



## Synthesis of Fatty Alcohols from Oil Palm Using a Catalyst of Ni-Cu Supported onto Zeolite

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**Abstract:** A series of Ni-Cu supported onto zeolite type ZSM-5 has been synthesized by direct hydrothermal method without template agent and characterized using XRD, FT-IR, NRM mass, SEM, CG and N<sub>2</sub> adsorption techniques. The catalytic performance of the obtained materials was evaluated and utilized for the hydrogenation of palm oil at 453 K and 40 atmospheres of pressure. The results show that the samples exhibited typical hexagonal arrangement of mesoporous structure with high surface area and the heteroatoms were probably incorporated into the framework of ZSM-5. Catalytic tests show that the bimetallic incorporated materials were effective as catalysts in the hydrogenation of oil palm producing fatty alcohols typical.

**Keywords:** Hydrogenation, Palm oil, Ni-Cu-ZSM5, Bimetallic Catalyst, Fatty alcohols.

### Introduction

The hydrogenation of vegetable oil is an important process in the oil and fat and the oleochemical industries both to modify the oil's physical characteristics for specific application and to increase its stability towards oxidation and decomposition. The vegetable oils are complex mixtures of triglycerides of fatty acids with 12-22 carbon atoms which may have 1-3 double bonds in each hydrocarbon chain. The industrial hydrogenation of palm oil in liquid phase is realized for convert the trienes and dienes, of the constituent fatty acids, at linolenic and linoleic respectively, selectively to the monoenes, oleic or to saturation, stearic, for use in frying and baking applications and by complete hydrogenation in the fatty alcohols respectively. Nickel catalysts supported on silica, alumina and Raney nickel which is an alloy with aluminum, are generally used in commercial hydrogenation. There are however some

concern on the toxicity of traces of nickel remaining in the oil<sup>1-4</sup>. Other catalysts including copper on silica<sup>3</sup>, nickel silver<sup>4</sup>, copper chromite<sup>5-8</sup> have been investigated. Noble metal catalysts are not generally used because of their high cost. However, their high activity in small quantity and the possibility of reuse with fixed bed reactor may offset the cost disadvantage. Palladium on carbon has been used in some process of commercial hydrogenation because of its high activity for linolenic acid and linoleic acid at low temperature<sup>9,10</sup>. It is also claimed to be cost effective for the production of pure margarine with a novel reactor design<sup>4</sup>. Platinum on carbon had been found to be highly active but with low selectivity producing the saturated fat<sup>11</sup>. A more recent report<sup>12</sup> found that a modified platinum on carbon catalyst by incorporating a small amount of ammonia in the hydrogen have high selectivity with low *trans*-isomerization.

Fatty alcohols are mainly derived from vegetable oils such as palm oil and coconut oil and serve as raw materials for various household products and surfactants. Fatty alcohols are produced by continuous hydrogenation of fatty acids or fatty acid methyl esters under high temperature (523–573 K) and high hydrogen pressure (25–35 MPa) in a liquid-phase slurry-bed process. The catalyst used in this process consists mainly of copper-chromite (Cu-Cr) oxide as a basic structure<sup>1-3</sup>. Although many modifications have been made for practical use, basic composition has not changed from the original. Safety is a major concern in using Cu-Cr catalyst since hexavalent Cr is discharged in catalyst manufacturing. Fatty alcohol producers and catalyst manufacturers have attempted to develop without Cr catalysts for many years; however, without Cr catalysts with equivalent performance to the Cu-Cr catalyst have not been developed to date. Catalysts must have high activity, selectivity and durability (catalyst life). We have developed an environment-friendly bimetallic catalyst Ni-Cu-Zeolite for used as a potential catalyst for selective hydrogenation direct for the oil palm being explored. The zeolite too is synthesized in this work without use template agent as support of the metals.

## Experimental

Refined oil palm (iodine value = 37) came from commercial sources. These were re-refined and bleached in the laboratory before hydrogenation in a local construction apparatus. Commercially available aluminum sulphate (E. Merck, Germany), sodium hydroxide (E. Merck, Germany), silica fumed (Sigma, St. Louis, MO, USA), hexadecyltrimethylammonium chloride (Fluka, Steinheim, Switzerland) were used for synthesizing the support. A mixture of oleyl alcohol, palmitoyl alcohol, 1-dodecanol, 1-tetradodecanol and lauryl alcohol (>99%) (Sigma Aldrich, US) was used for evaluate by GC the production fatty alcohols from hydrogenation with bimetallic catalyst; methanol (Merck, Germany); Butan-1-ol (Fisher, US); heptane and carbon disulfide (Merck, Germany); sodium chloride; anhydrous sodium sulfide and sodium hydroxide (J.T. Baker, US) were used without purification; acetate and nitrate of cooper and nickel (Merck, Germany). Palm oil (100% refined palm oil) was obtained from a local cultivates of area of Atlantic Coast in Columbia. The fatty acid composition was determined: 42.0% palmitic, 3.8% stearic, 38.7% oleic, 11.8% linoleic, myrastic 1.1% and 0.3% lauric acid.

### Procedures

The fatty alcohols composition of methylated reaction products were analyzed using a Hewlett Packard - 5890 GC gas chromatograph (GC) equipped with FID with a HP-5 (5% Phenyl Methyl Siloxane) capillary column-10 (*L*, 30 m; *i.d.*, 0.25 mm; thickness of film, 0.25  $\mu$ m) operated at 503 K and a temperature ramp between 323-503 K (293 K/min) with

nitrogen as carrier gas. For the quantitative determination of *trans*-isomers, the methyl ester obtained were dried under vacuum and then diluted with CS<sub>2</sub>, injected into a sealed liquid FTIR cell of thickness 0.1 mm with NaCl window using a Perkin-Elmer infrared Fourier transform model 2000 spectrometer equipped with a computer. The IR spectra at 4 cm<sup>-1</sup> resolution in the range from 1200 to 900 cm<sup>-1</sup> were collected. Calibration curve was previously obtained from standard mixtures containing from 3 to 51% *trans*-isomer, prepared from methyl oleate and methyl elaidate with total concentrations of between 20 and 30 mg mL<sup>-1</sup><sup>13-20</sup>. Determinations of FTIR spectrum for sample of oil palm before and after hydrogenation were made.

#### *Preparation of support, Zeolite ZSM-5*

NaZSM-5 with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 30 was synthesized without the use template in an autoclave under autogeneous pressure at 445 K. The autoclave was maintained at this temperature for 180 h for zeolites synthesized. Merck 35% silica, sodium aluminate, NaOH and water were used. The oxide compositions of the reactants used were SiO<sub>2</sub> = 0.8456, Al<sub>2</sub>O<sub>3</sub> = 0.03276, Na<sub>2</sub>O = 0.06354. After the specified crystallization time, the autoclave was cooled and the crystalline product was separated by filtration. The product was washed thoroughly with de-ionized water, dried overnight at 373 K and calcined at 823 K for 16 h. NaZSM-5 thus obtained was ion-exchanged three times with 0.5 M ammonium nitrate solution at 343 K. The NH<sub>4</sub>ZSM-5 thus obtained is dried overnight at 373 K and was then converted into its hydrogen form by calcination at 823 K for 7 h.

#### *Synthesis of Ni(II) and Cu impregnated ZSM-5*

Ni(II) and Cu(II)-impregnated ZSM-5 was prepared by mixing together equal amounts of ZSM-5 and nickel(II) nitrate or copper(II) nitrate, using minimum volume of water for wetting, followed by evaporation of the solvent at 393 K for 5 h and calcinations at 773-873 K for 10 h in air.

#### *Catalyst characterization*

Metal supported on ZSM-5 synthesized was confirmed by XRD measurements (Rigaku, Miniflex II, Cu K $\alpha$  radiation, U.S.). The changes in surface topography following metal impregnation were observed with SEM (Magellan™ XHR SEM FEI, US). The percentage of Ni(II) and Cu(II) entering into ZSM-5 is determined with atomic absorption spectrophotometer (Perkin Elmer Analyst 200, US). The catalysts were further characterized by FTIR measurements (Perkin Elmer spectrum RXI, range 4400-440 cm<sup>-1</sup>, MA, USA) using KBr self-supported pellet technique. The cation exchange capacity (CEC) of the catalysts was estimated using the copper bis-ethylenediamine complex method<sup>20</sup>. The N<sub>2</sub> sorption measurements of the sample previously treated at 423 K for 2 h under vacuum were made at the temperature of liquid N<sub>2</sub> on Autosorb 3B equipment (Quantachrome Corporation). The specific surface area (S<sub>BET</sub>) of ZSM-5, Ni-Cu-ZSM-5, Ni-ZSM-5 and CuZSM5 was calculated by the BET method from the amount of adsorbed N<sub>2</sub> in the range of 0.06 < P/P<sub>0</sub> < 0.24. The mean diameter of the mesopores (d<sub>mp</sub>) in these samples was determined by the model of DFT (Density Functional Theory).

#### *Hydrogenation of palm oil*

Catalytic capacity of the bimetallic catalyst synthesized was evaluated from a series of hydrogenation processes using oil palm at 40 atmospheres of pressure and temperature 453 K. The hydrogenation was made in Parr company a Shaker type hydrogenation equipment

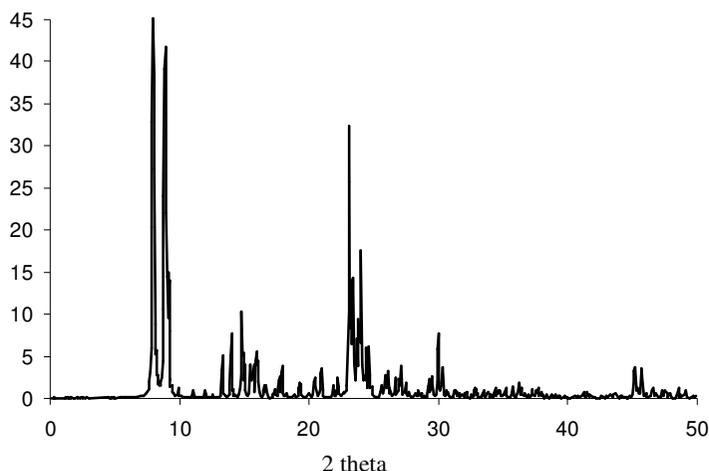
series 3916. The level of activity of each one was evaluated based in the consumption of hydrogen. The colloidal catalyst and 65 mL butan-1-ol were fed into the reactor. Hydrogen gas was charged several times to replace air and the catalyst was activated for 120 min with vigorous stirring. After the palm oil (1% w/w) was injected the reaction was started. The hydrogen consumption was monitored with a graduated gas burette. The reaction was stopped after 60 min. The partially hydrogenated palm oil were sampled at different intervals and analyzed by GC for determine the conversion to fatty alcohols<sup>21-22</sup>.

## Results and Discussion

### Catalyst characterization

#### XRD study

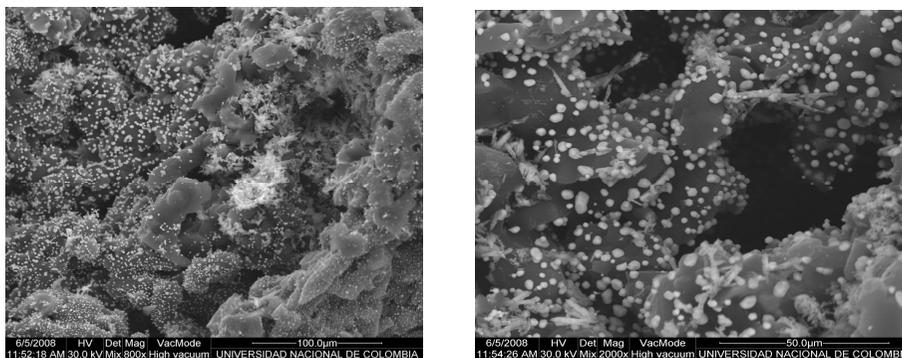
The x-ray diffraction patterns of the ZSM-5 sample without template are given in Figure 1. The sample show crystallinity and possess peaks characteristic of ZSM-5. Comparison of these values confirms that the major characteristic peaks of ZSM-5 are present on both the samples. Infrared spectra of the zeolites taken in the region 400-1400  $\text{cm}^{-1}$  give a clue as to the structural characteristics of the zeolites. The characteristic bands at 450  $\text{cm}^{-1}$  (O-O band), 550  $\text{cm}^{-1}$  (double ring) and 795  $\text{cm}^{-1}$  (symmetric stretch) are present in the sample confirming the ZSM-5 structural properties<sup>16-18</sup>. The ZSM-5 form showed three peaks at  $2\Theta = 2.363 \text{ cm}^{-1}$  ( $d = 37.32 \text{ \AA}$ ) and  $4.748 \text{ cm}^{-1}$  ( $d = 21.81 \text{ \AA}$ ). These results are in agreement with the literature values for ZSM-5<sup>17</sup>, known to give two to five reflections between 23 and 60  $\text{cm}^{-1}$  indicating long range order in them, although samples with more reflections have also been reported. In the present study, the ZSM-5 show two XRD peaks in the said region and the most prominent peak at  $2 \Theta = 2.467$  could be attributed to (1 0 0) reflection. The samples of ZSM-5 impregnated with Ni(II) and Cu(II) showed the following prominent peaks: (a) Cu(II)-ZSM-5: 3.398 ( $d = 26.05 \text{ \AA}$ ) and 3.928 ( $d = 22.49 \text{ \AA}$ ) and (b) Ni(II)-ZSM-5 2.998 ( $d = 29.46 \text{ \AA}$ ). The change in (1 0 0) reflection band and in the other characteristics due to metal-impregnation show that the structural regularity of the materials is affected to different extents as is also observed by other workers<sup>18</sup>. The incorporation of metal ions has led to distortion of the structure of zeolite regularity manifesting itself in peak landslide and the observed change.



**Figure 1.** The X-ray diffraction patterns of the ZSM-5 zeolite synthesized.

### Scanning electron microscopy study

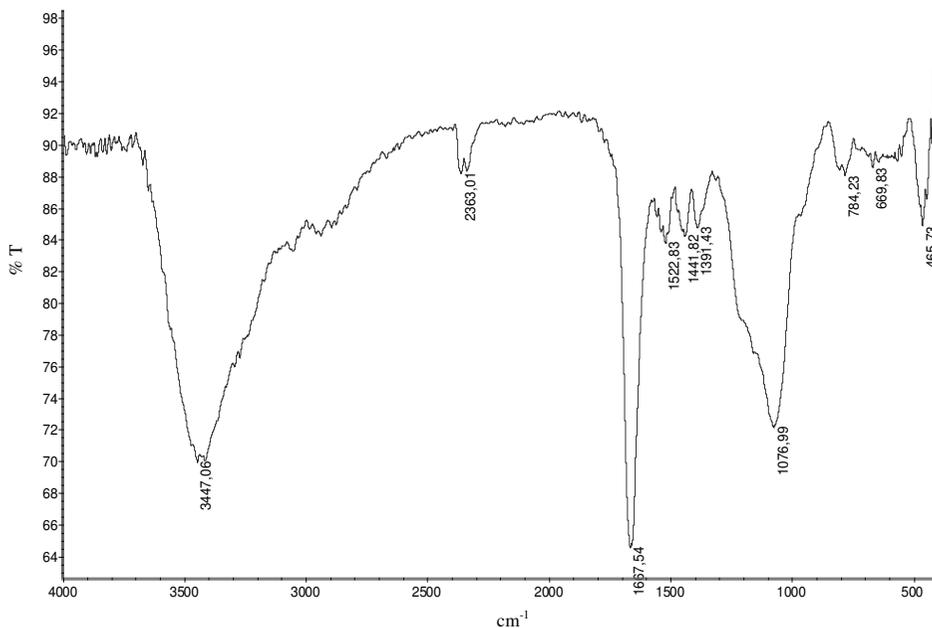
Scanning electron micrographs of samples of ZSM-5, Ni(II)-ZSM-5 and Cu(II)-ZSM-5 are shown in Figure 2(a) and (b). Introduction of Ni(II) and Cu(II) into ZSM-5 influenced the morphology regular of the porous structure of material. The grains of the salts could be clearly seen distributed over the ZSM-5 particles. A slightly difference could be observed between Ni(II)-ZSM-5 and Cu(II)-ZSM-5 with respect to morphology with the salt grains having some preferential distribution.



**Figure 2.** (a) SEM Ni(II)ZSM-5 catalyst (b) SEM Cu-ZSM-5 catalyst.

### FTIR study of catalyst Ni-Cu-Zeolite-5

FTIR spectra of samples of Ni-Cu-ZSM-5 show the characteristics bands (Figure 3). For example, Ni-Cu-ZSM-5, show IR bands characteristics between 500 and 964  $\text{cm}^{-1}$ . The band around 1000  $\text{cm}^{-1}$  is normally assigned to lattice defect and is correlated with the presence of tetrahedral framework linkages of the type  $\text{M}-\text{O}-\text{Si}^{21,18}$ .



**Figure 3.** FTIR spectra of Ni-Cu-ZSM-5 samples.

This band has been known to undergo slight red shift on metal-incorporation. Such shift was visible in all the cases in the present study. Assignment of this band to a Si-O vibration in Si-OH groups in siliceous ZSM-5 has also been suggested<sup>22</sup>. If this is the case, it is reasonable to attribute the red shift in metal incorporated ZSM-5 to the replacement of H from an OH group by a metal ion to form O-M type linkage. The broad absorption band between 3650 and 3400  $\text{cm}^{-1}$  in the FTIR spectra may be attributed to hydrogen-bonded vicinal pairs of silanol groups<sup>23</sup>. The broad band between 1000 and 1560  $\text{cm}^{-1}$  in the ZSM-5 samples may be assigned to the asymmetric stretching of Si-O-Si bridges. IR bands in the regions, 670-790  $\text{cm}^{-1}$  and 1400-1500  $\text{cm}^{-1}$  have been shown to correspond to aliphatic C-H bending vibrations and in the region, 2200-2400  $\text{cm}^{-1}$  to aliphatic C-H stretching vibration<sup>24</sup>. In the present work, no significant band was observed in the region of aliphatic C-H bending, but a few bands could be seen for aliphatic C-H stretching (2923  $\text{cm}^{-1}$  ZSM-5, 2930  $\text{cm}^{-1}$  Ni(II)-ZSM-5, 2920  $\text{cm}^{-1}$  Cu(II)-ZSM-5 and 2925  $\text{cm}^{-1}$  Ni(II)-ZSM-5). Some other bands observed in the present work (465  $\text{cm}^{-1}$  for example) could not be properly assigned. The C-H stretching and bending vibrations obviously refer to the presence of the other fragments in the material synthesized which might indicate that calcination did not completely remove materials used in synthesis of ZSM-5.

#### *Cationic exchange capacity (CEC)*

The CEC of ZSM-5 was established as 0,367  $\text{meq.g}^{-1}$ . There is a significant change in the introduction of the metal in the ZSM-5 by means of an impregnation technique in the CEC of Cu(II) and Ni(II) supported on ZSM-5 which increased from 0.384 to 0.385  $\text{meq.g}^{-1}$  respectively. The CEC of the two impregnated metals on ZSM-5 differs one from the other by a large amount and the difference is quite significant compared to the CEC of the ZSM-5 matrix. The ionic exchange capacity can be due to flaws in the structure and bond breaking and to the transfer of structural hydroxiles as it occurs in clays<sup>22</sup> and the values indicate that the Cu(II) and Ni(II) introduction increases the same in 4,7% and 4,9% respectively. The substitutions of the respective metals generate catalytic active sites. The protonation degree of the hydroxile groups will depend on the acceptor-electron interaction strength in the electrical field of the Si substituted metallic. Thus the catalyst activity will depend on that of the introduced cation in the lattice and this will increase insofar as the ratio charge/radius of the volume cation and of the porous diameter, under the synthesis conditions of these catalysts. This is related to the respective ion diameters.

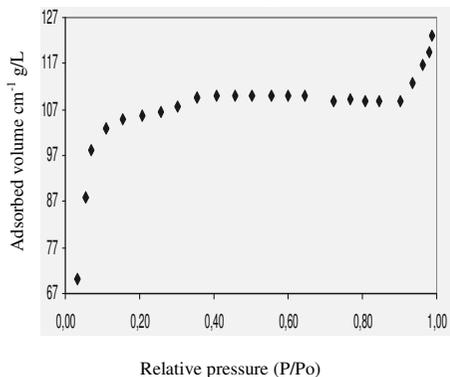
**Table 1.** Properties of the structure metal-ZSM-5 through the addition of different metals.

Samples	Metal/Zeolite ratio by, wt%	$S_{\text{BET}}$ , $\text{m}^2 \text{g}^{-1}$	Pore volume, $\text{cm}^3 \text{g}^{-1}$	Pore diameter, nm
ZSM 5	0	350	0.17	0.51
Ni-ZSM 5	4.9	390	0.26	2.57
Cu-ZSM 5	4.7	400	0.27	2.59
Ni-Cu-ZSM 5	4.2	440	0.27	3.83

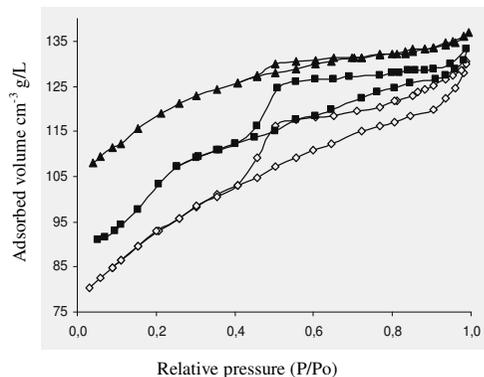
#### *The nitrogen adsorption isotherms of the samples*

The  $\text{N}_2$  adsorption isotherms of the zeolite ZSM-5 and Ni-Cu-ZSM-5, Ni-ZSM-5 and Cu-ZSM-5 samples are presented in Figures 4a and 4b. All samples show type IV isotherm patterns with H1-type hysteresis loop, which are the characteristics of the mesoporous zeolites with homogeneous pore-size distribution. These isotherms show an inflection near  $p/p_0=0.3-0.98$ . It represents mesoporous materials with cylindrical channels, indicating multilayer adsorption dominating the process and filling capillary condensation within the pores. Comparing the structure porous of the different catalyst, the formation of mesoporous

structure in Ni-Cu-ZSM-5 zeolite with major pore diameter that in Ni-ZSM-5 and Cu-ZSM-5, show that probably due the method employed in the synthesis and the presence of the two ions affect el diameter of pore.



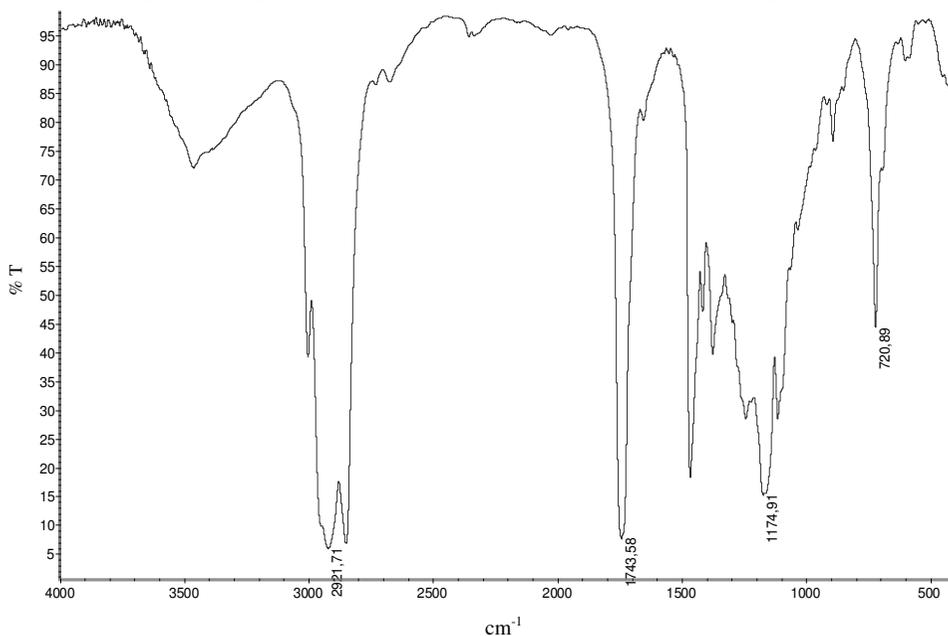
**Figure 4a.** N<sub>2</sub> physical adsorption isotherms ZSM-5.



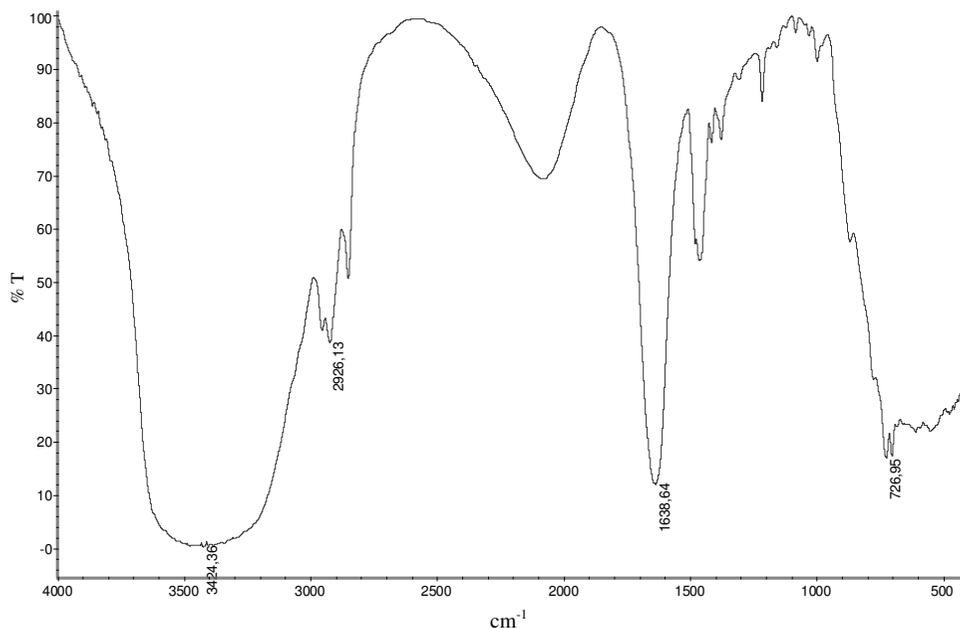
**Figure 4b.** N<sub>2</sub> physical adsorption and desorption isotherms: (▲) Ni-Cu-ZSM-5, (■) Ni-ZSM-5, (◇) Cu-ZSM-5.

*Palm oil hydrogenation with bimetallic catalyst*

Figures 5 and 6 shows palm oil FTIR spectrum before and after the hydrogenation with bimetallic catalyst synthesized in this work. The range of the bands between 3500 and 2900 cm<sup>-1</sup> shows the changes occurred during the hydrogenation process and the presence of the hydroxyls groups corresponding with fatty alcohols; additionally in the range 2200 and 1000 cm<sup>-1</sup> the corresponding changes of the palm oil and the hydrogenation products are shown. This proves that the hydrogenation is produced in the reactor and that fatty alcohols are generated as well.

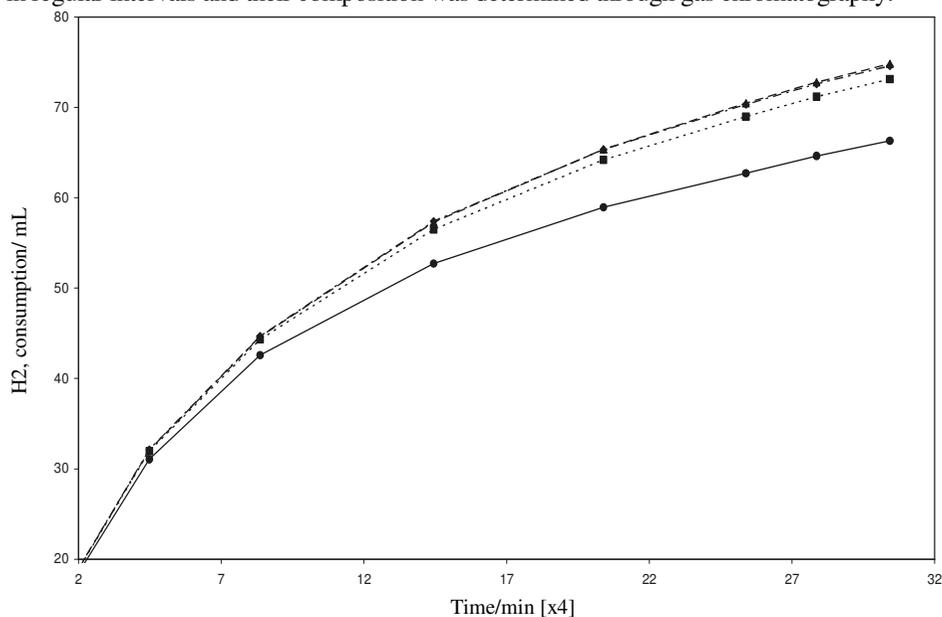


**Figure 5.** FTIR for refined palm oil.



**Figure 6.** FTIR spectrum of the palm oil hydrogenation products.

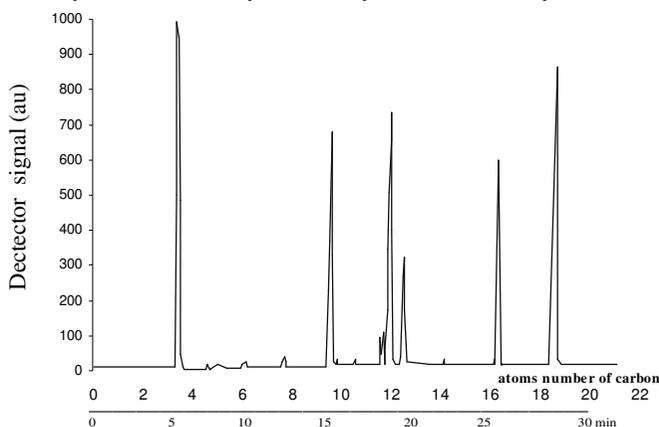
The hydrogen consumption through refined palm oil in butan-1-ol as solvent under experimental conditions were measured several times as shown in Figure 7 with different synthesized catalysts in this work. During the reaction course after several runs of 1 mL of the samples were removed in regular intervals and their composition was determined through gas chromatography.



**Figure 7.** Palm oil hydrogenation with different catalysts. Reaction condition: palm oil, 1% w/w; solvent, butan-1-ol; initial pressure, 30 atm; temp. 573K (■) Ni-ZSM-5; (●) Cu-ZSM-5 (◆) Ni-Cu-ZSM-5.

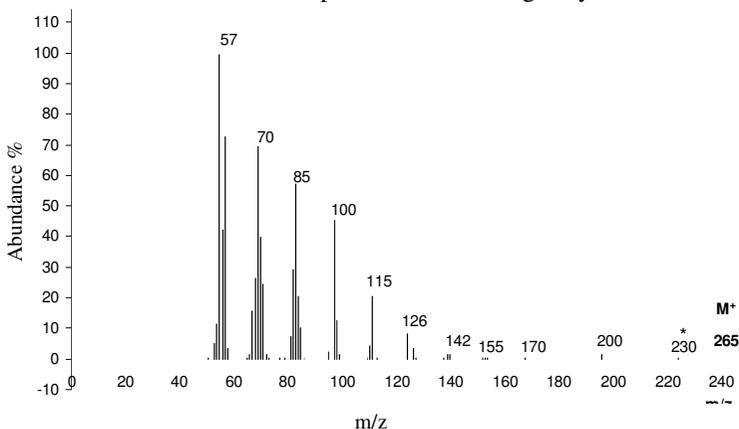
Figure 7 shows that the hydrogen initial consumption was fast, decreasing slightly with time until it reached a point that corresponds exactly to the necessary hydrogen amount to hydrogenate the trienes and dienes and the fatty acid esters to the moenes. Therefore the slope is less, which indicates an absorption rate of hydrogen slower than that of the corresponding monenes hydrogenation. The abrupt change in hydrogen consumption rate was probably due to the decrease of polienes, which confirms the oil composition. This is typical in the vegetable oil hydrogenation.

Figure 8 shows the chromatogram taken after running a sample of the hydrogenation reactor using the catalysts; the sample was taken after 45 minutes of reaction. The presence of fatty alcohols between C12 and C18 is observed. The chromatogram presented a great amount of peaks which according to the used standards permitted to establish that they corresponded to fatty alcohols, methyl esters, hydrocarbons, fatty acids and fatty esters.



**Figure 8.** Chromatogram of the samples taken after the hydrogenation reactor using the bimetallic catalyst.

The Figure 9 shows the mass spectrum obtained; this shows the presence of different compounds whose masses oscillates between 60 and 230 amu. The peaks of 170, 205 and 230 are to be highlighted since they are associated with the presence of myristic, lauric and palmitic alcohols. This corroborates the process of obtaining fatty alcohols.



**Figure 9.** Mass spectrum of palm oil hydrogenation products.

## Conclusion

The ZSM-5 synthesis was carried out without using template agent and the results show that a zeolite with typical characteristics is obtained. After being synthesized the copper, nickel, and copper nickel catalysts supported on ZSM-5 their behavior in the palm oil hydrogenation was analyzed; by using Cu-ZSM-5 and Ni-ZSM-5 catalysts it was detected production of fatty alcohols; however the activity of the bimetallic catalyst presented better properties respect to the others obtained showing that it is effective for the production of this type of alcohols according to the conditions of our experimentation. Fatty alcohols from C12 to C18 are detected by CG-MS technique finding the presence of other compounds which most probably correspond to fatty acids.

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