

A method for the Regeneration of used Fe-ZSM5 Catalyst in Fischer-Tropsch Synthesis

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Fischer–Tropsch synthesis (FTS) is a process for converting syngas from natural gas or coal to higher hydrocarbons. Due to the high FTS and water–gas–shift (WGS) activity, iron-zeolite catalyst is the preferred catalyst for FTS using low H₂/CO ratio syngas from coal gasification or CO₂ reforming of natural gas. Iron catalyst was prepared by co-precipitation method. Sufficient reagent grade ferric chloride and cupric nitrate caused to produce precipitate. The dried HZSM5 zeolite was mixed by iron catalyst. Iron - zeolite catalysts was agglomerated with silica solution. The catalyst was dried and calcinated in air. The catalyst characterized by AAS,XRD,SEM,TPR and BET. Catalytic reaction runs were conducted in a fixed-bed stainless steel reactor. The ability of regeneration of catalysts could increase economical benefit. In this paper, two types of used Iron-ZSM-5 catalyst regenerated by mixture of O₂/N₂ or air. Feed conversion and products selectivity after regeneration were investigated in different times, and the results are compared with fresh catalyst. In this method, used catalyst regenerate by air or O₂/N₂ mixture at 300-500 °C for 8 hours in atmospheric pressure. The catalyst reduced in to H₂/N₂ mixture then activated at 270 °C and 1 atm for 24 h. Finally, the regenerated catalyst tested in optimum reaction condition and experimental results collect by a Gas Chromatography.

1. Introduction

The Fischer-Tropsch Synthesis (FTS) has been recognized as a heterogeneous surface catalyzed polymerization process. During this process CH_x monomers, formed via hydrogenation of adsorbed CO on transition metals, produce hydrocarbons and oxygenates with a broad range of chain lengths and functional groups (Berton, 2009). FTS is an important step in the manufacture of hydrocarbon fuels from coal or syngas.



Although several metals are active for the FTS, only iron and cobalt catalysts appear economically feasible on an industrial scale. The use of iron-based catalysts is suitable not only due to their low cost and ready availability, but also due to their high water-gas shift activity which makes it possible to use these catalysts with low H₂/CO ratios. Iron catalysts are more versatile than cobalt catalysts, produce less methane and can be

geared for the production of alkanes, oxygenates and branched hydrocarbons, depending on promoters and the process conditions employed (Anderson et al,1984, Van der Laan, 1999). Due to the high FTS and water-gas-shift (WGS) activity, iron-zeolite catalyst is the preferred catalyst for FTS using low H₂/CO ratio syngas from coal gasification or CO₂ reforming of natural gas. Because the reserves of coal and natural gas are richer than that of crude oil, FT synthesis can supply plentiful liquid fuels for the world in longer times than petroleum refining. Fischer-Tropsch catalysts as composed mainly of iron oxide, are not usually regenerated when spent but are dumped. However, environmental and economic pressures are now requiring their regeneration (Andre Steynberg and Dry, 2007, Van der Laan, 1999). This paper will focus on regeneration of used Iron-ZSM-5 catalyst in Fischer-Tropsch synthesis by mixture of O₂/N₂ or air. Feed conversion and products selectivity after regeneration were investigated in different times in Fischer-Tropsch synthesis.

2. Experimental

2.1 Catalyst preparation

Iron catalyst was prepared by coprecipitated method. The Catalyst precursor batches were prepared in a continuous stirred precipitation reactor with built-in stirrer blades. The reactor was held at 80 °C in a constant- temperature bath. Sufficient reagent grade ferric chloride and cupric nitrate to produce precipitate. These two feed solutions were held at 75 to 80 °C before being charged to the precipitation. The salt solution and sodium carbonate solution were pumped to the reactor at equal rate to maintain an outlet pH of 7.0. The mixture was stirred vigorously for several minutes. When the precipitation was complete, the precipitate was washed with distilled water in a filter press to remove Na⁺ ions. The washed precipitate was reslurred with silicasol solution and impregnated with potassium nitrate. The HZSM5 zeolite (BET surface area, pore volume and Average pore diameter are: 313 m²/g, 0.16 cm³/g and 20.3 Å respectively) dried then zeolite and iron catalyst were each sieved to minus-100 mesh and thoroughly mixed. Iron - zeolite catalysts was agglomerated with silica- alumina solution. The resulting paste-like gel is dried on a perforated aluminum plate under reduced pressure to form to 4mm diameter and 3mm high cylinders using a pelleting press. The catalyst cylinders were dried and calcinated in air (Nakhaeipour, et al., 2008).

2.2 Catalyst characterization

BET surface areas were determined by nitrogen physisorption (Micrometrics ASAP 2010). Acidity measurement was conducted by ammonium adsorption/desorption in a quartz reactor with temperature increase of 10 °C/min from 100 to 500 °C, using frontal chromatography technique. Table 1 shows Surface area and acidity of iron-ZSM5 catalyst. XRD spectra of fresh and used catalysts were conducted with a Philips PW1840 X-ray diffractometer with monochromatized Cu (K α) radiation for determining of iron carbides phases. Temperature programmed reduction (TPR) profiles of the calcined catalysts were recorded using a Micromeritics TPD-TPR 290 system. The TPR

of 50 mg of each sample was performed using 5 % hydrogen in argon gas mixture. The samples were heated from 50 to 900 °C with a heating rate of 10°C/min.

Table.1: Surface area and acidity of iron-ZSM5 catalyst

Catalyst	Surface area (m ² /g)	Acidity (mmol NH ₃ /gcatalyst)
Fe-ZSM5(Fresh)	295	1.05
Fe-ZSM5(Used)	220	0.89

Figure.1 shows the XRD pattern of the iron-ZSM5 catalyst shows peaks from 10 to 80 correspond to magnetite (Fe₃O₄), hematite (Fe₂O₃) and ZSM5. The star sign shows ZSM5 and the other sign shows Fe₃O₄ and Fe₂O₃.

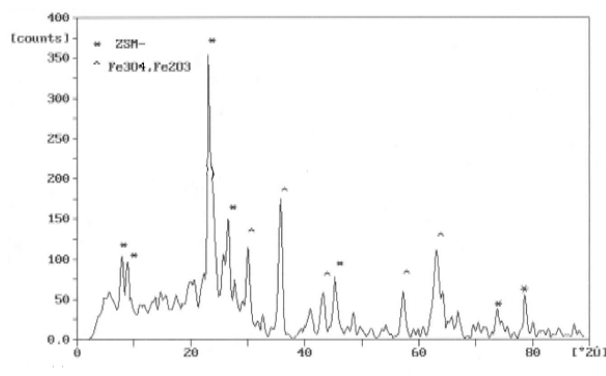


Figure.1: XRD spectrum of iron-ZSM5 catalyst (Fresh)

Figure 2 shows the H₂-TPR profiles of the Iron-ZSM5 catalyst. The reduction process in H₂ occurs in two stages in the temperature range between 200-850 °C. The first stage includes two small peaks corresponding to the transformations of the solid solution CuO to Cu and part of α -Fe₂O₃ to Fe₃O₄. CuO promoter facilitates the reduction of α -Fe₂O₃ when the two phases are well mixed; resulting in the reduction of α -Fe₂O₃ appears at much lower temperature. The second stage represents the transformation of Fe₃O₄ to α -Fe.

The catalyst was characterized by atomic absorption technique. The catalyst composition was designated in term of atomic ratio as 100Fe/3Cu/20SiO₂.

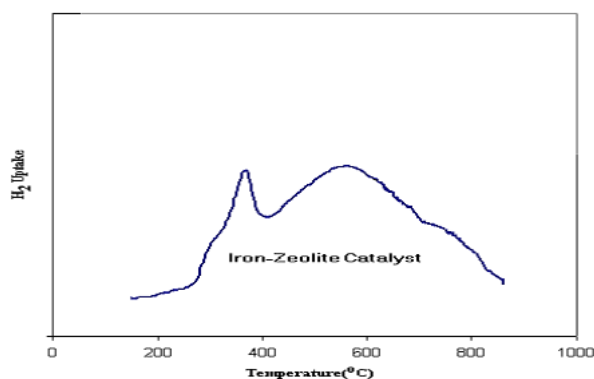


Figure 2: H_2 -TPR profiles of the Iron-ZSM5 catalyst

2.3 Cata-test system

Catalytic reaction runs were conducted in a fixed-bed stainless steel reactor. Gas flow rates and reactor pressures were controlled by electronic mass flow and pressure controllers. Four heating zone equipped with temperature controller and indicator supplied the required reaction heat. 1.5 g of used catalyst was loaded to the reactor. The used catalysts regenerated by air or O_2/N_2 mixture at 300-500 °C for 8 hours in atmospheric pressure then the catalyst was first pre-reduced by using a flow of %10 H_2/N_2 . Activation was followed in a stream of synthesis gas. Following reduction, the reactor pressure raised to 17 bar and temperature to 290 °C and reaction started in a stream of synthesis gas with $H_2/CO = 1$ and $GHSV = 2 \text{nl.h}^{-1}.\text{gFe}^{-1}$. The products were analyzed by three Chanel gas chromatograph: A Varian CP 3800 with three detector that two thermal conductivity detector (TCD) were used for analyzing H_2 , CO, CO_2 , CH_4 , and other non-condensable gases and a flame ionization detector (FID) was used for organic liquid products.

3. Result & discussion

Deactivation of bifunctional catalyst in syngas conversion can be the result of one or more following reasons: (i) Deposition of inactive carbonaceous layer. (ii) Sintering of metal particles. (iii) Phase transformations in the FT component. (iv) Coking of zeolitic component. Where, (i), (ii), and (iii) cause a decrease in the overall reaction rate of syngas with time on catalyst. The zeolite component deactivation in bifunctional catalyst by syngas conversion can be explained by the coking of the zeolitic component. This will cause that acidic sites of catalyst is decreased, so loss of available acidic sites in the conversion of olefins to aromatics is lead to reducing selectivity of aromatics. The regeneration process includes of contacting a deactivated Fischer-Tropsch catalyst with Air or O_2/N_2 stream for a sufficient period of time to remove formed cock over the Fischer-Tropsch catalyst.

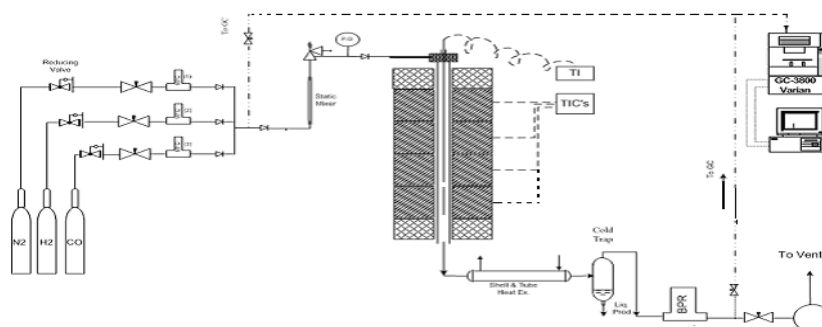


Figure 3: Cata-test system

Two methods exist for regeneration of catalyst: (i) Decreasing of GHSV (Zamni et al, European patent 2010) (ii) Using of Air or O_2/N_2 . The used catalysts are included of catalysts tested in the laboratory and Pilot for 700 h. In this study, we investigated regeneration of two types of catalyst by using of Air or O_2/N_2 : (1) Catalyst deactivated at Lab-test (CAT-L) (2) Catalyst deactivated at Pilot-test (CAT-P). Results of regenerated catalysts are shown in Fig.4 and Fig.5.

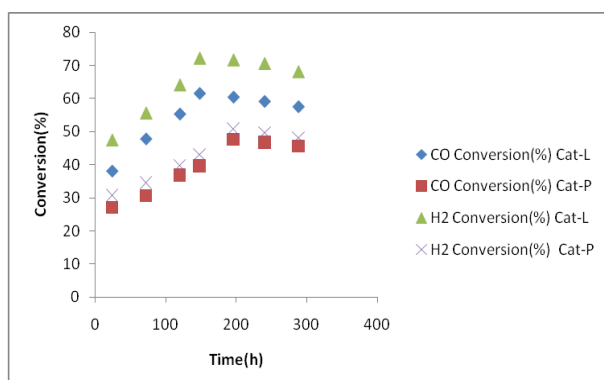


Figure 4: Carbon monoxide and Hydrogen conversion versus time

5. Conclusion

Iron catalyst produces mainly α -olefinic hydrocarbons but Iron-ZSM5 catalyst is an effective catalyst for gasoline production. With this catalyst, it is possible to minimize the formation of hydrocarbons beyond the gasoline-range product and obtain an appreciable amount of aromatics in the liquid product simultaneously. Pore structure of zeolite and its catalytic cracking action can limit the size of produced molecules. Zeolite presence shifts product distribution toward the formation of high-octane gasoline range isoparaffins and aromatics through the transformation of the primary FTS products on the zeolite acid sites, including

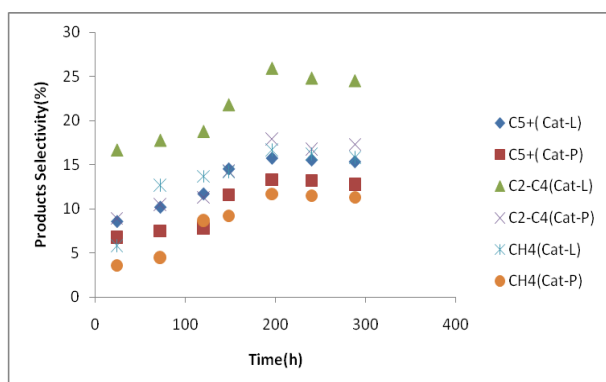


Figure 5: Products selectivity in different times

the cracking of C_{13}^+ hydrocarbons, skeletal isomerization, hydrogen transfer, and aromatization of the short-chain. Used Fe-ZSM5 catalysts were regenerated by removal coking, reduction of catalyst and formation of active phase (Iron carbides). Comparison of regenerated catalysts with fresh catalyst shows that about 80% of initial activity of fresh catalyst is returned by regeneration process.

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