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ABOUT HYDROCLEANING CATALYSTS

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ANNOTATION

Under hydrotreating conditions, the temperature, partial pressure of hydrogen and hydrogen sulfide are critical for maintaining the catalyst in sulfide form. It was found that molybdenum disulfide and mixed nickel sulfide have the highest activity.

Keywords: alumo-cobalt-molybdenum, breaking ties, catalyst

INTRODUCTION

In the processes of hydrotreating various petroleum fractions and products, any sulfur-resistant hydrogenation catalysts can be used, in particular, combinations of oxides and sulfides of cobalt (or nickel) with oxides and sulfides of molybdenum or tungsten, namely cobalt (or nickel) molybdates, nickel sulfate tungstates, and etc.

Alumo-cobalt-molybdenum (ACM) and aluminum-nickel-molybdenum (ANM) catalysts meet these requirements. In some cases, an aluminum-nickel-molybdenum silicate catalyst (ANMS) is also used.

All of these catalysts have high mechanical strength, resistance to poisons, and remain active for a long time. In catalysts, an important role is played not only by the content of active components, but also by the ratio of metals in them. So, in the catalyst

AKM the most effective ratio of the content of cobalt and molybdenum is 1: 5; it ensures its maximum activity in hydrodesulfurization reactions.

Such a catalyst has a very high selectivity, and the reactions of hydrocracking of C-C bonds or saturation of aromatic rings in its presence practically do not occur. In addition, it is practically insensitive to poisons, which are usually found in processed raw materials. Moreover, it is even preliminarily sulfided, and according to a number of data, this ensures its good performance in the hydrotreating system.

This catalyst has acceptable activity in the reactions of saturation of unsaturated compounds, cleavage of C - N, C - O bonds and is practically used in the hydrotreating of all petroleum fractions and products, with the exception of heavy petroleum residues. The active constituents of the catalyst are those that form octaeric oxide ions, i.e. CoO, CoMoO4 and "complex". It was found that the Co_2 + ion is evenly distributed between the tetrahedral and octahedral forms.

Another mass catalyst for hydrotreating is an aluminum-nickel-molybdenum catalyst (ANM). In terms of its activity, it is practically equivalent to ACM in the purification of distillates, but it is preferable for the purification of raw materials with an increased content of nitrogenous compounds and polycyclic aromatic hydrocarbons. In addition, it is 25% cheaper than the AKM catalyst and, when hydrotreating light fractions, allows the process to be carried out at a temperature 10-20 ° C lower than AKM.

In hydrotreating conditions, the temperature, partial pressure of hydrogen and hydrogen sulfide are critical for maintaining the catalyst in sulfide form. It was found that molybdenum disulfide and mixed nickel sulfide (NiS and NiS_2) have the highest activity.

The ANM catalyst requires preliminary sulfurization, while this requirement is optional for the AKM catalyst. During operation, a lot of coke, sulfur and metals are deposited on the catalyst - 7-20, respectively; 0.5-1.5 and 12-25% by weight of the catalyst. At the same time, it loses its activity, and the degree of desulfurization of products during its use decreases - normal aging of the catalyst occurs. The main sign of a drop in catalyst activity is an increase in the sulfur content in the hydrotreated product.

Hydrotreating catalysts are quite stable in oxidizing or reducing environments up to 550-600 ° C, however, prolonged exposure to the same conditions in an atmosphere of water vapor can lead to a decrease in its activity and strength. This reduces the active surface of the aluminum oxide and partly increases the volatility of the molybdenum oxide. Hydrotreating catalysts reduce activity mainly as a result of coke deposition in their pores, therefore, regeneration is carried out by burning out coke.

In the CIS countries, almost all ammonia and syngas (methanol) production units with a hydrosulfur treatment unit use the Co-Mo / Al_2O_3 catalysts AKM and GO-70 / Ryazan Refinery and foreign (S-49-1 / CCI, 41 -6 / ICI) productions.

Recently, nickel-molybdenum alumina catalysts have been increasingly used as catalysts for hydrotreating and hydrocracking processes. These catalysts are complex chemical systems, so the approach to their synthesis remains largely empirical.

The alumina-nickel-molybdenum catalyst, in comparison with the alumo-cobalt-molybdenum catalyst, has a higher activity by (15–20%) and a more developed (1.3–1.5 times) specific surface area. An important advantage is the absence of expensive and scarce cobalt in it, as a result of which the cost is 25% lower than the aluminum-cobalt-molybdenum catalyst.

Replacing expensive cobalt with nickel provides great savings in the production of the hydrogenation catalyst.

At JSC "Maxam Chirchik" studies were carried out to develop technologies for an aluminum-nickel-molybdenum catalyst based on cheap local raw materials - bentonite clays and reprecipitated aluminum hydroxide under production conditions in the catalyst shop and tested on a pilot plant in the methane conversion shop in the desulfurization department (AM-1). The tests have shown positive results. The production technology consists of the following stages:

- preparation of ammonium vapor molybdate solution with mass concentration (450-478) g / dm^3;

- preparation of a solution of nickel nitrate with mass concentration (689-799) g / dm^3;
- Moving the reprecipitated Al (OH) $_3$ with solutions
- Ferrous ammonium molybdate and nickel nitrate;
- Molding the catalyst mass in the form of extrudates, drying at 40-50 ℃ and calcining at 460-500 ℃ with a stepwise increase in temperature.

According to the developed technology, 17 tons of aluminum-nickel-lubdenum catalyst were produced.

Temperature ℃	Volumetric velocity	TG550 catalyst	AKM catalyst (Maxam-Chirchik)
300	300	90-93	92,0-94,0

The activity was determined on a microcatalytic unit according to the OST 3801130-77 method and compared with the activity of the TK-550 catalyst from Koldor Topsoe (Denmark). The activity of the catalyst is not inferior to the best world catalyst degree of butyl mercant conversion, s / o Table 1

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