Fuel Processing Technology 173 (2018) 56–65

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Active phase transformation in industrial CoMo/Al_2O_3 hydrotreating catalyst during its deactivation and rejuvenation with organic chemicals treatment

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ARTICLE INFO

Keywords:
Hydrotreating
CoMoS
Active phase
Catalysts
Rejuvenation
Organic acids
Glycols

ABSTRACT

Reactivation of industrial CoMo/Al_2O_3 hydrotreating (HDT) catalysts was studied. A spent catalyst was used in the ULSD production for about 2.5 years. It was oxidatively regenerated and rejuvenated by organic acids (citric and thioglycolic), glycols (ethylene and triethylene), and dimethylsulfoxide solutions. All solids were characterized by the elemental analysis, N_2 physisorption, X-ray powder diffraction, thermogravimetric analysis, high-resolution transmission electron microscopy, and X-ray photoelectron spectroscopy. Changes in the active phase composition and morphology during the CoMo/Al_2O_3 HDT catalyst operation, regeneration and rejuvenation were shown. The rejuvenated catalysts were tested in hydrodesulfurization (HDS) of dibenzothiophene and hydrogenation (HYD) of naphthalene. It was found that oxidative regeneration allowed restoring about 70–85% rel. of initial activity. Rejuvenation with organic chemicals resulted in the complete restoration of HDS and HYD activities. Resulting catalytic activity of the reactivated catalysts depended on the properties of the formed active phase species. These correlations are discussed in the study.

1. Introduction

Catalysts containing valuable metals such as nickel, cobalt and molybdenum on the γ-alumina support are commonly used in the oil industry and especially for hydrodesulfurization (HDS) processes. Hydrotreating (HDT) catalysts are in ever growing demand due to increasing consumption of low sulfur fuel and a tendency to process heavy distillate fractions [1,2]. These catalysts tend to deactivate with their time of use and require regeneration or replacement since catalyst deactivation results in a higher sulfur content [3,4]. Besides the growing fresh catalyst market, the regenerated HDT catalyst usage is also increasing. It is estimated > 30,000 tons every year worldwide [5]. The deactivation phenomenon occurs via various mechanisms: poisoning, thermal degradation, and coke and/or heavy metals deposition [6]. The deposition of coke is the main cause of catalyst deactivation in hydrotreating [7–9]. Regeneration can restore activity more or less efficiently for various catalysts. Carbonaceous species can be eliminated by using oxidizing atmosphere at temperature of 450–550 °C. This works well for conventional catalysts [3,10] while the oxidative treatment of new generation resulted in either to the formation of $CoMoO_4$ or $NiMoO_4$ if the regeneration temperature is too high or to an insufficient oxidation of S and C if the temperature is too low [11,12]. This can allow restoring HDS activity only partially. More recent class of HDS catalysts may need additional treatment to achieve better recovery of activity.

Chemical treatment after oxidizing regeneration is one of the most popular methods of spent catalyst rejuvenation. Various acidic or alkaline solutions such as oxalic acid, mineral acids, potassium hydroxide, acetic acid, and citric acid were used to recover spent catalysts. The rejuvenation mechanism and effects of different chemicals, concentrations, and operation conditions on catalyst regeneration vary depending on a spent catalyst and reliable information in open literature is limited by few researches and patents [13–18]. In addition, the difference between fresh and regenerated catalyst is not constant. It is usually higher at the start of its run than after several weeks of operation [19]. Therefore, the catalyst reuse has to be carefully examined on a per case basis.

The objective of the present study was to investigate changes in the

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https://doi.org/10.1016/j.fuproc.2018.01.008
Received 6 November 2017; Received in revised form 31 December 2017; Accepted 9 January 2018

active phase transformation and properties of an industrial CoMo HDT catalyst during its deactivation, oxidative regeneration and rejuvenation with various organic chemicals. With a view to expand the understanding of deactivation/rejuvenation mechanisms and to develop an efficient and cost-effective method of catalyst regeneration a study of alumina supported industrial CoMo HDT catalysts, spent and regenerated with various chemicals, has been undertaken. The effect of rejuvenation agents such as citric and thioglycolic acids and glycols on textural properties, composition and morphology of active phase species of regenerated and rejuvenated $CoMo/Al_2O_3$ catalysts have been studied.

2. Experimental

2.1. Preparation of rejuvenated catalysts

An alumina supported industrial CoMo HDT catalyst with MoO_3 and CoO loading equal to 16.2 and 4.6 wt%, respectively, was utilized as a reference sample. It was used for about 2 years and 2 months on a HDT unit for Ultra Low Sulfur Diesel production from Straight Run Gasoil (sulfur content 0.9 wt%). Operation conditions of the HDT unit was: pressure – 4.5 MPa, liquid hourly space velocity (LHSV) – 2.0 h^{-1}, H_2 in hydrogen-bearing gas – 96.2 vol%, starting temperature – 333 °C, temperature in the end of life cycle – 392 °C. Continuous temperature increasing was performed to compensate catalyst activity decreasing due to deactivation. The end of catalyst life cycle is defined as moment when catalyst does not allow producing hydrogenated product with total sulfur $<$ 10 ppm under the possible operating conditions – maximum temperature. The Mo and Co content in the catalyst was measured using an EDX800HS analyzer. The spent catalyst denoted as “Ind-S” was undergo the regeneration in a laboratory furnace at 500 °C for 2 h by small portions of 10–20 g of the catalyst in ceramic trays in oxidizing atmosphere; the regenerated sample was denoted as “Ind-C” and was used as an initial catalyst for rejuvenation with various chemicals. The Ind-C catalyst was treated by wetness impregnation with aqueous solutions of citric acid (CA), ethylene glycol (EG), triethylene glycol (TEG), a mixture of CA and EG (mole ratio 1:1), thioglycolic acid (TGA), and dimethylsulfoxide (DMSO). The molar ratio of the chemical to active metals content in the catalyst was 1:1. After impregnation, maturation was performed at room temperature for 12 h before being air-dried at 110 °C for 4 h. The obtained rejuvenated catalysts were denoted as “Ind-C-(*Used Chemical*)”. The fresh catalyst supplied by the industrial partner was also taken into account in the study.

2.2. Characterization of the catalysts

2.2.1. Carbon, hydrogen, nitrogen and sulfur (C,H,N,S) analysis

Spent and regenerated catalysts were analyzed for carbon, hydrogen, nitrogen and sulfur using an elemental analyzer EuroVector EA3000 according to ASTM D 5373. All the samples were studied in the sulfided state, except the spent Ind-S sample, firstly was washed with light petroleum fractions by a Soxhlet extraction to remove the adsorbed heavy compounds of feedstock.

2.2.2. Textural characteristics

The textural characteristics of the reference and rejuvenated catalysts were measured by low-temperature N_2 adsorption on a Quantachrome Autosorb-1 porosimeter. Before the adsorption measurement, catalysts were outgassed under vacuum ($< 10^{-1}$ Pa) at 350 °C (for sulfided samples) and 120 °C (for dried samples) for 4 h. Specific surface area (SSA) was calculated using the BET method. The total pore volume and pore size distribution were carried out from the desorption branch of the isotherm using the BJH model.

2.2.3. X-ray diffraction

X-ray powder diffraction measurements were performed on a Bruker D2 X-ray Diffraction system using Cu Kα radiation ($\lambda = 1.54056$ Å) with a scanning speed of 1.5°/min. The powders were loaded on a glass disk by packing the samples into a cavity on the disk. The diffractograms were analyzed using standard JCPDS files.

2.2.4. Thermogravimetric analysis

Simultaneous differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of the initial spent catalyst and rejuvenated ones were carried out using a NETZSCH STA 4449 F3 Jupiter apparatus in order to measure lost on ignition for fresh and regenerated catalysts. The TGA-DSC curves were recorded in flowing air in the range from room temperature to 600 °C (heating rate 10 °C/min). For analysis, 20 mg of a sample was loaded in a corundum crucible, calcined alumina being used as a reference sample. The findings on carbon and sulfur oxidation at various temperatures published by various authors [11,20–23] were used in interpreting the thermogravimetric analysis results.

2.2.5. X-ray photoelectron spectroscopy (XPS)

The sulfided catalysts were analyzed by XPS in order to identify the chemical species on the surface using a Kratos Axis Ultra DLD spectrometer with monochromatic AlK_α source ($h\nu = 1486.6$ eV, 150 W). For XPS analysis catalysts were sulfided in a quartz reactor at 400 °C in atmosphere of H_2S/H_2 (10/90 vol%) 4 h. After sulfidation complete the reactor was purged with argon and disconnected from the system. The insulated reactor placed in glovebox filled with argon. After purging the glovebox with 300 nL of argon, reactor was opened and sulfided catalyst was placed into a chemical vial under a layer of degassed n-heptane and transferred to spectroscopy laboratory. To record XPS spectra, the sample was dried under vacuum and moved to the cell of the spectrometer without contact with air. The binding energy (BE) scale of the spectrometer was preliminarily calibrated using the position of the peaks for the Au $4f_{7/2}$ (83.96 eV) and Cu $2p_{3/2}$ (932.62 eV) core levels of pure metallic gold and copper. The high resolution individual spectral regions were acquired to obtain BE of the peaks, assign the chemical state of the elements, and calculate the relative ratios of the elements on the catalyst surface. The collected spectra were analyzed using the CasaXPS processing software. The decompositions of the S 2p, Mo 3d, and Co 2p XPS spectra were performed according to [24,25] using the appropriate supported monometallic catalysts as oxidic and sulfided references.

Atomic concentrations of each element for every sulfided catalyst were determined. Relative concentrations of each species, cobalt oxide Co^{2+}, CoS_x, CoMoS, molybdenum oxide Mo^{6+}, MoS_xO_y and MoS_2, for every sulfided catalyst were determined. For example, the relative amount of Co in the CoMoS phase was determined using the following equation:

$$[\mathrm{CoMoS}\ ]\ (\%) = \frac{A_{\mathrm{CoMoS}}}{A_{\mathrm{CoMoS}} + A_{\mathrm{Co_9S_8}} + A_{\mathrm{Co^{2+}}}} \times 100\ , \tag{1}$$

where A_X represents the peak area of species x.

The effective Co content (wt%) in the CoMoS phase was determined as follows:

$$C_{\mathrm{CoMoS}} = [\mathrm{CoMoS}] \times C(\mathrm{Co})_{\mathrm{T}}, \tag{2}$$

where $C(\mathrm{Co})_{\mathrm{T}}$ represents the effective concentration of cobalt on catalyst surface determined by XPS (wt%).

The promoter ratio in the CoMoS phase slab was calculated using the following relations:

$$(\mathrm{Co/Mo})_{\mathrm{slab}} = \frac{C_{\mathrm{CoMoS}}}{C_{\mathrm{MoS_2}}}, \tag{3}$$

where C_{CoMoS} and $C_{\mathrm{MoS_2}}$ are absolute concentrations of Co and Mo in the CoMoS and MoS_2 species, respectively (at.%).

The promoter ratio in the slab edge of the active phase was calculated as follows: