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Maya crude hydrodemetallization and hydrodesulfurization catalysts: An effect of TiO_2 incorporation in Al_2O_3

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Abstract

Hydrotreating of Maya heavy crude oil over high specific surface area $CoMo/TiO_2–Al_2O_3$ oxide supported catalysts was studied in an integral reactor close to industrial practice. Activity studies were carried out with Maya crude hydrodesulfurization (HDS), hydrodemetallization (HDM), hydrodenitrogenation (HDN), and hydrodeasphaltenization (HDAs) reactions. The effect of support composition, the method of TiO_2 incorporation, and the catalyst deactivation are examined. Supported catalysts are characterized by BET specific surface area (SSA), pore volume (PV), pore size distribution (PSD), and atomic absorption. It has been found that sulfided catalysts showed a wide range of activity variation with TiO_2 incorporation into the alumina, which confirmed that molybdenum sulfided active phases strongly depend on the nature of support. The pore diameter and nature of the active site for HDS, HDM, HDN, and HDAs account for the influence of the large reactant molecules restricted diffusion into the pore, and/or the decrease in the number of active sites due to the MoS_2 phases buried with time-on-stream. The textural properties and hysteresis loop area of supported and spent catalysts indicated that catalysts were deactivated at the pore mouth due to the metal and carbon depositions. The atomic absorption results agreed well regarding the textural properties of spent catalysts. Thus, incorporation of TiO_2 with γ-Al_2O_3 alters the nature of active metal interaction with support, which may facilitate the dispersion of active phases on the support surface. Therefore, the TiO_2 counterpart plays a promoting role to HDS activity due to the favorable morphology of MoS_2 phases and metal support interaction.

Keywords: HDM; HDS; HDN; HDAs; Maya crude; $TiO_2–Al_2O_3$; CoMo catalyst; Deactivation; Heavy oil HDT; Support effect

1. Introduction

Hydrotreating is one of the most important processes in the petroleum refinery, because it is a process which mainly removes sulfur, nitrogen, and unwanted metals from hydrocarbons [1]. These molecules are the main source of environmental pollution, and also poison the catalysts used in various refineries operations [2]. For instance, metals need to be removed from hydrocarbons because they poison the catalyst and may cause corrosion even in minor quantities. During the hydrodemetallization, nickel and vanadium form sulfides, which results in pore mouth plugging and decreases catalytic activity by restricting the access of reactants to the catalytic sites. Thus, in the case of heavy oil processing, pore diameter is of equal importance as the active sites. A large variety of sulfur, nitrogen, and organometallic species, together with large molecules of asphaltenes, are present in heavy oil, which constitute the heaviest molecule in crude and are also responsible for catalyst deactivation during the hydrotreating processes [3]. Therefore, it is essential to conserve the catalysts using the meso or macro-porous and put them to maximum possible use with highly dispersed active sites.

Support effect in hydrotreating [4–6] catalysis, especially TiO_2 incorporation in alumina, is well reported for model molecules [7–13], but there is limited use of these catalysts in commercial studies [14,15]. However, due to the strength, low surface area, low pore volume, and high cost, pure TiO_2 is not a favorable support [16,17]. To overcome these problems, TiO_2 incorporation into the different oxides such as ZrO_2 [18], SiO_2 [19], and Al_2O_3 [7–13], was studied to modify the physico-chemical support properties. Apart from the wide range of studies using different model molecules and characterization on the $TiO_2–Al_2O_3$ supported catalyst, the application of this material in heavy oil hydrotreating is not common, with the exception of a few publications from our group [14,15], where

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we have reported that TiO_2–Al_2O_3 supported catalysts showed higher activity than reference catalysts. However, the stability of these catalysts was not as expected. That could be due to the support preparation, since the use of aluminum sulfate [15] as alumina source may generate strong acidity on a sulfided catalyst, if there were some SO_4^{-} ions remaining in catalyst; or, another reason is the feed composition employed in those studies [14,15], which could deactivate the catalyst at a very fast rate due to the precipitation of asphaltene in naphtha. Regarding to this aspect, Rayo et al. [14] presented a nice report about the effect of feed dilution on NiMo/Al_2O_3–TiO_2 supported catalysts.

In the present work, the effect of TiO_2 incorporation into the Al_2O_3 using different methods such as urea hydrolysis, ammonia hydrolysis, incipient wetness impregnation, and delayed precipitation of titania is reported. Among these techniques, urea hydrolysis offers advantages for hydrogenolysis (HDS, HDN, and HDM) activities while the delayed precipitation method showed lower activity due to the lower average pore diameter of the catalyst. However, the effect of individual activity on different catalysts is not very clear due to the similar composition of TiO_2 and Al_2O_3 [i.e. $TiO_2/TiO_2 + Al_2O_3 \approx 0.1$]. Different methods of support preparation showed variation in PSD, which may also cause some differences between the activities. The effect of PSD is confirmed by the comparison of fresh and spent catalyst textural properties as well as deposited metals. An increase in the hysteresis loop area is calculated and the results are discussed as an effect of metal poisoning and coke deposition near the pore mouth of catalyst after 120 h TOS.

2. Experimental

Al_2O_3–TiO_2 supports were prepared by using different methods employing aluminum nitrate solution (~1.5 M) and titanium tetra chloride or titanium *iso*-propoxide as source of Al_2O_3 and TiO_2, respectively. The composition of TiO_2 in the support was kept low (i.e. 10 wt.%) due to commercial importance of the catalyst. The Al_2O_3–TiO_2 sample is represented as AT, where different preparation methods will be indicated by 1, 2, 3, 4, 5, and 6.

1. AT-1 and AT-2, urea and ammonia hydrolysis co-precipitation methods respectively, which are reported in detail elsewhere [20]. Prior to the precipitation, the aqueous solution of $TiCl_4$ and aluminum nitrate was mixed together.
2. AT-3 is also similar to the ammonia precipitation except for the fact that the precursor of Ti is titanium *iso*-propoxide instead of $TiCl_4$.
3. AT-4 is titanium *iso*-propoxide, impregnated using incipient wetness impregnation over the γ-Al_2O_3 (550 °C).
4. AT-5 is titanium *iso*-propoxide, impregnated using incipient wetness impregnation over the boehmite phase of alumina (AlOOH).
5. AT-6, the urea hydrolysis delayed precipitation of TiO_2, aluminum nitrate was first precipitated, and after 30 min titanium *iso*-propoxide, considering the titania precipitates on the surface of the alumina particle.

The above calcined (550 °C) supports prepared with different methods were analyzed by atomic absorption and their compositions are reported in Table 1.

The molybdenum-supported catalysts were prepared using the incipient wetness impregnation method. An appropriate amount of ammonium heptamolybdate (AHM) (Fluka AR grade) was used and dissolved in ammoniac solution. The Co-promoted catalyst was also prepared by the sequential impregnation procedure on the Mo-loaded catalyst (dried at 120 °C and calcined at 400 °C). The cobalt nitrate salt was impregnated in aqueous medium. The final catalyst was dried in presence of air at 120 °C overnight and calcined at 450 °C for 4 h. The compositions of the supported catalysts are also reported in Table 1.

The BET SSA, PV and PSD analyses were carried out in Quantachrome Nova 2000 equipment. Nitrogen gas was employed for SSA measurements at liquid nitrogen temperature (−196 °C). Prior to the adsorption, the samples were degassed 3 h at 300 °C. X-ray power diffraction (XRD) patterns were collected on a Siemens D500 diffractometer using Cu Kα radiation.

The feedstock contains 50/50 (w/w) of Maya crude and diesel. Diesel was used as a diluent to avoid gum formation during processing. The feed composition is presented in Table 2. Metals (Ni, V) were analyzed in the feed and products using flame atomic absorption spectrometry (ASTM D 5863-00a method). The total S content was analyzed with the HORIBA model SLFA-2100/2800 using scattered spectroscopy by sulfur, generating energy dispersive X-ray fluorescence. The X-ray beam was separated selectively with the help

Table 1
Composition and textural properties of supported catalysts

Catalysts	Support $Al_2O_3/(Al_2O_3 + TiO_2)$	Catalyst composition (wt.%)		Textural properties		
		Co	Mo	SSA (m^2/g)	PV (ml/g)	APD (nm)
AT-1	0.908	2.13	5.53	230	0.4372	7.4
AT-2	0.901	2.16	5.52	255	0.4100	6.8
AT-3	0.902	2.25	5.53	260	0.3319	5.5
AT-4	0.906	2.20	5.50	206	0.3200	5.8
AT-5	0.905	2.21	5.65	232	0.3426	5.7
AT-6	0.911	2.02	5.57	231	0.3085	4.1