

The potential use of calcium-doped flamboyant char as a heterogeneous catalyst in triglycerides transesterification

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This study reports the synthesis of heterogeneous catalysts from flamboyant biomass and their evaluation on the transesterification reaction of safflower oil with methanol to produce biodiesel. The optimization of catalyst preparation conditions was performed. Results showed that the concentration of doping metallic specie was the main variable that affected the performance of flamboyant-based catalyst in the reactive system to obtain the biofuel where the highest formation of methyl esters was 93 %. Physicochemical characterization of the carbon-based catalysts was done with X-ray diffraction and FTIR.

Key words: Biodiesel, heterogeneous catalysts, flamboyant biomass, transesterification

INTRODUCTION

The increase of energy demand, fossil fuel costs and global warming have been the key factors to diversify the sources for obtaining low-cost and clean energy [1-3]. Biodiesel is an alternative to fossil fuels because of its renewability, biodegradability, ready availability, higher combustion efficiency, lower sulfur and aromatic content and higher cetane number [4]. It also has the potential capacity to satisfy the energy demand in the agriculture, commercial, industrial and transportation sectors [5]. To date, a number of studies has focused on the evaluation of methods for the biodiesel production. Transesterification of glycerides (mainly from biomass, vegetable oils or animal fats) is employed to produce biodiesel because its simplicity and cost [5-8,10,11]. Transesterification reaction is typically carried out in the presence of a catalyst [6]. The type of catalyst is one of the most important parameters in the transesterification reaction for biodiesel production. This parameter also contributes to reduce the biodiesel cost.

Heterogeneous catalysts have been widely utilized due to their advantages such as reuse and easy separation, low cost and green production [12]. Several heterogeneous catalysts have been reported for the biodiesel production. In particular, the carbon-based catalysts are attractive because of its chemical activity, thermic stability and the versatility to manipulate its physicochemical

properties [13]. These catalysts can be prepared from agricultural, forest and urban wastes, which have been suggested as low cost feedstocks because of their availability [11,13,14]. To improve its catalytic activity, the support surface can be modified to tailor its acidic or basic catalytic properties using active metal species, oxidizing atmospheres, bases, acids or oxides [15-17]. It is important to remark that the selection of the precursor and the preparation route are relevant parameters to improve the catalyst performance. The preparation route involves a wide variety of possibilities to synthesize versatile, biodegradable and effective catalysts for the biodiesel production. Therefore, it has been recognized that there is still the challenge of obtaining low cost materials with outstanding catalytic properties for the biodiesel production. This article reports the preparation and evaluation of flamboyant-based catalysts and its application in biodiesel production. The impact of synthesis route on catalyst performance for the transesterification reaction of safflower oil with methanol to produce biodiesel was analyzed.

EXPERIMENTAL

Preparation and evaluation of flamboyant-based catalysts

Flamboyant pods were used as precursors to synthesize the heterogeneous catalysts. This biomass was washed, dried, ground and sieved. Heterogeneous catalyst was obtained via the pyrolysis of this biomass to obtain a porous material, which was utilized to support calcium species that acted as the active phase. An experimental design

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was utilized to synthesize 16 samples of catalysts with the aim of identifying the best preparation conditions. The variables analyzed in this experimental design were the pyrolysis temperature and dwell time, the concentration of calcium nitrate solution used to modify the surface chemistry of the flamboyant-based support and the activation temperature. All the catalyst samples were evaluated in the transesterification reaction of safflower oil with methanol. Flamboyant-based catalytic supports were synthesized at different pyrolysis temperatures (600 – 900) under N₂ atmosphere with different dwell times (2 – 5 h) using a tubular furnace. These supports were modified using calcium nitrate with concentrations from 0.05 to 0.40 M and different impregnation temperatures (30 – 90 °C) during 5 h at constant stirring. Finally, the calcium-doped flamboyant chars were submitted to a thermal treatment at 400 – 700 °C for 2 h under N₂ atmosphere. All catalysts were washed to eliminate the excess of reagents and finally dried.

The reaction conditions to evaluate the catalysts performance were: alcohol to oil molar ratio of 15:1, reaction temperature of 80 °C, 5 % wt. catalyst with respect to the oil and 5 h of reaction time using a batch reactor. After 5 h, the mixture was centrifuged in order to separate the catalyst from the liquid phase containing the biodiesel. The excess of methanol was evaporated from the solution and fatty acid methyl esters content (FAMEs, %) was analyzed by gas chromatography. A Thermo Scientific Trace 1300 GC equipped with a flame ionization detector (FID) was utilized for these quantifications. Methyl esters content was determined using the methyl heptadecanoate reagent as internal standard.

Physicochemical characterization of catalysts

Selected samples of catalysts were characterized with X-ray diffraction and FTIR to analyze the surface chemistry of the flamboyant supports and

their corresponding catalysts. XRD patterns were recorded with a PANalytical Empyrean X-Ray diffractometer using the configuration of Bragg-Brentano with CuKα1. FTIR spectra were obtained using a Thermo Scientific Nicolet iS10 spectrophotometer where the catalysts samples were dispersed in KBr reagent to be measured as pellets.

RESULTS

Results of the best catalysts and their synthesis conditions are presented in Table 1. The percentages of FAMEs formation ranged from 77.3 to 90.1 %. ANOVA analysis of experimental design indicated that the calcium nitrate concentration was the main variable that impacted the catalyst performance. The best flamboyant-based catalyst was synthesized using a support obtained from the pyrolysis of flamboyant biomass at 600 °C for 4 h, which was modified with calcium nitrate at 0.4 M at 70 °C and submitted to a final thermal treatment at 700 °C. The highest FAMEs formation was 93 % of methyl esters. Kinetic studies were carried out with the best catalyst and results are reported in Figure 1.

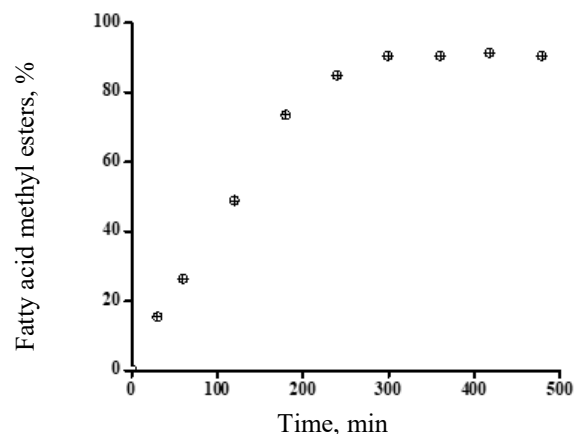


Fig. 1. Kinetics of transesterification reaction of safflower oil with methanol using a flamboyant-based heterogeneous catalyst.

Table 1. Synthesis conditions of flamboyant-based heterogeneous catalysts and their evaluation in the transesterification reaction of safflower oil with methanol to produce biodiesel.

Catalyst sample	Pyrolysis conditions to obtain the support		Modification of the support using calcium nitrate			
	Temperature, °C	Dwell time, h	Salt Concentration, M	Impregnation temperature, °C	Thermal treatment, °C	FAME formation, %
CC1	600	2	0.05	30	400	77.3±0.14
CC2	600	5	0.40	90	700	90.1±0.01
CC3	700	5	0.25	50	400	82.7±0.07
CC4	800	5	0.10	30	600	81.3±0.28
CC5	900	5	0.05	70	500	78.0±0.01
CC6	600	4	0.40	70	700	93.0±0.01

High FAMEs formation occurred at the first 3 h of reaction where 5 h was the equilibrium time. Kinetic experimental data were fitted to the pseudo-first and pseudo-second order models according to the next equations:

$$-\ln(1 - X_{BIO}) = k_1 t \quad (1)$$

$$\frac{X_{BIO}}{1 - X_{BIO}} = k_2 t \quad (2)$$

where X_{BIO} is the mass fraction of FAMEs, k_1 is the reaction rate constant in min^{-1} , k_2 is the reaction rate

constant in $\text{L mol}^{-1} \text{min}^{-1}$ and t is the time in min, respectively. Determination coefficients were 0.97 and 0.89 for pseudo-first and -second order models, respectively. The pseudo-first order equation was the best model to describe the kinetic reaction with a rate constant of 0.0072 min^{-1} .

Results of XRD characterization were used for phase identification of catalytic species, see Figure 2. The diffractograms of the flamboyant-based supports showed a wide peak at 25° that corresponded to the graphitic structure, which is typical of lignocellulosic-based materials [18].

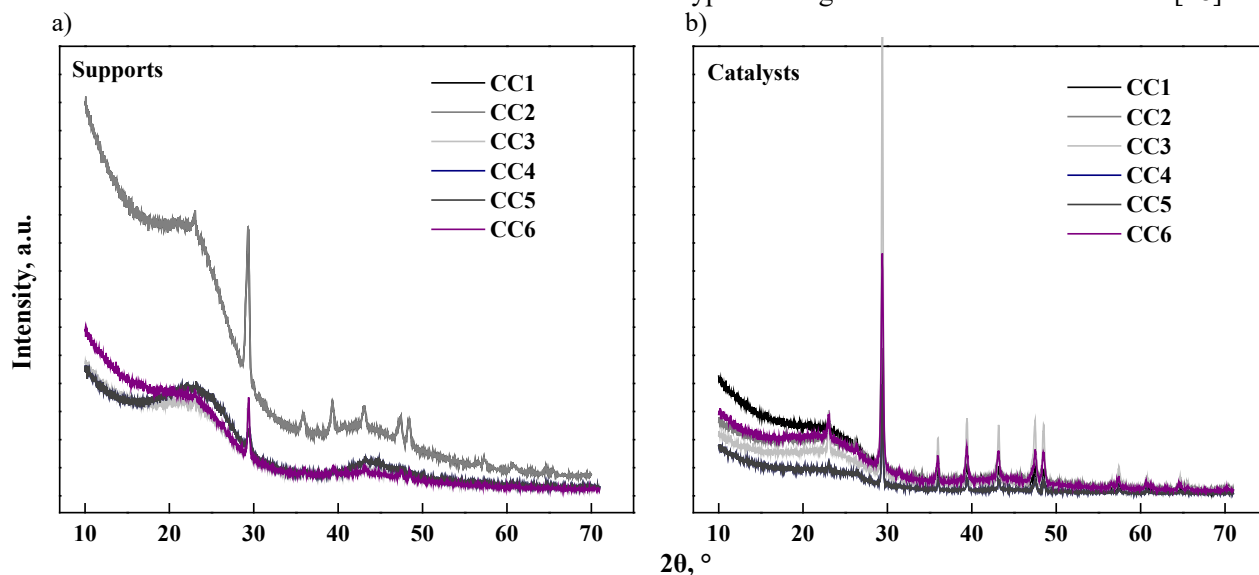


Fig. 2. XRD results of a) flamboyant-based supports and b) flamboyant-based heterogeneous catalysts.

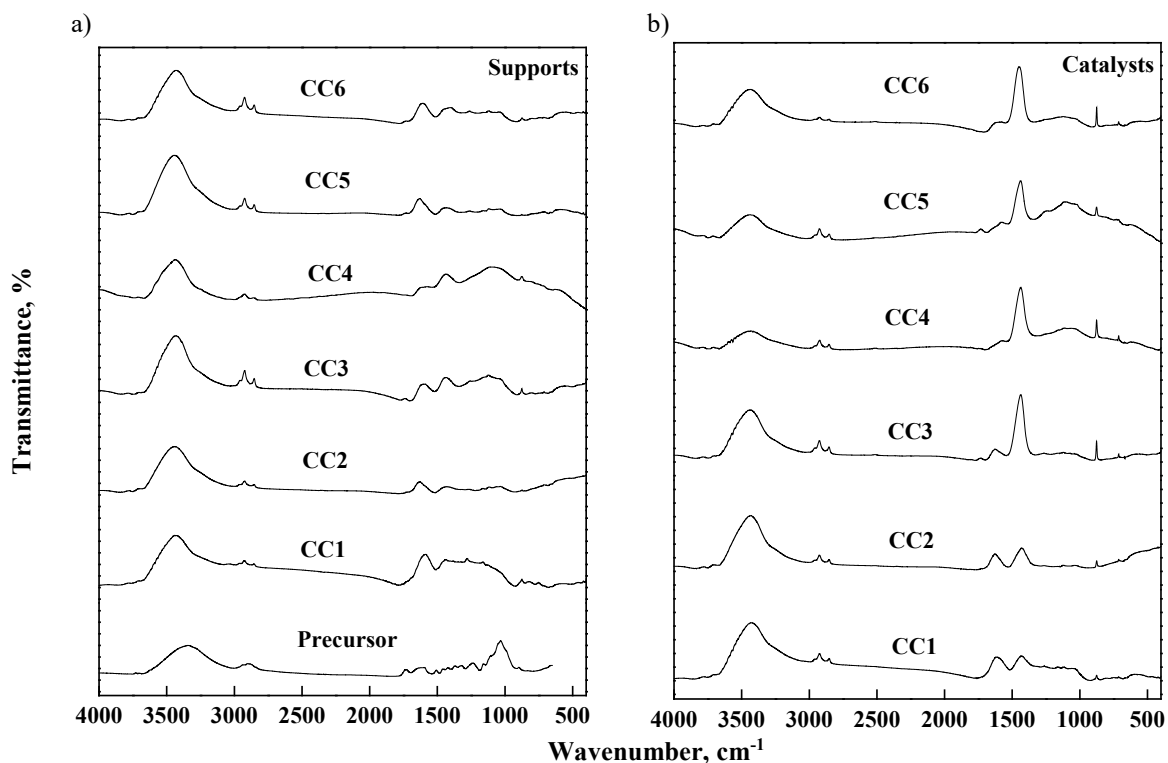


Fig. 3. FTIR spectra of a) flamboyant-based supports and b) flamboyant-based heterogeneous catalysts.

Catalyst diffractograms given in Figure 2b showed the characteristic peaks of CaCO₃ according to the PDF-2 database. FTIR results are reported in Figure 3. A band that corresponds to hydroxyl groups of phenols and alcohols [19] appeared in the region of 3500 – 3000 cm⁻¹ of FTIR spectra obtained for flamboyant supports. The bands corresponding to aliphatic groups were observed in the region 2916 – 2840 and 1504 – 1236 cm⁻¹. The bands at 1650 and 1520 cm⁻¹ were assigned to carboxylic groups and aromatic bonds. The bands at 1160, 1106 and 1029 cm⁻¹ can be attributed to the C – O vibration probably associated to acid, alcohol, phenol, ether and esters groups [20]. The band at 892 cm⁻¹ can be attributed to ring structures. For the catalyst samples (Figure 3b), the bands at 3500 – 3000 and 1650 cm⁻¹ showed a decrement in its intensity and a slight displacement, which were more remarkable as the calcium nitrate concentration and the temperature of thermal treatment increased during the catalyst preparation. The appearance of a band at 881 cm⁻¹ can be attributed to the presence of calcium carbonate [21]. These results confirmed the incorporation of calcium species onto the flamboyant-based support surface, which played a relevant role for FAMES transformation.

CONCLUSION

This report has demonstrated the importance of evaluating the route for the preparation of heterogeneous catalysts employed in transesterification reactions for biofuels production. The surface modification of a flamboyant char with calcium nitrate could be an alternative to improve the performance of the catalytic processes involved in the biodiesel production.

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