Friedel-Crafts Acylation of Furan: Development of A Green Process Using Chromium-exchanged Dodecatungstophosphoric Acid: Effect of Support, Mechanism and Kinetic Modelling

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Research Article

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Abstract

The Friedel-Crafts acylation of furan with acetic anhydride to produce 2-acyl furan is industrially important. With an aim of replacing the highly polluting process, it this study, supported but modified heteropoly acids were used. Metal exchanged dodecatungstophosphoric acid (DTP) was loaded on three different supports and its effect on acylation was evaluated. Thus, chromium exchanged DTP was supported on K-10, SiO_2, and ZrO_2 using the incipient wetness impregnation method. 20% w/w $Cr_{0.66}$-DTP/K-10 having the best activity for the acylation of furan with acetic anhydride was chosen for full characterization and reaction kinetics. Under optimized condition, the catalyst to furan ratio was 9.6%, significantly less as per prior art, which gave 88% conversion with 100% selectivity. The prepared catalysts were characterized by sophisticated techniques, namely, XRD, FT-IR, SEM, NH_3-TPD, TGA, and BET. The Eley-Rideal mechanism was found to fit the kinetic data. The activation energy was found to be 18.03 kcal/mol. The reaction is green and clean as no chlorinated chemicals, reagents, and catalysts were used.

Full Text

Due to technical limitations, full-text HTML conversion of this manuscript could not be completed. However, the latest manuscript can be downloaded and accessed as a PDF.

Tables

Table 1. NH_3-TPD and Surface area, pore volume, and pore diameter of K-10 supported catalysts.

Sr. No.	Catalyst	Acidity (mmol of NH_3 g-1)			Surface area (m^2g)	Pore diameter (nm)	Pore volume (cm^3/g)
		Weak	Moderate/Strong	Total			
1	K-10	0.68	0.19	0.86	240	6	0.39
2	20% w/w DTP/K-10	0.77	1.02	1.79	107.3	7.4	0.32
3	20% w/w $Cr_{0.66}$-DTP/K-10	0.85	1.22	2.07	145.6	7	0.3
4	Reused 20% w/w $Cr_{0.66}$-DTP/K-10	0.83	1.21	2.04	143.1	7.1	0.3

Table 2. Kinetic parameters of acylation of furan with acetic anhydride at various temperature.

Sr. No.	T (K)	k ($cm^6\ mol^{-1}\ g^{-1}s^{-1}$)	K_B ($cm^3\ mol^{-1}$)	Activation energy (E) (kcal mol^{-1})
1.	303	0.036	0.014	
2.	313	0.082	0.011	18.03
3.	323	0.240	0.007	
4.	333	0.510	0.004	

Figures

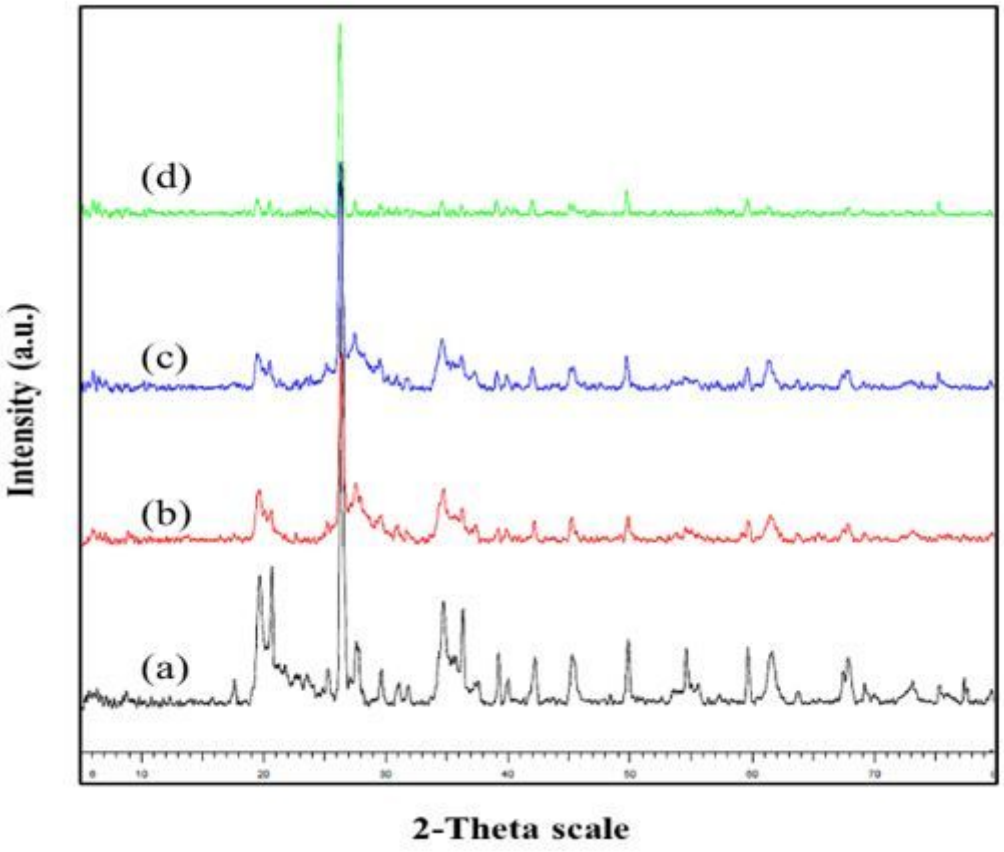

Figure 1

XRD of (a) K-10, (b) 20% w/w DTP/K-10, (c) 20% w/w Cr0.66-DTP/K-10, and (d) reused 20% w/w Cr0.66-DTP/K-10.

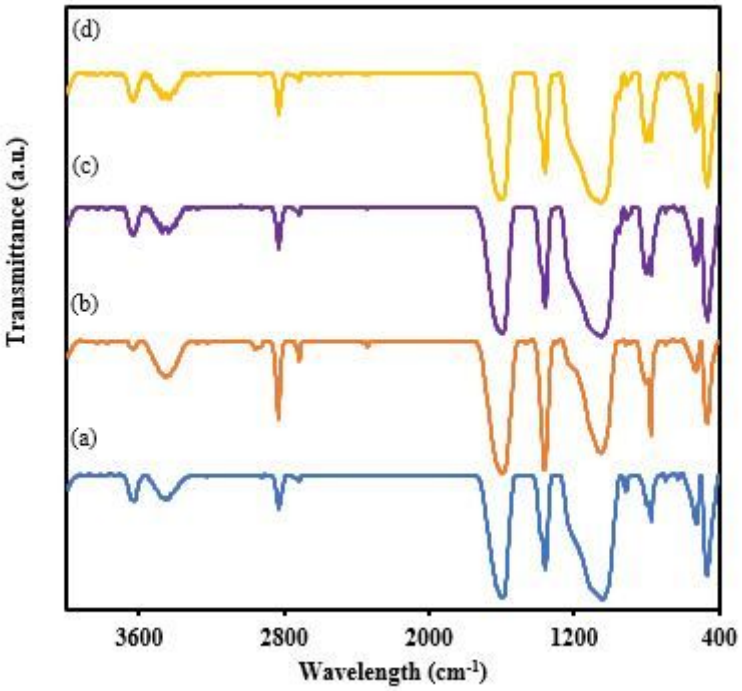

Figure 2

FT-IR of (a) K-10, (b) 20% w/w DTP/K-10, (c) 20% w/w Cr0.66-DTP/K-10, and (d) reused 20% w/w Cr0.66-DTP/K-10.

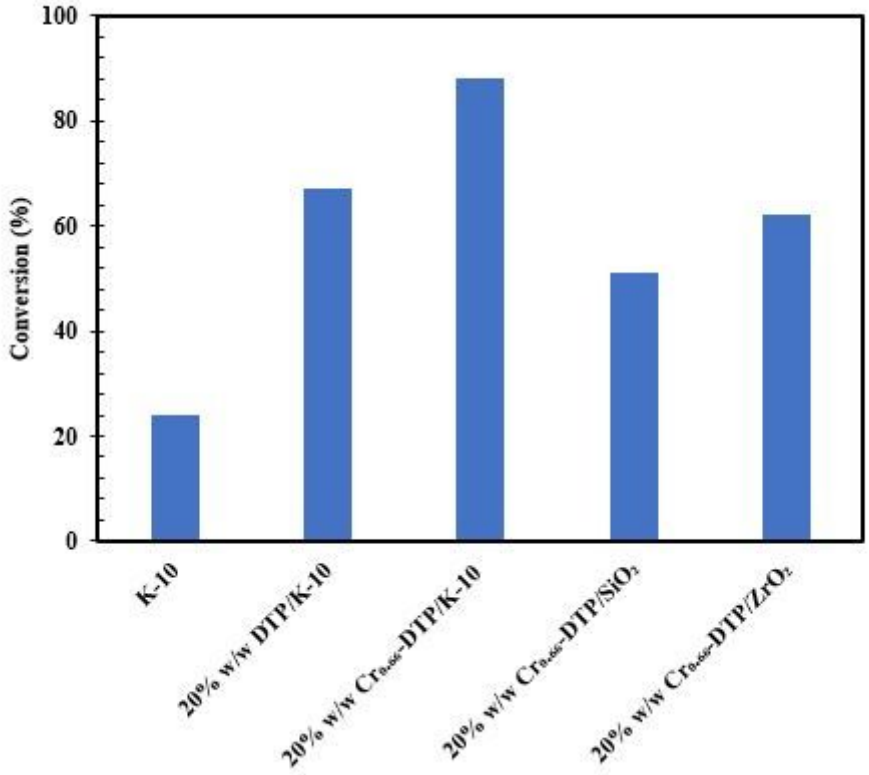

Figure 3

Effect of various catalysts on conversion of furan: Furan 2.50 g (0.036 mol), acetic anhydride 18.74 g (0.18 mol), catalyst loading 0.0125 g/cm3, speed of agitation 1000 rpm, temperature 50 ºC, total volume 20 cm3, reaction time 180 min.

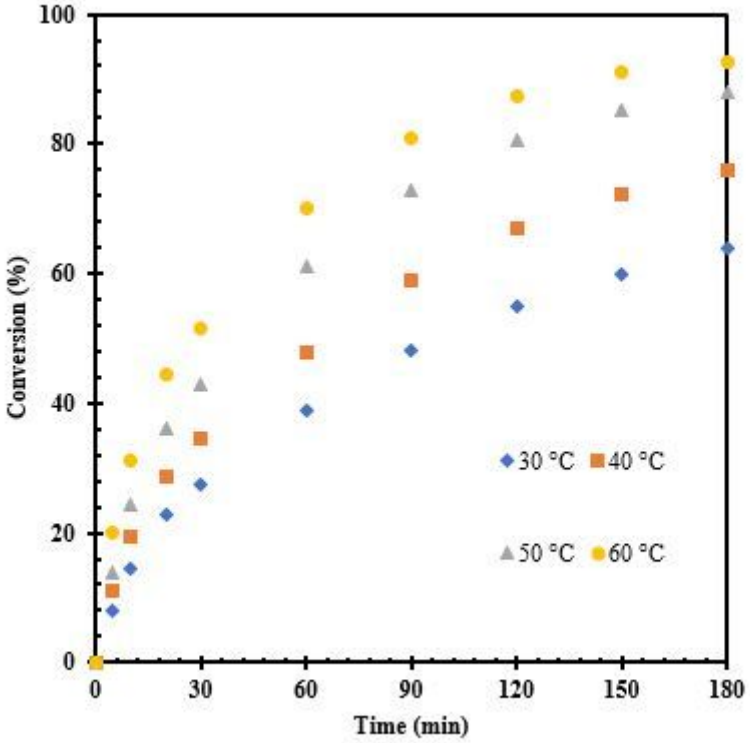

Figure 4

Effect of temperature on conversion of furan: Furan 2.50 g (0.036 mol), acetic anhydride 18.74 g (0.18 mol), catalyst loading 0.0125 g/cm3, speed of agitation 1000 rpm, total volume 20 cm3, reaction time 180 min.

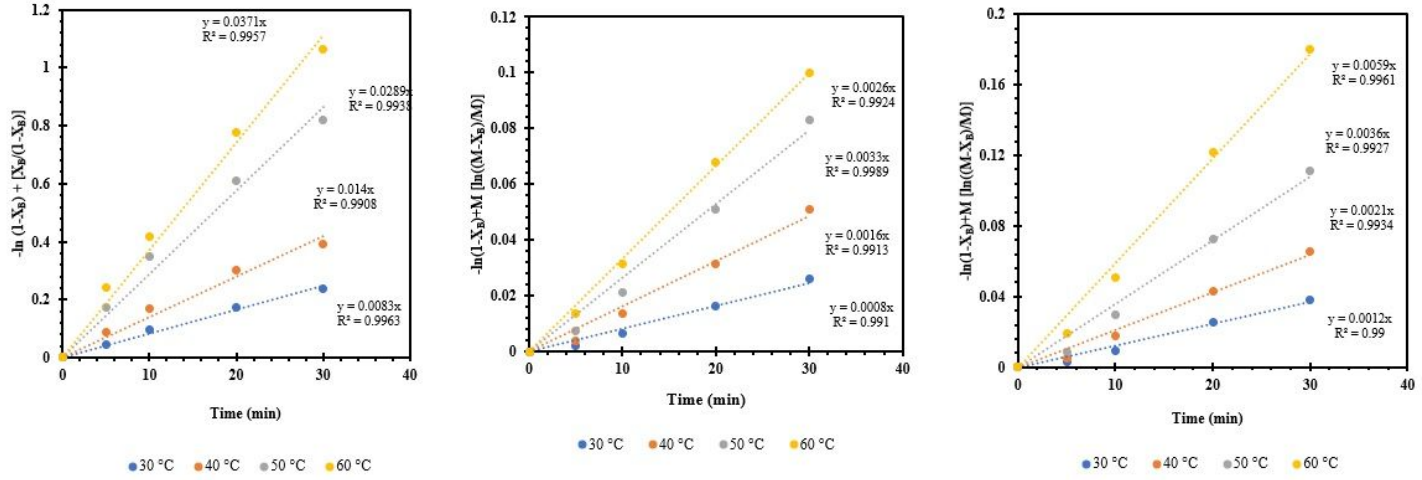

Figure 5

(a). Plot of -ln (1-XB) + [XB/(1-XB)] vs. time for M = 1.(b). Plot of ln (1 - XB) + M [ln ((M - XB)/M)] vs. time for M = 3.(c). Plot of ln (1 - XB) + M [ln ((M - XB)/M)] vs. time for M = 5.

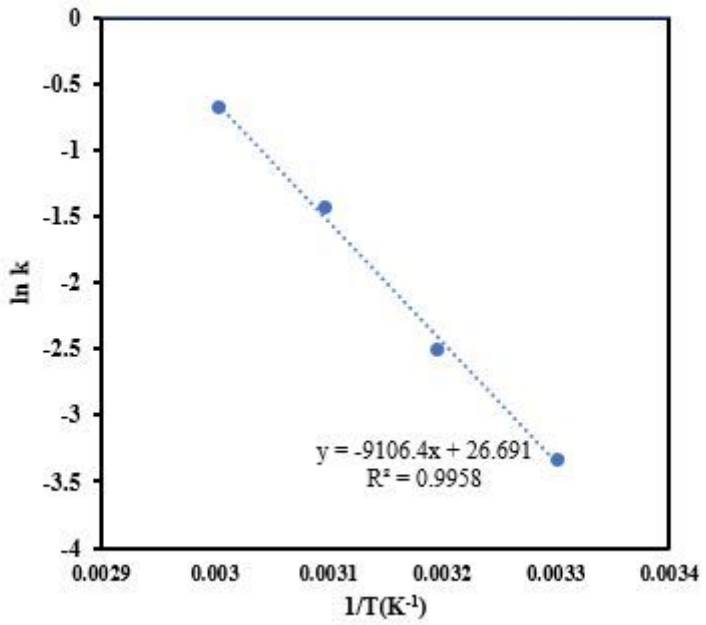

Figure 6

Arrhenius Plot

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