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Enhancement of Fischer-Tropsch Process using Four Different Types of Polymers Over Nano Iron-Paraffin/Polymer System

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Abstract: Four Fe-paraffin/polymers catalysts were prepared by thermal decomposition method, i.e., Fe-paraffin/PEG, Fe-paraffin/SBR, Fe-paraffin/PP and Fe-paraffin/PC and their Fischer-Tropsch Synthesis (FTS) activity and selectivity. The behavior of them were investigated and compared using a slurry reactor. We observed that the catalyst based on Propylene (PP) had the lowest initial activity but have more selectivity compared with other catalysts. The catalyst based on Polyethylene Glycol (PEG) and Styrene-Butadiene Rubber (SBR) showed enhancement of production of light olefins compared with the catalyst based on Propylene (PP) and Polycarbonate (PC). The obtained nanocomposites catalysts based on Fe-paraffin/Polymers (Fe-p/P) system have been characterized with AFM, XRD and have proven to be a dispersed form of Fe_3O_4 oxide nanoparticles. Methane, light olefins and CO_2 productivity and selectivity increased with time and temperature for all catalysts. The system Fe-paraffin/Polyethylene Glycol (Fe-p/PEG) have a great impact on CO conversion that reached up to 74% and a high yield of total hydrocarbons of 62 g/m^3.

Key words: Fischer-tropsch synthesis, Fe-paraffin/polymers catalyst, slurry reactor, SBR, polycarbonate, polyethylene glycol

INTRODUCTION

The high energy demand, oil prices and environmental pollution have received remarkable attention resulted to develop alternative technologies for the conversion of light hydrocarbons Gas To Liquid (GTL) for the manufacture of transportation fuels (Rahimpour *et al*., 2012; Rafiee and Hillestad, 2012; Glasser *et al*., 2012). In such GTL process, Fischer-Tropsch Synthesis (FTS) plays an essential role for reforming synthesis gas (CO and H_2 mixture in gas form) for the production of clean fuels, essential chemicals and other industrial hydrocarbons raw materials. The requirements for developing an effective catalyst have arisen, since, multistage reactor system is the most competitive challenge in FTS. Catalysts based on iron and cobalt are used for FTS mostly. The iron one have selectivity and activity for the FTS process and for the reaction of Water-Gas-Shift (WGS) as well. This can be considered an ideal for converting carbon monoxide-lean (low H_2/CO ratio) which normally derived from coal (Bae *et al*., 2009; Pour *et al*., 2010). Previous research shows a slurry of polymer-metal based catalysts have a great impact on stability, activity and selectivity of the catalysts compared to metal component alone (Kulikova *et al*., 2015a, b). Whereas catalyst composition exerts the greatest influence on the nanoparticles size distribution. Also, it is accepted that because of kinetic and thermodynamic limitations of such sort of reactions, bi-component catalysts system shall be more capable to boost up the value of the low carbon olefins and liquid hydrocarbons (Cooper and Frost, 1990; Mirzaei *et al*., 2010; Kulikova *et al*., 2015a, b). Many studies have indicated an improvement in selectivity and/or activity by using a metal dispersion in the polymer matrix to form a FTS catalysts (Kulikova *et al*., 2015a, b). Bondarenko *et al*. (2016) had proven that the addition of specific polymers would lead to increase the catalyst activity for both CO conversion and hydrocarbon productivity up to some level of degrees.

In this study, Four Fe-paraffin/Polymers (Fe-p/P) catalysts were prepared by thermal decomposition preparation technique to investigate activity and selectivity behavior during the FTS in the three-phase slurry reactor.

MATERIALS AND METHODS

Catalyst preparation: The catalyst based on iron was prepared by thermal decomposition method as follows, an

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aqueous solutions $Fe(NO_3)_3$. The $9H_2O$ (43.23 g) was dissolved in distilled water (20 mL), this was added drop wise to the paraffin (100 mL)/polymer (10 g) matrix under Ar and stirring at 280°C, for 4 h. This was following by downloaded the aged suspension nanoiron catalyst into slurry reactor. The FTS process was done with the catalyst suspended under the following conditions; pressure of 2 (MPa) and a syngas dose increment of 1.00-2.00 L/(g cat. h) (syngas with a molar ratio 1:1 of $CO:H_2$) the reaction mixture was warm slowly from 220-°C (20°C interval each 12 h).

Catalyst characterization

Particle size: Nanoparticles size determined by the means of scattering of dynamic light on a Malvern Zetasizer Nano ZS instrument. Sample preparation consisted of the dissolution of the sample 0.01 g in hexane 10 mL with the sodium dioctyl sulfosuccinate 5 wt.% was added as a surfactant.

Microscopy: The samples were analyzed using Atomic-Force (AFM) microscopy, an AFM type spectrometer with a PX Ultra multi-frequency controller and a Hybrid™ method controller. The probes used had the characteristics; CSG10. Freq. = 8.5 kHz, k = 0.07 N/m NSG01. Freq =187.2 kHz, k = 3.9 N/m. All measurements were performed using the Hybrid technique using the DMT Model to determine the nanoparticles in the inner side of the samples, the surface layer of paraffin was removed by hexane.

XRD analysis: The studies were carried out on a Shimadzu XRD-7000 apparatus using Cu Ka radiation. The voltage was 40 kV, the current strength was 30 mA and the scan rate was 2 sec. The purpose of this analysis was to obtain information on the phase composition of iron and paraffin compounds in the samples. By the intensity of the peaks and their position, using the image to the base of ethelon X-rays, a qualitative analysis was carried out.

RESULTS AND DISCUSSION

FTS reaction: The FTS was conducted with suspended catalyst at a range temperature of 220-320°C. The best yield of hydrocarbons was indicated at 300-320°C for all catalysts as well as a high formation of methane, light gases and CO_2 were also formed (Fig. 1-3). The selectivity towards unwanted products, like CO_2 and methane, dropped down quickly to CO_2 15% and methane 10% while those towards C5+ noticed a big change to more than 50 and 60%, respectively (Fig. 4). Of course this is a prove

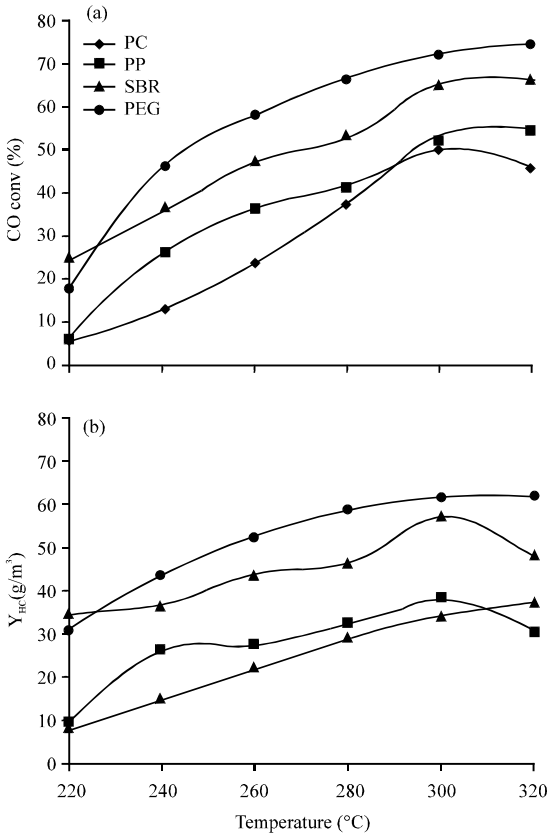

Fig. 1: CO conversion and formation of hydrocarbon liquid over nanoiron catalysts: a) CO-conversion and b) Yield of liquid hydrocarbons (C5+)

that the addition of polymer to the Fe-nanoparticales plays an essential rules to drive the reaction towards the desired products.

Characterization of the nanocomposites: The nanoparticles were prepared in paraffin/polymer as a matrix via. method described earlier by Kulikova *et al.* (2015a, b). Also the preparation of iron oxide nanoparticle by dissolving of iron (III) nitrate ($Fe(NO_3)_3.9H_2O$) in a molten paraffin/polymer matrix where polymer such as; Polyethylene Glycol (PEG), Styrene-Butadiene Rubber (SBR), Polypropylene (PP) and Polycarbonate (PC). The particles size distribution of the synthesized suspensions of catalysts before and after FTS are shown in Table 1.

All catalysts showed deformation and aggregation of nanoparticles. Deformation and aggregation depend on polymer type. The most effective catalysts have the least deformation and particle aggregation value and this is a clear indication of the stability of iron oxide (Fe_3O_4) on the surface of the paraffin/polymer matrix compared to the less effective catalysts that gave greater distortion and aggregation of the particles.

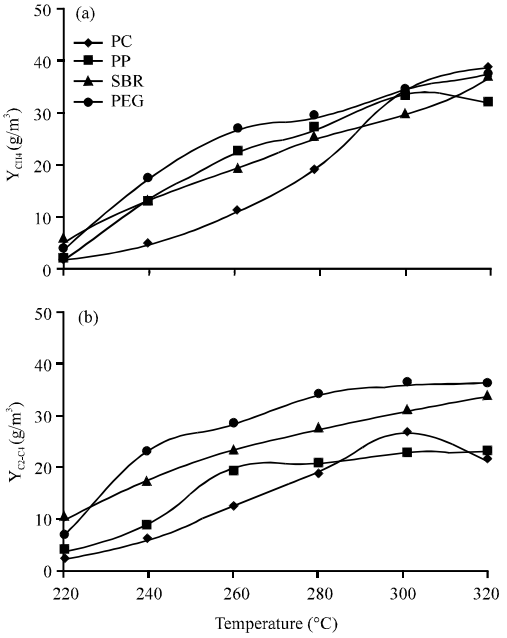

Fig. 2: Hydrocarbons gases formation over nanoiron catalysts: a) CH4-formation and b) C2-C4-formation

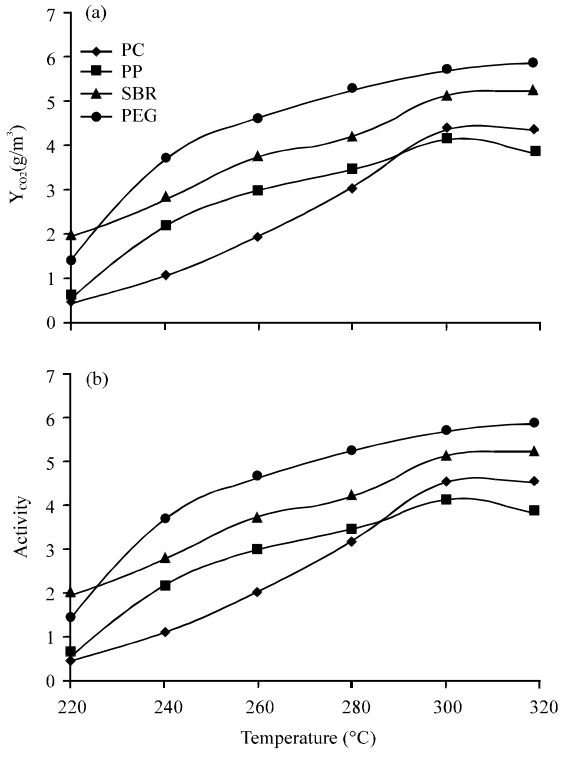

Fig. 3: CO2 formation and catalytic activity of nanoiron catalysts: a) CO2-formation and b) Catalytic activity

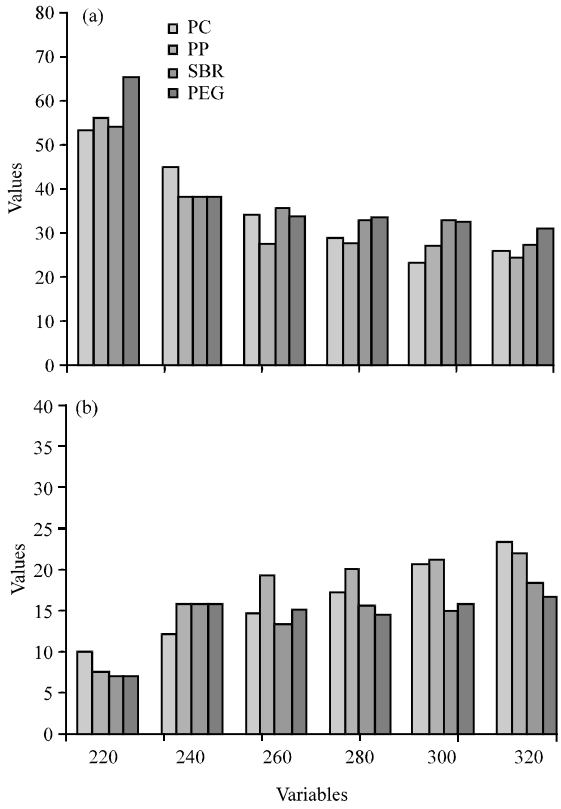

Fig. 4: C5+ and methane selectivity over nanoiron catalysts: a) C5+ selectivity and b) CH4 selectivity

Table 1: Particle size effect on FTS process of the working of catalytic

	Changes in particles size (nm) of iron nano-catalyst system before and after FTS			
	Before process		After process	
Nano-catalyst (Fe-p/P)	nm	Content (%)	nm	Content (%)
Fe-p/PEG	181.0	9.0	220.0	2.0
	655.0	91.0	842.0	98.0
Fe-p/PP	2.0	8.0	289.0	14.0
	488.0	92.0	953.0	86.0
Fe-p/SBR	312.0	6.0	1008.0	93.0
	644.0	94.0	2043.0	7.0
Fe-p/PC	85.0	6.0	899.0	93.0

The surface morphology

X-ray diffraction: Figure 5 represents the analysis of the XR-diffraction of all samples showed that have peaks indicating two phase of iron oxide Fe_3O_4 and δ-FeOOH. The catalyst based on polycarbonate and propylene were showed very weak peaks and the presence of a amorphous refer to δ-FeOOH compared as catalyst based on polyethylene glycol and styrene butadiene rubber where it was clear that there are peaks due to iron oxide Fe_3O_4 and varying degrees between the catalytic. In the case of polyethylene more powerful and clear at 2θ: 30,

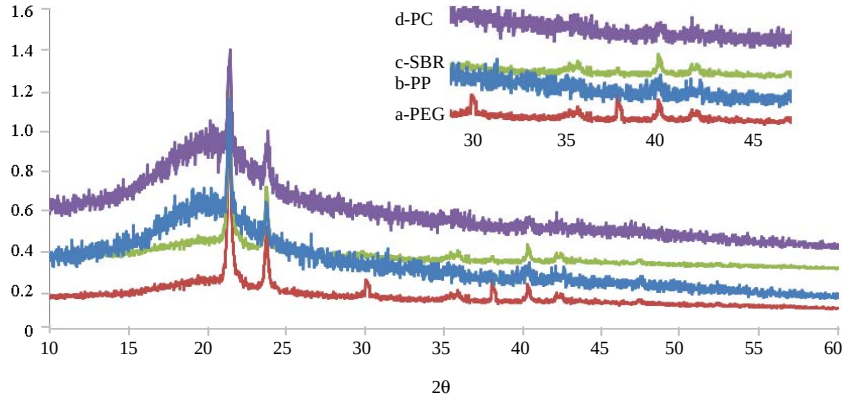

Fig. 5: XRD patterns of Fe-p/P catalysts based on: a) PEG; b) PP; c) SBR and d) PC

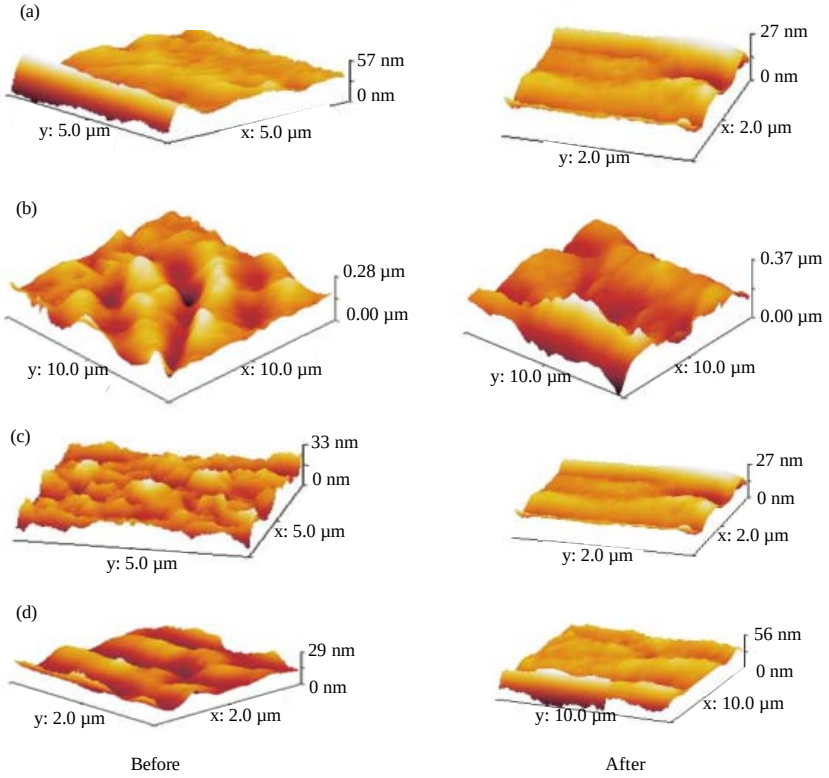

Fig. 6: AFM analysis of surface morphology of used system Fe-p/P catalysts before and after washed with hexane: a) PC; b) PEG; c) SBR and d) PP

38 and 42° which may refer to magnetite (Fe_3O_4) (Park *et al*., 2008; Zhang *et al*., 2007), this fact a strengthens peaks of catalysts are very effective compared as catalyst based on polycarbonate and propylene in the process of Fischer-Tropsch.

Atomic force microscopy analysis: The AFM analysis (Fig. 6) allows to evaluate the morphology and distribution of the nano iron, showing the existence of a close dependence between the distribution of the nanoiron and the polymer type during the synthesis of the catalyst.

The morphology of the surface of Fe-p/PEG looks more regular features with nearly sharp tips up wording outer of the surface of the particles and an approximate distances from surrounding tips and Fe-p/SBR catalysts clearly showing more regular and the distance between them about 2.66±0.44 µm with depth of 0.28 µm or in

another words 17 tips/100 μm^2 of area. And similar things appeared of the catalyst Fe-p/SBR with less regularity but more roughness. Whereas the other two catalysts the Fe-p/PC shows rounded tip groves with averaged distance between the of 2.125±0.375 μm and the Fe-p/PP shows similar surface feature with parallel groves of 1.8 μm between each other. Also Fig. 5 reveled that catalyst Fe-p/PEG and Fe-p/SBR both have more than one phase of crystallinity which improve the regularity of the surface of the catalyst particles. So, for the catalyst Fe-p/PEG, we believe with such pattern have great impact on C_{5+} selectivity at 220°C compared with other catalysts as shown in Fig. 6a.

CONCLUSION

Four Fe-p/P catalysts were prepared by thermal decomposition preparation technique. The catalyst Fe-p/PEG was the best for C_{5+} among the others at 220°C and the Fe-p/PC, Fe-p/PP, Fe-p/SBR investigated from activity and selectivity behavior during FTS in a slurry reactor. The following results can be concluded.

As comparison between the four Fe-paraffin/polymer catalysts; the CO conversions and liquid hydrocarbons formation of catalysts based on normal polymer (PP and PC) were the lowest and the CO_2 formation reduced to much better than the other two PEG and SBR polymer based catalysts.

All catalysts showed deformation and aggregation of nanoparticles after FTS reaction. Fe-p/PP and Fe-p/PC catalysts suppressed the methane and CO_2 formation better than the two other catalysts (Fe-p/PEG and Fe-p/SBR).

The Fe-p/PP and Fe-p/PC catalysts suppressed the methane formation far better than the two other catalysts. All catalysts led to reduced selectivity of liquid hydrocarbons at high temperature, at same time enhance selectivity CH_4 when the temperature rises from 220°C up to 320°C.

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