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Production of Biodiesel by Esterification of Free Fatty Acid using the Catalyst

$\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.7}\text{Ni}_{0.3}\text{O}_3$ (LSFN_x)

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ABSTRACT

In this work we have prepared oxide powders perovskite $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.7}\text{Ni}_{0.3}\text{O}_3$ by the method of sol-gel (combustion citrates), the powder is calcined in 700 ° C for 5 hours to obtain the pure phase. three compounds of this oxide (x = 0.0, 0.1 & 0.2), that the pure phase, were characterized by XRD, SEM, TEM and BET. We made this catalytic efficiency test for the three powders in the esterification reaction for biodiesel production, this transformation has been examined through the gas phase chromatography device to compare the three compounds and compare them with sulfuric acid (H_2SO_4). Biodiesel formation has been examined by using FT-IR spectrum.

Keywords: LSFN_x, Perovskite, catalysis, Biodiesel, Methyl Oleate, FAME, Esterification.

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INTRODUCTION

With over ten years of development and trade in Europe, biodiesel has proven its value as a fuel for diesel engines [1, 2]. The product is free of sulfur and aromatics, and, as is obtained from renewable sources, it reduces the lifecycle emissions of carbon dioxide by almost 70% compared to conventional diesel fuel.

The esterification reaction comprises the reaction of a fatty acid with an alcohol in the presence of an acid catalyst. The homogeneous catalytic reactions, generally, the strong mineral acids, exhibit excellent reaction yields, but they can cause equipment corrosion problems (for example H_2SO_4). However, the technological challenge is to make a biodiesel production process by esterification of acids using solid catalysts mixed acids. These materials must have high activity and stability, easy separation of the product and should not cause corrosion problems in the equipment. These properties could characterize them as environmentally friendly materials [3].

In this present paper, we have two objectives: Study of the catalytic power of LSFNx catalysts based on strontium doping rate and production of biodiesel by esterification reaction of oleic acid with methanol in the presence of a solid type of mixed oxide catalyst perovskite mesoporous (LSFNx) as powders synthesized by sol-gel process, there are three samples of perovskite $La_{1-x}Sr_xFe_{0.7}Ni_{0.3}O_3$ where ($x = 0.0, 0.1$ & 0.2) We will study the conversion of oleic acid to methyl oleate (methyl ester of oleic acid) in the presence liquid catalyst is sulfuric acid (homogeneous catalysis) and mixed solid catalyst, Lewis type acid (heterogeneous catalysis) is the perovskite LSFNx ($x = 0.0, 0.1$ & 0.2). Then and compared conclude the catalytic properties of the nanomaterial LSFNx ($x = 0.0, 0.1$ & 0.2).

EXPERIMENTAL

Catalysts synthesis and characterization

$La_{1-x}Sr_xFe_{0.7}Ni_{0.3}O_3$, ($x = 0.0, 0.1$ & 0.2) catalysts were synthesized by sol-gel combustion method. The starting raw materials used in this work were the Lanthanum nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$), ferric nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), strontium nitrate ($Sr(NO_3)_2$) and nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) as oxidizing agents, whereas citric acid ($C_6H_8O_7$) was used as fuel. All chemicals completely dissolved in 100 mL diluted water in a beaker under the constant stirrer at $100^\circ C$ until the homogeneous sol as solution formed. Afterwards, the homogeneous sol was heated slowly at $120^\circ C$ for a night. The solid dry gel was calcined at $700^\circ C$ in air for 5 h. The crystal structure and parameters were investigated by x-ray diffraction (diffractometer Bruker D8 Advance) using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) in 2θ range from 5° to 80° , treated using X'pert Highscore software. A Philips CM-200 and Joel JSM 2000 transmission and scanning electron microscopes (TEM and SEM), respectively, were used to check the morphology and particle sizes, using the high intensity XRD peak and calculated by Sherrer formula. BET technique was used to measure surface area, pore shapes and N_2 adsorption/desorption on catalysts area using a Surface Area and Porosity Analyzer, Micrometrics home (ASAP 2020 model).

Catalyzed methylic esterification of oleic acid

In this part, we use of Oleic acid (35.15ml) ($C_{18}H_{34}O_2$), Methanol (20ml) (CH_3OH), sulfuric acid

(1.77ml) (H_2SO_4 , 10 Wt%) and mixed oxides solid LSFNx ($x = 0.0, 0.1 \& 0.2$) catalysts as reagents. Catalyst is dissolved in methanol and adding oleic acid, the all are in round-bottom glass flask with two-neck cap.250 ml, the mixture is stirred to be homogeouned under heat. Four catalysts are tried in this esterification reaction: sulfuric acid catalyst (homogeneous catalysis) then, solid catalysts of the mesoporous perovskite $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.7}\text{Ni}_{0.3}\text{O}_3$ where ($x = 0.0, 0.1 \& 0.2$) (10% by weight, based on AGL).

Catalysis tests were carried out in the reactions and performed in a round-bottom glass flask with two-neck vol-250 ml equipped with a reflux condenser in a crystallizer. An excess of methanol was added to the flask containing the oleic acid in order to shift the equilibrium towards ester formation with a molar ratio of 1: 4.5 (oleic acid: methanol). Perovskite mesoporous (LSFNx) ($x = 0.0, 0.1 \& 0.2$) (10% Wt by weight, based on the oleic acid) was added to catalyze the esterification without it depends on the concentration of the reaction substrate. The crystallizer is placed on a hot plate about 70 °C with magnetic stirring about 450 rpm, maintaining the stability of the degree of the temperature through the thermocouple installed. Connecting the condenser in a small submersible pump placed in a water bath containing an amount of ice. This system condenses the vapor from the reaction to maintain the amount of the reactants. The esterification reaction is started and stay for three hours, several samples are taken at different times (0:10:30; 30: 30: 180 minutes) by Pasteur pipette, the samples are then separated by centrifuge. In order to regularise biodiesel acidity, biodiesel is placed in a separatory funnel 60 ml , washed with distilled water and then with dilute solution of sodium bicarbonate, until having a value (PH = 7) . Results are obtained from GC data and the conversion of methyl oleate (biodiesel) was calculated by the formula:

$$\text{Conversion \%} = \frac{\text{quantity of ester product after esterification (mol)}}{\text{initial quantity of free fatty acid (oleic acid) (mol)}} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

Characterization of catalysts LSFNx

X-ray diffraction

The x-ray diffraction (XRD) patterns of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{0.7}\text{Ni}_{0.3}\text{O}_3$, ($x = 0.0, 0.1 \& 0.2$) catalysts, calcined at 700°C for 5h are shown in [Figure 1](#). High crystalline and single phases confirmed, only in $\text{LSFN}_{0.2}$ patterns corresponding to LaNiO_3 . Furthermore, the product of the $\text{LSFN}_{0.0}$ sample was observed in orthorhombic perovskite structure with space group Pbnm, which is well consistent with the standard JCPDS card of perovskite $\text{LaFe}_{0.75}\text{Ni}_{0.25}\text{O}_3$ JCPDS37-1493). The lattice parameters slightly decreased with the value of doped Sr, due to the different in ionic radius, resulted small shifting of peaks to higher 2θ values. The average of crystallite size is calculated using the most intense peak ([Table 1](#)) [4].

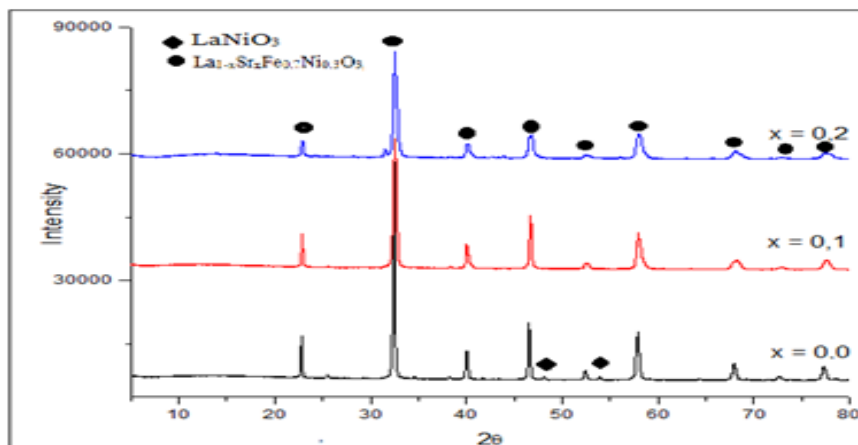
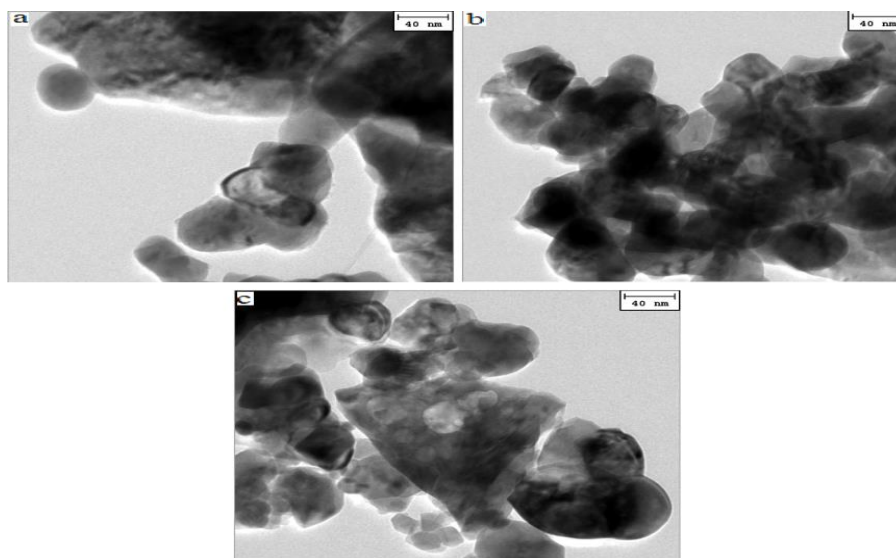

 Figure 1: XRD of LSFN_x catalysts

Table 1: Presents structural informations, and crystallite sizes calculated using Sherrer formula.

| Sample | Structure | Space group | Lattice parameters (Å°) | | | Unit cell volume (Å ³) | Crystallite size (nm) |
|----------------|--------------|-------------|-------------------------|----------|----------|------------------------------------|-----------------------|
| | | | <i>a</i> | <i>b</i> | <i>c</i> | | |
| <i>x</i> = 0.0 | Orthorhombic | Pbnm | 5.5360 | 5.5099 | 7.803 | 238.71 | 43.31 |
| <i>x</i> = 0.1 | Rhomboedric | R-3C | 5.529 | 5.529 | 13.354 | 367.78 | 31.50 |
| <i>x</i> = 0.2 | Rhomboedric | R-3C | 5.5160 | 5.5160 | 13.348 | 302.72 | 30.80 |

TEM & SEM images

TEM was employed to obtain direct information about the size and structure of the produced LSFN nanocrystals. Figure 2 presents a typical TEM image. It shows practically monodisperse particles with an average size about 30.8 – 43.31 nm, which are consistent with the average size obtained from the peak broadening in X-ray diffraction studied [5].


 Figure 2: TEM images of a) LSFN_{0.0} b) LSFN_{0.1} c) LSFN_{0.2}

SEM was employed to obtain information about particles agglomeration in area and pore shapes that improve BET results (Figure 3).

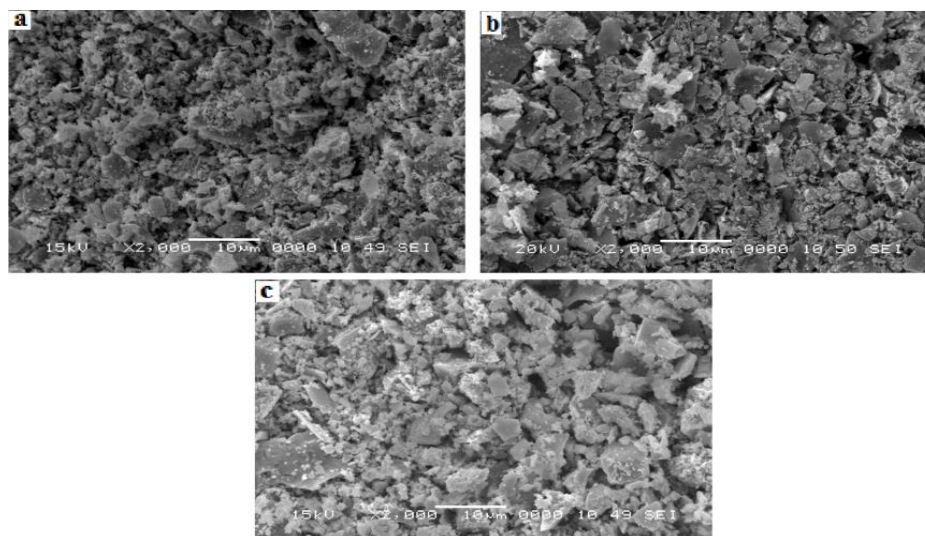


Figure 3: SEM images of a) LSFN_{0.0} b) LSFN_{0.1} c) LSFN_{0.2}

BET measurements

Surface areas of LSFN_x catalysts either pore sizes are gathered in Table 2, surface areas show important values, it explain high catalytic activity. Pore sizes shows that these materials are mesoporous (between 2-50 nm) [6].

Table 2: BET informations of LSFN_x mesoporous materials

| Sample | Surface area (m ² /g) | Pore size (nm) |
|-----------|----------------------------------|----------------|
| $x = 0.0$ | 5.66 | 25.52 |
| $x = 0.1$ | 20.67 | 13.43 |
| $x = 0.2$ | 7.68 | 20.66 |

Esterification of oleic acid

Chemical esterification reaction to produce biodiesel catalyzed with LSFN_x powders is shown in (Figure 4)

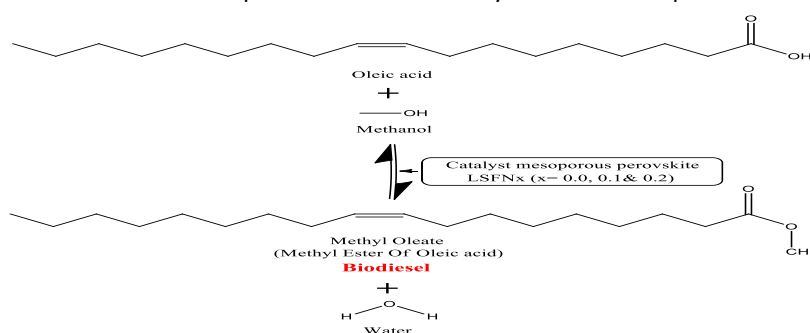


Figure 4: the esterification reaction of Oleic acid catalyzed by LSFN_x powders

The feasible procedure for recovery and reuse besides the high yields suggest that these catalysts are potentially useful for biodiesel production. Those authors proposed a mechanism of the catalytic action as described in (Figure 5) [7].

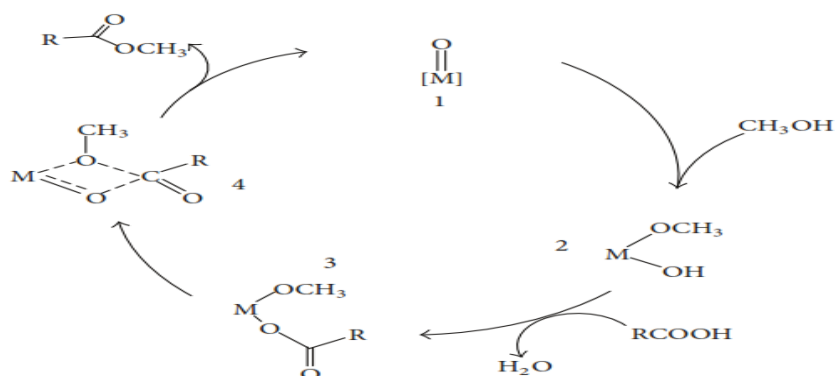


Figure 5 : Proposed mechanism for the esterification of FFA's catalyzed by Lewis acid metal oxides.

Characterization of biodiesel

Analysis of biodiesel synthesized by Gas chromatography (GC)

Analysis of biodiesel was performed on a GC 2014 chromatograph equipped with a flame ionization detector (FID) and a DB-5 column (30 m x 250 μm x 0,25 μm). Nitrogen is used as a carrier gas. The injection volume was 1 μL with split ratio 50. Setting oven temperature program . The temperatures of the injector and detector were set at 230 ° C and 270 ° C respectively. The oleic acid methyl ester was used as internal standard and was added before analysis by GC.

The biodiesel analysis by gas chromatography (GC-FID) was developed quantitative analysis (Figure 6), we enter the eight samples of each catalyst (H_2SO_4 and $\text{LSFN}_x = 0.0, 0.1 \& 0.2$) and calculate the conversion of oleic acid methyl oleate for each sample at different times for four catalysts to be able to compare the incentives and their impact on this type of reactions.

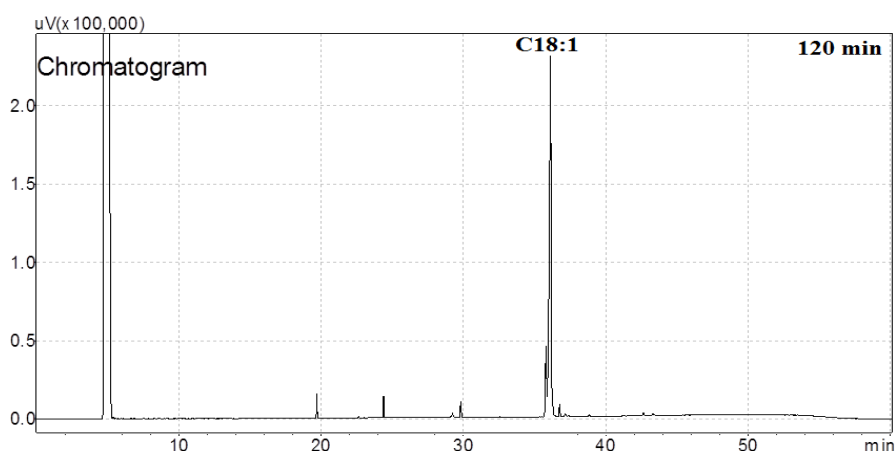


Figure 6: Chromatogram of the quantitative analysis of the biodiesel by GC-FID (Using $\text{LSFN}_x = 0.0$)

Note in chromatogram analysis of Biodiesel by GC-FID, large peak at 36 min peak distinguish this methyl oleate C18.1 (methyl ester of oleic acid), regarding the other peaks from (19,24,29) min has any other methyl ester free fatty acid, neglecting these peaks and is only interested in the big peak methyl oleate 18: 1.

Comparison between mixed oxide catalysts (LSFNx):

The figure (Figure 7) represents the conversion of oleic acid into methyl oleate as a function of reaction time under a temperature of 70 °C.

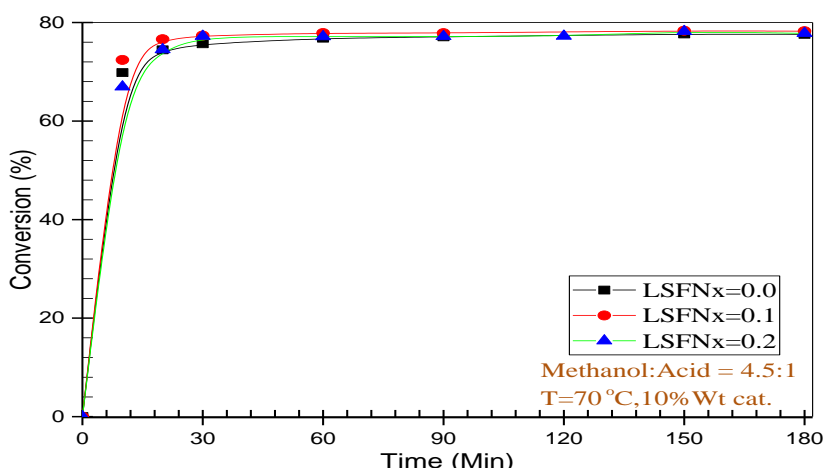


Figure 7: Catalytic Power of the Catalyst Compounds LSFNx

The compound x = 0.1 is the best catalyst in the series of LSFNx material, explaining the results of the specific surface measured by the BET method (Table 2). The catalytic power of compound x = 0.0 and x = 0.2 are converging in the interval III (90-120 min) (Figure 8) with superiority to compound x = 0.2 in most of the interval of time, explained by the limit substitution of strontium in the LFN matrix (20%) which creates secondary phases may cause a decrease in the value of specific surface area less than that of compound x = 0.1 [6] but the superimposition of the two curves, or the superiority of compound x = 0.0 in the beginning of the reaction can be explained by a small disturbance in operating conditions . The following order, than can be confirmed

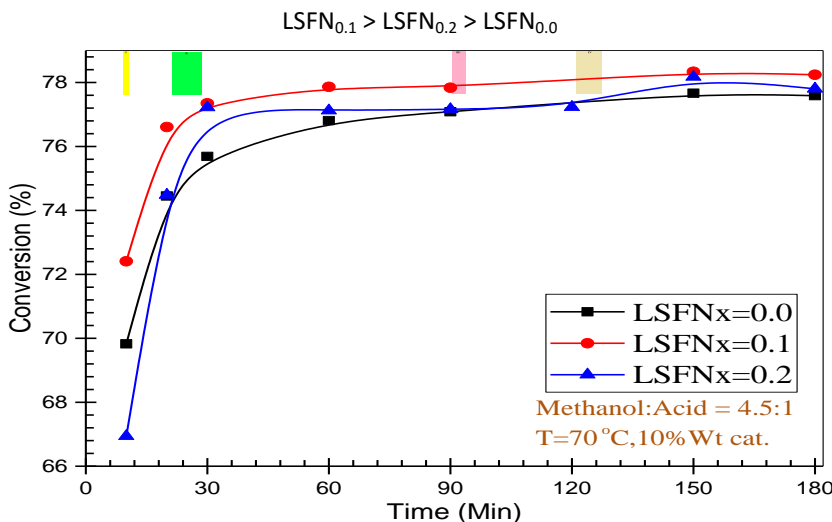


Figure 8: Catalytic power of compounds of LSFNx catalyst, divided into areas of time

Comparison between mixed oxide LSFN_x and H₂SO₄ in catalytic power

The sulfuric acid catalyst is often used to speed up the esterification reactions, for this, we made a comparison between the catalyst and the LSFN_{0,0} compound that has the last catalytic value by contribution to others. Figure 9 clearly shows that the LSFN_{0,0} catalyst is more effective than H₂SO₄ in the esterification reaction.

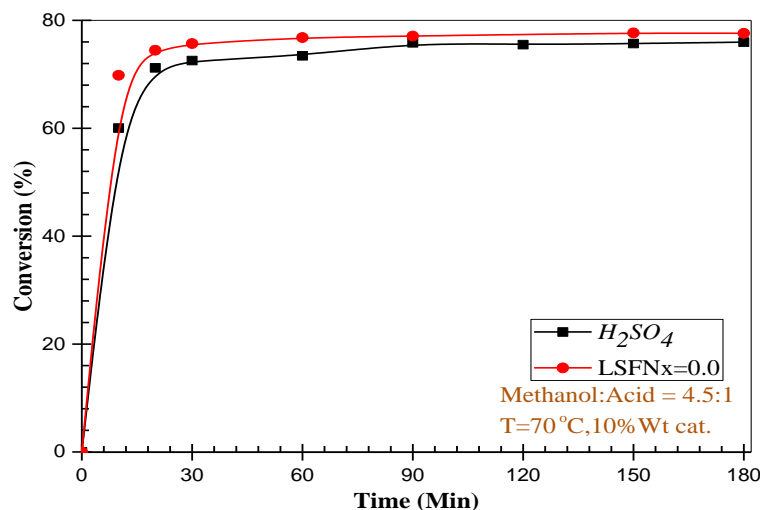


Figure 9: Comparison between the catalytic power of sulfuric acid catalyst and LSFN_{0,0}

Evolution of FT-IR spectra of biodiesel, product of esterification

To confirm the quality of our biodiesel we conducted an analysis by infrared spectroscopy [8]

The IR spectrum of biodiesel from oleic acid seed oil is shown in (Figure 10) IR spectrum of biodiesel showed a C = O stretching band of methyl esters at 1743 cm⁻¹ and C-O stretching bands at 1170, 1195 and 1246 cm⁻¹. The weak signal at 1654 cm⁻¹ may due to C=C stretching frequency. Strong and sharp signals at 2854 and 2926 cm⁻¹ are due to C-H stretching frequencies. The absorbance at 3005 cm⁻¹ indicates the =C-H stretching frequency. The observation of an absorption peak at 733 cm⁻¹ suggested the CH₂ rocking.

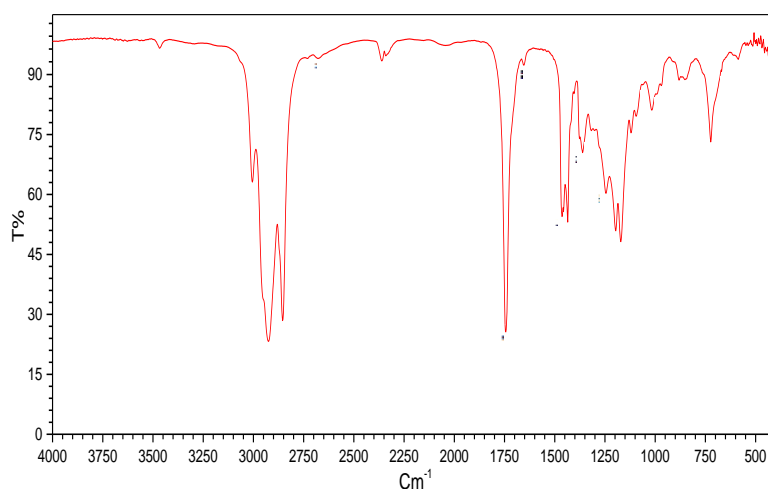


Figure 10: FT- IR spectrum of biodiesel from oleic acid

CONCLUSION

$\text{La}_{1-x}\text{Fe}_{0.7}\text{Ni}_{0.3}\text{O}_3$ Sr- doped is a cheap and good catalyst, strontium doping increase the catalytic power and $\text{LSFN}_{0.1}$ is the best compound in the series because of its specific surface, production of biodiesel by esterification of free fatty acids can be good catalyzed using this mesoporous perovskite.

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