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Copper-cobalt catalyzed liquid phase hydrogenation of furfural to 2-methylfuran: An optimization, kinetics and reaction mechanism study

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ABSTRACT

In the present work, the hydro-conversion of biomass derived furfural (FAL) into fuel additive 2-methylfuran (2-MF) is studied over Cu–Co/Al₂O₃ catalyst. The influence of various operating parameters such as temperature, pressure, catalyst amount, time and FAL concentration on the conversion of FAL to 2-MF was optimized using well known Taguchi method as statistical tool. According to Taguchi method, under optimum reaction conditions viz. temperature 220 °C, pressure 40 bar, reaction time 5 h, catalyst loading 0.75 g, and FAL concentration of 1.75 M, maximum 2-MF yield (87%) was obtained. The detailed kinetics of the liquid-phase hydrogenation of FAL to 2-MF in two steps was also studied in the range of temperatures from 200 to 220 °C and in the range of pressures from 20 to 40 bar. The initial rate of reaction for both conversion of FAL to FOL and FOL to 2-MF varied linearly with hydrogen pressure at various temperature and the catalyst loading, however, effect of reactant substrate behave distinctly. In case of FAL, rate of reaction varied linearly and order of reaction is found to be almost one, whereas, for FOL disappearance, order of reaction found to be almost zero beyond 2.25 gmol/L of FOL concentration. The experimental data could also be explained using Langmuir–Hinshelwood kinetics. A dual-site mechanism with dissociative adsorption of hydrogen and surface reaction as the rate-controlling step provided the best fit for the experimental data.

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1. Introduction

Over the years, substantial interest has been developed to the conversion of biomass derived commodities into biofuels which can replace finite fossil fuel resources and boost the economics of biofuels production (Corma et al., 2007). In this context, furfural (FAL) has been highlighted as a bio-based cost-effective source with a capability of conversion into a variety of valuable products ranging from biofuels, additives to other useful value added chemicals through several potential

routes (Butler et al., 2011). In the direction of chemicals and biofuels production through FAL, the most significant products identified are furfuryl alcohol (FOL) and 2-methylfuran (2-MF) (Gallezot, 2012; Yan et al., 2014). FOL is mostly used in resin industries however; 2-MF is used as a gasoline blend (Mariscal et al., 2016). The processes for the conversion of FAL to 2-MF were reported widely either in one step or in two steps via intermediate FOL in both liquid and vapour phase (Yan et al., 2014; Mariscal et al., 2016). In the vapour phase process, there are few reports available which addressed the detail

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Nomenclature

Symbol

FAL	furfural
FOL	furfuryl alcohol
THFOL	tetrahydrofurfuryl alcohol
2-MF	2-methylfuran
MTHF	2-methyltetrahydrofuran
1-PN	1-pentanone
2-PN	2-pentanone
1-PL	1-pentanol
2-PL	2-pentanol
1,2-PD	1,2-pentanediol
1,5-PD	1,5-pentanediol
IPA	2-propanol
k	rate constant
m	order with respect to substrate
n	order with respect to hydrogen
K_{FAL}	equilibrium adsorption constant for furfural
K_{FOL}	equilibrium adsorption constant for furfuryl alcohol
K_{H_2}	equilibrium adsorption constant for hydrogen
ΔH_{ads}	heat of adsorption
ΔS_{ads}	entropy of adsorption
ΔG_{ads}	Gibbs free energy for adsorption
RR	mean average of the relative residuals
RSS	residual sum of squares

kinetic studies for the conversion of FAL to 2-MF (Sitthisa et al., 2011a,b). Nevertheless, no work is reported till date highlighting the study of optimization and kinetics for the conversion of FAL to 2-MF through FOL in the liquid phase which is a necessary aspect in order to evaluate the reaction pathway for the liquid phase hydrogenation of FAL to 2-MF.

In liquid phase, just a few reports address the kinetics studies on the hydro-conversion of FAL to FOL only. For example, Vaidya and Mahajani (2003) have reported the kinetics study on the liquid phase conversion of FAL to FOL and depicted that the reaction order with respect to FAL is varied from zero to 0.86 depending on the concentration of FAL. They also proposed mechanism using LHHW model and suggested dual site molecular adsorption of hydrogen on the catalyst surface and surface reaction as the rate controlling step. Rojas et al. (2008, 2010) studied the kinetics of FAL hydrogenation to FOL using Ir supported on Nb_2O_5 and TiO_2 . Over both these catalysts, they proposed LH models considering single site having dissociative hydrogen adsorption on the catalyst surface and surface reaction as the rate controlling step. In our previous work, we have studied the effect of temperature on the hydrogenation of FAL to FOL over Cu–Co/SBA-15 and determined the activation energy for optimal conversion of FAL to FOL (Srivastava et al., 2015). In another work, we have successfully screened out bi-metallic (Cu–Co/ Al_2O_3) catalyst for the liquid phase hydrogenation of FAL to 2-MF (Srivastava et al., 2016).

Based on the above background, in present work, we report the optimization and detailed kinetics study along with mechanism for the liquid phase hydrogenation of FAL to 2-MF on a bi-metallic Cu–Co/ Al_2O_3 catalyst. The experiments were performed to understand the influence of reaction parameters like temperature, hydrogen pressure, catalyst amount, time and FAL concentration in order to optimize the yield of 2-MF in one step using Taguchi method and further investigated the

Table 1 – The factors and their levels in experimental design.

Factors	Levels			
	1	2	3	4
A (temperature, °C)	190	200	210	220
B (pressure, bar)	20	30	40	50
C (catalyst dosage, g)	0.5	0.75	1.0	1.25
D (time, h)	3	4	5	6
E (furfural con., gmol/L)	1.75	2.25	2.75	3.25

kinetics and reaction pathways of FAL hydrogenation towards 2-MF. Moreover, the role of individual metals viz. Cu, Co as well as their mixed oxides which was explored in our previous work (Srivastava et al., 2016), briefly discussed in the reaction mechanism section in order to ascertain the reaction pathways which might have a key impact on the study of other deoxygenating reactions involved in the upgrading of biomass-derived and/or bio-oil model compounds.

2. Experimental study

2.1. Material

Metal precursors such as cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$); chemicals such as furfural, furfuryl alcohol, 2-methyl furan, 2-methyltetrahydrofuran, 2-pentanone, and 2-pentanol (all GC grade) were purchased from Sigma–Aldrich, Mumbai, India. Support $\gamma\text{-Al}_2\text{O}_3$ having purity (99%) was purchased from the local vendor.

2.2. Catalysts synthesis

Bimetallic Cu–Co catalyst with molar ratio (Cu/Co = 1) over $\gamma\text{-Al}_2\text{O}_3$, was synthesized by impregnation method using the aqueous solutions of ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) as reported in our previous work (Srivastava et al., 2016). The doped catalyst was dried overnight at $100 \pm 2^\circ\text{C}$ and subsequently calcined at $450 \pm 5^\circ\text{C}$ for 4 h to obtain the final oxide catalyst in powder form. Thereafter, powder is converted into spherical pellets using balling (spherical agglomeration by a continuous rolling) using an appropriate solvent (Ratul and Baquee, 2013).

2.3. Catalytic activity study/design of experiments

Catalytic activity studies were performed in a 100 mL autoclave reactor using 2-propanol as a solvent. Briefly, in a typical experiment, appropriate amount of catalyst was pre-treated/reduced at $280 \pm 2^\circ\text{C}$ by passing H_2 at pressure of 1 MPa for 3 h. The reactor was then cooled down to room temperature and flushed with N_2 . Furfural was initially added into 2-propanol solvent, and charged into the reactor. The catalytic activity of prepared catalyst was investigated as per design of experiments, wherein, the reactions were carried out according to L_{16} array (Table 2) which was constructed based on the parameters and their levels (Table 1). Influence of various reaction parameters towards conversion of FAL to 2-MF was optimized by using Taguchi method (Ross, 1996; Taguchi et al., 2005). Detailed procedure regarding Taguchi method is described elsewhere (Srivastava et al., 2015). Experiments were set for five reaction parameters such as reaction temperature, hydrogen pressure, FAL concentration, catalyst amount and

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