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Catalysts based on amorphous aluminosilicates for selective hydrotreating of FCC gasoline to produce Euro-5 gasoline with minimum octane number loss

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ABSTRACT

The method for preparation of Co–Mo catalysts for one-stage hydrotreating of full FCC gasoline fraction is proposed. The main characteristic of the catalysts is the use of the supports based on amorphous aluminosilicate. Catalysts were characterized with nitrogen adsorption-desorption, HRTEM and XPS methods. It was shown that all catalysts containing aluminosilicates have similar textural characteristics and contain Co-Mo-S phase with similar morphology. The IR CO data indicate that sulfided catalysts contain different acid sites with the predominance of weak Lewis acid sites and Brønsted acid sites with the strength of 1190 kJ/mol. Catalysts were tested in hydrotreating of model fuel and full FCC gasoline fraction. It was shown that presence of amorphous aluminosilicates in catalysts results in the increase of catalytic activity in reactions of olefin isomerisation. Significant contribution of olefin isomerization reactions results in the prevention of octane number loss while high activity hydrodesulfurisation maintains.

1. Introduction

Nowadays the refining industry has a smooth pass to the production of gasoline that meets European quality standard Euro-5. According to this standard, sulfur content in gasoline has to be less than 10 ppm [1,2]. One of the main challenges facing the production of commercial gasoline is hydrotreating of catalytic cracking gasoline. FCC gasoline is one of the main components of blending gasoline. It is characterized by high sulfur content (150–3500 ppm) and high octane number (RON = 92–93 points) [2,3]. Hydrotreating of full FCC gasoline fraction results in inevitable octane number loss because of the hydrogenation of unsaturated high-octane compounds. Maximum permissible octane number loss after hydrotreating has not to exceed 1,5 point. Otherwise hydrotreated FCC gasoline is unfit for production of commercial gasoline with octane number more than 95.

There are many industrial processes for selective FCC gasoline hydrotreating [4,5]. These processes are based on previous rectification of full FCC gasoline fraction to light (with high olefin content) and heavy (high sulfur content) fractions followed by separate hydrotreating and blending [6]. However such processes are technologically complicated and require large energy consumptions.

Alternative way is a developing of selective hydrotreating catalyst of full FCC gasoline fraction. It permits the process to be carried out on traditional units for gasoline hydrotreatment. Currently there is no method of selective hydrotreating catalysts for hydrotreating of full FCC gasoline fraction without previous fractionating that provides to obtain gasoline with sulfur content less than 10 ppm with octane number loss less than 1,5 point.

Traditionally hydrotreating catalysts are Co(Ni)–Mo(W) systems supported on γ-Al_2O_3 and modified by different agents. The active component of these catalysts is Co-Mo-S phase. Its structure is well studied and described elsewhere [7,8]. The main problem of such catalysts is that the same active sites are responsible for reactions of hydrodesulfurisation (HDS) of sulfur compounds and undesirable hydrogenation (HYD) of high octane olefins [9–11]. Introduction of different additives that inhibit catalytic activity in hydrogenation usually leads to simultaneous decrease in HDS activity. Therefore such catalysts are typically accompanied by catalytic systems to restore octane number, e.g [12].

To increase catalyst selectivity, it is necessary to create active sites that are different from Co–Mo–S phase. The presence of these sites should promote HDS of sulfur components and isomerisation

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reactions of high-octane olefins and products of their hydrogenation into low-reactive components with high octane numbers. Formation of new acid sites can be achieved by introduction of amorphous aluminosilicate into support. Addition of amorphous alumosilicate into support is expected to result in the following effects: 1. the increase of cracking reactivity of catalyst will lead to the increase of catalyst HDS activity; 2. the presence of sites with high isomerisation activity will result in conversion of high-octane high-reactive olefins into high-octane less-reactive derivatives.

In present work Co–Mo catalysts based on amorphous aluminosilicate supports were studied. Influence of Si/(Si + Al) = 0.1, 0.15, 0.2, 0.5 ratios in initial amorphous aluminosilicate powders on catalytic activity and selectivity of the catalysts were studied. Finally the catalyst with high activity in HDS and isomerisation of olefins is defined. The catalyst ensures the production of hydrotreated FCC gasoline with less than 10 ppm of sulfur and minimum octane loss (<1,5 point).

2. Experimental

2.1. Preparation of supports

Initial amorphous aluminosilicate powders (hereinafter ASA) with ratios Si/(Si + Al) = 0.1, 0.15, 0.2, 0.5 were prepared by coprecipitation of aluminum sulfate and sodium silicate. Supports were prepared by extrusion of paste containing ASA and boehmite (Sasol, Germany GmbH) powders. Boehmite was used as a binding agent to form trilobe extrudates. Several supports differed in aluminosilicate were prepared to define the influence of Si content on catalyst activity and selectivity. Also two supports with Si/(Si + Al) = 0.2 were prepared with different ratio of aluminosilicate/boehmite equal to 90/10 and 70/30 to define the influence of ASA content. Supports were designated as ASA = Si/(Si + Al)(ASA/Al_2O_3). For example, the support with Si/(Si + Al) = 0.2 in initial ASA powder and ASA/boehmite = 90/10 is designated as ASA = 0.2(90/10) in the text.

2.2. Preparation of supported CoMo catalysts

Catalysts were prepared by impregnation of the supports with the solution containing ammonium heptamolibdate $NH_4Mo_7O_{24}·4H_2O$ and cobalt nitrate $Co(NO_3)·6H_2O$ followed by drying at 120 °C and calcination at 550 °C. Content of active metals in final catalyst was the following: Mo –3.3 ± 0.3% and Co –0.7 ± 0.1%. Low active metal content is based on several factors. First of all, it is well known that Co–Mo–S phase has high activity in HDS and HYD reactions. Therefore it is necessary to decrease its content in catalysts. Another factor is that composition of the support plays an important role. It can be suggested that if the support contains silica and alumina, active component will preferably localize on alumina than on silica due to stronger interactions. Thus, if we use low amounts of binding agent (10–30% wt.), it will be necessary to decrease active component content to avoid formation of massive structures of active component and to obtain high dispersed active component in catalyst composition. Typical content of active component in HDS catalysts of gasoline is about 10% of Mo and 3% Co. Content of alumina in the support is 30%. Therefore content of Mo was chosen to be about 3%. Catalysts based on ASA are designated as CoMo-ASA = Si/Al(ASA/Al_2O_3). Amorphous aluminosilicate powders, supports and catalysts were studied by HRTEM, nitrogen adsorption, chemical analysis, IR CO adsorption and XPS.

CoMo/γ-Al_2O_3 catalyst was used as a model pattern. To prepare γ-Al_2O_3 for the model pattern, boehmite Pural SB (Sasol GmbH, Germany) was used.

2.3. Sulfiding and testing in HDS

Catalysts were crushed to a particle size 0.25–0.5 mm and sulfided at atmospheric pressure in H_2S flow (500 h^{-1}). Sulfiding was carried out in two steps −2 h at 200 °C and 2 h at 400 °C.

All catalysts were tested in hydrotreating of model fuel. The most selective and active catalyst was tested in hydrotreating of real FCC gasoline produced by OAO Gazprom Neft—Moscow refinery.

Hydrotreating of model feed was carried out in a fixed bed reactor in the following conditions: LHSV = 10.0 h^{-1}, T = 220–260°C, P = 2.5 MPa, nm^3 H_2/m^3 feed = 200. The composition of model feed was the following: thiophene – 250 ppm in terms of S, toluene −40%, cyclohexane −40%, 1-hexene −20%. In such conditions the weight liquid product output was 94–98%. Composition of gas and liquid products was analyzed using fused silica column St® series of Chromos.

Hydrotreating of real FCC gasoline (produced by OAO Gazproneft-Moscow refinery) was carried out in the following conditions: LHSV = 2.2 h^{-1}, T = 260–280 °C, P = 2.5 MPa, H_2 nm^3/feed m^3 = 150. Characteristics of the feed are the following: sulfur content −130 ppm, RON = 93.0, MON = 80.5. Composition of gas and liquid products was analyzed using chromatographic analyzer Arnel 4050 (PerkinElmer Clarus 580) equipped with capillary column Rtx-DHA.

2.4. Characterisation techniques

2.4.1. XPS

Photoelectron spectra were recorded using SPECS spectrometer with PHOIBOS-150 hemispherical energy analyzer and AlKα irradiation (hν = 1486.6 eV, 200 W). Binding energy scale was preliminarily calibrated by the position of the peaks of Au4$f_{7/2}$ (84.0 eV) and Cu2$p_{3/2}$ (932.67 eV) core levels. For spectra recording the samples were supported on conductive scotch tape. The method of the internal standard was used for correct calibration of photoelectron peaks. For this peak of C1s with E_b = 284.8 eV was used.

To obtain correct atomic ratios of Si and Al, decomposition of overlapped Si2p and Al KLL peaks were made by XPS Peak 4.1 programm. Intergral intensity of Si2p line and, respectively, Si/Al was defined.

2.4.2. HRTEM

HRTEM images were obtained on a JEM-2010 electron microscope (JEOL, Japan) with a lattice-fringe resolution of 0.14 nm at an accelerating voltage of 200 kV. Local energy-dispersive X-ray analysis (EDXA) was carried out on an EDAX spectrometer (EDAX Co.) fitted with a Si (Li) detector with a resolution of 130 eV. Samples to be examined by HRTEM were prepared on a perforated carbon film mounted on a copper grid. The size of MoS_2 particles and the average number of layers in the package were determined using four different fragments of the sample under study, a total number of characterized particles being equal to 500.

2.4.3. Nitrogen adsorption-desorption

Textural properties of the catalysts and supports were determined by nitrogen physisorption using an ASAP 2400 (USA) instrument. Prior to analysis, samples were heated under flowing N_2 at 200 °C for 2 h. BET surface areas were calculated from the amount of nitrogen uptaken at relative pressures that ranged from 0.05 to 0.30. The total pore volume was derived from the amount of nitrogen adsorbed at a relative pressure close to unity (in practice, P/Po = 0.995) under the assumption that all of the accessible pores had been filled with condensed nitrogen in the normal liquid