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Review – Hydrocracking using Different Catalysts

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Abstract

The current demand is to produce quality fuel with high octane number which means better combustion properties from petroleum feedstock. Hydrocracking is a catalytic process upgrades petroleum feedstock by adding hydrogen. The coke yield was reduced significantly with use of catalyst, so to have environment friendly products the proper composition of catalyst is very important. This review focuses on different types of catalyst and catalyst loaded on supports for better understanding of characterization, the catalytic activity and other properties. Comparison between different catalysts for same support was studied to understand the properties of catalysts in an efficient way. Zeolites and silica-alumina were widely used catalyst supports which tend to show good catalytic activity with efficient loading of different metal catalyst.

Keywords: hydrocracking, catalyst, feedstock.

1] INTRODUCTION

With the growing population the demand for energy consumption is constantly increasing, resulting in rapid decrease in fossil reserves of earth [1-6]. The combustion of fossil fuel pollutes the environment and causes irreparable damage to the environment and create global problems [6]. Hydrocracking acts as a catalytic process which converts heavier fractions to lighter clean fuels thus making it an environment-conscience refining. This paper focuses on study of preparation of various catalyst for the hydrocracking process, which is one of the key process to convert heavy feedstock to high-quality fuels, for various types of feed and also study their different characteristics. Different feed stocks that can be used for hydrocracking as raw materials are asphaltenes, residual oil, vacuum gas oil, canola oil and paraffin wax. The catalysts that are used for hydrocracking are broadly divided into two types, an amorphous type (non-crystal) and a zeolite type (crystal). Amorphous type catalysts are composite oxide matrices primarily silica-alumina which can have controlled pore structure and acidity which leads to high yield of middle distillates. Due to this reason amorphous supports are used commercially whenever there is need to maximize the production of middle distillates or conversion to lube oil blending stock. The various form of amorphous supports are silica-alumina dispersed in alumina, alumina-boria, other acidic mixed oxides and fluorinated inorganic oxides. Zeolite type catalysts are crystalline aluminosilicate structure that have strong acidity and high catalytic activity but lower selectivity for middle distillates. Zeolites are important industrial catalyst. The main advantage of zeolites is the molecular shape-selectivity exerted by the pores for many catalytic process [7-16]. The characteristic of hydrocracking catalyst is that it has two types of active sites: acidic sites for isomerization and cracking function of C-C bonds from high molecular weight hydrocarbons; metal sites for hydrogenation and dehydrogenation function [17, 18]. Various catalysts like NiW, NiMo and CoMo bimetallic are paired with various supports which include zeolite, silica-alumina and ammonia [19-22]. In recent years Pd-based catalysts are finding application because of its high catalytic activity on hydrocracking of sulfur-free heavy hydrocarbons [24-27]. It was found that selectivity of catalyst depend not only on catalytic composition but also depends highly on the support materials and dispersion of metals in the supports and sequence in which the metals are impregnated on the support [26, 28].

1.1] Iron/Active Carbon-

The mixture of pyrite and active carbon when used for hydrocracking, required relatively low hydrogen pressure (7.0-10MPa). Hydrocracking of vacuum residue (300g) was carried out in a one-liter semi-batch magnetically stirred autoclave under constant hydrogen flow rate at 415-445ºC with varying hydrogen pressure 7.0-10MPa. The conversion rate was found high with low coke yield since thermal cracking of vacuum residue generated the free radical intermediates initially and are adsorbed on active carbon surface then stabilized by Iron after hydrogenation. The polycondensing is prevented since active carbon with mesoporous structure provides free radical intermediate with proper sites for adsorption. Thus at low hydrogen pressure the pyrite/active carbon mixture was found most effective for upgrading heavy oil [29].

1.2] Mud Catalyst-

Red Mud is general term for ferrous bauxite compounds containing high amount of iron oxide can be used as catalyst for the hydrocracking process of vacuum residue to increase the hydrocarbon yields and decrease coke yields by 92%. The benefit of red mud catalyst is that it can improve efficiency of energy attainment and the vacuum residue component of crude oil which was unattainable can be accessed thus enhancing sustainability of petroleum energy source. This is because the red mud facilitates the hydrogen uptake so the hydrocarbons that split into radicals react with hydrogen instead of themselves. The hydrocracking reaction was carried out under 490˚C for 2 hrs and activated red mud produced coke yield closer to 1.15 wt% whereas the un-catalyzed hydrocracking and phosphorous activated red mud produced 14.07 wt% and 1.63 wt% coke yield respectively. If a macro-mesoporous texture is induced to red mud molecule the production of coke remains fairly constant at a yield of about 0.33 wt% regardless of pore size, lighter liquid fractions production is favored by smaller pores of 150 nm pore diameter [30-31].

1.3] Mo/Mordenite Catalyst-

The mordenite catalyst was synthesized using mordenite, Al_2O_3 and nitric acid followed by extruding to band-form and drying was done at 120ºC and calcinated at 550ºC then 8 wt% Mo was loaded by cationic exchange approach and it has 18Å in pore diameter, 308 m^2/g in surface area, and 0.165 cm^3/g in pore volume. The hydrocracking reactions were carried out in a fixed bed reactor with gas and liquid sample collectors. The temperature was varied from 370 to 470ºC and hydrogen partial pressure kept in range of 30 to 55 kg/cm^2 with constant hydrogen flow rate at 100 sccm and H_2/phenanthrene molar ratio approached 20. With varying temperature the phenanthrene conversion at different hydrogen partial pressure were similar but the effect of hydrogen partial pressure impacted the phenanthrene conversion differently with changing temperatures [32-33].

1.4] USY Zeolite Catalyst-

In a comparative study of β- and USY zeolite with metal loading of varying composition of Al_2O_3 with impregnation of Ni and W salt solutions as active metal on these supports, in the hydrocracking activity for hydro-treated vacuum gas oil (HT-VGO) it was found that both are comparable to any commercial catalyst. The catalytic activity is dependent on the total acidity and the relative strength of acidic sites. The higher the reducibility gives higher hydrogenation activity and catalysts prepared on mixed supports gives higher amounts of saturates [34-36]. In another study of hybrid catalyst made of microcrystalline zeolite and silica alumina and 0.8 mass% Pt-loaded extrudates were calcinated at 500ºC for 1hr for the preparation of the hybrid catalyst and hydrocracking was carried out in a flow reactor where the catalyst are reduced at 340ºC for 1hr before the reaction starts. The hydrocracking for wax showed higher activity for hybrid catalyst than that containing only MC-USY and showed comparable selectivity as that of only silica-alumina because the silica-alumina in hybrid catalyst enhances the isomerization step which is considered the rate determining step for hydrocracking of wax. [37-40].

1.5] SBA-15 Catalyst-

In a study of hydrocracking for asphaltenes mesoporous SBA-15 support was used for catalyst with varying Fe loading of 4-30 wt% and 10wt% Ni metal loading at 573K and 5.0MPa hydrogen pressure. The SBA-15 support has the average pore diameter of 12 nm, pore volume of 2.6 cm^3/g and BET surface area of 790 m^2/g. Catalyst addition did not change the pore diameter, irrespective of metal type and loading, but lowered the pore volume and surface area, as expectable. The asphaltene conversion was higher and maltene yield was highest for 10wt% Fe loading whereas 10wt% Ni loading had lower conversion but higher yield than 10wt% Fe loading [41-43]. In another study of hydrocracking of DS-VGO it was observed that when mesoporous sieves of MCM-41 and SBA-15 are used as catalyst and it showed lower gas yield than those with USY zeolites [44].

1.6] Pt and Pd loading on β-SA-0.2

The amorphous type catalyst like silica-alumina has strong medium acidic site which gives high yield of middle distillates. The Pt and Pd was loaded by impregnation method on the silica-alumina carrier in which 40wt% is SiO_2 and it has 20wt% β-zeolite. The 0.8 wt% Pt loading catalyst showed that it had larger surface area and pore volume as compared to 0.8 wt% Pd loaded catalyst and had more stable catalytic activity during hydrocracking reaction while Pd loaded catalyst had higher gas selectivity and low middle distillates yield due to strongest acidic sites. The hydrocracking of wax was carried out at 260-300^{O}C temperature, 3.5 MPa pressure, 0.12 wt/wt ratio of H_2/wax and WHSV was considered 1-3 h^{-1}. After sometime the catalyst started deactivating and Pd loaded catalyst lost its activity after 38hr because of loss as only 20% of fresh catalyst reacted but the Pt loaded catalyst lost its activity after 200hr and 85% of fresh catalyst had reacted as it was well dispersed and stable [45].

1.7] Pd/$CoMoO_4$/silica and Pd/CNTs/$CoMoO_4$/silica Catalyst-

The preparation of a catalyst plays a major role in high quality products of hydrocracking. In an analysis of catalytic activity shown by both the catalyst for the hydrocracking of camellia fatty acid methyl esters it can be seen that different combination of loading and supports have different selectivity of cracking on heavy hydrocarbons. The hydrocracking reaction was carried out in a Parr reactor with 10wt% catalyst in feed at 300ºC temperature and hydrogen supplied at 450psi pressure. For the preparation of Pd/$CoMoO_4$/silica, both Pd and $CoMoO_4$ were loaded in mesopores of silica, where they were in close contact and react actively with feedstock. For the preparation of Pd/CNTs/$CoMoO_4$/silica (CNTs, Carbon Nano Tubes), Pd was loaded on surface of the CNTs and $CoMoO_4$ was loaded in the mesoporous silica to prevent aggregation. Thus CNTs separate Pd and $CoMoO_4$ by extremely small BET surface area. The reaction selectivity may vary because of different site of reaction (reaction site of mesoporous silica in first one and CNTs' surface in second one) and both the catalyst show high conversion [46].

1.8] Mo/Al_2O_3 Catalyst-

The 18wt% Mo metal was loaded on the mesoporous alumina of different pore size, i.e. 3.3, 9.0 and 18.9nm to study the hydrocracking of used motor oil (43.68 wt% residue) and residue oil (81.47 wt% residue). The effect of pore size on catalytic reaction was difficult to study directly because each catalyst has different properties. The catalyst with large pore surface area and high acid showed better hydrocracking activity because of high conversion of feedstock. The ratio of gasoline and kerosene to diesel yield also increased with increase in pore size. Thus catalyst pore size affects the liquid product distribution [47-48].

1.9] NiMo and Pt loading on γ-Al_2O_3 and Zeolite Catalyst-

Metal/acid bifunctional catalysts were generally used in hydrocracking reactions. Heavy hydrocarbons were dehydrogenated on the metal sites, and then isomerized or cracked on the acid sites and finally hydrogenated on metal sites. In a study of hydrocracking of extra heavy oil at 260-300ºC temperature with Hydrogen initial pressure of 5MPa and 5wt% catalyst it was found that NiMo/γ-Al_2O_3 are superior to NiMo/HZSM-5 because high conversion of 55.2wt% could be obtained and NiMo/HZSM-5 gave 46 wt% conversion. In an alternate way to produce biodiesel by hydrocracking of canola oil different catalysts – Pt/H-Y zeolite (2 wt% Pt), Pt/HZSM-5 (2 wt% Pt) and sulfide NiMo/γ-Al_2O_3 (0.8g S/g catalyst) was studied in an 80mL Batch reactor in ratio of 3wt% cat/wt. oil, temperature range of 300 to 400ºC and initial hydrogen pressures between 5 and 11 MPa among which NiMo/γ-Al_2O_3 gave highest conversion to liquid hydrocarbons in the boiling range of diesel fraction and Pt- zeolites have good catalytic activity therefore initial high hydrogen pressures were found to be required for good conversion and the time of reaction is dependent on type of catalyst. The advantage of NiMo/γ-Al_2O_3 catalyst was that it produced diesel (ca. 80%) from canola oil which is similar to petro diesel with advantage that former contains higher percentage of C_{17} and C_{18} hydrocarbons thus has a higher cetane number. The advantage of using Pt-Zeolite is that it has strong acid sites, which favors production of isoparaffins desirable in diesel to have a low pour point. The MFI nanosheets had similar shape selectivity to bulk ZSM-5 zeolite crystals and it grew in three dimensions. So it can also be used for hydrocracking patterns [49-53].

Conclusion

Hydrocracking of heavier fractions of crude oil to lighter clean fuels is counted recently as environmentally-conscience refining. Hydrocracking of higher hydrocarbons was studied by using different catalyst loading on suitable supports to get better yield of desired products. The reaction conditions used in the hydrocracking process were essential to get effective results. The composition and structure of catalyst is very important as it affects selectivity of compounds and catalytic activity. Still many innovations with different combinations of catalysts were under study and the improvement in the results can be achieved from it.

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