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Effects of Material Characteristics on the Performance of Hydrocracking Catalysts

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Abstract: Hydrocracking is a refinery process used to convert heavy hydrocarbon fractions to lighter cuts with high added value. The products that usually range from heavy diesel to light naphtha involving middle distillate as targeted cut are obtained as a result of hydrocracking process of feeding with higher molecular weights and lower hydrogen/carbon ratios. Hydrocracking reactions occur under high hydrogen partial pressures and temperatures in the presence of catalyst in order to remove impurities such as sulfur compounds and crack heavy hydrocarbon molecules to high added value lighter cuts. Hydrocracking catalysts are bifunctional in which metal function with hydrogenation consisting group VIB or group VIII B is for removal of impurities and acidic support consisting amorphous oxides and/or crystalline zeolites to realize cracking function. In this study, the association between the performance test results obtained from laboratory scale reactor system and the material characteristics of the catalysts are viewed. Selectivity, hydrocracking, and hydrogenation activities within the performance parameters of the catalysts are calculated based on the fraction ratios and feed-product properties. Furthermore, the effect of hydro-treating activity on hydrocracking activity is also highlighted. The surface area and pore size, crystallinity, chemical composition of the material and acidic properties are investigated within the scope of material characteristics of the catalysts by using BET, XRD, XRF, NH₃-TPD techniques, respectively.

Keywords: Hydrocracking; catalyst; characterization; structure-performance relationship.

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INTRODUCTION

Hydrocracking is a refining technology within the scope of hydro-processing which is used for the conversion of a variety of feedstocks to a range of products by adding hydrogen, removing impurities in the presence of catalyst. Hydrocracking technology for conversion of coal to liquid fuels was developed in Germany as early as 1915. The forerunner of the hydrocracking is Bergius process which may be considered as the first commercial plant and brought on stream in Germany in 1927 for hydrogenation of distillates derived brown coal (1,2). During World War II, hydrocracking processes played an important role in producing aviation gasoline. Nevertheless, after World War II, the emergent availability of Middle Eastern crude removed the incentive to convert coal to liquid fuels which caused the development of hydrocracking technology to become less important as newly developed fluid catalytic cracking processes were much more economical than hydrocracking for converting high-boiling petroleum oils to fuels. In the mid-1950s, manufacturing of high performance cars with high-compression ratio engines of the automobile industry required high-octane gasoline, where the switch of railroads from steam to diesel engines and the introduction of commercial jet aircraft in the late 1950s increased the demand for diesel fuel and jet fuel (1). Thus in the early 1960s, with the increasing demand for gasoline, diesel, and jet fuel, by-product hydrogen at low cost and in large amounts from catalytic reforming operations and environmental concerns limiting sulfur and aromatic compound concentrations, hydrocracking technology gained importance again. Moreover, in 1958, the first modern distillate hydrocracker had been put into commercial operation by Standard Oil of California (now Chevron). It grew in other parts of the world, starting in the 1970s primarily for the production of middle distillates, while hydrocracking was used in the United States primarily in the production of high-octane gasoline (1-3).

Hydrocracking reactions proceed through a bifunctional mechanism which is one that requires two distinct types of catalytic sites. These two functions to catalyze separate steps in the reactions are the acidic function, which provides for the cracking and isomerization and the metallic function which provides for the olefin formation and hydrogenation. The number and strength of the acid sites of the acidic supports consisting of amorphous oxides and/or crystalline zeolite plus binder, or a mixture of them, designate the acidic characteristics and thus the cracking function of the catalyst. The metals providing metal function consisting of noble metal or base metal sulfides from groups VIA and VIIIA, make the feedstock more reactive for cracking and heteroatom removal (4-6). In some studies, organic acids are reported to be used as modifying agents of supports that enhance activity and stability of the catalyst improving secondary pore volume, crystallinity, and silica-alumina ratio (7-10). Some studies are also related with uniformity of alumina-silica

dispersion to inhibit the molecular sieve agglomeration or channel blocking (11). Nevertheless, strength, ratio, balance, and distance of the acid and hydrogenation functions of the bifunctional catalyst are also important with regard to catalytic performance. For instance, a catalyst with a strong hydrogenation and a weak acidic function has low activity but good selectivity for middle distillates and requires low severe operating condition (12). Overall, the activity and selectivity within the relevant activities indicate the performance of the catalyst.

The selection of the hydrocracking catalyst concerning commercial units is a crucial step in terms of its performance, cost, and required operational conditions. The characteristics of the materials in terms of acidity, composition, surface area, pore structure, *etc.* strongly influence the hydrogenation and cracking activities of the catalyst as known from the literature. Therefore in this study, the association of the material characteristics and the performance of the relevant catalysts are viewed to investigate the consideration of the material characteristics for the selection of the hydrocracking catalyst in the future. The material characteristics of the catalysts are analyzed by several instrumental analysis methods using BET, XRD, XRF, NH₃-TPD techniques where the performance of the catalysts is calculated based on the laboratory scale test results. Furthermore in this study, the effect of hydro-treating activity on hydrocracking activity is also highlighted for revealing that the higher hydro-treating activity causes hydrocracking activity to enhance hydrocracking reactions.

MATERIALS AND METHODS

Chemicals

Three fresh, Ni-W-based hydrocracking catalysts coded as C(F), D(F), E(F) were selected for all performance tests and characterization.

Apparatus

All surface area and pore size measurements were carried out through BET (Brunauer–Emmett–Teller) technique with Micromeritics Asap 2020 N₂ Adsorption-Desorption. The crystal properties were investigated by XRD (X-ray Diffraction) analysis with Bruker – D8 Advanced. The chemical compositions of the material were carried out by XRF (X-ray Fluorescence) technique with Bruker – Tiger 8S and the acidic properties were characterized by NH₃-TPD (Temperature Programmed Desorption) analysis through Micromeritics Chemisorp 2750. The performance tests of the

catalysts were carried out in a laboratory scale reactor system, Parr 5402C providing a down flow continuous trickle bed operation in an isothermal mode by independent temperature control of three zone electric furnace (Figure 1). The distillation data of VGO (Vacuum Gas Oil) as feed and TLP (Total Liquid Product) which indicated hydrocracking activity of the catalysts were obtained through GC (Gas Chromatography) technique by AC Analytical Controls Simulated Distillation Analyzer on Agilent 7890. The sulfur & nitrogen content of the feed and the TLP which represented hydrotreating activity of the catalysts were analyzed by using Antek MultiTek N-S 115V/230V.

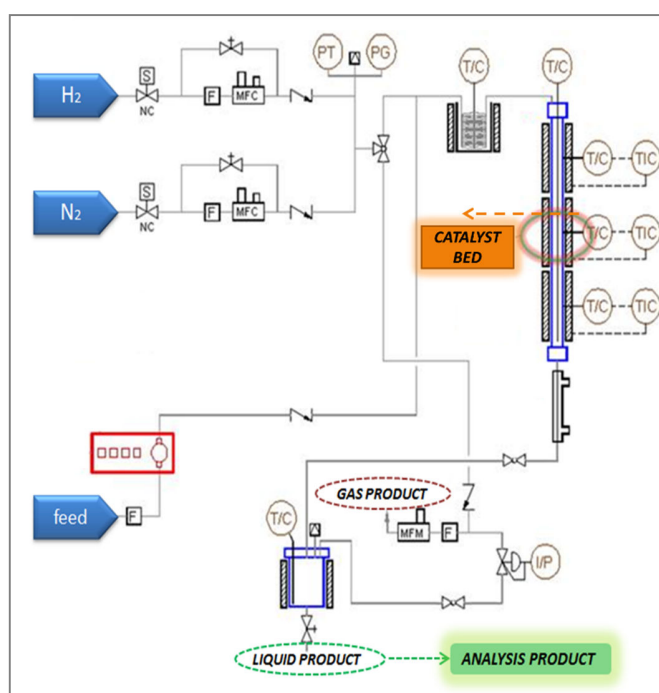


Figure 1. Schematic diagram of laboratory-scale reactor system.

Experimental procedure

The material characteristics of the catalysts were analyzed in terms of surface area and pore size by using BET (ASTM 3663, 4222, 4641, 4365), crystallinity by using XRD spectra with measurement range between 2θ degrees of $10-90^\circ$, chemical composition by XRF analysis and acidic properties by NH_3 -TPD analysis, respectively.

Process parameters that play an important role in the operation of the hydrocracking unit are reactor temperature, LHSV (Liquid Hourly Space Velocity), operating pressure and H_2 /oil ratio. These operating conditions held constant during the performance tests to avoid the effect of process parameters on the performance of the catalysts. The experiments of the performance

tests were performed at a temperature of 380°C, a pressure of 120 bar, a LHSV of 1.14, a H₂ flow rate of 400 mL/min and a feed flow rate of 0.33 mL/min over 17.54 mL of catalyst through a laboratory scale reactor system. Initially the hydrogen flow was set at a required level that has been calculated from LHSV and H₂/oil ratio of the commercial hydrocracker unit. The amounts of the catalysts were calculated according to the LHSV values and determined based on bulk densities of each catalyst. The catalysts are loaded to the reactor by mixing with an equal volume of SiC (Silicon carbide) to ensure homogeneous flow distribution and catalyst wetting through reactor during performance tests. The pressure of the reactor is controlled by a BPR (Back Pressure Controller) located at the gas outlet of high pressure separator.

At the end of the performance tests, the liquid and gas samples were collected for analysis of GC and product properties. Therefore, hydrocracking activity and selectivity of the catalysts were calculated as based on the distillation data of the feed and the TLP. The hydro-treating activity of the catalysts was also determined according to the total sulfur & nitrogen content of the feed and the TLP.

The surface area and the pore size are shown in Figure 2 revealing that the catalyst D (F) has the highest surface area with 270.2 m²/g but the lowest total pore volume with 0.368 cm³/g. The lowest surface area belongs to the catalyst C (F) having a higher total pore volume of 0.404 cm³/g.

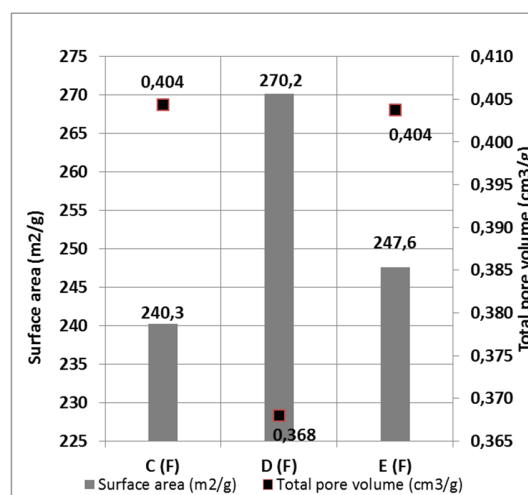


Figure 2. Surface area and pore size of the catalysts.

The content of NiO and WO₃ measured through XRF technique reveals that catalyst C (F) has the highest content of NiO and WO₃ where the content of NiO and WO₃ of the catalysts D (F) and E (F)

are similar and lower than that of catalyst C (F) as seen in Figure 3.

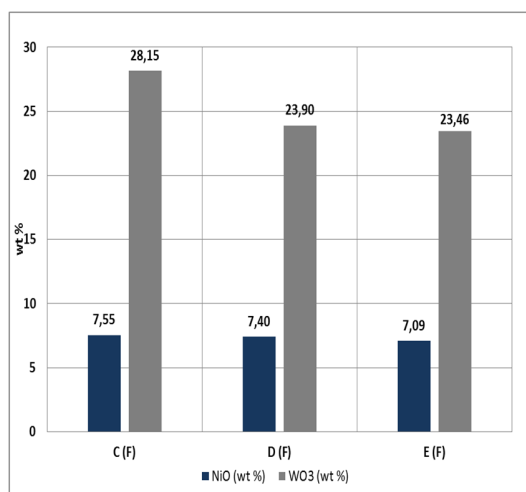


Figure 3. NiO and WO₃ content of the catalysts.

The crystallinity of the catalysts obtained from XRD patterns are given in Figure 4. According to the figure, catalyst C (F) and D (F) have zeolite structures whereas catalyst E (F) has an amorphous structure. The catalyst D (F) and E (F) are also assumed to have poor distribution of metal phase as WO₃ peaks are seen through related patterns.

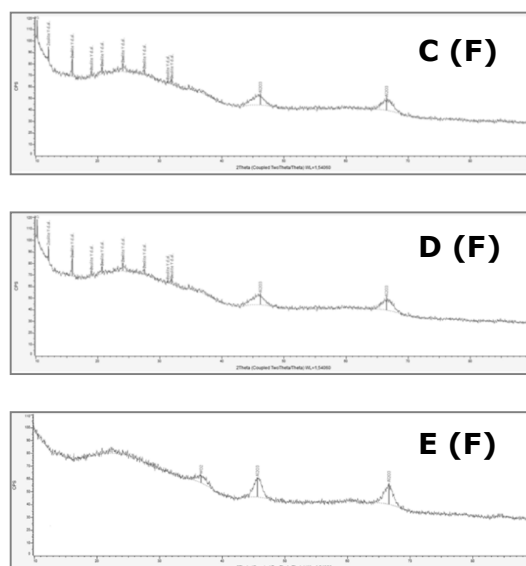


Figure 4. XRD patterns of the catalysts.

The acidic properties of the catalysts studied by NH₃-TPD analysis. According to the Figure 5, the catalyst D (F) has the highest total and medium acidic strength where the catalyst E (F) has the lowest total acidic strength.

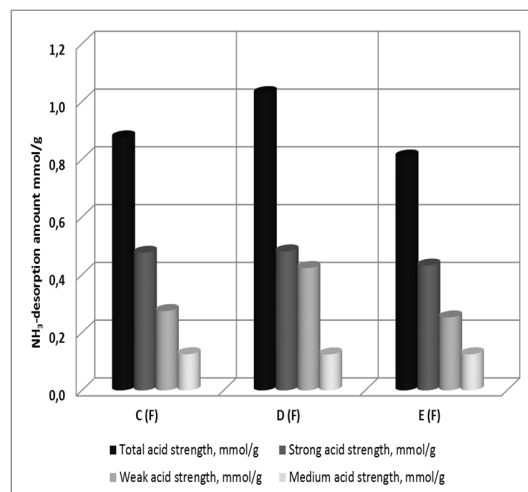


Figure 5. Acidic properties of the catalysts.

The hydrocracking and hydro-treating activities of the catalysts performed through the laboratory scale reactor system are given in Figures 6 and 7. The selectivity and hydrocracking activity of the catalysts are calculated through the distillation data of the TLPs which have been obtained from performance test of each catalyst.

According to Figure 6, the catalyst E (F) has the highest selectivity and conversion value as more fractions are observed and the amount of UCO (unconverted oil) in the TLP is the lowest. The catalysts C (F) and D (F) have similar values of selectivity and conversion due to similar fractions and UCO amount.

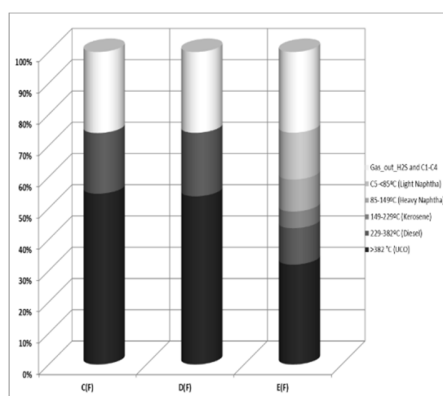


Figure 6. Selectivity and conversion performance of the catalysts.

The sulfur and nitrogen removal activities within the hydro-treating performance and the conversion activities within the hydrocracking performance of the catalysts are seen in Figure 7. The relevant activities are studied based on distillation data and sulfur and nitrogen content of both feed and TLP. The catalyst E (F) has both the highest conversion value and sulfur and nitrogen removal activity representing the hydrocracking and hydro-treating performances, respectively. The catalysts C (F) and D (F) have similar values of conversion and sulfur and nitrogen removal activity.

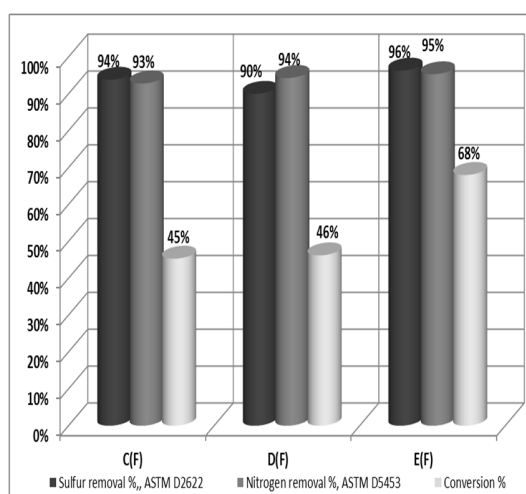


Figure 7. Hydrotreating activities and conversion performances of the catalysts.

RESULTS AND DISCUSSION

The metal phases of the catalyst C (F) are not bulk according to the XRD data. As a result, homogenous distribution of the available metal phases is observed to enhance the hydrotreating

activity (Figure 4). The similarity of the hydrocracking activities of the catalysts C (F) and D (F) even though the higher surface area and acidity of the catalyst D (F) may be associated with the higher total pore size and hydrotreating activity of the catalyst C (F) (Figure 5, 6 and 7).

The hydrotreating activity of the catalyst D (F) which has the lowest value may be associated with the lower content of NiO and WO₃ and poor distribution of metal phases of the catalyst (Figures 3 and 7). The WO₃ peak which is seen in XRD pattern also confirms the formation of the bulk metal phases in patches (Figures 4 and 7). The hydrocracking activity of the catalyst D (F) is relatively low despite high surface area and acidity of the catalyst. This may be explained by relatively lower pore size and hydro-treating activity of the catalyst D (F) (Figure 2, 4 and 7).

The enhancement of hydrotreating activity of the catalyst E (F) seen in Figure 7 may reveal the prospective metal-support interaction. Moreover, high mesopore/micropore ratio, large distribution of pore size, low SAR (Silica to Alumina Ratio) value, relatively high acidity and amorphous structure of the catalyst E (F) promotes high conversion activity of the catalyst even when using heavy feed such as VGO.

In general, the effect of hydro-treating activity on hydrocracking activity may be associated with consecutive nature of the hydrocracking and hydro-treating reactions. Therefore, the higher hydro-treating activity may promote hydrocracking activity to enhance hydrocracking reactions. It is concluded that the bulk metal formation of NiO and/or WO₃ phases or poor distributions of metal phases of the catalyst observed from XRD patterns has a negative effect on hydro-treating activity.

In future studies, the inclusion of the material characteristics for selection of the relevant hydrocracking catalysts within commercial unit operations will be investigated. Furthermore, the effect of hydro-treating activity on hydrocracking activity and the possible influence of consecutiveness of the hydrocracking and hydro-treating reactions will be examined in detail.

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Türkçe Öz ve Anahtar Kelimeler

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Melek Bardakcı Türkmen, Burcu Yüzüak, Deniz Onay Atmaca, Ayşegül Bayat, Volkan Balci, Seçil Ünsal, Can Erkey and Ersen Ertaş

Öz: Hidro-kraking ağır hidrokarbon fraksiyonlarını daha küçük ve katma değeri daha fazla olanlara çevirmek için kullanılan bir rafineri sürecidir. Hedeflenen kısımlar olarak orta distilatları içeren ağır dizelden hafif naftaya kadar uzanan bir seri elde edilir daha yüksek moleküler ağırlık ve daha düşük hidrojen/karbon oranları elde edilmiş olur. Hidro-kraking tepkimeleri yüksek hidrojen kısmi basınçları ve yüksek sıcaklıklarda, katalizör varlığında oluşur, kükürtlü bileşikler gibi safsızlıklar bu esnada ortamdan uzaklaştırılmış olur ve ağır hidrokarbon molekülleri yüksek katma değerli ve daha hafif türevlere dönüşür. Hidro-kraking katalizörleri iki fonksiyonludur ve VIB veya VIIIB grubundan bir metal hidrojenlemede safsızlıkları gidermek için ve amorf oksitler ve/veya kristal zeolitler de kraking işlevini yerine getirecek asidik fonksiyonları barındırır. Bu çalışmada, laboratuvar reaktor sisteminden gelen performans test sonuçları ile katalizörlerin malzeme karakteristikleri arasındaki uyum izlenecektir. Katalizörlerin performans parametreleri içindeki seçicilik, hidro-kraking ve hidrojenleme aktiviteleri fraksiyon oranları ve akış ürün özelliklerine dayanan hesaplamalarla bulunmuştur. Bunun ötesinde, hidrokraking aktivitesi üzerine hidro-muamele aktivitesinin etkisi de ortaya konmuştur. Yüzey alanı ve gözenek boyutu, kristallik, malzemenin kimyasal bileşimi ve asidik özellikleri sırasıyla BET, XRD, XRF, NH₃-TPD teknikleri ile yapılmıştır.

Anahtar kelimeler: Hidrokraking; katalizör; karakterizasyon; yapı-performans ilişkisi.

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