Fuel 237 (2019) 178–190

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

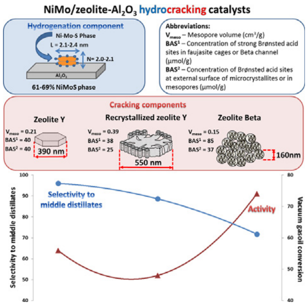
Full Length Article

Hydrocracking of vacuum gas oil over NiMo/zeolite-Al_2O_3: Influence of zeolite properties

P.P. Dik[a,*], I.G. Danilova[a], I.S. Golubev[a], M.O. Kazakov[a], K.A. Nadeina[a], S.V. Budukva[a], V.Yu. Pereyma[a], O.V. Klimov[a], I.P. Prosvirin[a], E.Yu. Gerasimov[a], T.O. Bok[c], I.V. Dobryakova[b], E.E. Knyazeva[b,c], I.I. Ivanova[b,c], A.S. Noskov[a]

[a] *Boreskov Institute of Catalysis SB RAS, Pr. Lavrentieva 5, 630090 Novosibirsk, Russia*
[b] *Department of Chemistry, Moscow State University, Lenin Hills 1/3, 119991 Moscow, Russia*
[c] *A.V. Topchiev Institute of Petrochemical Synthesis RAS, Leninskiy Prospect 29, 119991 Moscow, Russia*

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Hydrocracking
Vacuum gas oil
Catalyst
Zeolite beta
Micro-mesoporous zeolite Y
Recrystallization

ABSTRACT

Hydrocracking of vacuum gas oil has been studied over NiMo/zeolite-Al_2O_3 catalysts. Three different zeolites have been used for catalysts preparation: zeolites Beta (BEA) and Y (FAU) having small crystal size and zeolite Y modified by recrystallization (RFAU). HRTEM, low-temperature N_2 adsorption, FTIR of adsorbed CO and TPD-NH_3 showed that zeolites had different crystal sizes, mesopore volume, strength and concentration of acid sites. Sulfide active component particles have been revealed to be similar in all catalysts by HRTEM and XPS. NiMo/BEA catalyst having zeolite with the smallest average particle size and the highest concentration of Brønsted acid sites (BAS) demonstrated the highest hydrocracking activity. Selectivity to middle distillates decreased in the following order: NiMo/FAU > NiMo/RFAU > NiMo/BEA. This effect is accounted for by optimal zeolite acidity and improved availability of the acid sites for bulky molecules of the heavy feedstock.

1. Introduction

Hydrocracking is an oil refining process that converts petroleum fractions with high-boiling point, such as vacuum gas oil, deasphalted oil, atmospheric residue, and other heavy streams, into more useful products (gasoline, kerosene and low-sulfur diesel fuel) in the presence of H_2 and heterogeneous catalysts. Kerosene and diesel fractions obtained by hydrocracking have high quality due to high smoke point and cetane number, respectively, and low sulfur content. Therefore, middle distillates are the most valuable hydrocracking products [1,2].

---

[*] Corresponding author.
E-mail address: dik@catalysis.ru (P.P. Dik).

https://doi.org/10.1016/j.fuel.2018.10.012
Received 17 March 2018; Received in revised form 12 September 2018; Accepted 1 October 2018

Hydrocracking catalysts are bifunctional catalysts, which have two types of sites: hydrogenating and acidic [3]. Sulfides of transition metals (Mo, W), promoted by nickel [4,5] or cobalt [6–8], or noble metals, such as Pt [9,10], Pd [11,12] and their bimetallic compounds [13,14], are generally used as the hydrogenating components of hydrocracking catalysts. Hydrogenating activity of noble metals is higher than that of the transition metal sulfides, but NiW and NiMo catalysts are widely used in industry, because they are cheaper and more resistant to sulfur compounds.

Zeolites [4,10] and amorphous silica-alumina (ASA) [9,15], as well as their composites [16,17], are generally used as cracking components for preparation of hydrocracking catalysts. Selectivity of zeolite-containing catalysts to the middle distillates is lower than selectivity of the catalysts based on ASA [18,19]. This can be explained by the fact that the strength and concentration of acid sites in zeolites is higher than in amorphous silica-alumina. Besides, the size of the heavy feed molecules is often comparable or exceeds the size of the zeolite micropores. Therefore, zeolite-containing catalysts are more active in hydrocracking of C_{10}-C_{20} hydrocarbons, which results in overcracking of middle distillates and excessive production of light fractions [20].

Low activity of ASA can be compensated by an increase in process temperature, but it often causes rapid deactivation of catalysts and a decrease in the quality of the products due to the increase of aromatic compounds content [19,21]. Thus, an increase in the average pore size of zeolites combined with appropriate acidity and textural properties is necessary to enhance activity of catalysts in hydrocracking of heavy feedstocks [22]. For zeolite-containing catalysts, the concentration and strength of acid sites have a significant influence on activity and selectivity. Ding et al. [23] have shown that activity in hydrocracking of hexadecane increases with increasing acidity of the zeolite. Nowadays, ultra-stable zeolites Y are widely used as acidic component of commercial hydrocracking catalysts [24]. The unsteamed zeolite Y has a very high concentration of Brønsted acid sites, which results in very low selectivity to middle distillates. It is well known that an increase in the Si/Al ratio in zeolites leads to a decrease in the total number of acid sites, as well as to an increase in their thermal stability [25]. To increase a Si/Al ratio and selectivity to middle distillates, three different methods of zeolites dealumination are used: hydrothermal treatment, chemical treatment, and combination of hydrothermal and chemical treatment [26,27].

Another way to enhance selectivity of zeolites to middle distillates is to form additional mesopores. It is known that mesopores are formed during dealumination [28–30] and desilication [31]. Other promising approach to create mesoporosity in zeolites is recrystallization of zeolites with surfactants [32–38]. Recrystallization significantly increases the volume of mesopores and the accessibility of acid sites. The number and strength of the acid sites decrease with increasing the degree of recrystallization, while the accessibility of the sites is improved. It was shown previously for USY that the high selectivity of NiMo hydrocracking catalysts to middle distillates was the result of additional intracrystalline mesoporosity formed by recrystallization of the parent zeolite [39].

Another way to increase availability of acid sites is to reduce zeolites crystals size. Camblor et al. [40] have reported that activity and selectivity to middle distillates of hydrocracking catalysts based on zeolite Beta increases with decreasing size of zeolite crystals. Authors showed that activity of the catalyst based on the zeolite Beta with a crystal size of 10 nm was significantly higher than that of the catalyst based on zeolite Y. Moreover, the selectivity to middle distillates of the catalyst based on the nanocrystalline zeolite Beta was higher than the selectivity of zeolite Y based catalyst and even higher than that of ASA-based catalyst. Landau et al. [41] have found that activity of Pt containing hydrocracking catalyst based on zeolite Beta with crystal sizes of 10–30 nm is much higher than that of the hydrocracking catalyst based on zeolite Beta with crystal sizes of 200–500 nm. The influence of zeolite Y crystals size on the activity and selectivity to the middle distillates of NiW hydrocracking catalysts have been studied in the article [42], where it was shown, as in the article [40], that a decrease of zeolite crystals size resulted in an increase of selectivity to middle distillates and hydrocracking activity.

In a lot of works [17,40,43–47] zeolite Beta is used for hydrocracking catalysts preparation. A direct comparison have shown that the selectivity to middle distillates of hydrocracking catalysts based on zeolite Beta was lower than that of the catalysts based on zeolite Y, except the article [40], where zeolite Beta with a crystal size of 10 nm was used. It seems essential to compare different approaches for preparation of hydrocracking catalysts, which are more active and selective to middle distillates, by increasing availability of acid sites in zeolites. In this study, the influence of zeolites properties on catalysts performance in hydrocracking of VGO was investigated. Zeolites Beta and Y having small crystal sizes and zeolite Y modified by recrystallization were used for preparation of hydrocracking catalysts.

2. Experimental

2.1. Preparation

2.1.1. Preparation of zeolites

Reaction mixture for zeolite Y with small crystal size (denoted as FAU) synthesis was prepared by mixing sodium silicate, sodium aluminate, sodium hydroxide and silica. Zeolite FAU with $SiO_2/Al_2O_3 = 25$ was prepared by consecutive procedures of hydrothermal crystallization at 95 °C, deep ion exchange in NH_4NO_3 solution for residual sodium content 0,4 wt%, vapor treatment and acidic leaching with nitric acid.

Micro-mesoporous zeolite Y denoted as RFAU was prepared by hydrothermal treatment of dealuminated zeolite Y (CBV-720, Zeolyst) in a mixture of ammonia and hexadecyltrimethylammonium bromide aqueous solutions, according to [48].

Zeolite Beta with small crystal size denoted as BEA was synthesized from reaction mixture prepared from aerosil A300 (Degussa), sodium aluminate, sodium hydroxide and tetraethylammonum hydroxide (35% water solution, Sigma-Aldrich) as template. After hydrothermal crystallization at 135 °C, following preparation steps include washing, drying, calcination for template removing and ion exchange in NH_4NO_3 solution.

2.1.2. Preparation of the supports and catalysts

AlOOH boehmite (ISCZC, Russia) and zeolites were used for preparation of supports. Three supports with zeolite content of 30 wt% were prepared by mixing one of the zeolite RFAU, FAU or BEA with AlOOH followed by peptization with HNO_3 and extrusion by plunger extruder. Final trilobe extrudates were dried at 120 °C and calcined at 550 °C.

Catalysts were prepared by impregnation of the corresponding supports with aqueous solution prepared from nickel carbonate, ammonium heptamolybdate and citric acid with mass ratio of the components 1:2.9:2.5 (pH of the solution was 4). Impregnated catalysts were dried at 120 °C and calcined at 550 °C. Citric acid used for catalysts preparation because: it allows stable active metals solution to be prepared; Ni and Mo are located in close proximity due to complex formation [49]; favors high dispersion of active metals due to high viscosity of solution on the drying step [50]. Thus, the use of citric acid for catalysts preparation, even with the subsequent calcination of the catalysts, improves the deposition of active metals.

Ni and Mo content in the catalysts was 3.0 ± 0.1 and 9.8 ± 0.5 wt %, respectively. The catalysts were denoted as NiMo/FAU, NiMo/RFAU and NiMo/BEA.

Also, two additional catalysts – NiMo/Al_2O_3 and NiW/ASA-Al_2O_3 were prepared. NiMo/Al_2O_3 catalyst and NiW/ASA-Al_2O_3 were used as the first and second layers in a stacked bed to simulate industrial conditions in laboratory unit. NiMo/Al_2O_3 was prepared using similar