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Amorphous silica-alumina – perspective supports for selective hydrotreating of FCC gasoline: Influence of Mg

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ABSTRACT

CoMo/Al₂O₃-ASA catalysts with Mg were synthesized. Catalysts differed in the way of Mg addition: 1. Mg was added to ASA, 2. Mg was added to the kneading paste during the support preparation, 3. Mg was added before or after Co and Mo by the impregnation. Catalysts were characterized by the following techniques: low-temperature N₂ adsorption, IR of CO and CO₂ adsorption, X-ray photoelectron spectroscopy, high-resolution transmission electron microscopy. Synthesized catalysts were tested in hydrotreating of the model fluid catalytic cracking gasoline containing 250 ppm of sulfur from thiophene, 40 wt.% of toluene, 40 wt.% of heptane and 20 wt.% of *n*-hexene-1. It was found that the addition of Mg resulted in changes of physico-chemical properties of catalysts and their HDS and HYD activities. The way of Mg addition influenced the content of Lewis and Brønsted acid sites and morphology of sulfide active component. Mg increased HDS activity and decreased octane number loss. The catalysts with Mg in the kneading paste of the support and with Mg added after active metals showed the best combination of HDS activity and selectivity.

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1. Introduction

Catalytic cracking of heavy oil distillates refers to the processes that contribute 30–50% of gasoline to gasoline pool [1]. Fluid catalytic cracking gasoline (FCC gasoline) contains 20–40 wt.% of olefins, which provide a high octane number (up to 92 points). However, FCC gasoline is generally responsible for more than 90% of the sulfur compounds in the engine gasoline. The urgent demand to reduce exhaust emissions from gasoline-powered motor vehicles makes it necessary to control the sulfur content in gasoline.

Hydrotreating is the main process to decrease sulfur content in oil distillates. Since the initial research octane number of FCC gasolines does not usually exceed 93 points, it is possible to admit the decrease in the octane number during hydrotreating by less than 1–2 points. Otherwise, hydrotreated FCC gasoline is not suitable for obtaining commercial gasoline with a research octane number of at least 95. There are different variations of hydrotreating process for selective hydrotreating of FCC gasoline. They are based on separate desulfurization of light and heavy gasoline fractions. Many of these processes are technologically complex and power-consuming. On

the other hand, hydrotreating of FCC gasoline without previous fractionation results in the octane number decrease by at least 2 points. The main reason for the octane number decrease is the use of non-selective catalysts, which along with the desired desulfurization reactions of sulfur containing compounds catalyze undesirable hydrogenation reactions of high octane olefins. Therefore, there is an urgency for new catalysts characterized by increased activity in hydrogenolysis reactions of sulfur-containing compounds, with minimal activity in the hydrogenation of high-octane olefins. Therefore, the search of new solutions, such as development of new selective catalytic systems, plays an important role in the production of ultra-low sulfur gasoline.

Currently, a large amount of scientific information on the composition and structure of the sulfide active component of hydrotreating catalysts has been accumulated. In accordance with generally accepted concepts, the active component of hydrotreating catalysts comprises molybdenum sulfide particles decorated with cobalt atoms [2]. The main difference between the sulfide active component in the catalysts for the hydrotreating of FCC gasoline from hydrotreating catalysts of other fractions is its selectivity, expressed in the ratio of the rates of target hydrogenolysis reactions of sulfur-containing compounds and undesired reactions of olefin hydrogenation. The degree of the saturation of olefins during hydrotreating of FCC gasoline over selective and unselective cat-

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alysts at equal desulfurisation degree can differ up to 4 times [3]. A number of studies have shown [4–6] that the selectivity of catalysts in hydrogenation reactions is almost completely determined by the properties of the sulfide active component and depends little on the nature of the support. The selectivity of the cobalt (nickel)-molybdenum (tungsten) hydrotreating catalysts without modifying agents is influenced by three parameters: a) atomic ratios of Co/Mo or Co/Mo/W in the sulfide active component [3,7]; b) concentration of active component in the catalyst [8]; c) the dispersion of the active component, which is determined by the linear dimensions of its particles and the stacking number of the CoMoS phase [5,9,10].

However, other studies have shown that the addition of modifying additives to the catalyst allows one to influence the properties of the active phase or directly affect the activity of the catalyst in certain reactions. Thus, the catalysts with amorphous silica-alumina (ASA) supports were shown to have high selectivity in hydrotreating of FCC gasoline [11,12]. High isomerization activity of high-reactive high-octane olefins into low-reactive high-octane derivatives provided high selectivity of these catalysts. However, the use of ASA in supports of hydrotreating catalysts has some disadvantages, for example, sufficiently low mechanical strength, that makes it necessary to use binding agent. Moreover, increase of ASA content in the catalyst will inevitably increase the cost. Therefore, the question arises whether it is possible to increase the selectivity of the catalysts based on amorphous silica-alumina?

In order to increase the selectivity of catalysts for the hydrotreating of FCC gasolines, in particular to suppress undesirable reactions of hydrogenation of high-octane olefins, catalysts are modified by various acidic or alkaline components. Alkali metal compounds – sodium, potassium and magnesium, are most often used. A number of studies have not revealed a clear effect of modifying alkaline additives on the state of metals in the composition of the active component [4,5,10], but only an indirect effect on the morphology of the CoMoS particles is shown, which is more dependent on other factors. It was shown in [13] that the addition of Na additive to the catalyst composition resulted in a strong decrease in both the hydrogenating and desulfurization activities that was not favorable for the FCC hydrotreating catalysts. On the contrary, it was shown in [14], that when potassium was introduced into CoMo catalysts based on Al_2O_3 or hydrotalcite, there was a slight decrease in desulfurizing activity and a sharp decrease in hydrogenating activity and a proportional increase in a selectivity factor. The introduction of 2.7 wt.% K into the industrial CoMo/ Al_2O_3 catalyst HR306 results in a sharp increase in the selectivity of the hydrotreating, but the desulfurization activity was somewhat reduced [15]. Thus, the data published in the literature suggest that the modification of CoMo/ Al_2O_3 by alkaline additives slightly increases the selectivity of the catalysts for the hydrotreating of FCC gasoline. However, they almost always reduce the desulfurization activity. The main reason is that addition of alkali metals have slight positive effect on electronic properties of the active component or, on the contrary, blocks sites of desulfurization [16,17]. The effect on the support consists in changing the acid properties of the already formed surface, and practically does not affect the structure of the support itself. Consequently, when modifying the support or the catalyst with alkali metal compounds, one should not expect a sharp positive effect, ultimately resulting in the preservation of the octane number of FCC gasolines during their hydrotreating. A much greater positive effect should be given either to the use of components that radically alter the structure of the support, or to use additives that already have a structure. Mg compounds, whose introduction into the support can result in the formation of surface spinel-like structures, are promising as such additives. The structure and acid properties of Mg spinel-like structures differ fundamentally from the properties

of alumina, and, at the same time, they remain in the composition of granular supports and catalysts.

The use of Mg hydrotalcites as components of a composite support (Al_2O_3 /hydrotalcite weight ratio = 1/3) in Co-Mo FCC hydrotreating catalysts is described in [14]. The authors found that although hydrotalcite-based catalysts are somewhat inferior in hydrodesulfurization activity to the catalyst based on Al_2O_3 , they are characterized by high selectivity and, as a consequence, greater preservation of the octane number. This allows us to consider hydrotalcites as promising components in the preparation of supports for selective hydrotreating catalysts. However, the preparation of supports generally includes a calcination step at a temperature of about 550°C. At this temperature, hydrotalcite decomposes to form mixed aluminas and, for example, magnesium. Accordingly, it is possible that the support, and further a catalyst with similar properties, can be obtained from other Mg and Al compounds, excluding the synthesis stage of the hydrotalcite itself. In addition, the introduction of Mg compounds to a support or catalyst based on alumina or amorphous aluminosilicate can result in the formation of hydrotalcites and at the same time have a positive effect on the structural and catalytic characteristics of the support and the catalyst as a whole. On top of that several patents recommended the use of MgO-supported catalysts for the selective HDS of FCC gasoline [18,19]. It is believed that Mg forms sites with their own acid-base properties that changes morphology of active component and, therefore increases proportion of hydrodesulfurization sites to hydrogenation one [20]. Among these, catalysts containing Mg in their composition, besides the conventional CoMo components, were found to be promising for preparation of hydrotreating catalysts of FCC gasoline. However, most works, which are devoted to the influence of Mg, refer to CoMo/ Al_2O_3 -MgO. Influence of Mg on catalysts with silica containing supports is not present in the literature.

In this investigation, we attempted to increase selectivity of CoMo/ASA- Al_2O_3 catalysts for FCC gasoline selective HDS, investigated the physicochemical properties of catalysts with Mg and the selective HDS performance thereof, and presented a reasonable explanation for the enhancement of HDS selectivity.

2. Experimental

2.1. Preparation of supports and catalysts

Initial amorphous silica-alumina powder (hereinafter ASA) with ratio $\text{Si}/(\text{Si} + \text{Al}) = 0.5$ was prepared as it was described in [21]. 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. Ratio of aluminosilicate/boehmite was 70/30.

Catalysts were prepared by impregnation of the supports with the solution containing ammonium heptamolibdate $\text{NH}_4\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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 wt. % and Co – 0.7 ± 0.1 wt. %. Co to Mo ratio is 0.2 in the catalysts.

Mg was added at different stages: 1. during preparation of ASA; 2. during preparation of the kneading paste of the support; 3. before the impregnation of the support by Co and Mo compounds (by the impregnation of the support with $\text{Mg}(\text{NO}_3)_2$ solution followed by drying and calcination); 4. after the impregnation of the support by Co and Mo compounds (by impregnation of the support with $\text{Mg}(\text{NO}_3)_2$ solution followed by drying and calcination). Mg content was about 1 wt.% in all the samples.

Also, CoMo/ASA- Al_2O_3 without Mg were prepared for comparison.

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