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Characteristics of Maya crude hydrodemetallization and hydrodesulfurization catalysts

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Abstract

Hydrotreating of Maya crude is carried out under conditions close to the industrial operation. Various catalysts are prepared in the laboratory and the results are compared with a reference catalyst. Catalysts for such hydrotreating process are designed with high porosity and low active metal content considering metal deposition during the reaction and consequently the stability. Information regarding the activity and deactivation of the catalyst is discussed on the basis of catalyst porosity and deposited metal characterization. It was found that supports prepared by ammonium carbonate and urea hydrolysis methods have macro pore size distribution (PSD) as well as comparatively higher pore volume. The hydrodemetallization (HDM) activity increases while the hydrodesulfurization (HDS) activity decreases with increasing the average pore diameter (APD). The results of HDM and hydrodeasphaltenes (HDAs) activities of catalyst protrude distinct contribution of macro PSD of support which has more capabilities to retain metal deposition and better diffusion of complex organo-chelating metals. The spent catalysts are characterized by PSD, temperature-programmed reduction (TPR), in situ Fourier transform infrared (FT-IR), and transition electron microscopy (TEM). The spent and fresh catalysts characterization results are in well agreement with the activity. It has also been proposed that deposited vanadium sulfide may act as auto-catalytic activity for HDM and HDAs instead of being poison. It is also found that the deposition of metal depends on the porosity and surface area of the catalyst.

Keywords: HDS; HDM; HDAs; Catalyst deactivation; Metal deposition; FT-IR; TPR; Spent catalyst; Maya crude

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1. Introduction

Upgrading the bottom of the barrel is one of the toughest challenges in heavy oil processing. The demand for heavy oil decreased recently due to their invaluable use as heavy feedstock while the need in light and middle distillate has moved to the opposite direction. The trend has indicated the importance of heavy oil processes which convert the heavy oil fraction into more valuable and environmental clean products. Therefore, now the important task in hydrotreating is heavy oils processing in which there is a lack of detailed knowledge about the feed composition. The composition and different molecular structure of crude oils consist predominantly of high concentration of heteroatoms hydrocarbons and vary with their origin [1,2]. Metals (V and Ni) are invariably the most abundant heteroatom impurities in heavy crudes. In general, metalloporphyrins are concentrated in the resin and mainly in the asphaltenes, which are building blocks of pyrrole. Nitrogen is present in the form of basic nitrogen compounds containing the pyridine nucleus, while the rest is mainly present in relatively non-basic compounds containing the pyrole nucleus [3]. Thus, the high-molecular-weight molecules are porphyrinic configurations of complex nickel and vanadyl radicals but these porphyrinic structures are not only metal carriers but also other hydrocarbons such as asphaltenes.

The hydrodemetallization (HDM) ends up in the metal sulfide accumulation onto the catalyst surface, and as a result, blocking of the active sites and pores [1,2,4]. This becomes more complicated since virtually infinite number of complex hydrocarbons like asphaltenes together with the molecules containing heteroatom, mainly S, N, V, Ni, etc., are present in high concentration [5]. In order to draw the concept governing the effect of support preparation in HDT catalysts performance, different γ-Al_2O_3 support preparation methods

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have been employed to vary the porosity and PSD which play an important role in stability as well as in metal retention capacity on the surface of catalyst [1]. The different characterization of the catalysts before and after reaction provides important information about the role of textural properties on metal deposition. In general, the HDM catalysts behavior can be observed in two ways which depend on the textural properties of the catalyst, e.g. (a) micro-porous and low-range meso-porous catalyst decreases activity rapidly due to the pore mouth blockage and diffusion of complex molecules into the pores, (b) the catalysts containing macropores, in which deposited metal sulfides (V and Ni) behave themselves as catalytic sites, and those catalysts showed comparatively more stability during the time-on-stream (TOS). The metals from this hydrogenolysis are deposited on the catalyst in sulfided state, so that the reaction active sites were created with TOS; however, the original catalytic Mo sites may decrease due to the deposition of metal and asphaltenes [6].

Various researchers [7–14] focused on the effect of metallic deposits, mainly vanadium and nickel sulfides, which confirm that the decrease in activity is due to the metallic deposition on the catalyst surface. But only few characterization studies [15–18] have been carried out on spent catalysts. Toulhoat et al. [15,16] reported that nickel is always associated to vanadium and its crystallite size ranged from 5 to 30 nm, which grew up perpendicular to the alumina platelets. Kawada et al. [18] found that metals exist as the sulfide compounds using X-ray diffraction patterns. Smith and Wei [19–21] studied transition electron microscopy (TEM), EDX, STEM, and XPS for model molecules such as nickel etioporphyrin and vanadyl etioporphyrin on deactivated catalysts and concluded that nickel and vanadium sulfides deposited on HDM catalyst are in the form of relatively large spatially dispersed crystallites. Takeuchi et al. [6] reported X-ray power diffraction (XRD), ESR, and SEM on spent catalysts to find out the shape of deposited V and Ni sulfide crystallites. On the other hand, the surface deposited metal composition and its effect on the textural properties of spent catalyst at different catalyst beds is reported by Fleisch et al. [22].

In this publication we try to embark on an effect of support using different porosity and its influence on various catalytic activities such as HDM, hydrodeasphaltenes (HDAs), and hydrodesulfurization (HDS). The performance of the catalyst based on the pore size distribution (PSD) showed that larger the pore higher the HDM activity while the HDS activity decreases. The metal deposition capacity increases with high porosity which represents better stability of catalyst. The characterization results of fresh and spent catalysts showed that the number of catalytic sites altered after the reaction which is due to the deposited metal during the reaction. To show the chemical form of deposited species different analysis such as textural properties, TEM, FT-IR, and temperature-programmed reduction (TPR) characterization were carried out and the results indicated that the deposited species may have some catalytic activity.

2. Experimental

γ-Al_2O_3 supports were prepared by using different precipitation agents such as urea (γ-Al_2O_3-u), ammonium carbonate swing method (γ-Al_2O_3-acs), and ammonium hydroxide (γ-Al_2O_3-am). The details of the preparation of support are given elsewhere [23]. The Co–Mo promoted catalysts were prepared by the sequential incipient wetness impregnation method. The textural properties of these catalysts are given in Table 1.

The specific surface area (SSA), pore volume (PV), and PSD were carried out in a Quantochrome Nova 2000 equipment using N_2 adsorption–desorption at −196 °C. X-ray power diffraction patterns were collected on a Siemens D500 diffractometer using Cu Kα radiation. The TEM experiments were done in Jeol 100CX-II equipment.

TPR experiments were carried out in a flow apparatus, which consisted of a quartz reactor of 6 mm inner diameter designed by Altamira equipped with gas mass flow controllers. Feed gases were Ar (99.999% purity) and 10% H_2 (99.999% purity) balance in Ar. A thermal conductivity detector (TCD) was used to monitor the concentration of referred gases. Prior to each reduction experiment, the samples were pretreated at 450 °C (at the rate of 10 °C min^{-1}) with a flow of dry and purified Ar for 2 h. The experimental conditions for a TPR were a flow of 30 mL min^{-1}, with a 20 mg catalyst and a heating rate of 10 °C min^{-1}; final temperature was 1000 °C. The gas flow rate precisely controlled with an optional mass flow

Table 1
Textural properties of fresh and spent catalysts

Catalysts	Fresh catalysts			Spent catalysts		
	SSA (m^2/g)	PV (mL/g)	APD (nm)	SSA (m^2/g)	PV (mL/g)	APD (nm)
CoMo/γ-Al_2O_3-u	136	0.39	9.4	78	0.20	8.0
CoMo/γ-Al_2O_3-acs	160	0.47	11.2	80	0.25	7.2
CoMo/γ-Al_2O_3-UB	160	0.47	11.2	97	0.30	6.4
CoMo/γ-Al_2O_3-am	169	0.27	6.5	123	0.16	4.6
RC	175	0.56	12.7	140	0.21	6.0

SSA; PV; APD, average pore diameter; RC, reference catalyst for HDM feed, γ-Al_2O_3 + Ti 3.7 wt.%; U, spent catalyst (fixed bed 60 h TOS); BU, spent catalyst (batch reactor 6 h TOS).