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Solvent free synthesis of HMF levulinate using tin exchanged tungstophosphoric acid supported on K-10 catalyst

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Introduction
The three fold challenge of continuously decreasing crude oil resources, increasing energy demand and tightening emission controls have resulted in increased efforts for renewable energy sources for eg. biofuels and biofuel-additives. Biomass has emerged as one of the prominent alternatives not only to fossil fuels but also as a source for renewable platform chemicals. Lignocellulosic biomass has been well explored and used to get several useful platform molecules such as ethanol, furfural, lactic acid, 5-hydroxymethyl furfural (HMF) and levulinic acid. HMF and LA can be transformed into several high value products including next generation biofuels and fuel additives, such as HMF levulinate. HMF esters can be synthesized by esterification of HMF with bio-based acids such as lactic acid, pyruvic acid, acetic acid and levulinic acid. HMF levulinate has several applications in chemical and pharmaceutical industries, fuel-additives, fungicides and surfactants.

Heteropoly acids (HPA) possess high activity due to the super acidity of these acids. Dodecatungstophosphoric acid (DTP) is reported to be most widely used HPA because of its better thermal stability and higher acidity [3]. In the present work, tin exchanged tungstophosphoric acid supported on K-10 was synthesized and characterized by using different techniques such as FT-IR, XRD, UV-Vis, SEM, and acidity measurements. The catalytic activity of tin exchanged tungstophosphoric acid/K-10 with varying tin substitutions was evaluated in esterification of HMF to HMF levulinate, and the reaction conditions were optimized for high selectivity to HMF levulinate.

Materials and Methods
Tin exchanged tungstophosphoric acid supported on K-10 catalysts (20% w/w Sn-DTP/K-10) was prepared by sequential incipient wetness technique using Sn(II)Cl2 and DTP 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. All the reactions were performed in 20 ml glass reactor equipped with magnetic stirrer at 80°C for 2h and periodically taken samples were analyzed 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
Characterization of catalyst
XRD patterns of K-10, DTP/K-10 and Sn-DTP/K-10 are shown in Figure 1. DTP is highly crystalline as shown in the insert and after the exchange with tin the intensity of peaks decreases slightly but sharp peaks confirm the crystalline nature of Sn-DTP. The loading of DTP and Sn-DTP on K-10 does not change the overall XRD pattern of catalyst, indicating the structure of K-10 clay is retained after impregnation.

Catalyst comparison and optimization
The scheme 1 represents the esterification of HMF with LA. The reaction parameters such as catalyst weight, temperature, and mole ratio HMF to LA were studied to maximise the yield of HMF levulinate. With increase in temperature the rate of reaction increased linearly indicating the reaction is under kinetic regime and any diffusion limitation was absent (Figure 2). Under the optimized conditions of 0.2 g catalyst weight, 1:5 mole ratio of HMF and LA, and 110°C temperature 90% conversion of HMF was achieved within 2h. Further the kinetic model was developed using Langmuir Hinshelwood Hougen Watson (LHHW) adsorption mechanism and rate constants were calculated. The apparent activation energy was found to be 28.4 kJ/mol. The observed activation energy is larger than the activation energy of diffusion in liquids (12-21 kJ mol-1), thus confirming the absence of external mass transfer and intra-particle diffusion resistances.

Scheme 1: Esterification of Levulinic acid with HMF

Significance
Facile, efficient and selective catalytic protocol for esterification of HMF to HMF levulinate has been developed using 20% w/w Sn-TPA supported on K-10 as catalyst. Process was optimized to obtain 90% yield of HMF levulinate at 110°C. The advantages of this process are high yield of HMF levulinate, low catalyst cost and negligible side product formation, such as furanic polymers. The process is green and clean as no effluent with spent mineral acids were generated.

References