



## Hydrocracking of vacuum gas oil over NiMo/Y-Al<sub>2</sub>O<sub>3</sub>: Effect of mesoporosity introduced by zeolite Y recrystallization

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### ABSTRACT

Hydrocracking of vacuum gas oil was studied over micro-mesoporous zeolite based catalysts, obtained by zeolite Y recrystallization. The contribution of mesoporosity in recrystallized materials was varied by adjusting the content of alkali and the temperature of hydrothermal treatment. The increase of recrystallization degree results in the increase of mesopore to micropore volume of zeolite Y as well as to the decrease of the contribution of strong Brønsted acid sites in faujasite cages and the increase of the contribution of Brønsted acid sites in mesopores. The highest hydrocracking activity and middle distillates yield is achieved over NiMo catalyst obtained with micro-mesoporous material with low degree of recrystallization. This effect is due to the improved accessibility of active sites and easier transport of bulky molecules provided by mesopores, on the one hand, and optimal zeolitic acidity, on the other hand. The highest selectivity to middle distillates is achieved over catalyst with the highest degree of zeolite recrystallization. This observation can be explained by the decrease of the contribution of strong BAS (bridging Si-O(H)-Al groups) accompanied by the increase of concentration of BAS in mesopores.

### 1. Introduction

Hydrocracking is one of the main processes in oil refinery for the conversion of a wide range of low-value heavy feedstocks into high-quality products, mainly transportation fuels [1,2]. This technology is extremely versatile and provides the production of middle distillates of superior quality: diesel fuel with high cetane number, low aromatics and sulfur content, good cold flow properties and jet fuel with high smoke point and low freeze point. Hydrocracking catalysts are bifunctional catalysts, comprising both hydrogenation and acid functions. Cracking as well as isomerization activity is provided by the acidic component, while the supported metals provide hydrogenation activity [3]. Typically, mixed transition metal sulfides (NiMo or NiW) [4–8] or noble metals (Pt or Pd) [9–11] are used in hydrocracking catalysts. Noble metals possess much higher hydrogenation activity, however, they can be used only in a low-sulfur or sulfur-free environment, i.e. in hydrocracking units with a separate recycle system for the second-stage operation. In the presence of hydrogen sulfide and organic sulfur compounds as well as ammonia and nitrogen compounds, i.e. single-stage hydrocracker or first-stage operation, mixed metal sulfides are

preferred. NiMo catalysts are used when a supplementary hydrodenitrogenation (HDN) activity is required, while NiW catalysts are used when hydrogenation activity is a priority [12].

Depending on the support composition, hydrocracking catalysts are classified into non zeolite catalysts, based on amorphous silica-alumina (ASA), and zeolite catalysts, which can be grouped into low zeolite and high zeolite content catalysts [1,13]. Amorphous catalysts are less active for hydrocracking than zeolite catalysts, however they provide higher selectivity to middle distillates [14]. Zeolite catalysts are substantially more active due to higher acidity. Higher activity allows operating the process at lower temperatures and provides middle distillates of higher quality. At present, zeolite commercial hydrocracking catalysts are based on ultrastable Y zeolites (USY) [12,13]. The activity and selectivity of a catalyst and products distribution (gases, naphtha, kerosene, diesel) are determined by the balance between acid function and hydrogenation function [1,15,16]. Catalysts with high acidity but weak hydrogenation function produce light products such as naphtha and gases, whereas catalysts with lower acidity and enhanced hydrogenation activity produce middle distillates. At the same time, the accessibility of zeolite acid sites should be taken into account, since

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diffusion limitation may play a major role in the conversion of large molecules due to zeolite microporous structure. As has been shown by hydrocracking of model compounds of different molecular sizes and atmospheric residue [17,18], enhanced mesoporosity of zeolite Y is favorable for hydrocracking of heavy feeds.

The most generally applied approach to increase the accessibility of active sites and minimize diffusion limitation is the creation of mesopores inside the microporous zeolite crystals [19–21]. A wide variety of methods have been developed for generating mesopores in zeolites, however the most common approach is based on the removal of framework aluminium (dealumination) or silicon (desilication) atoms [22]. One of the promising strategy for the preparation of zeolites with a secondary mesoporosity, which are referred to as micro-mesoporous zeolite materials, is zeolite recrystallization with surfactants [23–29]. The procedure involves zeolite dissolution leading to partial destruction of a zeolite and extraction of zeolitic fragments and the following re-assembling of the dispersed species into mesoporous phase. Depending on the degree of zeolite recrystallization, micro-mesoporous materials can be obtained as mesoporous zeolite crystals, coated with thin films of mesoporous materials, composite materials consisting of two co-crystallized zeolitic and mesoporous phases or mesoporous materials with zeolitic fragments in the walls [28]. Recrystallization significantly increases the volume of mesopores and the accessibility of acid sites. With increasing the degree of recrystallization the number and strength of the acid sites decreases, while the accessibility of the sites is improved. Superior performance of recrystallized materials with respect to parent zeolites have been confirmed in a wide range of reactions including alkylation of aromatics on recrystallized mordenite [30], methanol dehydration on recrystallized ZSM-5 [31], skeletal isomerization of 1-butene on recrystallized ferrierite [32,33], hydroisomerization of octane and hexadecane on Pt-containing recrystallized mordenite [34], hydrodealkylation, transalkylation and disproportionation of alkylaromatics on recrystallized mordenite [24,35,36], cracking of vacuum gas oil (VGO) on recrystallized faujasite [27,37]. NiW-modified micro-mesoporous zeolite material obtained by recrystallization of BEA showed higher activity and selectivity for middle distillates in hydrocracking of Daqing vacuum residue than parent BEA, MCM-41 and the mechanical mixture of BEA and MCM-41 [38].

The advantages of the strategy for the preparation of micro-mesoporous zeolite materials by zeolites recrystallization can be used to increase the selectivity to middle distillates of USY-based hydrocracking catalysts. In this work we present the results on the effect of mesoporosity introduced by zeolite Y recrystallization on the performance of NiMo/Y-Al<sub>2</sub>O<sub>3</sub> catalyst in hydrocracking of vacuum gas oil. Hydrocracking was performed with non-pretreated feed and stacked catalyst beds [39]: the top layer – hydrotreating catalyst, the interlayer – ASA-based hydrocracking catalyst and the bottom layer – hydrocracking catalyst based on micro-mesoporous zeolite Y. This approach allows simulating commercial process conditions for single-stage hydrocracker or first-stage operation, when zeolite catalyst operates in the presence of NH<sub>3</sub>, H<sub>2</sub>S and small amounts of unconverted organic hetero compounds.

## 2. Experimental

### 2.1. Preparation

#### 2.1.1. Preparation of micro-mesoporous zeolites Y

Micro-mesoporous zeolites Y were obtained by hydrothermal treatment of dealuminated zeolite Y denoted as FAU (CBV-720, Zeolyst) in a mixture of ammonia and hexadecyltrimethylammonium bromide aqueous solutions according [40]. Contribution of micro- and mesoporosity in micro-mesoporous zeolites Y was varied by altering the concentration of ammonia solution and the temperature of hydrothermal treatment. The recrystallized materials were denoted as RFAU.

#### 2.1.2. Preparation of the supports and catalysts

AlOOH boehmite produced by ISCZC (Russia) and RFAU zeolites were used for the preparation of supports.

Four supports denoted as FAU-Al<sub>2</sub>O<sub>3</sub> and RFAUx-Al<sub>2</sub>O<sub>3</sub> (where x – RFAU sample number) with zeolite content of 30 wt% were prepared by mixing of zeolite and AlOOH followed by peptization with HNO<sub>3</sub> and extrusion of obtained paste using plunger extruder. The obtained trilobe extrudates were dried at 120 °C and calcined at 550 °C.

NiMo/FAU-Al<sub>2</sub>O<sub>3</sub> and NiMo/RFAUx-Al<sub>2</sub>O<sub>3</sub> 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. Impregnated catalysts were dried at 120 °C and calcined at 550 °C. Ni and Mo content in the catalysts was 3.0 ± 0.1 and 9.8 ± 0.5 wt% respectively.

Also, two catalysts NiMo/Al<sub>2</sub>O<sub>3</sub> and NiW/ASA-Al<sub>2</sub>O<sub>3</sub> were prepared. NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst and NiW/ASA-Al<sub>2</sub>O<sub>3</sub> were used as the first and second layers in a stacked bed to approximate conditions in laboratory unit to industrial ones. NiMo/Al<sub>2</sub>O<sub>3</sub> was prepared using similar impregnation solution but without calcination after drying at 120 °C [41]. Ni and Mo content in NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst was 3.7 and 12.5 wt% respectively. NiW/ASA-Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by impregnation with the aqueous solution prepared from nickel carbonate, ammonium paratungstate and citric acid followed by subsequent drying at 120 °C and calcination at 550 °C [42]. Ni and W content in NiW/ASA-Al<sub>2</sub>O<sub>3</sub> catalyst was 3.1 and 17.4 wt% respectively.

### 2.2. Characterization

Elemental analysis of the catalysts was carried out using the method of atomic emission spectroscopy with inductively coupled plasma (ICP-AES) on Optima 4300 DV.

Low temperature adsorption-desorption of N<sub>2</sub> for zeolites was measured at 77 K using an automated porosimeter (ASAP 2000 Micromeritics). The BET method was applied to calculate the total surface area, which was used for comparative purposes. The t-plot method was used for determination of microporosity. The total sorbed volumes, including adsorption in the micropores and mesopores, were calculated from the amount of nitrogen adsorbed at a relative pressure  $P/P_0$  of 0.95, before the onset of interparticle condensation. Pore size distribution was calculated by BJH method using the adsorption branch of the isotherm.

Textural properties of the catalysts and supports were determined by nitrogen physisorption using an ASAP 2400 Micromeritics instrument.

HRTEM images were obtained on a JEM-2010 electron microscope (JEOL) with a lattice-fringe resolution of 0.14 nm and operated at an accelerating voltage of 200 kV. The high-resolution images of periodic structures were analyzed by the Fourier method. Samples to be examined by HRTEM were prepared on a perforated carbon film mounted on a copper grid.

Temperature programmed desorption of ammonia (TPD-NH<sub>3</sub>) was performed on chemisorption analyzer USGA-101 (production of UNISIT Ltd., Russia) equipped with TC detector.

Surface acid sites of the zeolites were characterized by IR spectroscopy of adsorbed carbon monoxide. IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer within the spectral range of 700–6000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> and 500 scans for signal accumulation. The powder samples were pressed into thin self-supporting wafers (0.004–0.006 g/cm<sup>2</sup>) and activated in the special IR cell at 773 K for 2 h in dynamic vacuum of 10<sup>-3</sup> mbar. CO was introduced at liquid nitrogen temperature by doses up to an equilibrium pressure of 13 mbar. The strength of Brønsted acid sites (BAS) was estimated by the method of hydrogen bonds based on the change in the stretching vibration frequency of the OH groups that occurred under CO adsorption. The higher the shift of IR band of OH stretching vibration of the hydroxyl groups ( $\Delta\nu_{\text{OH}}^{\text{OH}\cdots\text{CO}}$ ), the stronger is the acidity of OH group.

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