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Synthesis of Biodiesel from Transesterification of Jatropha Oil with Methanol Using Double Metal Cyanide as Catalyst

Praveen Kumar, Vimal Chandra Srivastava, and Mithilesh K. Jha

***Abstract*—Fe-Zn double-metal cyanide catalysts were synthesized by co-reaction of zinc chloride with potassium ferrocyanide in presence co-complexing agent and complexing agent. Acidity, basicity, morphology and textural characteristics of catalysts were studied using CO_2- and NH_3-temperature-programmed desorption (TPD), X-ray diffraction (XRD), scanning electron microscopy (SEM) and liquid N_2-sorption data. Fe-Zn-1 catalyst with highest basicity was found to be more effective for transesterification of Jatropha oil with methanol to form biodiesel in a batch reactor. It was further used for optimizing the reaction condition such as effect of methanol/PC molar ratio and reaction time; and studying its reusability.**

***Index Terms*—Transesterification of Jatropha oil, Fe-Zn double metal cyanide, Biodiesel.**

I. INTRODUCTION

Biodiesel is green alternative fuels resource. It is a non-toxic, biodegradable, renewable alternative of the conventional diesel fuel. Biodiesel has lower emission, no sulfur content, high flash point and high centane number [1]-[3]. High production cost and insufficient feedstock are the major hurdles in the very large scale production of biodiesel. In this context, low cost non-edible oil such as karanja oil, Jatropha oil, waste cooking oil, etc. can improve the economical feasibility of the production of biodiesel [1]-[3].

Various types of homogeneous catalysis (acid and base) are used for the synthesis of biodiesel due to faster conversion and high yield. However, homogeneous catalyst has many drawbacks such as equipment corrosion, tedious separation process due to formation of emulsion, removal of catalyst and its disposal. To overcomes these problem, heterogeneous catalysts such as CaO, ZnO, SrO, Al_2O_3 ZrO_2 and MgO are used for biodiesel production. However, low yield, reuseability and leaching are some of the drawbacks of these atalysts [4], [5]. In the present study, Fe-Zn based double metal cyanide catalyst was synthesized and used for biodiesel production. A series of double metal cyanide (DMC) particularly Fe-Zn catalyst were synthesized and used for transesterification of Jatropha oil to produce biodiesel. The synthesized catalysts were characterized for N_2-sorption, X-ray diffraction (XRD), NH_3- and CO_2-TPD for studying acidity, basicity and morphology of the catalysts using scanning electron microscopy (SEM). The synthesized catalysts were then tested for biodiesel production from transesterification of Jatropha oil with methanol.

II. EXPERIMENTAL

A. Materials

Zinc chloride hydrous ($ZnCl_2$) and Potassium ferrocyanide ($K_4[Fe(CN)_6]$) and were purchased from Himedia Chemical, India. Methanol and tert-butanol were purchased from Loba chemical, India. Poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (PEG-5800) was purchased from Aldrich chemical, India. All chemicals were used of analytical grade (AR). Deionized water was obtained from *Milli-Q water* filtration station (Millipore).

B. Catalyst Preparation

For **s**ynthesis of Fe-Zn catalyst, potassium ferrocyanide (0.01 mol) was dissolved in deionized water (40 mL) used for prepration of solution 1. In the another beaker, $ZnCl_2$ (0.1 mol) dissolved in deionized water (100 mL) and tert-butanol (20 mL) to prepare solution 2 and in another beaker 15-g of tri-block copolymer(PEG-5800), 40 mL of tert-butanol and 2 mL deionized water were added in a third beaker to prepare solution 3. After that, the solution 2 was added drop-wise to the solution 1 at 50 ℃ for 1 h under vigorous stirring till white color precipitate was formed. After that, solution 3 was added under vigorous stirring condition at 50 ℃ for 5–10 min to the product formed from solution 1 and 2. The solution was further stirred for 2 h at room temperature. The white colour precipitate was washed with deionized water to remove all of the uncomplexed ions and dried at room temperature for 24 h and then activated at 180 ℃ for 6h (Fe–Zn-1). PEG-5800 works as a co-complexing agent and tert-butanol acts as a complexing agent. Fe-Zn-2 catalyst was prepared in absence of co-complexing agent (PEG-5800) and Fe-Zn-3 in absence of both complexing agent (tert-butanol) and co-complexing agent (PEG-5800) agents for synthesis [6], [7].

C. Catalyst Characterization

The Fe-Zn catalysts were characterized by various characterization techniques such as N_2-sorption, XRD, NH_3-TPD, CO_2-TPD, SEM-EDX and ICP-OES. Textural properties of the synthesized catalysts were investigated with

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micromeritics ASAP 2020 at -195°C using N_2 sorption. Specific surface areas and pecific pore volumes of the catalysts were estimated with Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method, respectively. XRD pattern of catalysts were estimated with Brueker AXS, Germany with D8 diffractometer (40 kV/30 mA) with (λ= 1.5406Å) at Cu Kα radiation with step size 0.02 over a 2θ range of 5°-60°. Crystalline size was investigated with ICDD-JCPDS. Crystal sizes (L) and lattice strain were calculated from the Scherrer's equation:

$$L = \frac{K\lambda}{\beta cos\theta} \tag{1}$$

where, K is the Scherrer's constant (K=0.94), β is the full width of the reflection at half maximum (FWHM), λ is the wavelength of X-ray radiation is equal to 1.54051 Å, and θ is the Bragg angle. Acidic and basic properties of the synthesized catalysts were determined by TPD of NH_3 and CO_2 with micromeritics Chemisorb (model- 2720) with (TCD) thermal conductivity detector. The sample (50 mg) was placed in a quartz U-tube for 6 h at 200 ℃ under helium flow. Adsorption/saturation of NH_3 was performed with 20 cm^3 min^{-1} flow rate for 30 min after that dispersed with helium for 1 h at room temperature. The desorption of NH_3 was investigated from 30 – 900 ℃ at 10°C min^{-1} under helium flow (20 cm^3 min^{-1}) and evolved NH_3 was estimated with TCD detected. Similarly, same process was used for CO_2-TPD to estimate the acidic properties of the catalysts. Elemental compositions and morphology were determined by SEM-EDX from Model 200-FEG, QUANTA, Netherlands at 15 kV. Actual metal composition estimated with the EDXRF spectrometer (MiniPal-2) from PANayltical, Netherlands.

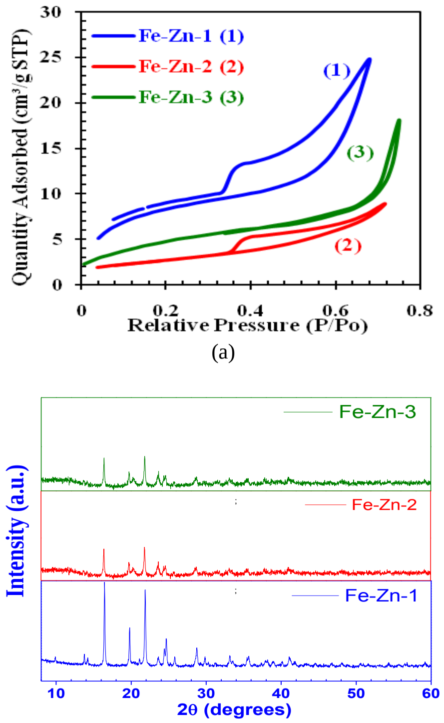
D. Catalytic Activity

Catalytic activity of the synthesized catalysts was tested for transesterification of Jatropha oil with methanol for biodiesel synthesis in a stainless-steel autoclave (500 mL) reactor attached with mechanical stirrer. Initially, the reaction was filled with required amounts of Jatropha oil, catalysts and methanol and the reactor was flushed with nitrogen. The reactor was heated with desired temperature with heating rate of 10 ℃.min^{-1} and with constant stirring 450 min^{-1}. The progress of reaction was studies by Thin Layer Chromatography (TLC), solution was prepared with the composition of glacial acetic acid (1.5 ml): diethyl ether (13.5 ml): petroleum ether (85 ml) mixture as the mobile phase. After completion of the reaction, the product mixture was transferred to separate from glycerin with catalyst in lower phase and biodiesel in upper phase. The product was estimated in terms of conversion (%) by using Gel Permeation Chromatography (GPC) technique, which consist PL gel column (5 nm × 7.5 mm) with refractive index detector THF as carrier solvent with flow rate 1 $cm^3.min^{-1}$.

III. RESULTS AND DISCUSSION

A. Catalyst Characterization

N_2 sorption. Specific surface area (S_{BET}) of Fe–Zn-1, Fe–Zn-2 and Fe–Zn-3 were found to be 125 $m^2.g^{-1}$, 85 $m^2.g^{-1}$ and 75 $m^2.g^{-1}$, respectively. Pore volume of Fe–Zn-1, Fe–Zn-2 and Fe–Zn-3 were found to be 0.1395 $cm^3.g^{-1}$, 0.0308 $cm^3.g^{-1}$ and 0.0355 $cm^3.g^{-1}$, respectively (see Table I). All the catalysts exhibit type IV isotherm with H3 hysteresis (see Fig. 1(a)), which corresponds to porous substances with wide range of pore sizes. Such porous substances show adsorption behavior extending from monolayer to multilayer and ultimately to capillary condensation.



(a)

(b)

Fig. 1. N_2 adsorption-desorption isotherm & XRD of the synthesized catalysts.

TABLE I: N_2 SORPTION AND METAL COMPOSITION OF THE SYNTHESIZED CATALYSTS

Catalyst	BET Surface Area ($m^2.g^{-1}$)	Pore Volume ($cm^3. g^{-1}$)	Actual values		Actual values from ED-XRF analysis		Actual values from EDX analysis	
			Fe	Zn	Fe	Zn	Fe	Zn
Fe-Zn-1	126	0.139	0.4	0.6	0.39	0.61	0.38	0.62
Fe-Zn-2	85	0.030	0.4	0.6	0.38	0.62	0.39	0.61
Fe-Zn-3	71	0.035	0.4	0.6	0.38	0.62	0.38	0.62

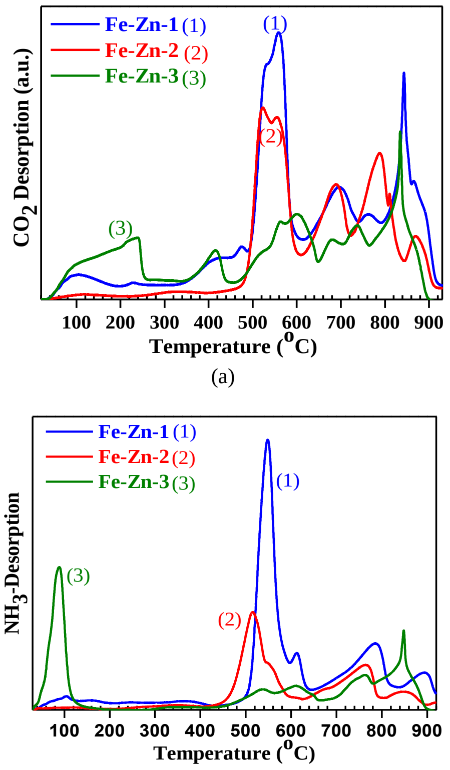
XRD. X-ray diffraction patterns of synthesized Fe–Zn catalysts are shown in the Fig. 1(b). The synthesized catalysts are highly crystalline. XRD patterns of Fe-Zn-1 catalyst showed peaks at 16.45 (111), 19.84 (200), 21.91 (210), 24.64 (211), and 28.84 (221) corresponding to a cubic structure with space group of Fm-3m. Fe-Zn-1, Fe-Zn-2 and Fe-Zn-3 catalyst formed hydrated $K_2Zn_3[Fe(CN)_6]_2.xH_2O$, hydrated $K_2Zn_3[Fe(CN)_6]_2$ and hydrated $K_2Zn_3[Fe(CN)_6]_2$, respectively. Fe-Zn-1 catalyst was found to possess 19.6 nm crystalline size and 0.0125 lattice strain. Fe-Zn-2 and Fe-Zn-3 were prepared in absence of complexing and co-complexing agents but with difference reagents and could be indexed to a mixture of cubic [6], [7].

NH_3-TPD. Acidity of the synthesized catalysts was performed by NH_3-TPD and the results are shown in Fig. 2(a) and Table II. The CO_2 / NH_3-TPD profiles are classified such as: weak, moderate, and strong with the temperature range corresponding (< 200°C), (200-450°C) and (> 450°C), respectively. The basic site density depends upon the temperature at which peaks exist. Low temperatures desorption of the NH_3 as weak basic sites in the catalysts and higher temperature desorption of NH_3 shows strong basic sites. The total amount of NH_3 desorbed from the Fe–Zn-3, Fe–Zn-2, and Fe–Zn-1 catalysts was: 16.83, 11.16 and 18.54 mmol.g^{-1}, respectively. Total desorbed amount of NH_3 was found to be in the following order: Fe–Zn-2 < Fe–Zn-3 < Fe–Zn-1. Fe–Zn-1 catalyst is found to posses highest acidic sites in all regions. Overall the co-complexing agent and complexing agent affect the acidic properties of the catalysts.

TABLE II: TPD ANALYSIS USING ABSORBED NH_3 AND CO_2 OF SYNTHESIZED CATALYSTS

	TPD analysis of absorbed NH_3 (mmol/g)			Total
Catalyst	Weak (< 200 ℃)	Moderate (200-450 ℃)	Strong(> 450 ℃)	evolved NH_3 (mmol/g)
Fe-Zn-1	-	-	13.66 (548), 1.31 (612) & 3.57 (785)	18.54
Fe-Zn-2	-	-	7.19 (515), 3.95 (764) & 0.65 (847)	11.16
Fe-Zn-3	6.55 (89)	0.15 (334)	1.93 (539) 2.01 (760) & 6.19 (848)	16.83
	TPD analysis of absorbed CO_2 (mmol/g)			Total
Catalyst	Weak (< 200 ℃)	Moderate (200-450 ℃)	Strong (> 450 ℃)	evolved CO_2 (mmol/g)
Fe-Zn-1	0.61 (106)	0.29 (229) & 0.63 (430)	4.51(558), 0.71 (694) & 4.69 (843)	11.44
Fe-Zn-2	-	-	3.57 (524), 1.94 (689) & 3.01 (788)	8.52
Fe-Zn-3	0.74 (110)	0.67 (239) & 0.85 (416)	2.39 (600), 1.45 (737) & 1.99 (835)	8.09

Temperature (℃) at maxima is given in brackets.



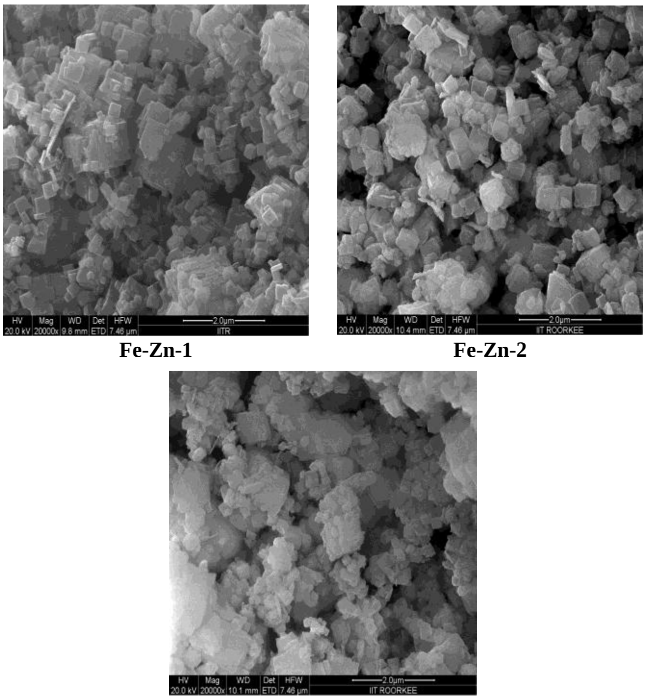
(a)

(b)

Fig. 2. NH_3 and CO_2 TPD of the synthesized catalysts.

CO_2-TPD. The basic properties of the synthesized catalysts were investigated by CO_2-TPD and results are shown in Fig. 2(b) and CO_2 desorption values are shown in Table II. Strong basic sites of medium strength are due to the presence of low-coordinated O^2 and presence of M^{n+}-O^{2-}on the surface and weak basic sites are due to surface O-H$^-$ groups. The total amount of CO_2 desorbed from the Fe–Zn-1, Fe–Zn-2, and Fe–Zn-3 catalysts shows 18.54, 11.16 and 16.83 mmol.g^{-1}, respectively. Total desorbed amount of CO_2 was found to be in the following order: Fe–Zn-3 < Fe–Zn-2 < Fe–Zn-1. Thus, Fe–Zn-1 catalyst most basic and that the Fe–Zn-3 is least basic. It may be noted that amount of acidic and basic sites are more in Fe-Zn-1 and this catalysts have been found higher specific surface area as compared toFe-Zn-2 and Fe-Zn-3.

Surface morphology and elemental analysis. SEM image images of the synthesized Fe-Zn-1, Fe-Zn-2 and Fe-Zn-3 catalysts are shown in the Fig. 3. All the catalysts, shows the squire and rectangular morphology, heterogeneous and crystalline structure. Fe-Zn-1 catalysts show sharp cube shaped structure, however, Fe-Zn-2 and Fe-Zn-3 show undeveloped or broken cubes.



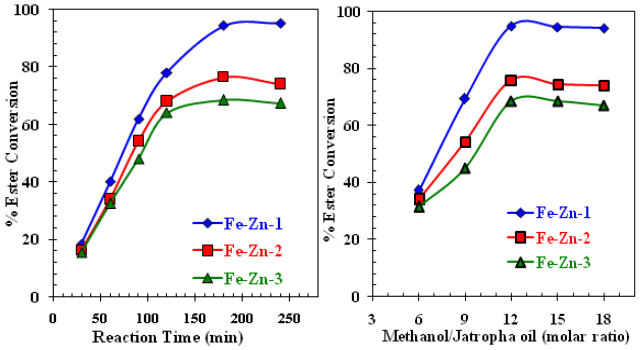
Fe-Zn-1 **Fe-Zn-2**

Fe-Zn-3

Fig. 3. SEM image of the synthesized catalysts.

The activity of the Fe-Zn-1, Fe-Zn-2 and Fe-Zn-3 synthesized catalyst were evaluated in terms of ester conversion. Activity of the synthesized catalysts was checked at the initial pressure of 2-5 bar and the final pressure of 20-25 bar; catalyst mass =3 wt% of Jatropha oil and reaction temperature = 160 ℃.

The effect of reaction time on ester conversion at different reaction time is shown in Fig. 4(a). It can be seen in the Fig. 4(a) that the ester conversion increases with the increases with time up to 180 min and after that only marginal changes occur in the ester conversion. Fig. 4(b) shows the methanol/Jatropha oil molar ratio on ester conversion. It may be seen that the conversion increased with increase in the methanol/Jatropha oil molar up to a ratio of 12 after that marginal changes in the ester conversion are observed.



(a) (b)

Fig. 4. (a) Effect of reaction time and, (b) Effect of methanol/ Jatropha oil molar ratio on transesterification reaction.

Fe-Zn-1 catalyst was found to give maximum 94.5% ester conversion at 3 wt.% catalyst dose for reaction time of 180 min. Fe-Zn-2 and Fe-Zn-3 catalyst gave only 76.5% and 68.6% ester conversion, respectively at these conditions. It can be seen in the catalysts characterization and the activity of the catalysts has reasonable correlation with the basicity and surface area of the catalysts. The recovered (Fe-Zn-1) catalyst was further for tested for reusability of catalyst without any intermediate regeneration process. No significant loss of activity was observed for transesterification of Jatropha oil for 5 runs. Average 93% conversion was observed in these runs [8], [9].

IV. CONCLUSION

Fe-Zn double metal cyanide was found to be highly active catalysts for production of biodiesel from transesterification of Jatropha oil with methanol. In the synthesis of catalysts, both cocomplexing agent (PEG-5800) and complexing agent (tert-butabol) were found to significantly affect physical (crystallinity and surface area) and catalytic properties. Fe-Zn-1 catalyst gave maximum 94.5% ester conversion in 180 min at 3 wt.% catalyst dosage with methanol/Jatropha oil molar ratio of 12 and temperature 160°C. Fe-Zn-2 and Fe-Zn-3 catalyst gave 76.5% and 68.6% ester conversion, respectively at these conditions. Basicity and surface area of the catalysts were found to significantly affect the activity of the catalysts.

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