



Research article

Comparable investigation of spillover and cobalt promoter effects in CoMoS/CoS_x/SiO₂ catalysts for selective hydrotreating of model FCC gasoline



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ABSTRACT

Co_x-Co₂Mo₁₀/SiO₂ and Co₂Mo₁₀/Co_x/SiO₂ catalysts with various Co/Mo ratios and active species compositions are prepared using H₆[Co₂Mo₁₀O₃₈H₄] heteropolyacid, CoCO₃ and citric acid. Catalysts are characterized using the following techniques: low-temperature N₂ adsorption, temperature-programmed reduction, high-resolution transmission electron microscopy, and X-ray photoelectron spectroscopy. Catalytic activities of the synthesized catalysts are examined in hydrotreating of model fluid catalytic cracking (FCC) gasoline that contains 1000 ppm of sulphur from thiophene and 36 wt.% of n-hexene-1. As the Co/Mo ratio increases, hydrodesulphurization (HDS) and hydrogenation (HYD) activities of the prepared catalysts significantly builds up. The changes of catalytic properties and specifically of the HDS/HYDO selectivity factor of the synthesized CoMo catalysts arise from two effects: an alteration of the promotion degree of CoMoS active phase particles and a hydrogen spillover from CoS_x species to active sites. The developed silica-supported CoMo catalysts may be a prospect for selective HDS and hydro-upgrading of FCC gasoline.

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1. Introduction

Compliance with environmental specifications for sulphur and other contaminants in diesel or gasoline usually requires hydrotreating (HDT) of oil cuts and residues by transition metal sulphides supported on high surface areas materials. Co(Ni)Mo(W)/Al₂O₃ is the formulation most widely used as a catalyst in HDT processes. Despite significant advances in the development of HDT catalysts as a whole, further improving catalytic properties of hydrodesulphurization (HDS) catalysts for processing various feedstocks remains important. Fluid catalytic cracking (FCC) gasoline poses two major challenges: removing a large sulphur concentration and retaining all olefins. Thus, HDS of sulphur-containing compounds is a desirable reaction, whereas hydrogenation (HYD), especially of olefins (HYDO), is undesirable. Successful FCC gasoline refining requires HDT catalysts with the highest possible HDS/HYDO selectivity.

Various approaches have been proposed to improve catalytic properties of sulphide catalysts for FCC gasoline HDT. New and modified supports, including advanced amorphous aluminosilicates [1–10], various precursors and ways of forming supported active phases [11–14] or bulk sulphides [15] as well as various additives [16–23] have been

aimed at a direct formation of active phase species with specified properties and low HYDO activity. Some recently published researches are focused on a very fundamental and key question about the interrelationship between active phase composition of the CoMo HDS catalysts and HDS/HYDO selectivity in hydrodesulphurization and touched on such points as effect of sulphur defects in MoS₂ crystallites [15].

Along with the mentioned approaches, Jin et al. [24] has recently reported high HDS/HYDO selectivity of alumina-supported nickel sulphide catalysts in thiophene HDS, which can be useful in selective HDT of FCC gasoline. In our previous researches [11,25–29], supported transition metal sulphide catalysts obtained through heteropolyanions (HPAs) with Anderson structures were successfully studied in HDS and hydrodenitrogenation (HDN) reactions. Later, the hydrogen spillover (Hso) effect was investigated in HDS and HDN reactions over bi-component supported catalysts CoMoS/MS_x/Al₂O₃, consisting of nanosized CoMoS species formed from Co₂Mo₁₀HPA entities and MS_x species, where M is Ni, Co, Mn, or Zn [30–32]. It was shown that the existence of MS_x species on the catalyst surface, which are able to activate molecular hydrogen, can be an additional key factor to increasing the turnover frequency of HDS, HYD and HDN reactions on CoMoS sites and improving catalytic activity in diesel HDT. Despite the fact that Hso has been studied since 1969 [33] and that the literature communicates several beneficial effects for HDS [34–36], HYD [34,36] and HDN [37,38] reactions and HDT of real feedstock [36,39–41], it has not been

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so far investigated in selective HDS of FCC gasoline. Taking the above into account, the aim of this work is to investigate the Hso effect in selective HDS of model FCC gasoline over CoMoS/CoS_x/SiO₂ catalysts. The novelty of the research consists in the investigation of the Hso effect for the purposes of selective HDS of FCC gasolines and its quantitative comparison with an effect of the active phase promotion by cobalt in the case of Co_x-CoMoS/SiO₂ catalysts.

2. Experimental

2.1. Catalyst preparation

Three types of catalytic systems with comparable metals loading and various active species composition and distribution are used in the research. The first series of the Co_x-Co₂Mo₁₀/SiO₂ catalysts differ in promotion ratio $\lambda = \text{Co}/(\text{Co} + \text{Mo})$ and are prepared using decamolybdodicobaltate heteropolyacid H₆[Co₂Mo₁₀O₃₈H₄], which is synthesized according to [42] (named as Co₂Mo₁₀HPA), commercial cobalt (II) carbonate (CoCO₃, from Fluka, Co conc. = 43–47%) and commercial citric acid (CA, from Sigma-Aldrich, 99% purity), Co/CA mole ratio is equal to 1.0. Co₂Mo₁₀HPA is prepared from ammonium heptamolybdate tetrahydrate and cobalt (II) nitrate (from Fluka, 99.0 and 98.0% purity, respectively) as described earlier [43,44]. Catalysts are prepared via wetness impregnation of commercial SiO₂ (Sigma-Aldrich, specific surface area (SSA) 320 m²/g, pore volume 0.95 cm³/g and effective pore radius 45 Å) with an aqueous solution, containing the appropriate concentration of Co₂Mo₁₀HPA, CoCO₃ and CA. The reference catalyst Co₂Mo₁₀/SiO₂ is prepared using only Co₂Mo₁₀HPA.

The second type of catalysts, with Co₂Mo₁₀/Co_x/SiO₂ composition are synthesized by impregnation of Co-modified supports Co_x/SiO₂ with aqueous solutions containing the required amounts of Co₂Mo₁₀HPA and differ from each other in the content of cobalt sulphide in support “x”. Co-modified supports Co_x/SiO₂ are prepared by wetness impregnation of commercial silica with cobalt (II) nitrate water solution. Then the impregnated samples are dried at 60, 80, and 110 °C (for 2 h) and sulphided at 400 °C (2 h) in H₂S/H₂ atmosphere (15 vol.% H₂S, flow rate is 2.0 L/h).

The third series are separated cobalt and molybdenum sulphides supported on silica denoted as CoS_x/SiO₂ (4.0 wt.% of cobalt) and MoS₂/SiO₂ (12.7 wt.% of molybdenum), respectively. The samples are prepared by wetness impregnation of initial silica with cobalt (II) nitrate or molybdophosphoric acid (from Sigma-Aldrich, 99% purity) water solution accompanied with further sulphidation procedure. These catalysts are used to investigate the influence of active metals interaction on the results of selective HDS of FCC gasoline.

2.2. Characterization of catalysts

2.2.1. Textural characteristics of the catalysts

Textural characteristics of the prepared materials are determined by nitrogen adsorption at low temperature (77 K) on Quantachrome Autosorb-1 adsorption porosimeter. The SSA is calculated using the Brunauer-Emmett-Teller (BET) method at relative partial pressure P/P₀ of 0.05–0.3. The total pore volume and pore size distribution are measured by a desorption curve using the Barrett-Joyner-Halenda (BJH) model at relative partial pressure P/P₀ of 0.99. The samples are vacuum-dried before the adsorption measurement at 350 °C for 6 h at P < 10⁻¹ Pa.

2.2.2. Temperature-programmed reduction (TPR)

The TPR analysis of cobalt and molybdenum sulphides supported on silica are carried out with a thermal conductivity detector (TCD). TPR experiments are performed with various charges of the reactor: MoS₂/SiO₂ and CoS_x/SiO₂ catalysts are charged separately as well as by mechanical mixture with various CoS_x/SiO₂ to MoS₂/SiO₂ weight ratios (1/1, 1/3 and 1/5) diluted with SiO₂.

Catalysts are first sulphided in a quartz reactor at 400 °C for 4 h with a mixture of H₂S and H₂ (10 vol.% of H₂S) at a heating rate 5 °C/min, then cooled to room temperature and charged to the reactor without contact with air. The analysis is performed in a mixture of H₂ and N₂ (5 vol.% of H₂) under the following conditions: gas flow rate of 30 mL/min, temperature range from 20 to 900 °C with holding period at 900 °C for 1 h, a heating rate of 10 °C/min.

2.2.3. High-resolution transmission electron microscopy (HRTEM)

HRTEM images of the CoMo catalysts are obtained on a Tecnai G2 20 electron microscope with lattice-fringe resolution of 0.14 nm at 200 kV accelerating voltage. The high-resolution images of periodic structures are analysed by the Fourier method. The samples examined by HRTEM are prepared on a perforated carbon film mounted on a copper grid.

The average length of the slab (\bar{L}) and the stacking degree (\bar{N}) are calculated and averaged using the data obtained from 8 to 10 transmission electron microscopy (TEM) micrographs (an equivalent of at least 400 crystallites) for each catalyst. The average length (\bar{L}) approximately corresponds to the diagonal dimension of the observed MoS₂ platelet. The dispersion of edge and corner Mo atoms (denoted as D) is also calculated. In this calculation, it is assumed that MoS₂ is a perfect hexagon in accordance with Kasztelan [45]. The D value is statistically evaluated by dividing the total number of Mo atoms at the edge surface by the total number of Mo atoms using the crystallite sizes determined from HRTEM:

$$D = \frac{Mo_E + Mo_C}{Mo_T} = \frac{\sum_{i=1..t} 6n_i - 6}{\sum_{i=1..t} 3n_i^2 - 3n_i + 1}, \quad (1)$$

where Mo_E , Mo_C and Mo_T are numbers of Mo atoms located on edges, corners and total number, respectively, in average MoS₂ crystallite (evaluated from HRTEM), n_i is the number of Mo atoms along one side of the MoS₂ slab determined from its length and t is the total number of slabs in the TEM micrographs.

The average stacking degree (\bar{N}) is calculated by the following equation:

$$\bar{N} = \frac{\sum_{i=1..t} n_i N_i}{\sum_{i=1..t} n}, \quad (2)$$

where n_i is the number of stacks in N_i layers.

2.2.4. X-ray photoelectron spectroscopy (XPS)

The XPS spectra are obtained on a Kratos Axis Ultra DLD spectrometer using monochromatic AlK_α source (hν = 1486.6 eV, 150 W). The analysis procedure is described in detail in [42]. The XPS decomposition allows the determination of the absolute quantification of each type of species:

$$C(j)_T(\%) = \frac{A_j/S_j}{\sum_{i=1..t} A_i/S_i} \times 100, \quad (3)$$

where A_i is the measured area of the species i , S_i is the sensitivity factor of the atom related to the species i (provided by the manufacturer), and $C(j)_T$ is the absolute amount of the species j .

The relative concentrations of each species, cobalt oxide Co²⁺, CoS_x, CoMoS, molybdenum oxide Mo⁶⁺, MoS_xO_y and MoS₂, for every

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