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Analysis of the hydrotreatment of Maya heavy crude with NiMo catalysts supported on TiO_2-Al_2O_3 binary oxides
Effect of the incorporation method of Ti

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Abstract

Heavy Maya crude has been hydrotreated with NiMo/alumina-titania catalysts in which titania was incorporated by two different methods. Titania added to boehmite followed by calcination in order to promote formation of Ti–O–Al bonds, and Ti added to alumina in order to promote the formation of TiO_2 structures on the surface. The reaction results indicate that hydrodesulfurization (HDS), hydrodemetallization (HDM) and hydrodenitrogenation (HDN) activities are improved by the incorporation of Ti to the catalyst. In all cases, catalysts prepared by the method leading to the formation of surface TiO_2 structures show superior performance in the three functionalities (HDS, HDM and HDN). Raman analysis of the supports gives clear evidence of the differences in Ti oxide structures on the surface. The characterization of the catalysts indicates that Ti-modified catalysts have increased surface acidity (evaluated by pyridine adsorption) and greater number of coordinatively unsaturated sites (titrated by NO adsorption). Ti-containing catalysts seem to be also more stable with time-on-stream.

Keywords: NiMo catalysts; Hydrodesulfurization; Hydrodemetallization; Hydrodenitrogenation; Titania-alumina supports; Maya crude

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1. Introduction

The need for better hydrodesulfurization catalysts capable of complying with the present and future environmental regulations has promoted research on the use of new supports and active phases. Among the new supports, titania [1–3] and alumina-titania [4–8], have shown interesting properties. Mo or W-based catalysts supported on Al-Ti oxide supports have been successfully used for the hydrodesulfurization of sulfur refractory molecules such as 4MDBT, 4,6 DMDBT or even real feeds [9–13].

An additional problem facing the petroleum industry is that a significant part of the world reserves consists of heavy petroleum with high content of contaminants like sulfur, nitrogen, aromatics and metals such as Ni and V. These heavier feeds often contain a greater proportion of sulfur molecules resilient to HDT (the so-called refractory compounds) such as substituted dibenzothiophenes, 4 methyl dibenzothiophene (4MDBT) or 4,6,dimethyl dibenzothiophene (4,6 DMDBT), which are very difficult to hydrodesulfurize [14–20]. These heavier petroleum cuts also contain important amounts of basic and non-basic nitrogen compounds, considered as responsible for color and gum formation, and which strongly poison the HDT active sites [21–24].

The fundamental studies with model molecules performed so far indicate that Ni(Co)-Mo(W) catalysts supported on Ti-modified alumina are among the catalysts with interesting properties to be used for the hydrotreatment of heavy petroleum. The causes for the good performance of Ti-containing catalysts in the hydrodesulfurization of the most refractory sulfur molecules have been well explained in ref. [20]. Essentially, under the reducing atmosphere prevailing at reaction conditions, some surface Ti^{4+} is reduced to Ti^{3+}, which can easily donate an electron and therefore act as an electronic promoter of the Mo or W sulfided phases facilitating the formation of sulfur vacancies (CUS) and causing an increase in

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their number. This leads to an increase in the hydrodesulfurization and hydrogenation functions of the catalyst.

Not all the surface species of Ti perform equally in HDS. The activity of Ti-containing catalysts depends significantly on the micro structural nature of the Ti oxide species present on the catalyst surface [20]. Because of this, the method of incorporating Ti to the catalyst support is of great importance to the activity of the catalyst. Some of the above advantages of Ti-containing catalysts have been put in evidence in experiments with model molecules and real feeds such as gasoils [1,2,4–13]. However, little work has been performed with heavier feeds containing high concentration of contaminants (sulfur, nitrogen and metals) and aromatics. In the present work, we analyze the behavior of NiMo catalysts supported on Al-Ti binary oxides during the hydrotreatment of heavy Maya petroleum with respect to the different functionalities (hydrodesulfurization, hydrodemetallization and hydrodenitrogenation). Particular attention is paid to the study of changes induced in catalytic activity, during the hydrotreatment of heavy Maya petroleum, by variations in the method of incorporating Ti to the alumina support. To this end, NiMo catalysts supported on Al-Ti supports with 5 wt% Ti were prepared by two methods: (a) incorporating the Ti precursor to boehmite followed by drying and calcination and (b) incorporating Ti to the surface of an already calcined alumina. It is expected that these two methods of incorporating Ti to the alumina surface will lead to different structures of the Ti oxide overlayer. Essentially, the degree of polymerization of the surface Ti–O–Ti species will be low with the first methodology and high for the second one. The supports and catalysts are characterized by nitrogen physisorption, FTIR of adsorbed pyridine, UV–vis-DR and Raman spectroscopies and dynamic NO adsorption.

2. Experimental

2.1. Feed composition

The results from chemical analysis performed to the feed used in the experiments are presented in Table 1. The feedstock was prepared as a 50/50 wt% mixture of partially hydrodemetallized Maya petroleum (Maya HDM) and diesel. The final column in Table 1 gives the analysis of the mixture used as feedstock.

2.2. Supports preparation

2.2.1. Alumina support

Alumina extrudates were prepared from commercial boehmite (Catapal C1) supplied by Condea-Vista as follows: a small portion (10%) of the total amount of boehmite was made into a paste (binder) by mixing it with HNO_3 (10%). Then, slowly, the rest of the boehmite and deionized water were incorporated under agitation until a homogeneous paste was formed. This paste was extruded to obtain pellets of 1/16 in. diameter. The pellets were dried in an oven at 393 K during 3 h and calcined at 823 K for 3 h.

2.2.2. TiO_2/Al_2O_3 support

Alumina support previously calcined was impregnated using the pore volume method with a solution containing the required amount of titanium isopropoxide in isopropanol to obtain a support with 5 wt% Ti. The sample was left overnight at room temperature and then it was dried in air at 393 K for 3 h and calcined at 823 K during 4 h.

2.2.3. TiO_2-Al_2O_3 support

This support was prepared by mixing boehmite (Catapal C1) with the required amount of a solution of titanium isopropoxide in isopropanol to achieve a titanium concentration of 5 wt%. After that, HNO_3 (10%) and deionized water were added under agitation until a homogeneous paste was obtained. This paste was extruded into 1/16 in. diameter cylindrical pellets. The pellets were dried in an oven at 393 K during 3 h and calcined at 823 K for 3 h. Hereafter, the supports will be named Ti-Al or Ti/Al when Ti is impregnated on boehmite or on alumina, respectively.

2.3. Catalysts preparation

Using the above supports a series of NiMo catalysts was prepared by simultaneous pore volume impregnation of Mo and Ni, using the required amounts of aqueous solutions (pH 9–9.5) of ammonium heptamolybdate and nickel nitrate. The Mo and Ni contents were 10 and 4.3 wt%, respectively. After impregnation, the samples were left overnight at room temperature; dried at 393 K for 3 h and calcined at 773 K during 4 h. Hereafter, NiMo catalysts prepared by simultaneous impregnation will be named Si-Ti-Al or Si-Ti/Al, according to

Table 1
Feed characterization

Properties	ASTM Method	Maya HDM	SRGO	Feedstock Maya HDM/SRGO 50/50 wt%
Density (20/4 °C)	D-1298	0.9044	0.8267	0.8693
Nitrogen (wt%)	D-4629	0.1842	0.0226	0.1180
Sulfur (wt%)	D-4294	1.21	0.0379	0.80
Asphaltenes (wt%)	D-2007	6.8	–	5.5
Metals (ppm)	D-5863			
Ni		50.1	–	20.2
V		173.7	–	67.6
Ni + V		223.8	–	87.8

the method of Ti impregnation. The Si-Al sample represents the NiMo catalyst supported on pure alumina, where “Si” means simultaneous impregnation of Mo and Ni.

2.4. Catalyst and support characterization

BET specific surface area (SSA), pore volume and pore size distribution (PSD) measurements were carried out by nitrogen physisorption at 77 K in a Quantachrome Nova 2000 equipment. Prior to the adsorption, the supports and catalysts were outgassed for 3 h at 573 K. X-ray powder diffraction spectra were obtained using a Siemens D500 diffractometer from 10 to 70 2θ with a scan rate of $2.5^\circ\ \mathrm{min}^{-1}$ using Cu Kα radiation. The quantitative analysis of metals, Ni and V, was carried out in a Perkin-Elmer 2380 atomic absorption spectrophotometer.

The electronic spectra were obtained in a Cary 500 Scan Varian UV–vis-NIR spectrometer. The Raman measurements were recorded in a Nicolet FT-Raman 950 instrument at room temperature using a resolution of $4\ \mathrm{cm}^{-1}$ and 500 scans.

Dynamic adsorption of NO was performed in a Micromeritics Pulse Chemisorb apparatus using helium as carrier gas. Pulses of 1.68 μmol of NO were injected until saturation of the sample.

Pyridine adsorption experiments were performed using pressed disks of the pure catalysts. The wafers were first pretreated in oxygen at 723 K for 2 h and then outgassed at the same temperature for 1 h from the IR cell connected to a conventional gas manipulation-evacuation apparatus. The FTIR spectra were registered at room temperature, 373, 473 and 573 K with 100 scans and $4\ \mathrm{cm}^{-1}$ resolution.

2.5. Catalytic activity test

The reactor was loaded with equal volumes of catalyst and carborundum (0.2 mm size) used as diluent. Prior to sulfidation, the catalyst was dried at 393 K and atmospheric pressure during 2 h in a nitrogen stream. After drying, the catalyst was soaked at 423 K for 2 h using straight-run gas oil (SRGO, 1.7 wt% S). Then, the feed was changed to a mixture of the same SRGO added with dimethyl disulfide (DMDS, 1 wt%). Sulfidation was carried out at $28\ \mathrm{kg/cm^2}$ under a two level temperature program, 533 K (3 h) and 593 K (5 h), using a H_2/HC ratio of $2000\ \mathrm{ft^3/bbl}$ and $2.0\ \mathrm{h}^{-1}$ LHSV. The detailed sulfiding procedure is reported elsewhere [25].

The reaction experiments were conducted in a continuous flow microplant unit equipped with a 0.5 in. diameter tubular reactor to which 7.4 g of catalyst were loaded. In each catalytic test, the catalyst was kept under reaction conditions during 120 h. Other experimental conditions were: total pressure of $54\ \mathrm{kg/cm^2}$, reaction temperature of 653 K, LHSV of $1.0\ \mathrm{h}^{-1}$ and hydrogen-to-oil ratio of $356\ \mathrm{m^3/m^3}$.

The feedstock used in the reaction experiments was a 50/50 wt% mixture of partially hydrodemetallized Maya crude and SRGO. Total sulfur and nitrogen were determined with an Antek analyzer. The asphaltene content was defined as the amount of compounds insoluble in n-heptane ($n\mathrm{C}_7$). Ni and V contents were analyzed by atomic absorption.

Table 2
Textural properties of support and catalysts

Sample	Textural properties		
	SSA ($\mathrm{m^2/g}$)	PV (ml/g)	APD (nm)
Al	217	0.5	9.3
Ti-Al	215	0.35	6.5
Ti/Al	195	0.44	9.0
Si-Al	171	0.37	8.7
Si-Ti-Al	179	0.27	6.0
Si-Ti/Al	152	0.33	8.6

SSA, Specific surface area; PV, pore volume; APD, average pore diameter.

3. Results

3.1. Characterization of supports and catalysts

The results from the textural characterization of supports and catalysts are presented in Table 2. The supports show variations in textural properties depending on the method of Ti incorporation. Incorporating Ti to boehmite leads to greater surface areas but also to smaller pore volume and average pore diameter with respect to incorporating Ti to the surface of alumina (see Fig. 1). The same tendency is observed for the corresponding NiMo catalysts. About 20% of the surface area of the supports is lost by the impregnation of metals. The small difference observed between the average pore diameter of supports and catalysts suggests an even distribution of the metallic phases on the surface of the different supports.

The X-ray diffractograms of the mixed oxide supports and catalysts are presented in Fig. 2. The XRD patterns of the supports show the typical reflections of poorly crystallized γ-alumina but also a small additional peak corresponding to the main reflection of TiO_2-anatase, (1 0 1), suggesting the formation of small TiO_2 particles on the alumina surface.

In the oxide catalysts, no reflections corresponding to NiO were evident, however, in the Si-Ti/Al catalyst a small broad peak at $2\theta = 27.3^\circ$, hinted the presence of small amounts of MoO_3 because the main reflection of this oxide, given by the

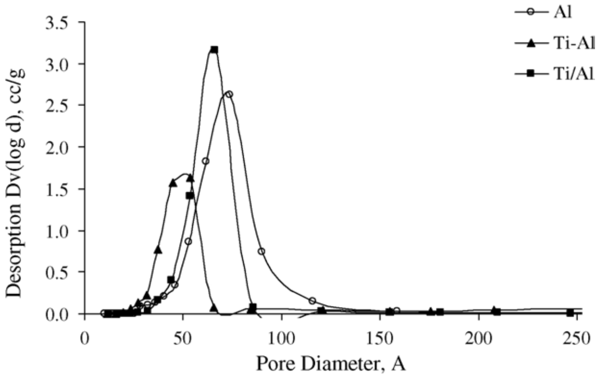

Fig. 1. Pore size distribution of supports.

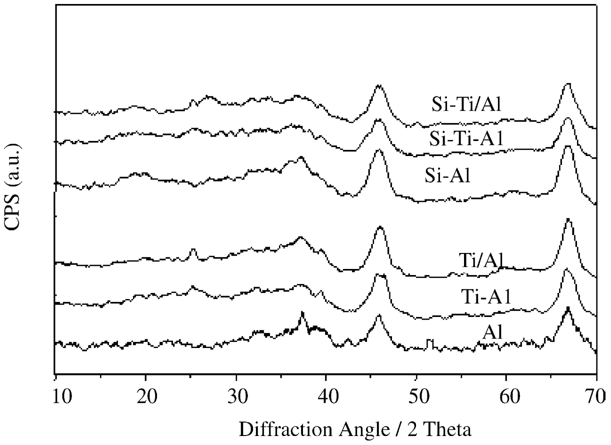

Fig. 2. X-Ray diffractograms of supports and catalysts.

(0 2 1) planes, is observed at this angle. These results suggest that the metallic phases in the catalysts did not block the pores and were well dispersed on the support surface.

3.2. Catalytic activity

The catalytic activity tests were performed during 120 h time on stream in order to achieve the steady state of the catalyst. Fig. 3 shows the behavior of the HDS reaction with time-on-stream for the Si-Al, Si-Ti-Al and Si-Ti/Al catalysts. Clearly, the Ti-containing catalysts present greater stability and HDS conversion.

Fig. 4 presents a comparison of the conversion achieved in the different catalyst functionalities (HDS, HDM and HDN), after 120 h under reaction conditions.

For HDS, Fig. 4a, the catalyst in which Ti was incorporated in an eggshell mode on the alumina surface (Si-Ti/Al) showed the highest activity compared with Ti incorporated on boehmite (Si-Ti-Al) or on pure alumina (Si-Al). The conversion for the former was 55% versus 46% and 40% for the others, respectively. In line with our previous findings in experiments with model reactions using CoMo and NiMo catalysts supported on Al_2O_3-TiO_2 mixed oxides, high concentration of TiO_2 structures on the surface leads to higher HDS activities. The fact that Si-Al and Si-Ti-Al have almost the same HDS activity suggests that incorporating Ti to boehmite followed by calcination, changes little the properties of the support surface.

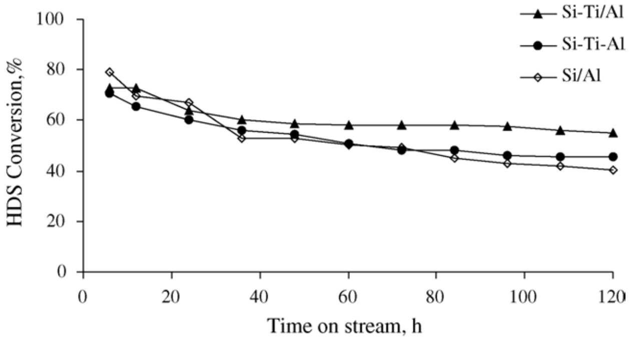

Fig. 3. HDS conversion with time-on-stream.

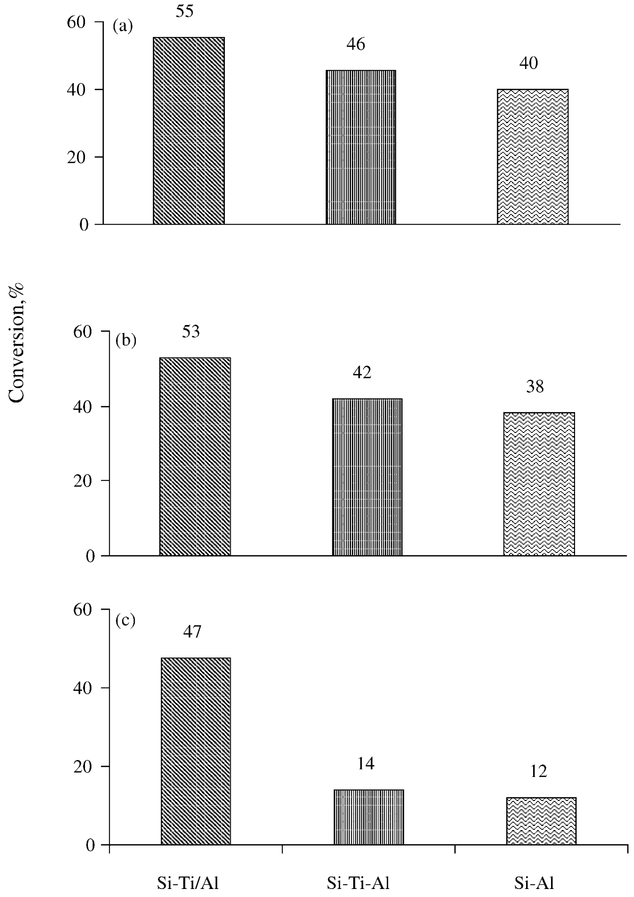

Fig. 4. Conversion at 653 K and 120 h time-on-stream for (a) HDS, (b) HDM and (c) HDN.

It has been shown before that when Ti is incorporated during the synthesis of an Al-Ti mixed oxide support, for Ti contents below 50 mol%, the support surface is enriched with alumina [26].

The HDM results are shown in Fig. 4b. The activity of the catalysts follows the same trend with the support composition than that found for HDS. The total HDM conversions (Ni + V) were 53, 42 and 38% for the Si-Ti/Al, Si-Ti-Al and Si-Al catalysts.

Usually, the hydrodemetallization reaction depends strongly on the textural properties of the catalyst since bulky molecules have to enter into the pores to be demetallized. If the composition of the support had no influence on this reaction, the most active catalyst should be the one supported on alumina because this catalyst has the biggest pore volume and average pore diameter; however, this is not the case. Following the same line of thinking the Si-Ti-Al catalyst having the smallest pores should be the less active catalyst. However, due to the presence of Ti on the support surface the activity trend is Si-Ti/Al > Si-Ti-Al > Si-Al. Clearly the Ti-containing catalysts are more active despite their smaller pore volume and average pore diameter (see Table 2). It appears then that in the hydrotreatment of heavy petroleum like Maya, the presence of TiO_2 on the catalyst surface increases the activity and stability of the hydrodemetallization functionality.

Concerning the HDN functionality, Fig. 4c presents the HDN conversion observed for the different catalysts at 120 h time-on-stream. In this case, the conversion achieved with the Si-Al and Si-Ti-Al catalysts was similar (12 and 14%, respectively), and the conversion exhibited by the Si-Ti/Al catalyst was very high (47%), compared with the other two catalysts. So, the catalyst with high Ti content on the surface performs better in the hydrodenitrogenation of heavy crudes. It is well known that for HDN to occur is necessary to hydrogenate first the aromatic ring containing the heteroatom. Thus, it is normally found that a hydrotreating catalyst with high hydrogenating functionality performs well in HDN. Previously published results proved that high concentrations of TiO_2 on the catalyst surface increases the hydrogenation of aromatics [20]. According to this, it is then not surprising that the Si-Ti/Al catalyst, which has an egg shell like layer of TiO_2 covering the alumina surface, showed the best HDN activity.

To corroborate the suggestion that the Si-Ti/Al catalyst had more TiO_2 structures on the surface, FT-Raman analysis was performed on the three catalyst supports. Fig. 5 shows that, as suggested, the Raman signal for the Al and Ti-Al supports is similar, showing a broad absorption due to fluorescence phenomena caused by some impurity in the alumina support. Only a very small peak at 146 cm^{-1}, which is the most intense Raman peak of the titania-anatase phase, indicates the presence of some TiO_2 structures on the surface of this support. In contrast, for the Ti/Al support, intense and well defined peaks typical of titania-anatase appear at 146, 398, 520 and 640 cm^{-1}, with almost no signal due to fluorescence, indicating clearly that the nature of the support surface is mostly TiO_2-anatase.

It has been mentioned earlier that the acidity of the support is beneficial to HDS and some correlation has been found between the acidity of the oxide catalysts precursors and the catalytic activity of the catalyst in the sulfided state. This has been related to a better dispersion of the active phase precursors, obtained during catalyst preparation in the impregnation steps [4,27]. To analyze this point, some acidity measurements were performed in our catalysts. Fig. 6 shows the results of pyridine adsorption on the oxide catalysts. The results show that a greater number of acid Lewis sites are present in the Ti-containing catalysts and that Si-Ti/Al is the most acid, with Si-Al showing the smaller number of acid sites. The acidity values obtained after desorption of pyridine at higher temperatures (up to 573 K) indicate that the strength of the acid sites follows the same tendency with support composition (Si-Ti/Al > Si-Ti-Al > Si-Al).

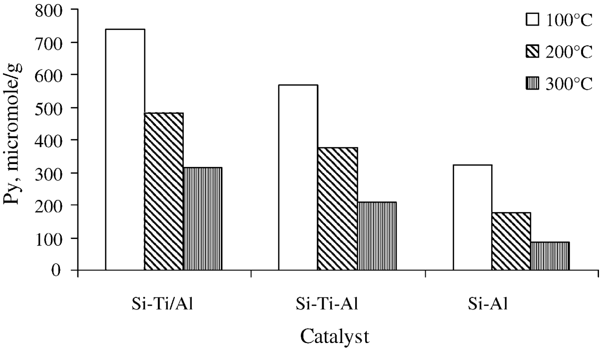

Fig. 6. Pyridine adsorption for oxide catalysts at different outgassing temperatures.

Concerning the structure of the Mo and Ni species existing on the Ti-containing catalysts, it has been well established that the presence of TiO_2 on the surface induces the formation of more Mo in octahedral coordination [20]. However, little has been said about the changes induced on the Ni promoter. To enquire on this, UV–vis-DRS characterizations were performed. Fig. 7 shows the electronic spectra of the three catalysts in their oxide state in the 500–900 nm region. In the 415 nm zone, where typical absorption of octahedral Ni appears, no clear difference between the catalysts was observed. However, some differences are evident in the 500–900 nm region where contributions of tetrahedral Ni (595–615 nm, shoulder) and octahedral Ni in NiO (730 nm) are detected. Respect to the other two catalysts, the maximum of the spectrum of the Si-Ti-Al catalyst shifted towards higher wavelengths and appears at 730 nm, in contrast to the other two catalysts that present the maximum at 650 nm. This indicates that in the Si-Ti-Al sample

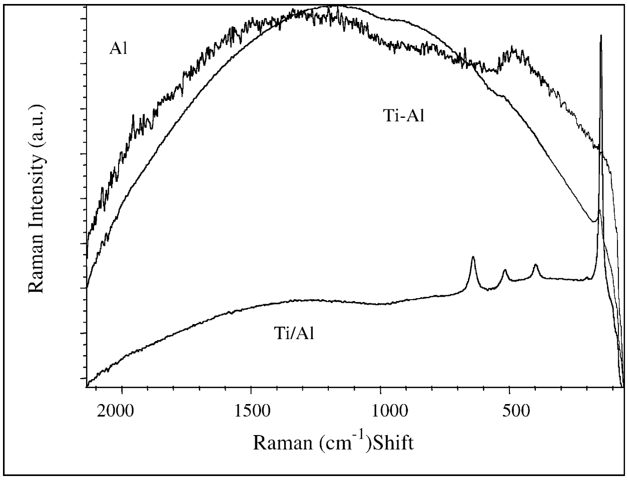

Fig. 5. FT-Raman spectra of supports.

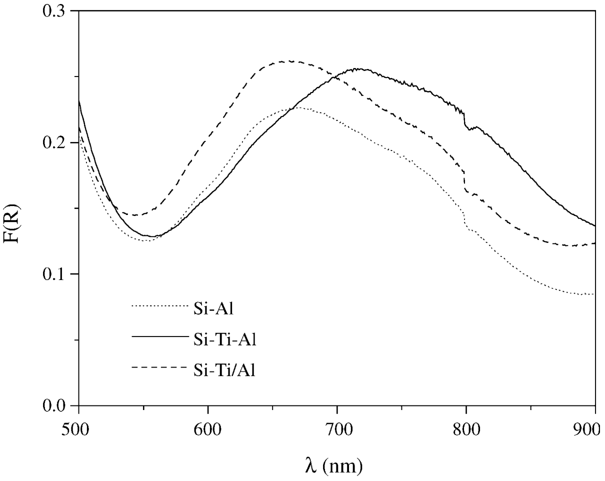

Fig. 7. Electronic spectra of oxide catalysts in the 500–900 nm region.

a greater amount of segregated NiO particles is present. However, if they were present in significant amounts, these NiO particles would be smaller than 40 Å in size since no NiO phase was detected by XRD.

4. Discussion

The above results indicate that the incorporation of Ti to the alumina support in NiMo catalysts induces higher HDS, HDM and HDN during the hydrotreatment of heavy Maya crude. This increase in activity is significantly affected by the way in which Ti is incorporated to the support. Incorporation of Ti to boehmite leads to smaller activities than incorporating Ti to alumina. As the Raman results show, incorporation of Ti to boehmite appears to form, most probably during the calcinations step, greater amount of Ti–O–Al bonds and a low concentration of TiO_2 structures. On the contrary, adding Ti to the surface of alumina leads to the formation of TiO_2 structures, which cover most of the alumina surface, since almost no fluorescence is evident in this sample and the Raman peaks characteristic of TiO_2-anatase are well defined and intense. Previous studies with mixed oxides prepared by sol–gel have led to the conclusion that when Ti–O–Al bonds are dominant the activity of the catalyst supported on the mixed oxide resembles that of an alumina supported catalyst. In our case, according to the Raman characterization, the reaction of titanium isopropoxide with the highly hydroxylated boehmite leads after calcination to a surface with few TiO_2-anatase structures.

The contaminants and aromatics present in the heavy feed used in this study seem to affect less the catalysts with Ti incorporated than those supported on pure alumina. This effect could be related to the greater hydrogenating capability of Ti-containing catalysts [20], which will enhance HDN and prevent coking. The more stable operation of the Ti-containing catalysts with time-on-stream is in line with this suggestion.

The catalyst acidity is also affected significantly by the way in which Ti is incorporated. The catalysts with more TiO_2 on the surface present higher acidity, greater number and strength of acid sites. A clear explanation of the effect of acidity with such a complex feed as the one used here goes beyond the scope of the present work. Nevertheless, the mild acidity presented by the catalysts, which does not appear to be strong enough to promote enhanced poisoning by coke, followed the same trend as catalytic activity.

To analyze the state of dispersion of the sulfided phase in the three catalysts, NO adsorption was performed on the sulfided samples. It is well known that NO titrates the sulfur vacancy sites on the sulfides (CUS), which are associated with the active sites in hydrotreatment. Fig. 8 shows the results of NO adsorption normalized per square meter of catalyst surface. In line with the results obtained above, the Si-Ti/Al catalyst showed a greater number of CUS (0.06 μmol NO/m^2) compared with Si-Ti-Al (0.03 μmol NO/m^2) or Si-Al (0.01 μmol NO/m^2). Not surprisingly, this trend is the same as the one observed for catalytic activity. It appears then that the incorporation of Ti to the catalyst support increases the number of sulfur vacancies associated to the active sites. This can also be an indication of increased dispersion of the sulfided phase. These effects lead to enhanced catalytic activities in the different functionalities of the catalyst.

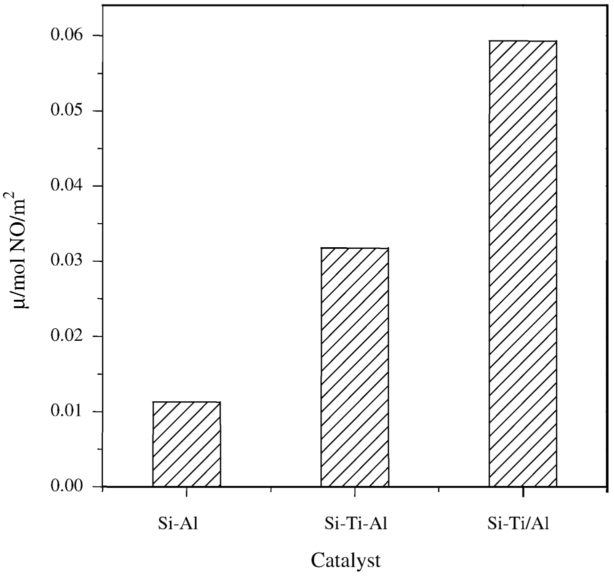

Fig. 8. Dynamic NO adsorption over sulfided catalysts.

5. Conclusions

In the present study, heavy Maya crude was hydrotreated with three different NiMo catalysts in order to analyze the effect that over the different catalyst functionalities (HDS, HDM and HDN) has the presence of Ti and the mode in which it is incorporated to the catalyst support. The above results allow us to conclude the following:

(a) For the hydrotreatment of heavy Maya crude, the incorporation of Ti to the alumina support surface in NiMo catalysts leads to enhanced HDS, HDM and HDN activities.
(b) The method of incorporating Ti to the alumina surface is of significant importance to catalytic activity. High activity is obtained when the method of incorporating Ti promotes the formation of TiO_2 structures on the surface of the support.
(c) Ti-containing catalysts present higher acidity (number and strength of acid sites), and greater number of coordinatively unsaturated sites (CUS), associated with the active sites in hydrotreatment.
(d) The beneficial effects induced by Ti render the catalysts not only more active but also more stable towards poisoning by the different components of the heavy feed used in this work.

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