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# Effect of silicon content on active catalytic phase for hydrocracking of heavy crude oils

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#### ABSTRACT

The silicon composition effect on acidic properties of Ni[sbond]Mo catalysts was investigated for hydrocracking reaction, where an optimal Si and Al ratio is required for the formation of Brønsted acid sites and as well as of Al<sup>3+</sup> (IV) tetrahedral coordinated sites. The support composition affects the Si[sbond]OH[sbond]Al network, where cations (Al<sup>3+</sup> or Si<sup>4+</sup>) have a coordination number of IV generating higher Brønsted acidity and macro-pores. The supports and fresh catalysts were characterized by atomic absorption, nitrogen physisorption, FT-IR of CO and pyridine adsorption and <sup>27</sup>Al MAS NMR.

#### **KEYWORDS**

heavy crude oils; hydrocracking; hydrodeasphalting; Ni[sbond]Mo catalysts; SiO<sub>2</sub>[sbond]Al<sub>2</sub>O<sub>3</sub>

# 1. Introduction

Hydrocracking is one of the main refining processes where the heavy crude oil and heavy fractions are changed to light products with better quality, becoming essential for product selectivity toward middle distillates; however, pore diffusion limitations preventing the access of large molecules as asphaltenes to the active sites and the rapid deactivation of the catalyst by coke and metal deposition is the main task (Speight 2019) that has to be solved. One way is by bifunctional catalysts that promote hydrogen transfer reaction associated with hydro/dehydrogenating function, while isomerization and cracking of the hydrocarbon skeleton occur on Brønsted sites of the acidic component (Hensen et al. 2010), as well as, the textural properties, which can be controlled by the selection of the proper support composition and its preparation method (Ali, Tatsumi, and Masuda 2002). The present work aimed to study the effect of Silicon content on the acid sites formation and the electron deficiency of active metals species related to hydrocracking reaction. The study makes a significant contribution in developing a catalyst which would be able to have higher cracking function due to the support contribution.

# 2. Experimental

## 2.1. Synthesis of supports and catalysts

A series of SiO<sub>2</sub>[sbond]Al<sub>2</sub>O<sub>3</sub> supports, and Ni[sbond]Mo supported catalysts were synthesized according to as reported elsewhere (Leyva et al. 2009), for obtaining Mo and Ni contents of 5 and 2 wt%, respectively, on the final catalytic materials. Four supports were obtained and labeled as SA-0.04, SA-0.09, SA-0.22, and SA-0.46; the number indicates the Si/(Al+Si) atomic ratio. The catalysts were denoted as NM/SA-0.04, NM/SA-0.09, NM/SA-0.22, and NM/SA-0.46.

Sample	SSA, m²/g	APD, nm	TPV, mL/g	Micropore	Mesopore	Macropore
Supports						
SA-0.04	376	6.2	0.55	0.8	98.5	0.7
SA-0.09	317	6.6	0.51	0.2	97.4	2.4
SA-0.22	295	8.4	0.63	1.6	93.8	4.6
SA-0.46	223	13.7	0.76	1.2	71.0	27.8
Catalysts						
NM/SA-0.04	327	5.8	0.48	1.1	98.3	0.6
NM/SA-0.09	349	5.6	0.49	1.7	97.6	0.7
NM/SA-0.22	255	8.5	0.54	1.2	93.5	5.3
NM/SA-0.46	167	14.0	0.58	1.4	73.9	24.7

Table 1. Textural properties supports and catalysts.

Micropore <2 nm, mesopore 2–50 nm, macropore >50 nm.

## 2.2. Characterization

Textural properties were analyzed in a Quantachrome Nova 4000 equipment with nitrogen gas at liquid nitrogen temperature (77 K =  $-196^{\circ}$ C). The samples were degassed for 3 h at 300°C. For FTIR spectra, a Nicolet 710 FTIR spectrometer with MCT and DTGS detectors using a resolution of 4 cm<sup>-1</sup> was employed. The catalysts were sulfided in situ in the IR cell under a flow of 10% H<sub>2</sub>S in H<sub>2</sub> (30 mL/min) at 3°C/min up to 400°C for 4 h. <sup>27</sup>Al MAS NMR analyses were recorded at 104.3 MHz on a Bruker Fourier 300 spectrometer, using short and powerful radio frequency pulses (0.6 µs, equivalent to 10° pulse angle).

# 2.3. Catalytic activity evaluation

Firstly, the cumene hydrocracking (HCR) was used as a model reaction to determine relative acidity of the catalysts. 200 mg of the catalyst with a particle size of 0.4-0.8 mm was sulfided at 400°C for 3 h in a flow of 50 mL/min of hydrogen saturated with CS<sub>2</sub> in a fixed-bed glass reactor at atmospheric pressure with a GC Varian 3700 equipped with FID/TCD detectors.

The mild hydrocracking of heavy crude oil (21.4 API, 12.7 wt% asphaltenes content) was carried out in a stainless-steel tubular fixed-bed up-flow reactor. 10 mL of the catalyst was loaded and sulfided at 2.8 MPa and 320°C for 5 h, and the reaction was carried out at 5.4 MPa and 380°C for 200 h.

# 3. Results and discussion

#### 3.1. Textural properties

The influence of the increasing amount of  $SiO_2$  is evident for the textural properties (Table 1), especially for the specific surface area (SSA), which decreases as the silica content increases as well as with the incorporation of Ni and Mo. The intercalation of silicon-aluminum influences on the porosity of silica–alumina composite, this can be attributed to a dense silica–alumina phase formation, and it fills the interlayer region would not give rise to the high surface area. At higher silica content, there is a significant growth in macropore porosity, which indicated the effect of silica in macropore structure formation. These results may correspond to the improving reactants diffusion and active sites accessibility on the one hand, but decreasing the dispersion of the active phase on the other hand.

# 3.2. FTIR of pyridine adsorption

The pyridine (py) adsorption results for supports and catalysts at  $150^{\circ}$ C is shown in Figure 1. Strong IR bands assigned to Lewis acid sites (LAS) are observed for SA-0.04 and 0.09 at  $1450 \text{ cm}^{-1}$ , and at



Figure 1. Comparison of IR spectra of thermodesorption of pyridine at 150 °C of supports and catalysts.

Si/(Si + Al)		LAS, $\mu$ mol g <sup>-1</sup>			BAS, $\mu$ mol g <sup>-1</sup>			
	100 °C	200 °C	300 °C	400 °C	100 °C	200 °C	300 °C	400 °C
0.04	182.8	95.5	40.7	17.9	0.00	0.00	0.00	0.00
0.09	110.2	90.4	46.2	21.3	1.57	0.71	0.5	0.20
0.22	147.2	77.0	34.8	16.3	3.8	1.4	1.0	0.7
0.49	103.7	64.7	38.4	21.8	17.3	7.7	1.4	0.9

Table 2. Py adsorption results on supports.

1617 cm<sup>-1</sup>, which are due to vibration modes of chemisorbed pyridine on coordinative unsaturated  $Al^{3+}$  sites (tetrahedral  $Al^{3+}$  (IV) and octahedral  $Al^{3+}$  (VI) environments, respectively) (Rajagopal, Marzari, and Miranda 1995). The Brønsted acid sites (BAS) appears at around 1545 cm<sup>-1</sup> being more visible for SA-0.22, and SA-0.46 supports, and 1640 cm<sup>-1</sup> band characteristic of the pyridinium ions was found for SA-0.46 indicating the presence of strong BAS. For supported catalysts, the intensity of the bands 1450 and 1545 cm<sup>-1</sup> is reduced due to the deposition of nickel and molybdenum; this indicates that the amount of acid sites has decreased; however, the nature and the strength of these sites are not modified. The concentrations of LAS and BAS according to py adsorption-desorption temperature (Table 2), were estimated from the intensity and areas of IR bands at *ca*. 1450 and 1545 cm<sup>-1</sup>, respectively, using the molar extinction coefficients (Emeis 1993). The number of LAS is higher than BAS in a global way, excluding for SA-0.04 support, which does not have evidence of BAS. Instead, the opposite behavior was observed for the highest silica content support (SA-0.46); this can be attributed to an optimum ratio of silicon atoms and aluminum atoms which promote the formation of BAS at this silica concentration.

# 3.2. FTIR of hydroxyl groups

The CO adsorption on  $SiO_2[sbond]Al_2O_3$  supports are shown in Figure 2. For SA-0.04 and SA-0.09, Al[sbond]OH bands were detected at 3790–3780, 3730–3725, 3700–3675 cm<sup>-1</sup>, indicating



Figure 2. CO adsorption on silica-alumina supports at 1 Torr of equilibrium.

the presence of alumina. The band at  $3770 \text{ cm}^{-1}$  has been assigned to isolated Al IV[sbond]OH groups bonded to tetrahedral Al, and the bands at 3727, 3732, and  $3678 \text{ cm} \text{ cm}^{-1}$  to bridging Al<sup>VI</sup>[sbond]OH[sbond]Al<sup>IV</sup>, Al<sup>IV</sup>[sbond]OH[sbond]Al<sup>VI</sup> and (Al<sup>VI</sup>)<sub>3</sub>[sbond]OH (Omegna, van Bokhoven, and Prins 2003). These bands are intense for low silica content supports but tend to disappear when SiO<sub>2</sub> content increases. For SA-0.46, a band at  $3745 \text{ cm}^{-1}$ , which corresponds to the silanol groups, is observed. For SA-0.22, the silanol band is visible as well, and other two broad shoulders are also observed at 3528 and  $3628 \text{ cm}^{-1}$ , these correspond to the contribution of alumina OH groups, and the interaction of silanol groups with water molecules, respectively.

#### 3.3. CO adsorption on sulfide catalytic phases

The dispersion of Mo and Ni phases was determined by CO chemisorptions over sulfided catalysts (Figure 3). Vibration frequencies of CO adsorbed on the LAS, and BAS are similar, indicating that the acid strength of the support is not significantly modified by the sulfide phase. Different bands were observed at around 2127, 2111, 2080, and  $2070 \text{ cm}^{-1}$ , which correspond to the adsorption of the sulfided sites of the supported catalysts due to Ni on the edges of MoS<sub>2</sub> (NiMoS), non-promoted sixfold coordinated Mo sites, and fivefold, and fourfold coordinated Mo sites at the vicinity of Ni promoter, respectively (Travert et al. 2001). The sulfide phase is notable for NM/SA-0.04 to NM/SA-0.09 by ~15%, indicating an increase of the dispersion of the sulfide phase. For higher silicon loadings, the opposite behavior is observed. For NM/SA-0.22 to NM/SA-0.46 a shoulder between 2130 and 2120 cm<sup>-1</sup>, and bands at 2090 cm<sup>-1</sup> and at 2060 cm<sup>-1</sup> were detected and correspond to CO adsorption on the Ni promoter; on pure nickel sulfide phase; and Mo sites of the partially Ni substituted on Mo on the edges, respectively (Crépeau et al. 2006).



Figure 3. CO adsorption on NiMo sulfided supported catalysts at 1 Torr at equilibrium.

# 3.4. Nuclear magnetic resonance (NMR)

 ${}^{27}Al MAS NMR$  spectra of SiO<sub>2</sub>[sbond]Al<sub>2</sub>O<sub>3</sub> supports were obtained (not shown). Three components at around 60, 25, and 0 ppm that are due to aluminum in tetra- (Al<sup>3+</sup> IV), penta- (Al<sup>3+</sup> V), and octahedral (Al<sup>3+</sup> VI) oxygen-aluminum coordination, respectively, were obtained. The generation of acid centers is due to the isomorphous substitution of Si<sup>4+</sup> by Al<sup>3+</sup> in the silica lattice. When an ordinarily six-coordinated Al atom is placed in a four-coordinated structure, a net unit negative charge is created, that can be compensated by the addition of proton, in this way BAS are created (Hensen et al.2010). In this sense, the SA-0.46 support possesses a more significant amount of Al<sup>3+</sup> (IV) atoms thus higher amount of BAS.

# 3.5. Catalytic activity for cumene hydrocracking

Same behavior for supports and catalysts was obtained (Figure 4). The maximum cumene hydrocracking reaction rate corresponds to the amount of BAS sites generated according to the silicon content. The cumene HCR reaction rate is related to of  $Si^{4+}$  and  $Al^{3+}$  in a tetrahedral environment of shared oxide ions. The SA-0.46 support has a more significant amount of  $Al^{3+}$  (IV) atoms, having a high hydrocracking activity, this suggests that the composition of this support possess an optimal  $Si^{4+}-Al^{3+}$  network ratio to form the required BAS for enhancing the acidic function. Meanwhile, the SA-0.04 and SA-0.09 shown low hydrocracking activity, this can be attributed to the small ratio octahedral  $Al^{3+}$  than tetrahedral than SA-0.22, and SA-0.46 supports, the ratio of formation octahedral  $Al^{3+}$  than tetrahedral is increasing as the silica content increases until ~50 wt% of SiO<sub>2</sub>. For catalysts behavior, the number and the interaction of [sbond]OH group of support with molybdenum and nickel provokes a decrease in Brønsted acidity (Navarro et al. 1996). However, during sulfidation, Mo supported  $Al_2O_3$  catalyst created acid sites, which are stronger than those of the support. Thus, the cracking activity is a contribution of both the acid sites of the support and supported sulfide phases (Muralidhar, Massoth, and Shabtai 1984).



Figure 4. Comparison of the HCR activities of supports and Ni-Mo catalysts respect to amount of BAS.



Figure 5. Effect of support composition on the hydrodeasphalting of heavy crude oil.

#### 3.6. Hydrodeasphalting (HDAs) catalytic activity

The catalytic activity of supported catalysts for hydrodeasphalting reaction is presented in Figure 5. The presence of acid sites affects asphaltene conversion, the higher acidity containing catalyst (NM/SA-0.46) has higher HDAs. This can be explained in two ways, either due to the pore diameter or due to the acidity. The HDAs results correlate to the HCR of cumene (acidity) and average pore diameter (large pore). The existence of BAS on SiO<sub>2</sub>[sbond]Al<sub>2</sub>O<sub>3</sub>, enhances the rate of hydrocracking, because of the BAS presented on the surface can donate a proton required for hydrocracking reaction and represents another form of surface hydrogen. The [sbond]SH groups on the surface of the catalyst have the proton-donating ability as well (Furimsky 2007). For molecules possessing a double bond (olefin and aromatics), they can readily accept a proton and form a carbocation. Otherwise, a carbocation could be formed by donating a hydride  $H^-$  from hydrocarbon to a LAS on the catalyst surface.

# 4. Conclusions

The aim of the cracking activities results is to find out a balance between acidity and textural properties of the sulfided catalysts, which is responsible for the cracking activity of heavy oil molecules. The silicon content contributes to the acidic nature as well as textural properties of the support. Additionally, the surface of the support is responsible for the active metal dispersion through its nature of interaction and facilitation toward the activation of catalysts. The introduction of the acid component in  $Al_2O_3$  modifies the metal support interaction of active metals, which has a corresponding effect on the activity.

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