Influence of the Nature of Molybdenum Compounds on the Activity of Mo/γ-Al₂O₃ and NiMo/γ-Al₂O₃ Hydrotreating Catalysts

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Abstract—The influence of the nature of molybdenum compounds on the catalytic activity of sulfided NiMo/γ-Al₂O₃ catalysts was studied. The samples were prepared by impregnating the support with mixed aqueous solutions of nickel nitrate and molybdenum-containing compounds: ammonium paramolybdate and the 6-series heteropoly compounds (HPCs) ammonium molybdonickelate and ammonium molybdenum phosphomolybdate. Complexing agents (tartaric acid or a solution of NH₃) were used for stabilizing mixed aqueous ammonium paramolybdate and nickel nitrate solutions and for simultaneously producing an acidic or alkaline medium. The starting molybdenum compounds and catalysts in the oxide form were characterized using IR spectroscopy and X-ray diffraction analysis. The activity of catalysts based on NiMo/γ-HPC in the hydrodenitrogenation of thiophene and in the hydrotreating of the diesel fraction was higher than that of catalysts based on ammonium paramolybdate: at 320°C, the degree of sulfur removal from the diesel fraction was higher by 13–16% and the average degree of hydrogenation of polycyclic aromatic hydrocarbons was higher by 14–15%. It was also found that the use of AlMo₆-HPC does not cause such an effect.

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INTRODUCTION

Hydrotreating catalysts always contain cobalt or nickel oxide as a promoter in addition to molybdenum or tungsten oxide; the mixed oxide phase, which is most often supported on γ-Al₂O₃, is converted into a sulfide phase during the necessary stage of sulfiding. In many studies, it has been reliably found [1] that the activity of promoted sulfide catalysts is related to the occurrence of a phase like CoMoS on the catalyst surface; this implies the occurrence of a CoO(NiO)–MoO₃(WO₃) mixed phase in the oxide precursor. It has not been ascertained what procedure for the synthesis of this oxide phase affords the maximum activity of the resulting catalysts in the hydrogenolysis of sulfur-containing compounds and the hydrogenation of aromatic compounds. Undoubtedly, the specific properties of this phase, as well as the preparation procedure, are mainly responsible for the properties of the sulfide phase. However, studies of the oxide precursor of the active phase or the procedure of the production of this phase on the support surface are of lesser interest than a comparison between the results of these studies and catalytic activity.

Catalysts of the NiMo/γ-Al₂O₃ type can be synthesized in several ways. The procedure in which a support (for example, γ-Al₂O₃) is impregnated with a mixed aqueous solution of molybdenum and nickel compounds, dried, and calcined is of the greatest interest. In this case, as mentioned above, the desired molecular contact between nickel and molybdenum compounds takes place at all of the stages of the catalyst synthesis. However, the mixed neutral aqueous solution of ammonium paramolybdate and nickel nitrate is unstable; various precipitates are formed from this solution depending on pH. Various compounds are added to stabilize the mixed aqueous solution; phosphoric acid is most frequently used in industrial practice [2–8]. After calcination, phosphorus compounds remain as catalyst constituents to affect catalytic activity.

We formulated the problem of studying the effect of the composition of a mixed impregnating solution of molybdenum and nickel compounds on the catalytic activity of sulfided NiMo/γ-Al₂O₃ catalysts. To stabilize the mixed aqueous solutions of ammonium paramolybdate and nickel nitrate and simultaneously produce an acidic or alkaline medium, we used compounds that did not change the catalyst composition. Tartaric acid and an ammonia solution were used as these compounds. The mixed solutions were stabilized by binding the Ni²⁺ ion in a complex with tartaric acid or an ammonia complex, respectively; this complexation prevented the formation of insoluble compounds of this cation and molybdenum-containing anions. In addition to ammonium paramolybdate, the following molybdenum 6-series heteropoly compounds (HPCs) were also used for the synthesis of catalysts: ammonium molybdonickelate and ammonium molybdoaluminate. Thus, the component compositions of all of the...
synthesized catalysts were the same: they contained either MoO₃ and Al₂O₃ or MoO₃, NiO, and Al₂O₃. The catalysts differed only in the molybdenum compounds used for the preparation of the mixed impregnating solution. This allowed us to study the effect of starting molybdenum compounds on the activity of catalysts in the hydrogenolysis of thiophene and in the hydrotreating of the diesel fraction.

**EXPERIMENTAL**

The following two series of catalysts were synthesized: Mo/γ-Al₂O₃ (series I) and NiMo/γ-Al₂O₃ (series II). γ-Al₂O₃, which was prepared from commercial aluminum hydroxide manufactured from sulfate by continuous precipitation, extrusion molding, drying, and calcination, was used as a support [9, 10]. The texture characteristics of the resulting alumina were determined from nitrogen adsorption at 77 K on a Micromeritics ASAP 2020 adsorption porosimeter. The specific surface area was calculated using the BET method at a relative partial pressure of P/P₀ = 0.2. The total pore volume and pore size distribution were determined from an adsorption curve using the Barrett–Joiner–Halenda model at a relative partial pressure of P/P₀ = 0.99. The specific surface area was 315 m²/g, and the apparent pore diameter was 110 Å. The catalysts were prepared by the incipient wetness impregnation of γ-Al₂O₃ with a particle size of 0.25–0.50 mm.

The ammonium salts of 6-molybdonickelic (NH₄)₆[Ni(OH)₆]Mo₆O₁₈·nH₂O (NiMo₆-HPC) and 6-molybdooaluminic (AlMo₆-HPC) heteropoly acids were synthesized in accordance with published procedures [11, 12]. The IR spectra of crystalline NiMo₆-HPC, AlMo₆-HPC, and ammonium paramolybdate samples, which were predried at 110°C and pelletized with KBr, were recorded on an Avatar-360 (FTIR) instrument (Fig. 1). The phase composition of the synthesized HPCs and catalysts was determined on a DRON-2 x-ray diffractometer (CuKα radiation).

Aqueous solutions of the following molybdenum compounds were used to prepare catalysts from series I: ammonium paramolybdate (reagent grade) in the presence of a solution of NH₃-I, ammonium paramolybdate and tartaric acid (I-2), NiMo₆-HPC (I-3), and AlMo₆-HPC (I-4). Mixed aqueous solutions of the above molybdenum compounds and nickel nitrate hexahydrate Ni(NO₃)₂·6H₂O (analytical grade) were used to prepare catalysts from series II (II-5 to II-8). A solution of NH₃ (catalyst II-5) and tartaric acid (catalyst II-6) were used to stabilize the mixed solution of ammonium paramolybdate and nickel nitrate. The samples were dried at 80, 100, and 120°C and calcined at 400°C for 2 h. Before testing, the catalysts were sulfidized: impregnated with di-tert-butyl polysulfide taken in a stoichiometric ratio of S/(Mo + Ni) = 1 and heated at 350°C in an atmosphere of hydrogen (5 l/h) for 2 h. Optimum sulfidization parameters were chosen previously [13]. Table 1 summarizes the conditions of the synthesis and the concentrations of active components and active sulfur in the prepared catalysts before and after testing in a flow unit.

The catalytic activities of all of the samples in the hydrogenolysis of thiophene were determined in a pulse microcatalytic system over the temperature range of 300–400°C at a step of 20 K. The catalyst weight was 25 mg, and the volume of thiophene was 0.2 µl. The reaction products were separated on an OV-101 fused-silica capillary column. The UniChrom software was used in the recording and processing of the chromatograms.

Catalysts from series II were tested in a hydrodesulfurization process in a laboratory flow system at the pressure of hydrogen. The system contained units for specifying, maintaining, and controlling the temperature, pressure, and hydrogen-containing gas and feed flow rates. The reactor temperature, pressure, and feed hydrogen flow rates were maintained to within ±2 K, ±0.05 MPa, ±0.2 ml/h, and 0.2 l/h, respectively. A mixture of 50 vol % straight-run diesel fraction and 50 vol % catalytic cracking light gas oil was used as the feed in the hydrotreating process. The composition of the chosen model feed is close to that of feeds actually used at petroleum refineries; thus, the catalytic tests were performed under severe conditions because cata-