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Comparative study of nano iron catalysts in the presence of the crude polymer matrix and their cross link polymer in the Fischer-Tropsch synthesis

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Abstract. A new metal-polymer catalyst in a stable colloidal system, were prepared. Iron-paraffin catalysts, nano sized particles, with different polymers have been matrixes were used to examine the effects of polystyrene and their derivatives on chemical/structural properties through Fischer–Tropsch synthesis (FTS) and the yield as well. Nano size iron-containing particles distributed are suspended in the hydrocarbon medium of the slurry-reactor were found to have great impact and high percent conversion of CO to more than 70%. Polystyrene derivatives found to interact with Fe species by the formation of Fe₃O₄ oxide and amorphous hydrolyzed δ-FeOOH which were formed at the given conditions. All catalysts with a polymer found to have a bimodal distribution particle. In structural aspects, polystyrene derivatives increases the dispersion of Fe species and inhibits the coagulation of active iron particles, and on other hand, the chemical and structural effects would cause the increase of the FTS efficiency towered the selectivity of heavy hydrocarbons and olefins during the FTS. The state of iron and polymer-paraffin matrix were examined utilizing XRD and AFM techniques which showed the forms of ground state of iron as Fe₃O₄ oxide and amorphous hydrolyzed δ-FeOOH were exists. When the polystyrene derivatives are introduced, the proportion of amorphous paraffin found to be less than that in a crystalline state. The maximum conversion of CO (71%) and the yield of liquid hydrocarbons (63g.m⁻³) based on a cross-link polymer such as a polystyrene divinylbenzene (PS-DVB) used. A very interesting fact that the risen temperature found to have a small decrease in selectivity and an increase in conversion efficiency, this was observed in all reactions.

1. Introduction.

Fischer-Tropsch synthesis (FTS) was discovered nearly 95 years ago. It have a great industrial importance due to its wide applications and a great variety of products obtained, such as paraffin's, olefins and alcohols. It converts syngas (CO+H₂) to hydrocarbons in the range C₁ to C₁₀₀ [1]. The benefits of FTS were well documented. One of its application include the generation of liquid fuels free of sulfur and aromatic compounds which normally found in the crude oil distillates and fuels. Iron-based catalysts provide three advantages: cheaper, less selective towards methane and promotes the water gas that compared to cobalt based catalyst [2].

There are many methods used in reforming includes, slurry and fixed reactors, slurry reactors were applied in a wide range of chemical processes, at both laboratory and industrial scales [3]. The main uses of FTS that for the generation and reforming sulfur free hydrocarbons as well as aromatic contains products than those found in crude oil distillates.

During the last two decades, nanoparticles, received a great attention, due to their properties and the wide applications. Indeed, extensive and intensive work has been done on the synthesis of polymer/nanoparticles composite materials as a catalyst, due to their direct importance reforming and cracking hydrocarbons [4]. It is therefore very important to find synthetic methodology to produce



nanoparticles that have significant impact on changing of physical and chemical properties of such materials, so they should be well investigated [5-9].

The effect of using polymers as stabilizers in the synthesis of cobalt and iron based nanoparticles was studied by Claver [10]. The difficulty of synthesizing the metal's nanometer-sized particle is to keep it stable and free standing nanoparticles. Such materials are highly reactive and have tendency to combined together, leading to lose their unique properties. Therefore, to keep their main properties without any change it was necessary to embed them in a matrix polymer [11-14].

The aim of the present work is prepare FTS's catalysts over iron nano-sized particles inserted in the paraffin and polymers to be loaded in dispersion medium to investigate the catalytic properties: activity, selectivity, and conversion of CO efficiency in FTS.

2. Experimental.

To produce iron Nano-sized catalyst Fe-paraffin/polystyrene (Fe-P/PS) and compare it with its derivatives: Fe-paraffin/polystyrene cross-linked hosting polymer as with divinylbenzene (Fe-P/PS-DVB) and Fe-paraffin/butadiene-styrene rubbers (Fe-P/SBR) systems. The Fe-paraffin/polymer catalysts were prepared via a thermal decomposition method [14]. Which in brief, add solutions containing $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to a paraffin (mark - 2) and 6 wt % of one of the following polymers (PS), (PS-DVB) and (SBR) matrixes at 280°C under stirring and argon gas as an inert atmosphere stream.

The experiments were conducted the catalyst suspended in a slurry reactor at a pressure of 2 MP. All catalysts were activated by CO gas at 300°C for 24h, that for all the experiments. A 100 ml of catalyst was loaded into the reactor under syngas load of 1–2 L/(g cat h) and molar ratio of $\text{CO}:\text{H}_2 = 1 : 1$. Temperature ranges of $220\text{--}320^\circ\text{C}$ were maintained. The temperature was increased stepwise (by 20°C each 12 h period). The gas was analyzed on line by gas chromatographs (GC) (Models Kristallyuks- 4000 M) with a thermal conductivity detector array and helium as a carrier gas.

The liquid products in the cold traps were collected over 72 h and analyzed using liquid chromatographs (LC) (Models Kristallyuks- 4000 M).

The particle size was determined by Malvern Zetasizer Nano ZS instrument for each synthesized catalyst. In succinct, a 0.01 g dissolved from suspended catalyst in 10 ml of hexane with the addition of 5 wt % of a surfactant (sodium dioctyl sulfosuccinate).

In order to obtain the catalysts, the following reagents were used:

- Paraffin grade P-2 (GOST 23683-89) - a mixture of high-molecular hydrocarbons $\text{C}_{18}\text{--}\text{C}_{35}$, mainly aliphatic structure, obtained by distillation of oil.
- Iron (III) nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) nanohydrate, "extra pure" brand, manufactured by Scharlau Chemie S.A.
- polymers : PS = $[\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)]_n$, SBR = $[(\text{C}_6\text{H}_5)\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2]_n$ and PS- DVB = $[\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)]_x[\text{CH}_2\text{CH}[\text{C}_6\text{H}_4(\text{CHCH}_2)]]_y$.

3. Results and discussion.

3.1. Particle size distribution.

The particle sizes were examined using dynamic scattering technique in order to evaluate the changes in the particle size distribution of the dispersed phase of the synthesized suspensions. Nano catalyst includes SBR polymers and PS-DVB which brought into the required metal nanoparticles size, that have clear effect in the range of 170 to 660 nm in diameters as compared to the Nano catalyst structure, which is falls on the range from 2 to 670 nm diameter for the (Fe-P/PS) system [14] (Table 1).

In all period of production a systems were gave bimodal distribution [14].

PS introducing has lead to the formation of smaller particles (2 nm), it is going to affects their actions as compared with the catalysis based on SBR and PS-DVB polymers that has active Nano catalyst. It could be implicit that bimodality is connected with the stabilizing Fe possibility with each of polymer and paraffin. By another way, we demonstrate that Nano catalyst suspensions treatment with the CO:

H₂ combination in the temperature range 220-320 ° C for 5 days was the risen of the particles to the size mentioned in Table 1.

Table 1. The effect of polystyrene derivatives on the particles size.

Nano catalyst type	Particles size, nm			
	Before FTS		After FTS	
	nm	% content	nm	% content
Fe-P/PS	2	9	220	2
	677	91	842	98
Fe-P/PS-DVB	171	10	1283	84
	664	81	1643	16
Fe-P/SBR	312	22	540	14
	644	78	953	86

3.2. FTS performance.

The products, liquid and Gas have been sampled for an analysis. The catalysts activity had evaluated in terms of the next parameters:

The catalysts activity is calculated according to the following representation:

$$\text{Specific activity} = \frac{(\text{gram of CO})_{\text{in}} - (\text{gram of CO})_{\text{out}}}{\text{M.Wt of CO} \times (\text{gram of Cat.} \times \text{second})}$$

And the CO conversion (%) can be calculated according to:

$$\text{CO conversion (\%)} = \frac{(\text{gram of CO})_{\text{in}} - (\text{gram of CO})_{\text{out}}}{(\text{gram of CO})_{\text{in}}} \times 100$$

Also the selectivity of liquid hydrocarbons (%) can be calculated according to the following equation:

$$\text{Selectivity of C}_{+5} \text{ (\%)} = \frac{(\text{gram of Carbon})_{\text{in}} - (\sum \text{gram of Carbon})_{\text{out}}}{(\text{gram of Carbon})_{\text{in}} - (\text{gram of Carbon in C5+})_{\text{out}}} \times 100$$

The Product yield also calculated according to:

$$\text{Product yield} = \frac{\text{Amount of the product in grams formed}}{\text{gram of Cat.} \times \text{h}}$$

The entire synthesized catalysts display high catalytic activity in hydrocarbons liquid preparation from CO and H₂ throughout the progression. Whereas the catalyst introduction depend on SBR and

PS-DVB which led to an increase of the amount of CO gas conversion as compared with the catalysis structure PS polymer in the Fe-Paraffin-Polymer system.

The maximum CO gas conversion shown in (Fig 1) has been achieved was 71%, with the system Fe- P/PS-DVB and the hydrocarbons liquid formation was (63 g/m^3) as in (Fig 2). Whereas utilizing the system of Fe-P/SBR the conversion of CO gas had reached 65%, and the liquid hydrocarbons formation reached (63 g/m^3). Catalyst based on PS had been led to 15% conversion of CO, and the liquid hydrocarbons formation was (26 g/m^3) (Fig 2). Significant rise in conversion of CO in systems based on the SBR and PS-DVB can be attributed cross link structure of the system, which had the capability to react with the metal (iron) much better than that inserted in the PS polymer. That also believed the iron nanoparticles have tendency of agglomeration in PS system compared with the others.

We believe also system based on cross-link acts as a stabilizer which could help to prevents sedimentation and leads to the formation of a completely new active catalyst system and that these catalysts could give some selectivity towards the control on distribution of the nanoparticles over the cross-link systems network structure of polymers and its concentration can be conceded evenly distributed as mentioned previously.

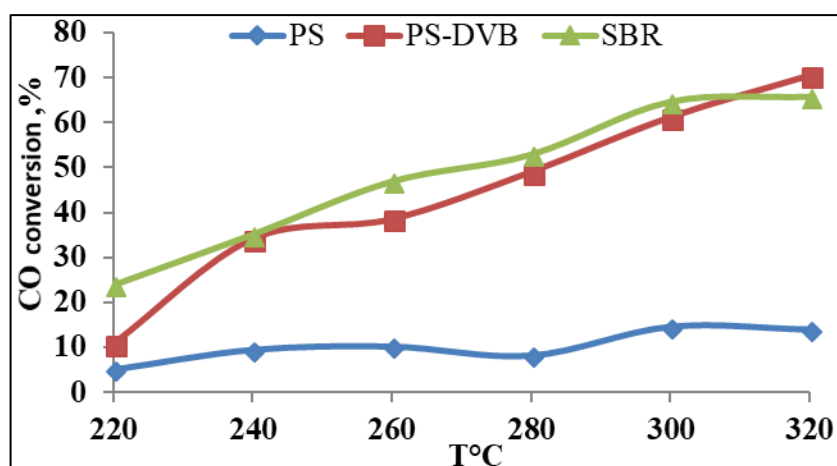


Figure 1. Temperature dependence of CO conversion of the Fe–paraffin–polymer Nano catalyst system: PS, PS-DVB and SBR.

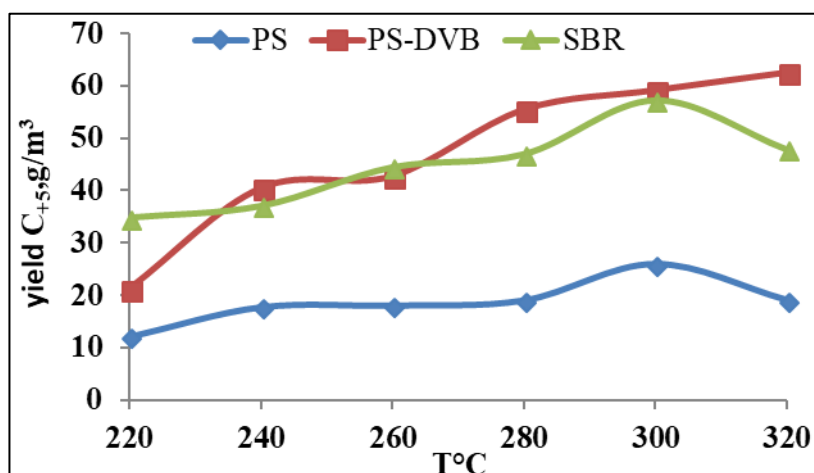


Figure 2. Dependence of the yield of C₅₊ liquid hydrocarbons on the synthesis temperature in the presence of the Fe–paraffin–polymer Nano catalyst system: PS, PS-DVB and SBR.

This network structure may play the center roles of adsorption of the reactive gases (CO:H_2). The polystyrene derivatives influence on the essential parameters of the Fischer-Tropsch catalysts based on Fe-paraffin-polymer are represented in Table 2. As well known at such conditions of optimum metal content in classical catalysts for the three-phase Fischer-Tropsch synthesis shall not more than 20% because would suffer from agglomeration. That what we have done to solve such problem by using polymer systems as a stabilizer.

Table 2 and figure (3,4), shows that the synthesized samples with nano catalysts based on PS it's important to notice that the yield of the main byproduct formed in the presence of iron Nano catalysts gaseous hydrocarbons (C_1 , $\text{C}_2\text{-C}_4$ and CO_2) yield found to depend on the type of the polymer used. The nanocatalysts depend on polystyrene used have a low yield gaseous hydrocarbons: C_1 and ($\text{C}_2\text{-C}_4$) from 4 to 33 g m^{-3} , CO_2 from 21 to 208 g m^{-3} respectively.

Table 2. The influence of polystyrene derivatives on the products of the Fischer-Tropsch synthesis ($T=220\text{-}320^\circ\text{C}$, $P=20\text{ atm}$, $\text{CO:H}_2 = 1:1$).

Nano catalysts	$*X_{\text{CO}}$, %	Yield of Hydrocarbons, g m^{-3}				Liquid hydrocarbon selectivity, %
		C_1	$\text{C}_2\text{-C}_4$	C_{5+}	CO_2	
Fe- P/PS	15	4	4	26	21	88
Fe- P/PS-DVB	71	33	33	63	208	74
Fe- P/SBR	65	30	31	57	190	54

$*X_{\text{CO}}$, % = Conversion of CO, %.

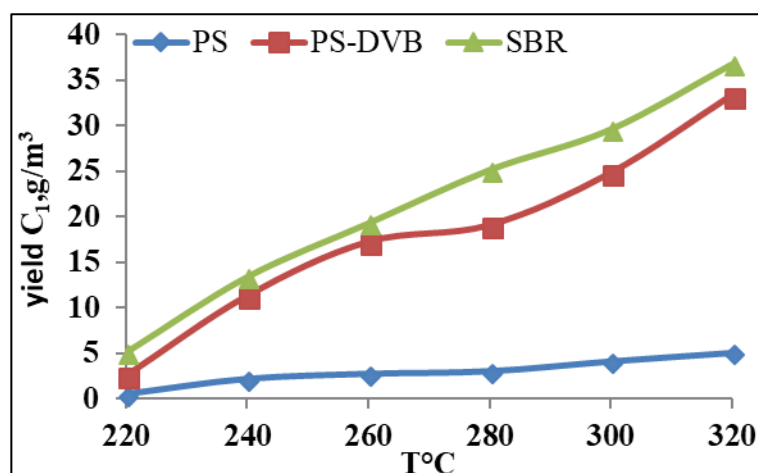


Figure 3. Dependence of the yield of CH_4 gas hydrocarbons on the synthesis temperature in the presence of the Fe-paraffin-polymer Nano catalyst system: PS, PS-DVB and SBR.

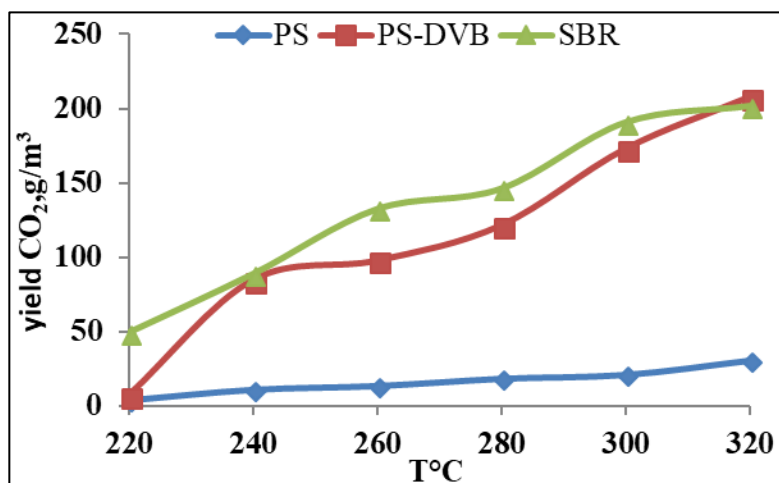


Figure 4. Dependence of the yield of CO₂ gas on the synthesis temperature in the presence of the Fe–paraffin–polymer Nano catalyst system: PS, PS-DVB and SBR.

The Fe–paraffin suspensions include the various polymers displayed different actions and different selectivity for the aimed product it could be implicit that the promoting effect had attributed directly to the structure and features of the polymer elements ^[14] figure 5.

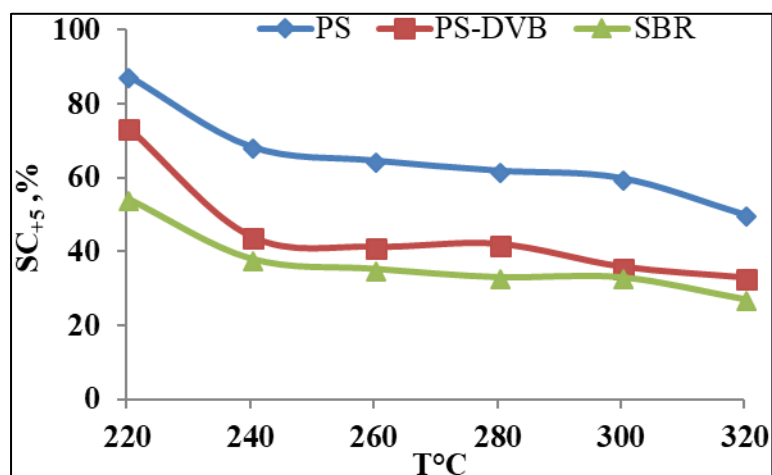


Figure 5. Dependence of the C₅₊ liquid hydrocarbon selectivity on the temperature in the presence of the Fe–paraffin–polymer Nano catalysts based on: PS, PS-DVB and SBR.

In table 3, we displayed the hydrocarbons liquid analysis which it obtained in the temperature range 220–320 °C. Which is clearly showing the PS derivatives (n-paraffin, iso-paraffin and olefin) have an influence on the composition of liquid hydrocarbon production and on the incomplete composition (gasoline C₅–C₁₀, kerosene C₁₁–C₁₈ and wax C₁₉₊).

Polystyrene derivatives compared into the Nanocatalyst suspension composition had lead to reduce the unsaturated compounds fraction that in contrast with the polystyrene sample and the paraffin fraction had also changed. Whereas using SBR copolymer had led to an increase in the paraffin yields (from 60 to 75%), whilst using PS polymers had led enhance the olefins yield from 7 to 18%. Additives of copolymer (PS-DVB and SBR) also had an influence on the liquid products fractional composition table 3. the quantity of the C₁₉₊ heavy fraction in the composition of C₅₊ hydrocarbons increased from 31 to 57%.

Table 3. Listing the selectivity effect of group composition associated with catalyst type on hydrocarbon yields.

Iron Nano catalyst	Group composition, %			Yield Fractional composition, %		
	n-paraffins	isoparaffins	olefins	C5-C10	C11-C18	C19+
Fe- P/PS	60	21	18	13	56	31
Fe- P/PS-DVB	52	31	17	20	46	34
Fe- P/SBR	75	18	7	6	37	57

3.3. Atomic Force Microscope (AFM).

The surfaces morphology of the synthesized materials revealed to see the texture of the surface Figures 6, 7 and 8. The sample was dissolved in hexane to get rid of the wax layer which coats the polymer. Clearly revealed the wavy textured surfaces in all figures, compared with that washed with hexane of less featured about plane surface. Thus in the case of a polystyrene with catalyst Figure 6, which shows the nanoparticles had been still fixed after treatment with hexane, that to explain its activity might be connected to polystyrene to alter the synthesized catalysts surface. Though most of the surface shows variation in partial size as compare with each other, while on the PS-DVB the one could found the surface turn to be more homogenous compared with surface before washing, Fig. 7. So, any changes, in the catalytic surface would lead to variance in activities and selectivity as well, that because change the active sites either shape or area diameters. In Figure 8, iron had fixed and have more featured sets and regular distribution on both x and y-axis on the catalyst surface compared the that washed and the later shows two folds of waves and three meniscuses along the y-axis of the surface of course all such variations can cause grate differences on the yield of the catalyst system used.

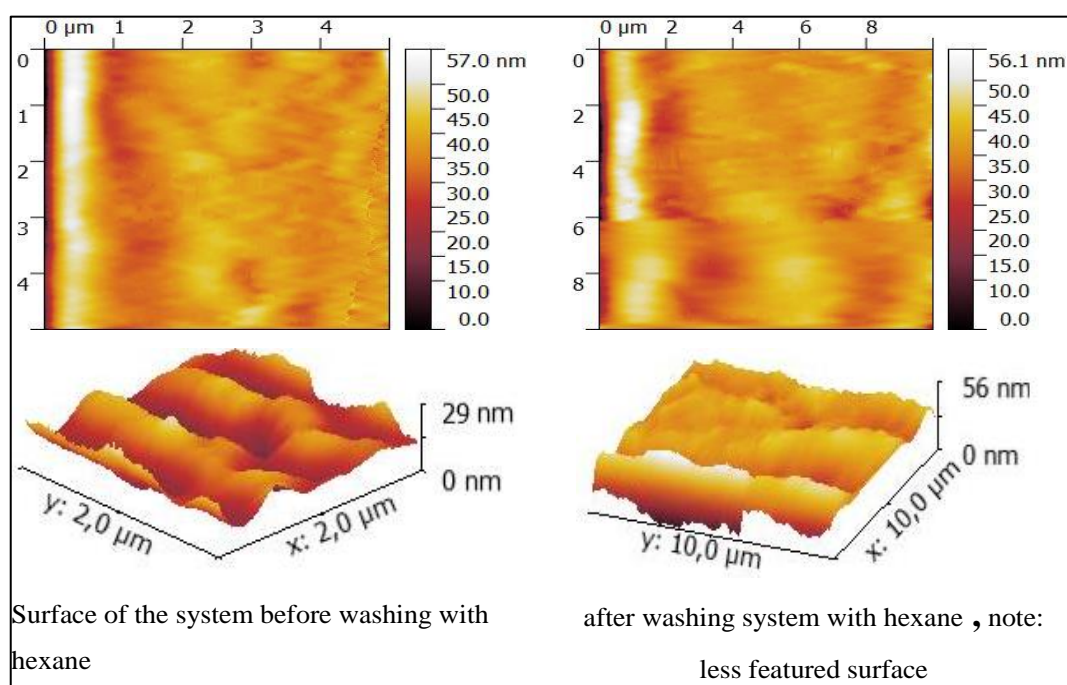


Figure 6. AFM morphology, for iron-containing solid catalyst Fe-paraffin-PS before and after washing down with hexane.

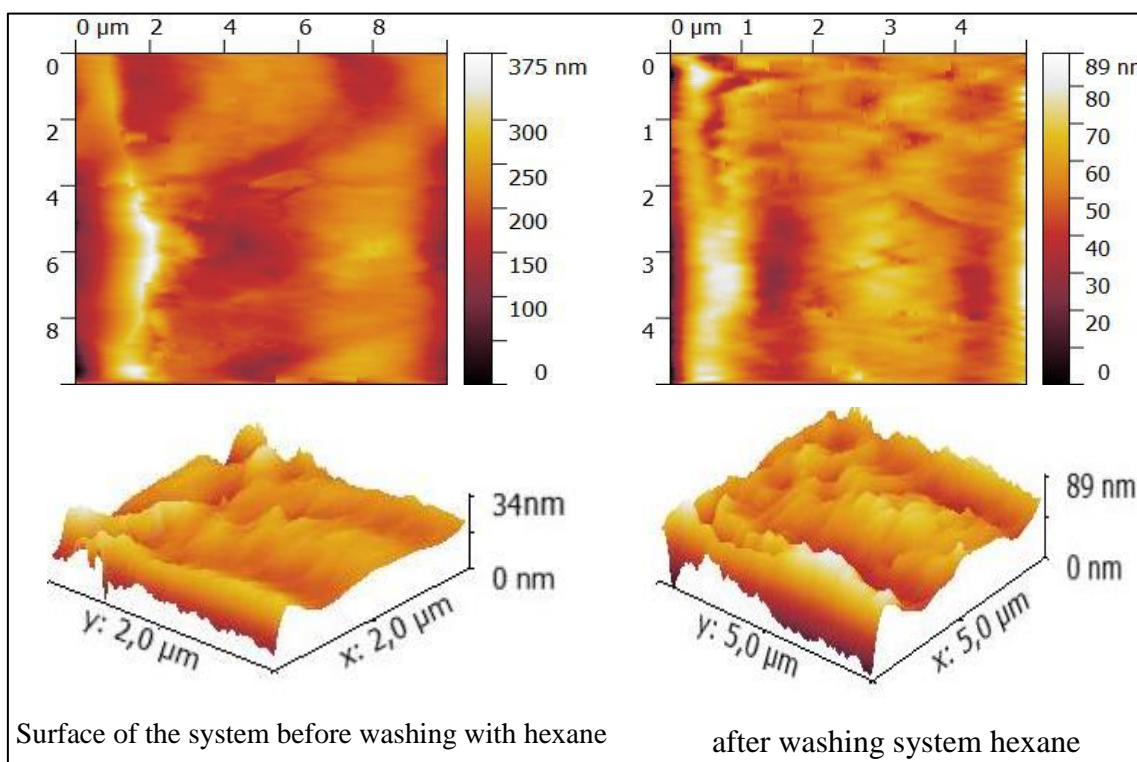


Figure 7. AFM morphology, of iron-containing solid catalyst Fe-paraffin-PS-DVB.

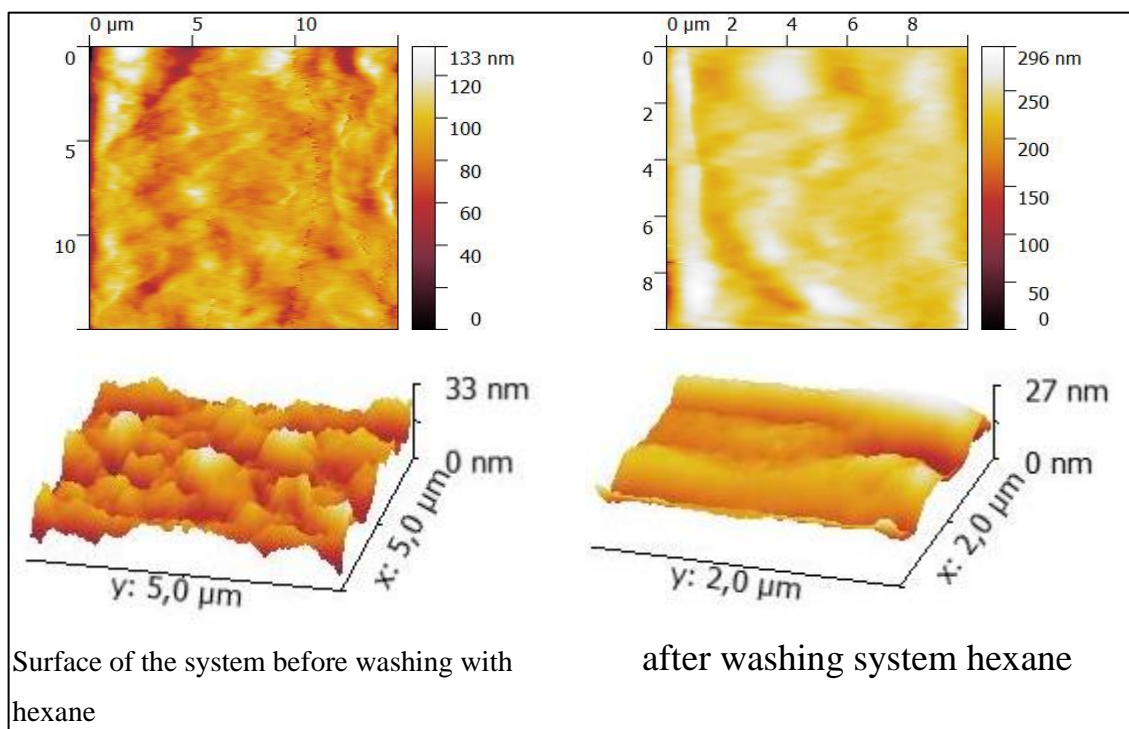


Figure 8. AFM morphology, of iron-containing solid catalyst Fe-paraffin-SBR. The surface morphology AFM.

3.4. XRD Pattern

The iron state and polymer-paraffin matrix had studied using XRD technique (Figure.9). The basic states of the catalysts used throughout the experiment were in amorphous state. At reduced temperature, catalysts reviled a crystalline phase. The iron ground state as Fe_3O_4 oxide found to have crystal properties and hydrolyzed $\delta\text{-FeOOH}$ to be in amorphous form. In factor this system iron-paraffin-polymer the iron oxide nanoparticles stabilized in PS polymer and paraffin. In the case, we investigated the nanoparticles iron oxide Fe_3O_4 stability gained from paraffin and polymer which it in charge for selectivity and activity.

In the composites of XRD patterns of the polystyrene (Fig. 9a), there are no peaks to refer to any crystallinity of the sample. This is mean there is only $\delta\text{-FeOOH}$ which might be due to the low contact with the metal-containing with polystyrene in the composite and may be caused by a change of matrix. The amorphous paraffin presence was evident, that iron nanoparticles catalyst- poorly stabilized with polymer and paraffin. Also, the particles size proves this attribution. Another results had gained for a catalyst with styrene butadiene rubber (SBR) and a polystyrene cross-link with divinyl benzene (PS-DVB) (Fig. 9b,9c) respectively that we could observe the iron oxide presence, which may be connected to the high magnetite of (Fe_3O_4) presence^[15]. These peaks will be more intensive in cases of the composite studied includes such magnetite of quantity. For reactions based on SBR, weak peaks at $2\theta = 30^\circ$ and sharp peaks are obviously appeared at $2\theta = 36^\circ$; were observed, those might be connected to the attendance of magnetite (Fe_3O_4) quantity^[16-18]. For sample based on PS-DVB, weak peaks at $2\theta = 36^\circ$ and 42° were observed, which can be related to the attendance of magnetite (Fe_3O_4) too.

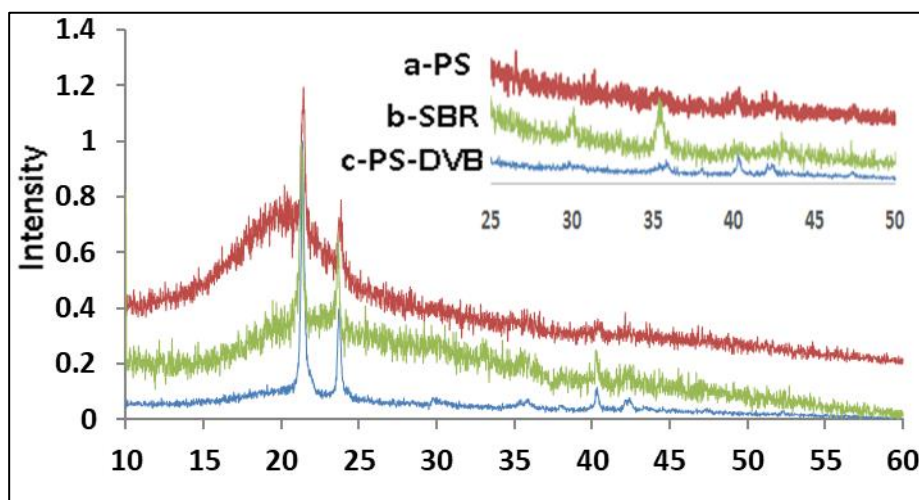


Figure 9. XRD patterns of Nano iron -paraffin-polymer catalysts : a- pristine PS, b- pristine SBR, and c-PS-DVB.

4. Conclusions.

The goal behind this work was to compare and synthesis of new Nano size iron-polymer catalysts for the three-phase Fischer-Tropsch process. Suspensions system (Iron-Paraffin-Polystyrene or Polystyrene derivatives) were applied in Fischer-Tropsch process as a Nano-catalysts; and throughout the present time polymers suggested for the synthesis of Nano-catalysts were used in FTS to be stable at high temperatures. Which reverberate on the steadiness of the Nano-catalyst as long as it not cause the Nano catalyst poisoning. The influence of polystyrene derivatives on the Nano catalyst structure has also proven by XRD and AFM measurements. We explained also the raise in the formation of targeted product and CO conversion. we notice, that Nano catalysts are more valuable in the process of Fischer Tropsch with the cross linked polymers concerned in the composition, compared with the raw polymer .The selectivity of various systems on the production of liquid hydrocarbons also proven.

In another way, revealed the cross linked polymers nature have an important influence on the iron nanoparticles stabilization properties and changes iron nanoparticles size in particularly.

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