted in complete removal of H^+ ions and the activity decreased as shown in Figure 1.

Process parameters including catalyst loading, Sn_x loading, furfuryl alcohol : butanol mole ratio and reaction temperature were optimized. The optimum conditions using 20% w/w Sn_1TPA/K-10 catalyst resulted in complete conversion of furfuryl alcohol with 98% selectivity to butyl levulinate. The catalyst stability was also investigated and found to be heterogeneous in nature. The catalyst was successfully recycled for three runs without losing activity.

Significance

Highly efficient and selective catalytic protocol for alcoholysis of furfuryl alcohol has been developed by using Tin exchanged Tungestophshphoric acid supported on K-10 as catalyst. The advantages of this process are high yield of butyl levulinate, negligible side product formation of polyfurfuryl alcohol, low catalyst cost. The process is green as no solid waste being discharged from the neutralization of spent mineral acid.

References

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[2] Tiwari M.S., Yadav G. D., *RSC Advances* **2016**, 6, 54, 49091.