



Activity and sulfidation behavior of the CoMo/Al₂O₃ hydrotreating catalyst: The effect of drying conditions

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ABSTRACT

The influence of drying condition of the CoMo/Al₂O₃ catalyst prepared using citric acid as a chelating agent on the sulfidation behavior and on the catalytic activity to hydrodesulfurization of straight-run gas oil (SRGO) was investigated. The catalysts dried at 110, 220, 300 and 400 °C were studied using Raman, IRS and DTG techniques. The sulfidation behavior with straight-run gas oil spiked with dimethylsulfide (DMDS) was investigated using gas chromatography (GC) with a thermal conductivity detector and GC with an atomic-emission detector for analysis of gas and the liquid phases, respectively. It was shown that the sulfidation behavior of the catalysts prepared using the chelating agents depends on the drying condition: the lower drying temperature, the later DMDS conversion and oxide precursor sulfidation starts. A higher activity in SRGO desulfurization was obtained with catalysts dried at 110 and 220 °C. This phenomenon was accounted for by the stabilization effect of chelating agent that retards precursor sulfiding but provides favorably the formation of active CoMoS phase and achieving the highest activity.

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1. Introduction

The ever toughening standards on the content of harmful compounds in exhaust gases of motor vehicles make it necessary to effectuate new specifications for motor fuels. Since 2005 the European fuel regulations require the maximum diesel sulfur content of 50 ppm and require no more than 10 ppm of sulfur after January 1, 2009 [1]. In Russia, the EURO-3 standards (350 ppm of sulfur) came into force on January 1, 2009 and EURO-4 (50 ppm of sulfur) will be put in force on January 1, 2012 [2]. The production of fuel to meet these regulations will need new effective hydrotreatment catalysts.

The conventional catalysts for hydrodesulfurization of diesel fractions are the Co–Mo/Al₂O₃ and Ni–Mo/Al₂O₃ sulfide systems. It is well accepted that the active component of hydrotreatment catalysts comprises nanosized MoS₂ particles with cobalt or nickel atoms decorated their edges and corners; the particles form the so-called Co(Ni)–Mo–S phase [3–11]. Two types of the Co(Ni)–Mo–S phase are described in the literature. The Co(Ni)–Mo–S phase of type I is characterized by the strong interaction with the support due to the formation of Mo–Al–O bonds and by low degree of

sulfidizing. In the Co(Ni)–Mo–S phase of type II, the particles are fully sulfidized and only Van der Waals forces hold them on the support surface [4–7,9], the specific activity (per number of Co atoms in the Co–Mo–S phase) of type II phase being considerably higher than the activity of type I [4,10]. The modern catalysts for fine hydrotreatment of diesel fuel are very efficient due to high concentrations of the active components (a disperse Co(Ni)–Mo–S phase of type II) on the alumina surface [11].

Among the methods to form preferably active type II Co(Ni)–Mo–S phase on the support surface is supporting the active components from solutions containing chelate agents [9,12–30]. There are numerous examples reported in the literature on improving the activity of Co(Ni)Mo sulfide catalysts using chelating ligands: nitrilotriacetic, ethylenediaminetetraacetic and cyclohexanediaminetetraacetic acids [9,12–24], citric [24–28] and thioglycolic acids [29,30].

In opinion of some researchers, chelating additives favor the dispersion of active components through the support surface [14–17], diminish the interaction of the active component (Mo) and promoter (Co) with the support to form the type II active sulfide phase [10,18–20]. In addition, in the presence of chelate ligands, sulfidation of Co(Ni) starts at a higher temperature simultaneously with [29,30] or after [12,13,31–35] the formation of Mo sulfide. Such a sulfidation order minimizes the probability of Co segregation into an individual phase and favors its arrangement on side faces of Mo sulfide to give rise to the formation of the active Co–Mo–S phase.

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It is reported [6,13,17–22,26,33] that the higher activity to hydrodesulfurization is observed when the catalysts prepared using chelate ligands are not calcined before being sulfidized. At the same time, some contrary data are available in literature [36–39]. For example, the calcinations of catalysts, in which NTA was added before the sulfidation, influenced favorably the HDS activity [36]. When calcined, the Co–Mo/MgO–Al₂O₃ catalysts prepared with CyDTA as the chelating agent were more active to thiophene hydrodesulfurization [37]. Diammonium ethylenediaminetetraacetate (diA-EDTA) was used as the chelating agent for the preparation of the commercial CoMo on alumina HDT catalysts [38]; the resulting catalyst was more active to tetralin hydrogenation when the preparation procedure included not only drying but also drying and calcination.

To clarify more the influence of the thermal treatment condition on the hydrodesulfurization activity we try to follow the sulfidation behavior of the Co–Mo/Al₂O₃ catalysts prepared using citric acid as the chelate ligand with the subsequent drying at the different temperatures: 110, 220, 300 and 400 °C. The conditions of sulfidation (gas or liquid phase, hydrogen pressure) influence considerably the formation of the Co–Mo–S phase [39–41]. While organosulfide compounds are used for activation of commercial hydrotreating catalysts, straight-run oil gas spiked with dimethyldisulfide (DMDS) was used for the studies. Gas chromatograph (GC) equipped with a thermal conductivity detector and an atomic-emission detector was used for analysis of gas and liquid phases, respectively, to understand regularities of the sulfidation.

2. Experimental

2.1. Preparation of the complexes and catalysts

The bimetallic compound for catalyst preparation was synthesized from the ammonium salt of the tetrameric citrate anion [Mo₄(C₆H₅O₇)₂O₁₁]⁴⁻, which was prepared via dissolution of 44.8 g (0.234 mol) of citric acid C₆H₈O₇·H₂O and 57.92 g (0.328 mol of Mo) of ammonium heptamolybdate (NH₄)₆Mo₇O₂₄·4H₂O in a small amount of distilled water, followed by the addition of more water to obtain exactly 200 ml of solution. Adding solid Co(CH₃COO)₂·4H₂O to the solution containing ammonia salt of [Mo₄(C₆H₅O₇)₂O₁₁]⁴⁻ anion in proportions equivalent to a Mo/Co = 2 atomic ratio, Co₂[Mo₄(C₆H₅O₇)₂O₁₁] was obtained [42,43]. The resulting solution, under ethanol precipitation gave a rose-colored powder of Co₂[Mo₄(C₆H₅O₇)₂O₁₁].

Catalysts were prepared by impregnating alumina granules with a solution of CoMo complex. γ -Al₂O₃ granulated in the form of trilobe extrudates with diameter of 1.4 mm and length/diameter ratio equal to 3–5 (from JSK “Promkataliz”, Ryazan) was used as the support. The specific surface area of 285 m²/g, total pore volume of 0.82 cm³/g and average pore diameter of 115 Å are characteristic of the support. The resulting wet catalyst was dried at 110 °C for 8–10 h (sample CoMo(110)). Several catalyst samples were dried in a muffle furnace at temperatures 220, 300 and 400 °C, they were labeled CoMo(220), CoMo(300) and CoMo(400), respectively.

2.2. Testing of the hydrotreatment catalysts

A three-phase down-flow reactor (internal diameter 16 mm and isothermal zone 300 mm in length) was used for sulfiding of the catalysts and its testing in hydrotreatment of straight-run gas oil (SRGO). The feed was fed to the reactor using a HPLC pump; hydrogen was portioned using an automated Bronkhorst flow mass. The desired pressure of hydrogen was controlled by back pressure regulator. For each test 10 ml of catalyst granules were mixed with fine carborundum particles (fraction 0.25–0.5 mm) at

the ratio 1:1 and loaded in the isothermal zone of the reactor [44]. Carborundum is also loaded below and above the catalyst bed.

Catalysts were sulfided in the reactor by a straight-run gas oil containing extra sulfur (0.6%) as a constituent of dimethyldisulfide (DMDS). The procedure included several steps [39,45,46]:

- Drying in flowing hydrogen at 120 °C for 5 h.
- Wetting the catalyst by the feedstock and increasing hydrogen pressure in the reactor up to 3.5 MPa.
- Temperature elevation up to 230 °C at the rate of 25 °C/h.
- Sulfiding at 230 °C for 5 h (low-temperature stage).
- Temperature elevation up to 340 °C at the rate of 25 °C/h.
- Sulfiding at 340 °C for 8 h (high-temperature stage).

In the course of sulfiding, the flow rate of the sulfiding feed was 2 h⁻¹ and hydrogen/oil ratio equaled 300, SRGO being used for preparation of the sulfiding mixture. Transformations of DMDS in the presence of catalysts were studied by following the changes in the concentrations of DMDS and products of DMDS decomposition in the sulfiding mixture, in the concentrations of methane and hydrogen sulfide in the effluent gas at all the steps of sulfiding.

Catalytic properties of the samples were characterized by the residual sulfur content in the straight-run gas oil after the latter was subjected to hydrotreatment at 340 °C, 3.5 MPa, flow rate 2 h⁻¹, and hydrogen/oil 300. Properties of the initial SRGO are summarized in Table 1. Residual sulfur content was the average of three samples of hydrotreated product picked up in 10, 11 and 12 h after beginning of each next stage differing by the experimental conditions.

An Agilent 6890N chromatograph equipped with an atomic-emission detector was used for determining sulfur content (with reference to the line of atomic sulfur emission at 181 nm, S¹⁸¹ nm) in the hydrotreated product, as well as for quantitative identification of the products of DMDS decomposition in the sulfiding mixture. A capillary chromatographic column HP-1MS (60 m length, 0.32 mm internal diameter, and 0.25 μ m thickness film) was used for the separation of components of SRGO at the temperature in the chromatograph thermostat elevated from 40 up to 240 °C at the rate of 2 °C/min and then up to 260 °C at the rate of 10 °C/min.

Liquid feed was sampled for analysis at 30 min intervals. Quantitative analyses were carried out in terms of the areas of the S¹⁸¹ nm peaks at retention times of 3.43, 3.60, 3.90, and 6.75 min. These peaks were identified as hydrogen sulfide, methanethiol, dimethylsulfide and DMDS, respectively (Fig. 1).

Concentrations of hydrogen sulfide and methane in the outlet gas were determined using a thermal conductivity detector with hydrogen as gas carrier. The compounds were separated at 120 °C and flow rate of 30 ml/min of the gas carrier in a chromatographic column (2 m length and 2 mm internal diameter) filled with Chromosorbe-104.

2.3. Characterization techniques

The atomic adsorption method was used for measuring contents of main components (Co and Mo) in the oxide species of the catalyst. In the sample calcined at 550 °C for 4 h,

Table 1
Characteristics of SRGO.

Sulfur concentration, ASTM D 4294 (wt%)	1.104
Total aromatics, IP 391/395 (wt%)	30.86
Density at 15 °C, ASTM D 4052 (g/ml)	0.855
Boiling point distribution, ASTM D 2887 (°C)	
10%	241
50%	286
90%	341

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