



## Influence of Iron Nano Co-polymer Catalysts on the Liquid Hydrocarbons Production in the Synthesis Fischer Tropsch

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### Abstract

In this paper the synthesized composites were used in the Fischer - Tropsch reaction (FT) which compared the catalytic activity of catalysts based on Co-polymer (COP) such Styrene Butadiene Rubber (SBR) and Polyethylene terephthalate (PET) with catalysts. The COPS were supported within polypropylene (PP) in the system nano Fe-Paraffin-polymer. The behavior of Co-polymers gave significant effects in the creation of nano catalysts by stabilizing the nanoparticles, and producing new active sites for synthesized hydrocarbons from CO and H<sub>2</sub> as sources of energy. Catalytic materials shows sensitivity and selectivity in the Fischer-Tropsch process with three phase slurry reactors. The greatest conversion of CO was obtained in 66%, which forming hydrocarbons liquid reach to 60g/m<sup>3</sup> for catalysts copolymer (SBR), whilst using catalyst with PP reduce the conversion of CO to 50% which also forming 38g/m<sup>3</sup> of hydrocarbons. The iron nano particles were characterized by AFM technique and XRD in the polymer-paraffin matrix.

**Keywords:** Fischer-Tropsch (FT), Three phase slurry reactor, Polymers.

### Introduction

Fischer-Tropsch synthesis (FTS) constitutes an area of catalytic hydrogenation chemistry have been the subject of intense research that demonstrated by many researchers in the latest years [1, 7]. Cobalt and Iron were widely used by Fischer and Tropsch which employed as catalysts for the formation of hydrocarbons and fuels [8]. Out of two methods, the slurry reactors and fixed reactors; the former one was used in many chemical processes, in the lab scale and in the industrial sector [9]. The most crucial key step in the development of FTS is how to produce highly active catalyst and highly selectivity as well [10, 11].

Hao and co-workers used FTS in the slurry reactor with iron-based catalyst and studied the pressure effect on the iron based catalyst selectivity and activity. The stabilization effect of the polymers in the formation of Co and Fe nano particles have studied by Claver [12] when reported that stabilizers show a good activities with small size thus used as stabilizer [13] such Iron. In this study the catalyst was prepared through the thermal decomposition of metal solution in a dispersion medium of wax and polymer in an inert gas argon (Ar), in addition, bottom-up

used to be suitable approach to prepare the catalyst [13]. A new nano metal-paraffin/polymer nano catalyst was stable colloidal system. Nanoscale iron oxide-containing particles are distributed in to the dispersion hydrocarbon media of the slurry reactor [13]. Concern climate change due to huge amount of fuels consumption and sustain ability. Clearly, it is a great interest to chemists to be able to find alternative method to produce liquid fuels and chemical products. The aim of our work is preparing nano catalysts Iron- Paraffin (mark-2)-Co-polymer matrix with normal polymer and tests the activities in FT process.

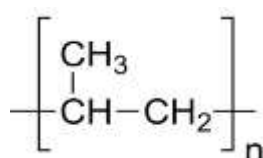
### Experimental

#### Material and Methods

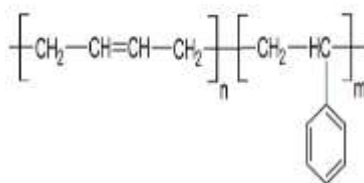
The catalyst (Fe-paraffin-polymer) was synthesized as described by thermal decomposition [14]. Briefly; a flow catalytic reactor with the suspended catalyst in liquid slurry under pressure 2 MPa, and 1 to 2 L/ (g cat h) of syngas load in 1:1 molar ratio of CO: H<sub>2</sub> at range of temperature 220-320 °C. The reaction mixture was slowly warmed (20°C every 12 h). The initial syngas and the gaseous products of the reaction have

analyzed using gas-solid chromatography with Kristallyuks 4000 chromatograph which supplied by the carrier gas (helium) and thermal conductivity detector and with two columns were used. The CO and N<sub>2</sub> has separated using 3 m × 3 mm column packed with CaA molecular sieves in an isothermal mode at 80°C; CO<sub>2</sub> and C<sub>1</sub>-C<sub>4</sub> hydrocarbons were separated on a HayeSep R-packed column (3 m × 3 mm) at controlled temperature 80 to 200°C at 8°C/minutes.

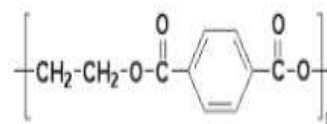
Ultrafine iron catalysts for FTSs were prepared via thermal decomposition at 280°C and stirring under inert gas (Ar) stream in a dispersion medium composed of molten oil paraffin (mark - 2) and a 6wt %, addition the polymers: Polyethylene terephthalate, butadiene-styrene rubbers and polypropylene.



Polypropylene (PP)



Styrene-Butadiene Rubber



Polyethylene Terephthalate

The additive materials were represented by PET, SBR, and PP respectively. The particle size of the synthesized samples was determined by the scattering of dynamic light on a Malvern Zetasizer Nano ZS apparatus. Sample preparation consisted of the dissolution of 0.01 g of the sample in hexane 10 mL, sodium dioctylsulfosuccinate (5 wt %) was added as a surfactant.

The following reagents were used for the preparation of nano-sized catalysts; the first one is paraffin mark -2 (GOST 23683-89)- which is a mixture of high molecular weight hydrocarbons C<sub>18</sub>-C<sub>35</sub>, mainly aliphatic structure. The second reagents was Iron (III) nitrate (Fe (NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) hydrate, "extra pure", purchase from Scharlau Chemie S.A. While the polymer was include three materials as shown below.

## Results and Discussion

### Particle Size Distribution

The dynamic scattering was used to study the products and to assess to follow the variation in the distribution of the particle size of the dispersed phase for the suspensions. The nano catalyst contains the PET, SBR or PP polymers have found that the clear effect of the metal nanoparticles size. The catalyst based on Polypropylene have small metal nanoparticles size distribution from 2 nm to 488 nm with compared to nano catalyst supported by SBR

and PT which has the metal nanoparticles size distribution in the regions of 212 and 312 to 644 nm which that have clear effect in the this range [15] (Table 1). The nanocatalyst based on PET, SBR and PP polymers have bimodal particle size distribution [13]. The PP leads to the formation of smaller particles size at 2 nm, compared with the catalyst supported with PET and SBR polymers. It can be assumed that bimodality is associated with possibility of stabilizing Fe with both paraffin and polymer. It depends on the nature of the polymer. Table. 1.

Table 1: Influence of copolymer on the size of particles

Nano catalyst Fe - Paraffin/polymer	Particles size, nm	
	nm	Content,%
Fe - P/PP	2	8
	488	92
Fe - P/PET	212	6
	541	94
Fe - P/SBR	312	22
	644	78

### FTS Performance

Gas and liquid were analyzed, and the activities of the catalysts were estimated in terms of the parameters below:

- Specific activity: number of moles of CO that reacted for each gram of Fe in second.

- Yield of product: the grams of formed product per cubic meter of normalized syngas passed that through the catalyst.
- Selectivity: the percentage ratio of consumed carbon to the total amount of carbon that introduced into the reaction area, and efficiency (the amount of yield per kilogram of catalyst each hour).
- CO conversion: percentage ratio of the amount of reacted carbon monoxide to the amount of fed CO into the reaction area.

All synthesized catalysts showed high catalytic activities in the preparation of liquid hydrocarbons using CO and H<sub>2</sub> during the process. Whilst, introducing the catalyst based on SBR and PET led to an increased conversion of CO gas in comparison to the catalysis using PP polymer in the system Fe-Paraffin-Polymer [13]. Table 2, shows change in activity (CO conversion) and C<sub>5+</sub> selectivity

at 300°C for PP and PET, 320°C for SBR. Catalytic activity increased gradually with increased temperature, but CO conversion at 66% was kept for 72 hours with C<sub>5+</sub> selectivity at 54% (Table.2). The greatest conversion of CO gas with the system Fe-paraffin-SBR (6 grams and 6% weight of iron of polymer) (Fig 1), and the formation of liquid hydrocarbons (Fig 2), also using Fe-paraffin-PET conversion of CO gas was obtained in 56% and the formation of liquid hydrocarbons is 54 gm<sup>-3</sup> (Table.2), we observed rise in CO conversion in the systems based on the SBR and PET because of the existence of copolymer in the system catalyst which has the ability to interact with the metal (iron) and thus believe that these polymers are working to reduce the agglomerate of nanoparticles comparison with catalyst based on PP which gave CO conversion 50% and liquid hydrocarbons is 38gm<sup>-3</sup> (Table.2).

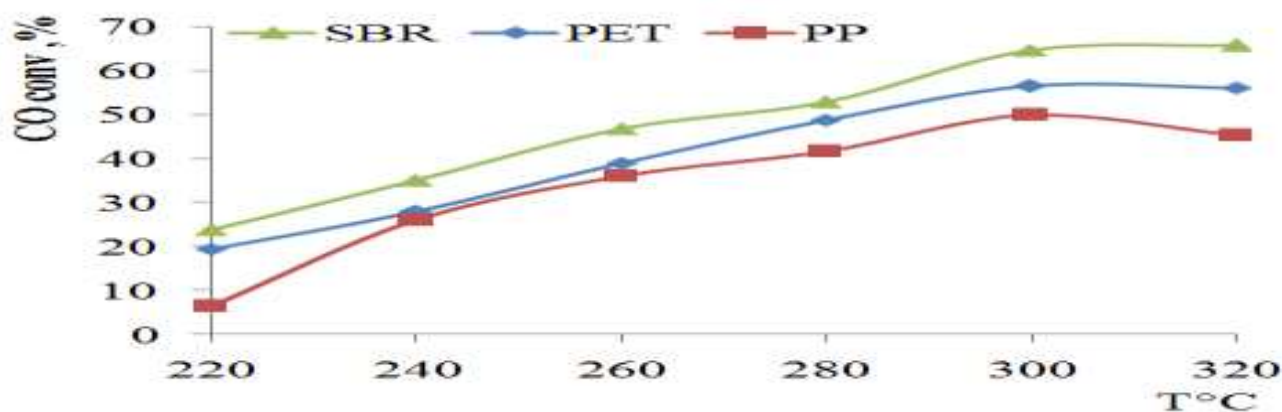


Fig.1: Temperature versus CO conversion

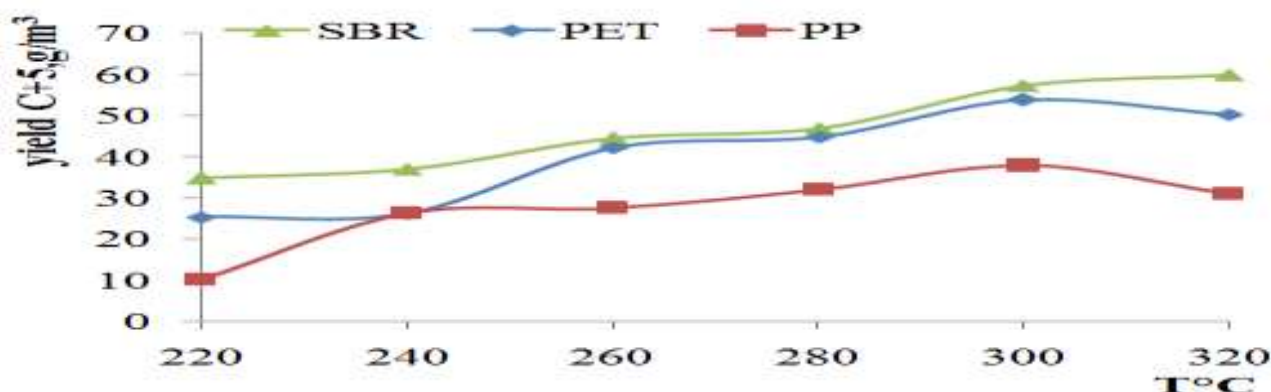


Fig.2. Yield of C<sub>5+</sub> liquid hydrocarbons versus temperature

Table 2 shows that the samples with copolymers have high yield of liquid hydrocarbons comparing to nano catalysts that based on normal polymer. However, it is significant to mention that the side-product yield which formed in the existence of iron nano catalysts gaseous hydrocarbons (C<sub>1</sub>, C<sub>2</sub>-C<sub>4</sub> and CO<sub>2</sub>) depends on the type of the

polymer used (table 2). The Fe-paraffin-polymer nano catalysts based on normal polymer (PP) showed a low yield gaseous hydrocarbons (C<sub>1</sub>, C<sub>2</sub>-C<sub>4</sub> and CO<sub>2</sub>), CH<sub>4</sub> from 37 to 17 gm<sup>-3</sup>, CO<sub>2</sub> and C<sub>2</sub>-C<sub>4</sub> gases from 190 to 140 g m<sup>-3</sup> and 31 to 23 g m<sup>-3</sup> respectively (Table 2, Fig. 3, 4).

Table 2: Influence of copolymer of the products (T=220 to 320°C, P=20 atm, CO: H2 = 1)

Sample	CO%Conv.	Yield of Hydrocarbon ,g m <sup>-3</sup>				selectivity%
		C <sub>1</sub>	C <sub>2</sub> -C <sub>4</sub>	C <sub>5+</sub>	CO <sub>2</sub>	
Fe- paraffin-PP	50	17	23	38	140	56
Fe- paraffin-PET	56	31	27	54	168	49
Fe- paraffin-SBR	66	37	31	60	190	54

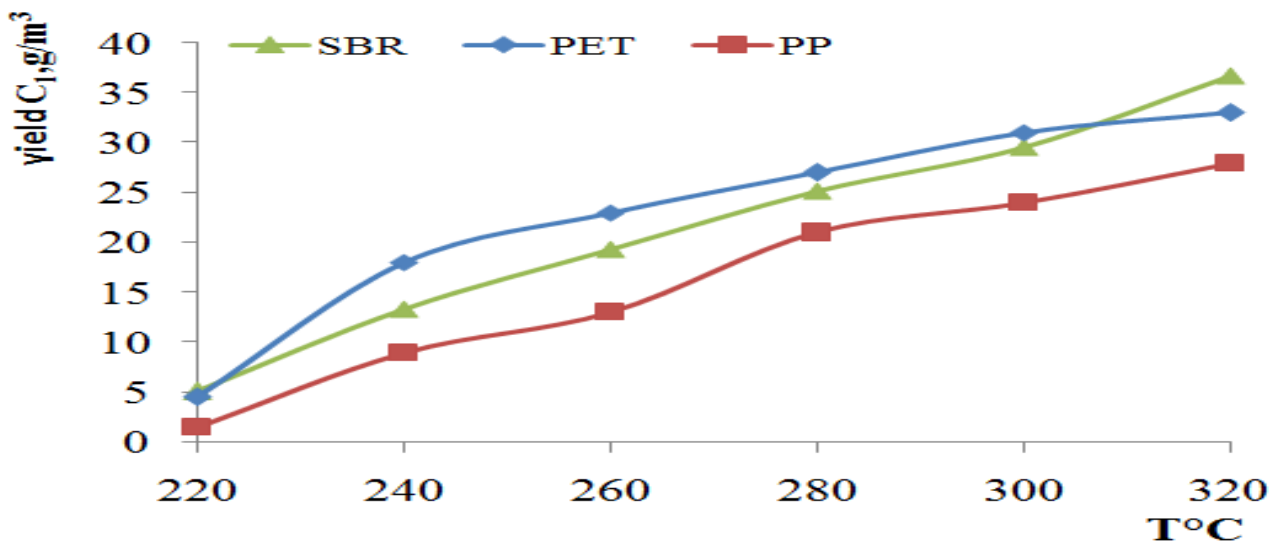


Fig.3: CH4 gas yield versus temperature

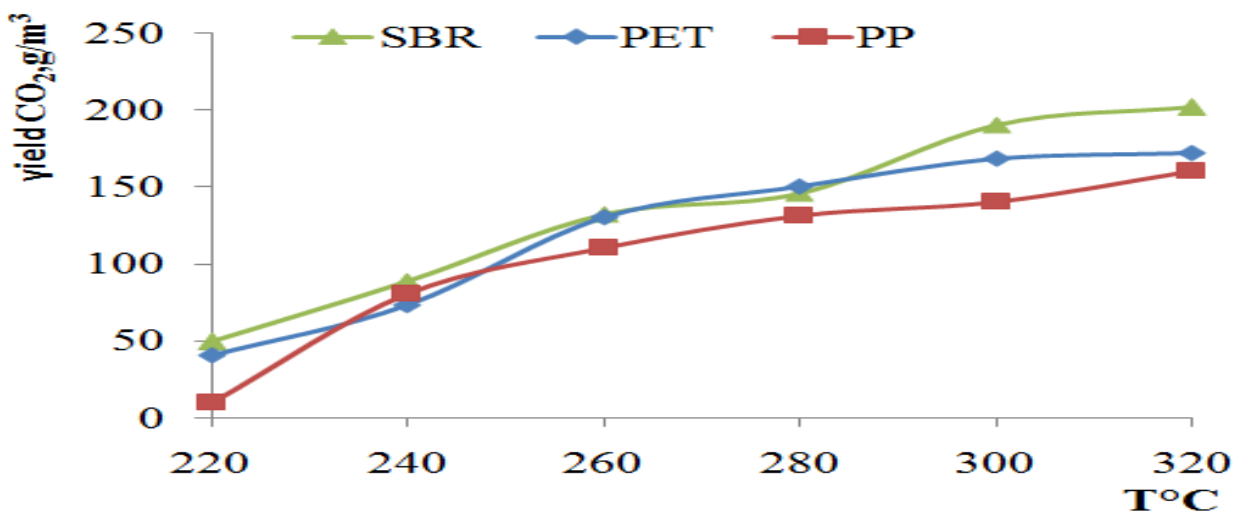


Fig.4: CO2 gas yield of hydrocarbons versus temperature

The selectivity of liquid hydrocarbons C<sub>5+</sub> for nanocatalysts based on PP,SBR and PET were close to each other , 56%,54% and 49% respectively.

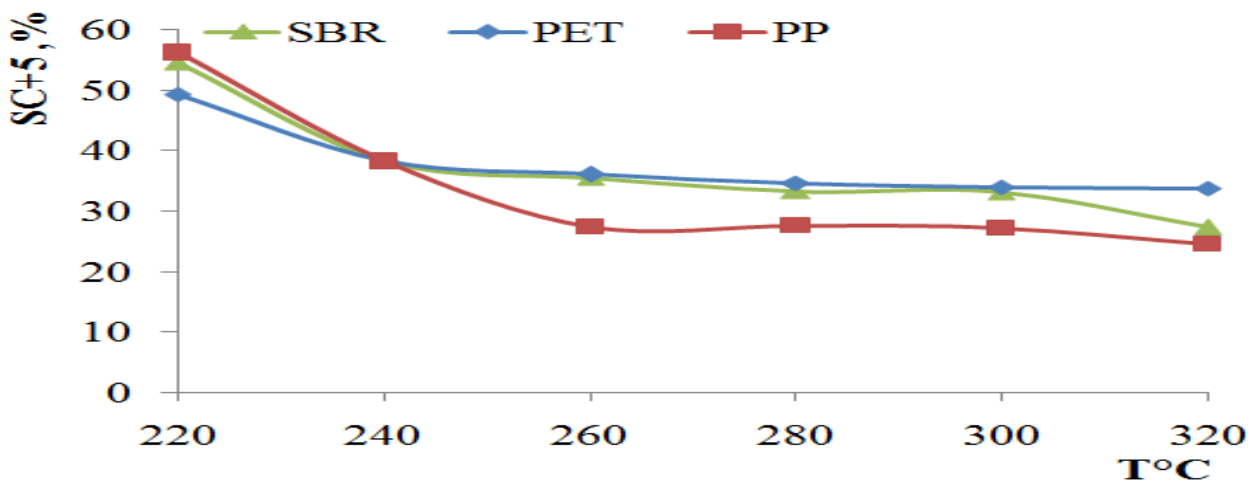


Fig. 5: The selectivity C5+ versus temperature

The Fe-paraffin suspensions consist of different polymers exhibited various activities and selectivity for the product [16]. It is assumed that the effect of promotion is directly attributed to the properties and the structure of the polymer component [13]. In Table 3 we have shown that the analysis of liquid hydrocarbons that obtained at the temperature 220-320°C. Catalyst with copolymers had an effect on the fractional composition (gasoline C<sub>5</sub>-C<sub>10</sub>, kerosene C<sub>11</sub>-C<sub>18</sub> and wax C<sub>19+</sub>), and the group composition of liquid production (n-paraffin, isoparaffin and

olefin) too. Nano catalyst suspension based on copolymers (SBR and PET) leads to a decrease in the fraction of unsaturated compounds (olefin) to 7% compared with Nano catalyst based on normal polymer (PP) which was 24%. The fraction of paraffin also changes, in particular, the use of the SBR copolymer leads to a twofold increase in the yield of paraffin (from 51 to 75%) and the amount of the heavy fraction C<sub>19+</sub> was increased from 21 to 57%, whilst use the PP polymer leads to a twofold increase in the yield of gasoline C<sub>5</sub>-C<sub>10</sub> (from 6 to 23%).

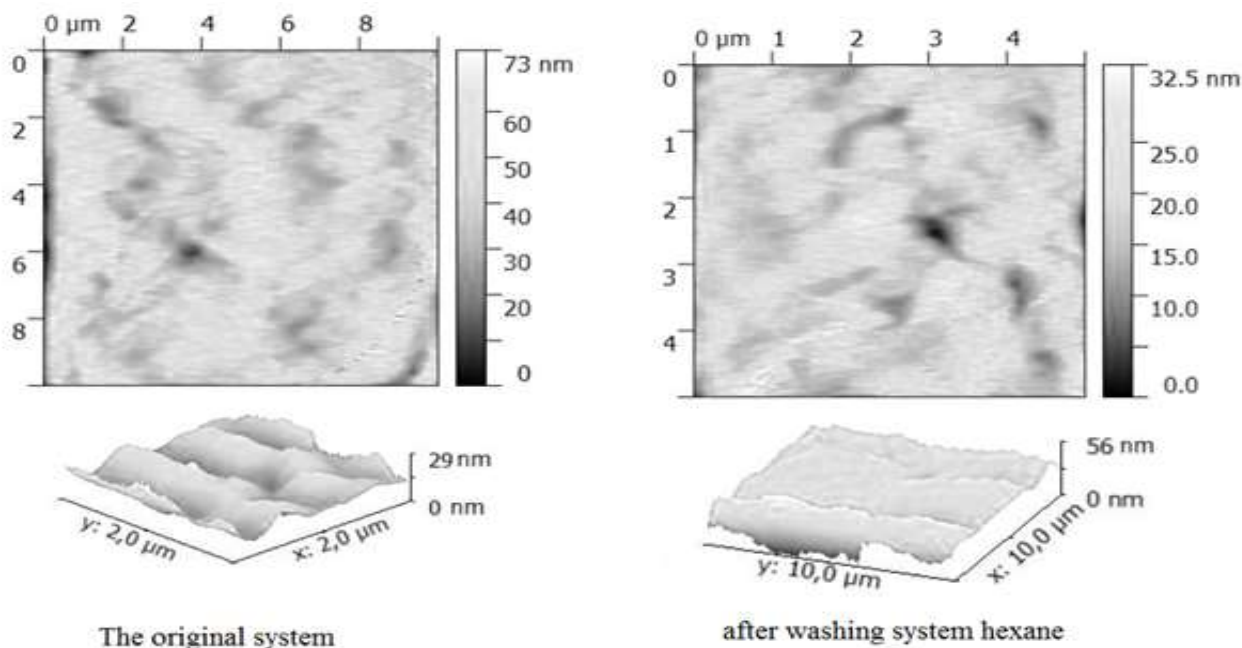
**Table 3: Fractional and group composition of liquid products of FTS on system Fe- paraffin - polymer (PET, SBR and PP)**

Sample	Group composition, %			Fractional composition, %		
	n-paraffins	isoparaffins	olefins	C <sub>5</sub> -C <sub>10</sub>	C <sub>11</sub> -C <sub>18</sub>	C <sub>19+</sub>
Fe- paraffin-PP	51.0	25.0	24.0	23.0	56.0	21.0
Fe- paraffin-PET	60.0	21.0	18.0	13.0	56.0	31.0
Fe- paraffin-SBR	75.0	18.0	7.0	6.0	37.0	57.0

### Atomic Force Microscope (AFM)

In this work the morphology of surfaces for the formed substances was used to analyze the nature of surfaces. The sample was dissolved in hexane, for remove the wax layer, which confirmed when the wavy wax disappeared and formed visible lamellae of crystalline polymer. The catalytic activity can be related to the stability of iron nanoparticles in the paraffin and polymer matrix. In the case of catalyst based on PP (Figure 6) which appears reduced in results from CO converted and formation liquid hydrocarbons. the stability of small nanoparticles in the polypropylene matrix with leaving large nanoparticles with

paraffin by hexane, which resulted in a clear change in the catalytic surface as well as we can observed smooth surface before treatment with hexane. The case of catalyst with PET, and SBR as shown in Fig. 7 and Fig 8, respectively, the bit ratios of nanoparticles were migrated with paraffin after washing and stability of large iron nanoparticles in the polymer matrix. It is also possible to observe the irregularity on the heterogeneous surface which gives the catalytic effect due to the ease of the nano-iron stability on it. The distribution of nanoparticles between the polymer and paraffin with changed the particle size and stabilities in matrix are responsible for the effectiveness of the catalyst.



**Fig.6: Analysis of current state of Fe-containing solid catalyst Fe-paraffin-PP**

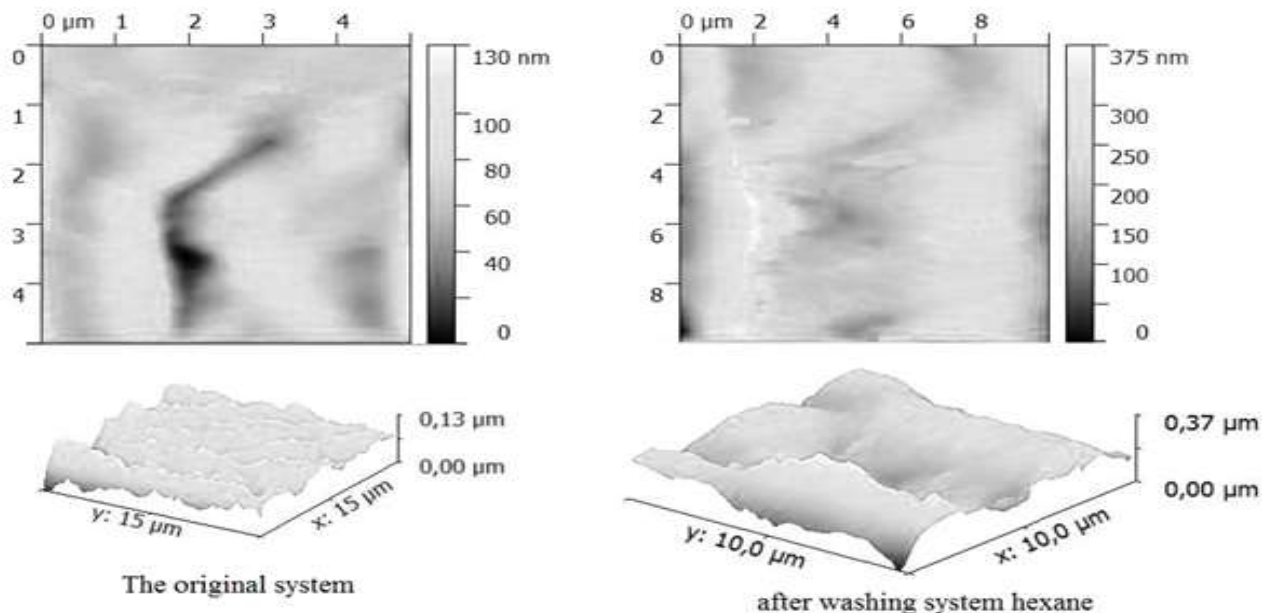


Fig.7: Analysis of current state of Fe-containing solid catalyst Fe-paraffin-PET

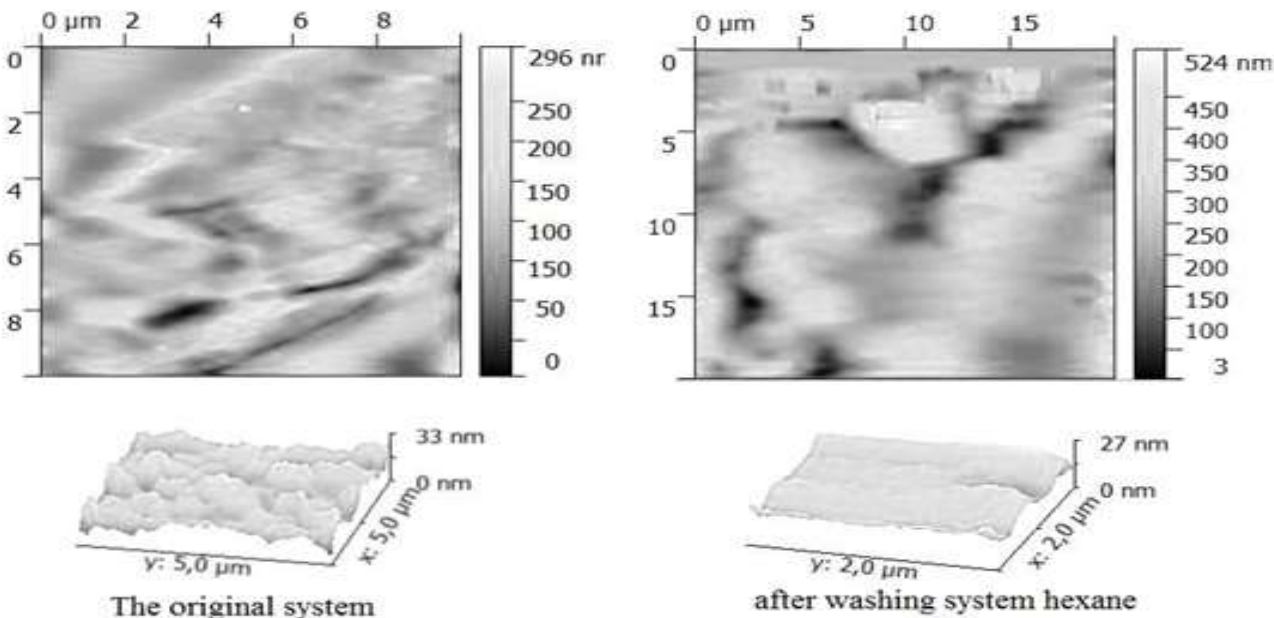


Fig.8: Analysis of current state of Iron-containing solid catalyst Fe-paraffin-SBR

### XRD Technique

The states of iron and polymer-paraffin matrix were studied by XRD spectroscopy (Figure 8). The initial form of iron is oxide, mainly  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ . During activation, it is restored. Active particles in the catalytic cycle may be intermediates with chemical bonds of iron-carbon or iron-hydrogen. The ground state of iron in  $\text{Fe}_3\text{O}_4$  and in amorphous  $\delta\text{-FeOOH}$ . In fact, in iron-paraffin-polymer system the iron oxide nanoparticles were fixed with paraffin and polymer. The stability of nanoparticles iron oxide  $\text{Fe}_3\text{O}_4$  in paraffin and polymer which responsible for activity and selectivity of Nano catalyst in the matrix (Fe-paraffin-polymer). The XRD patterns in Fig.8a of the Polypropylene (PP) composites observed

weak beaks can attributed to amorphous phase of iron oxides which refer to  $\delta\text{-FeOOH}$ . The last properties may refer to lack of contact of the metal with PP in the composite. Other results were obtained for the catalyst with a copolymers styrene butadiene rubber SBR which plotted in Fig. 8b and Polyethylene terephthalate PET in Fig. 8c. The last two figures shows that presence of iron oxide, may refer to magnetite ( $\text{Fe}_3\text{O}_4$ ) [17, 18] which more intensive. The sample which supported by SBR have weak peak at  $2\theta = 30^\circ$ , also have sharp peak at  $2\theta = 42^\circ$  which can be related to the presence of magnetite ( $\text{Fe}_3\text{O}_4$ ) [19, 20]. On other hand for sample based on PET we can observe peaks at  $2\theta = 30^\circ$ ,  $36^\circ$  and  $42^\circ$ , can related to the presence of magnetite ( $\text{Fe}_3\text{O}_4$ ) too.

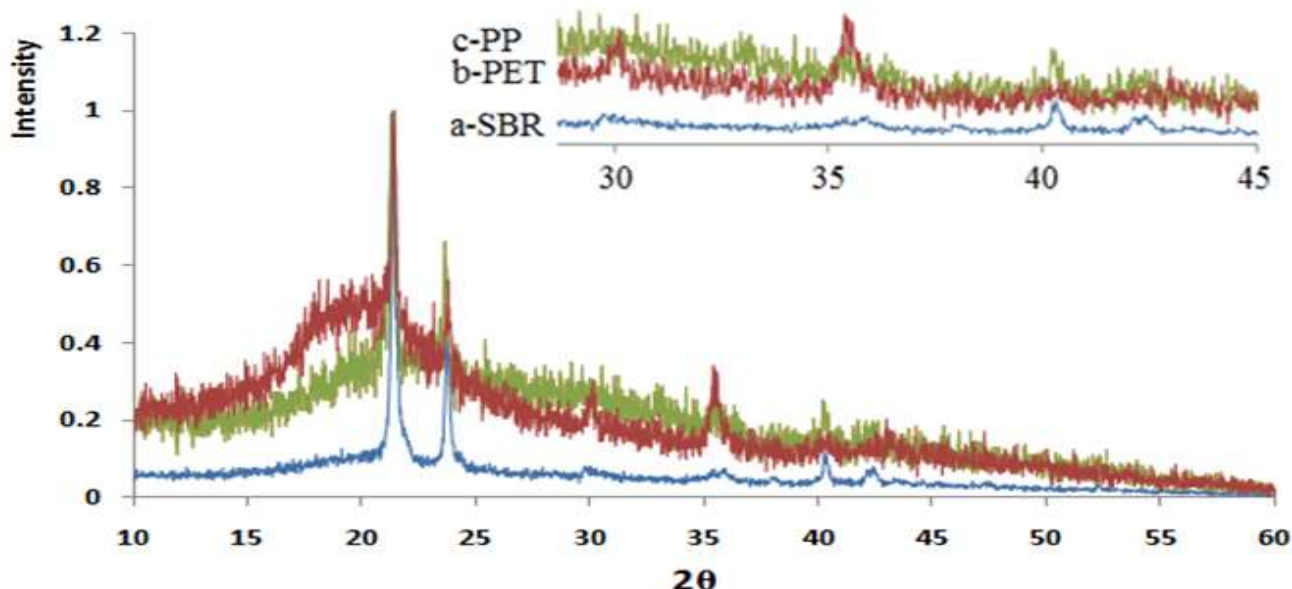


Fig.8: XRD patterns: a- SBR, b- PET and c-PP

## Conclusion

Clear effect by copolymer on the nano catalyst structure which supported by XRD and AFM to an increase in the conversion CO and formations of target product .The Nano catalyst was more effective in FTS with the copolymer involved in the component as compared to the linear polymer, and in contrast, the selectivity of liquid hydrocarbons was reduced. The nature of the Co-polymers has a significant effect on the stabilization of iron nanoparticles and changes size. The stability of nano iron

particles is measured in paraffin and polymer, as well as the active catalyst is one which shows a change on surface when dealing with hexane

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