

Liquid Phase Acylation of 2-Methylfuran with Fatty Acid Anhydride

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Introduction. Lignocellulosic biomass is a renewable source of furans which can be upgraded to commodity chemicals and fuels. Park et al. [1] showed that a new class of renewable surfactants known as oleo furan sulphonate (OFS) surfactants can be synthesized from biomass-derived furans and fatty acids or anhydrides via Friedel Crafts acylation. The furan ring substitutes the benzene ring of the conventional petrochemical based linear alkylbenzene sulphonate (LAS) surfactants as the aromatic linker, connecting the long hydrocarbon tail to the hydrophilic head group. In comparison to LAS surfactants, these biorenewable surfactant molecules exhibit improved detergency properties such as stability in hard water, low Krafft temperature, and comparable critical micelle concentration. Friedel Crafts acylation of furan for the formation of alkyl furan ketones is the key reaction involved in the tunable and selective synthesis of OFS surfactants for specific applications. Solid acid catalysts have been studied for acylation of furanics and other aromatic substrates [2-4]. However, such reactions are prone to catalyst deactivation by coke formation or high-molecular weight products. This study aims to determine the kinetics and the mechanism of acylation of 2-methylfuran using long chain anhydrides (C₈ or higher) as the acylating agent and mesoporous Al-MCM-41 as the solid acid catalyst. The reaction is studied using a high-pressure liquid phase fixed-bed reactor.

Materials and Methods. Al-MCM-41, purchased from Sigma Aldrich, was calcined at 450 °C for 4 hr using an air flow rate of 63 ml/min. The experiments were performed in a liquid phase flow reactor operated at 29 bar. The feed solution containing 0.06 M 2-methylfuran, 0.09 M n-octanoic anhydride and an internal standard, n-decane in heptane was flowed at 1.0 ml/min through the reactor. The reaction was monitored by collection of liquid samples every 15 minutes for 240 minutes time on stream at 100°C. The liquid samples were analyzed using a gas chromatograph (Agilent 7890A) equipped with a flame ionization/ Polyrac™ detector. To account for catalyst deactivation over the course of the reaction, a bracketing method was employed. An activity factor was obtained by subjecting the catalyst bed to a fixed reference condition mentioned above. In this way, the effects of different reaction conditions were compared.

Results and Discussion. The reaction of 2-methylfuran with n-octanoic anhydride formed acyl furan ketone and n-octanoic acid over Brønsted acid catalyst, Al-MCM-41. Figure 1 shows the reaction scheme and time on stream rate of formation of the acylated product. The initial rapid reduction in the rate was due to catalyst deactivation. After 4 hr time on stream, a bracketing technique was employed to obtain the steady state reaction rates under differential conditions (<10% conversion). Using these rates, an apparent activation energy of 13.64 ± 1.34 kcal/mol (std. error) was obtained over a temperature range of 343-400 K (Figure 2). This value compared well with the literature value for the acylation reaction of 2-methylfuran [2]. Determination of reaction orders aided in further elucidating the rate expression and active site mechanism.

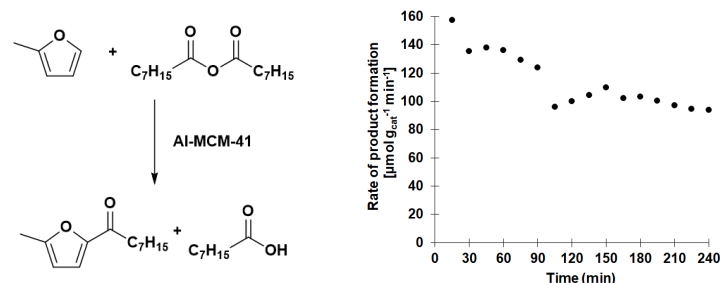


Figure 1. (Left) Reaction scheme and (Right) rate of formation of the acylated product over Al-MCM-41. Reaction conditions: 105 °C, 29 bar maintained using He gas flow, 75.8 mg Al-MCM-41, 1 ml/min liquid flow, 0.0656 M 2-methylfuran, 0.0998 M n-octanoic anhydride in heptane (n-decane is used as internal standard for GC analysis). Carbon Balance: 96-111 %.

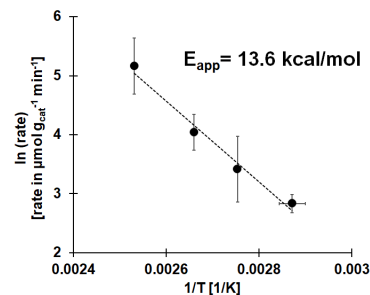


Figure 2. Apparent activation energy for acylation reaction of 2-methylfuran with n-octanoic anhydride. Reaction Conditions: 29 bar, 1 ml/min liquid flowrate, 0.067 M 2-methylfuran, 0.095 M n-octanoic anhydride. Solvent: heptane. Error bars are 95 % confidence intervals.

Significance. The acylation reaction is the key synthetic step for producing OFS surfactants. The use of long chain anhydrides as the acylating agent for furanic substrates is not well-reported in the literature. A better understanding of the mechanistic pathway and kinetic parameters benefit the design of catalysts and the scale-up of this reaction.

References

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