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Niobium oxide (Nb_2O_5) as support for CoMo and NiW catalysts in the hydrodesulfurization reaction of 3-methylthiophene

Avaliação de Catalisadores CoMo e NiW suportados em Óxido de Nióbio em reação de Hidrodessulfurização de 3-metiltiofeno

Evaluación de Catalizadores de CoMo y NiW soportados em Óxido de Niobio em Reacción de Hidrodesulfuración de 3-metiltiofeno

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Abstract

The efficiency of niobium oxide as catalytic support of hydrodesulfurization (HDS) catalysts (CoMo and NiW) has been investigated in the HDS of a model molecule representative of sulfur compounds present in FCC gasoline (3-methylthiophene: 3MT). The NiW catalyst presented higher catalytic activity than CoMo calcined and non-calcined catalyst, however a better ratio pentane/pentene has been achieved by CoMo catalysts, which implies a lower formation of hydrogenated products. Indeed, the activity order for the catalysts evaluated is: NiW/Nb_2O_5 > CoMo/Nb_2O_5 calcined support > CoMo/Nb_2O_5 non-calcined support, despite the ratio pentane/pentene which has the inverse order. Furthermore, textural and chemical characterization techniques have been performed. From NH_3-TPD analysis it was observed an acidity profile with a predominance of weak/strong and weak/moderate acid for CoMo and NiW catalysts, respectively. Meanwhile, the BET analysis has shown a low specific surface area for the catalysts supported by niobium oxide. Concerning the structure characteristic, the XRD analysis has suggested an amorphous phase in all catalysts analyzed.

Keywords: Hydrodesulfurization; FCC gasoline; 3-Methylthiophene; Niobium oxide; Interaction metal-support.

Resumo

A eficiência de óxido de nióbio como suporte para catalisadores de hidrodesulfurização (HDS), CoMo e NiW, foi investigada na reação de HDS de uma molécula modelo representativa de compostos sulfurados presente na gasolina de FCC (3-metiltiofeno). O catalisador NiW/Nb_2O_5 apresentou a maior atividade catalítica, seguido pelo catalisador CoMo/Nb_2O_5 calcinado e por fim o catalisador CoMo/Nb_2O_5 não calcinado. Entretanto, apesar da menor atividade catalítica, o catalisador CoMo/Nb_2O_5 apresentou uma melhor razão pentano/penteno, fato que implica em uma menor formação de produtos hidrogenados. Além disso, caracterizações químicas e texturais foram realizadas a fim de investigar a estrutura dos catalisadores preparados. A partir da análise de TPD-NH_3 observa-se um perfil de acidez com predominância de ácidos fracos/fortes e fracos/moderados para os catalisadores CoMo e NiW, respectivamente. A análise de área superficial específica (BET) apresentou uma baixa área especifica em todos os catalisadores CoMo e NiW, devido principalmente a baixa área supercial do óxido de nióbio. Por fim, a análise estrutural por difração de Raio-X (DRX) sugere que os catalisadores preparados não possuem uma forma cristalina.

Palavras-chave: Hidrodesulfurização; Gasolina de FCC; 3-Metiltiofeno; Óxido de Nióbio; Interação metal-suporte.

Resumen

La eficiencia del óxido de niobio como soporte para catalizadores de hidrodesulfuración (HDS), CoMo y NiW, se investigó en la reacción HDS de una molécula modelo representativa de los compuestos de azufre presentes en la gasolina FCC (3-metiltiofeno). El catalizador NiW/Nb_2O_5 mostró la mayor actividad catalítica, seguido por el catalizador CoMo/Nb_2O_5 calcinado y el catalizador CoMo/Nb_2O_5 no calcinado. Sin embargo, a pesar de la menor actividad catalítica, el catalizador CoMo/Nb_2O_5 mostró una mejor relación pentano/penteno, hecho que implica una menor formación de productos hidrogenados. Además, se llevaron a cabo caracterizaciones químicas y de textura para investigar la estructura de los catalizadores preparados. A partir del análisis de TPD-NH_3 se observa un perfil de acidez con predominio de ácidos débiles/fuertes y débiles/moderados para los catalizadores de CoMo y NiW, respectivamente. El análisis del área superficial específica (BET) mostró un área específica baja en todos los catalizadores CoMo y NiW, principalmente debido a la baja área superficial del óxido de niobio. Finalmente, el análisis estructural por difracción de rayos X (DRX) sugiere que los catalizadores preparados no tienen forma cristalina.

Palabras clave: Hidrodesulfuración; Gasolina FCC; 3-Metiltiofeno; Óxido de Nióbio; Interacción metal-soporte.

1. Introduction

The reduction of pollutants in fossil fuels is a challenge in the refineries taking into account more strict regulations and the development of environmentally friendly energy. In order to achieve the requirement for environmental regulations, different alternatives need to be evaluated aiming at reducing contaminants present in the motor vehicle fuels (Lu et al., 2020; Santos et al., 2019). Hydrotreatment process is one of the alternatives and consists in removing impurities (S, N, O) from crudes under high partial pressure of hydrogen. Regarding the hydrodesulfurization process of FCC gasoline, the challenge is to selectively hydrodesulfurize the sulfur species (HDS) and to avoid the hydrogenation of olefins (HYD) in order to preserve the octane number of the fuel (Silva & Secchi, 2018).

Due to the presence of sulfur compounds, the hydrotreatment process needs specific catalysts that combine high thioresistance and catalytic activity. In this regard, hydrotreating catalysts are usually in form of transition metal sulfides (TMS) such as molybdenum and tungsten (VIB group) promoted by elements of VIIIB group such as nickel or cobalt and supported on alumina, silica or aluminosilicates. Thus, the usual industrial catalyst for the hydrodesulfurization processes is the molybdenum sulfide catalysts promoted by nickel or cobalt, depending on the feed to be hydrotreated, with a Co(Ni)/[Co(Ni)+Mo] molar ratio between 0.3-0.6 (Santos et al., 2019). Furthermore, the catalytic support is responsible for loading the active components and disperse the active phase, improving the reaction effectiveness. It is the catalytic support that influences the diffusion, adsorption and determines the accessibility of reactants towards the active sites (Gutierrez et al., 2017; Huirache-Acuña et al., 2012). This fact presents the relevant importance of the support and the interaction metal-support in the preparation step of a hydrotreatment catalyst.

Currently, Brazil has more than 90% of the world's natural resource of niobium (Nb) and it is considered the largest explorer country in the world for this metal. In the hydrotreatment field, the literature has shown an increase in the number of publications about activity and selectivity enhancement as well as the chemical stability of traditional catalysts when a small amount of niobium is added (Aray et al., 2014; Méndez et al., 2017). Gaborit et al. (2000) used niobium as a dopant for hydrotreating NiMo catalyst to investigate the hydrodesulfurization of dibenzothiophene (DBT) and hydrogenation (HYD) of tetraline at $P = 33$ bar and $T = 300$ºC. The use of niobium as a dopant has increased the catalytic activity in both, HDS and HYD, model reactions where the highest activities were obtained with an optimum niobium content of 5%. In the case of DBT hydrodesulfurization, the selectivity for cracked products increased and isoalkylbenzenes appeared when Nb was added, which demonstrated that niobium sulfide enhanced the catalytic acidic properties. Since then, a crescent interest in the application of these materials has been noticed, especially with studies about niobium oxides as active phase or catalytic support. The Nb_2O_5 has already been used as support to Mo and Co (Ni) Mo as well as a precursor of active phase such as niobium sulfide (Faro et al., 2006; Kaluza & Zdražil, 2018; Méndez et al., 2017). For instance, Faro et al. (2006) have investigated the HDS of thiophene at 2.8 MPa and 523–573 K and concluded that the degree of niobium sulfidation increases in the following order: $Nb_2O_5 < Ni/Nb_2O_5 < Mo/ Nb_2O_5 < NiMo/Nb_2O_5$. Moreover, it was concluded that niobium sulfide has a strong influence on the activity of the niobium-supported catalysts in the cumene hydrocracking reaction.

Furthermore, the selective hydrodesulfurization reaction has also been studied over supported tungsten catalyst promoted by nickel under specific operating conditions, due mainly to the promising HDS activity over the WS_2 slabs. Indeed, León et al. (2017) have studied the HDS of 3-methylthiophene at $T = 280$ºC and atmospheric pressure over a supported NiW catalyst under different supports. In this study, the catalytic performance of the NiW was attributed to an efficient metal-support interaction, particularly with the samples that used the proposed mixed supports.

In order to further increase the catalytic activity through enhancing the interaction of metallic ions, numerous studies have been published in the literature by using a chelating agent in the hydrotreatment catalysts (CoMo and NiMo, NiW) preparation (Haandel et al., 2017; Pereyma et al., 2018; Valencia et al., 2014; Valencia & Klimova, 2012). The chelating agent are molecules composed by two or more atoms donors of electrons that works as a ligand of a metallic ion behaving as acid/base of Lewis. This reaction occurs with a great contribution of entropy, due to the water molecules surrounding of metallic ion replaced by a ligand chelating (Kaluza et al., 2012). In the literature, the citric acid and ethylene diamino tetracetic acid (EDTA) have been studied as a chelating agent in the in the preparation step of catalysts for hydrotreatment of sulfur compounds such as thiophene and benzothiophene with NiMo, CoMo and NiW catalysts (Castillo-villalón et al., 2014; Kaluza & Zdražil, 2018; Lélias et al., 2010; Pereyma et al., 2018). Indeed, Kaluza & Zdražil (2018) have applied the nitrilotriacetic acid (NTA) in the preparation of CoMo catalyst supported in niobium in order to improve its activity in the HDS of thiophene at 1.0 MPa and 400ºC. A pronounced improvement (5.7 times) has been noticed when compared the specific activity normalized per total BET surface area with the commercial catalyst, which was attributed to a positive effect of NTA in the preparation of supported niobium catalyst as well as the high activity per m^2 of $CoMo/Nb_2O_5$ catalyst. The citric acid as a chelating agent was also used in the preparation of a supported NiW catalyst in the investigation of the effect of catalytic thermal treatment in the HDS of dibenzothiophene (T = 280ºC, P = 35 bar, H_2/feed = 500 m^3/m^3) (Pereyma et al., 2018). In this study, a direct correlation between the thermal treatment temperature and the catalytic activity of DBT HDS has been found and attributed to an increasing in the stacking degree of WS_2 while maintaining a small length of sulfide slabs.

This paper focuses on the efficiency of niobium oxide as a support for two types of catalysts, CoMo and NiW, in the hydrodesulfurization of a model sulfur molecule (3-methylthiophene) representative of sulfur species present in the FCC gasoline. The role of the support as well as the active phase will be investigated through a catalytic activity test and explained by the proposed characterizations aiming at achieving the selective hydrodesulfurization of model molecule by avoiding the hydrogenation of olefins.

2. Experimental Part

2.1 Catalyst and chemicals

The CoMo catalyst precursors were prepared using Ammonium Heptamolybdate Tetrahydrate - AHM (Sigma Aldrich, Prod. No.1.01182) and cobalt nitrate hexahydrate - CoN (Vetec, Prod. No. 295). Meanwhile, the NiW were prepared with Ammonium Metatungstate - AM (Sigma Aldrich, Prod. No. 463922) and Nickel Nitrate - NiN (Sigma Aldrich, Prod. No. 301100025414). The Citric Acid - CA (Sigma Aldrich, Prod. No.1001727327) was used as a chelating agent in the preparation of both types of catalysts (CoMo and NiW). Niobium oxide hydrate ($Nb_2O_5.xH_2O$) was provided by Companhia Brasileira de Metalurgia e Mineração in the form of fine powder.

The support for the catalysts (Nb_2O_5) has been calcined in a muffle for 4 hours at 400°C. Afterward, the sample was used for metal wet impregnation with a molar ratio CA/precursor = 1. The mass of precursors as well as the molar ratio Co:Mo and Ni:W for the catalysts prepared are presented in Table 1.

Table 1. Theoretical mass of precursors and the molar ratio of each metal used in the catalyst preparation.

Compound	$CoMo/Al_2O_3$[1]	$CoMo/Nb_2O_5$ non calcined support	$CoMo/Nb_2O_5$ calcined support	NiW/Nb_2O_5 calcined support
CoO (wt%)	3.0	3.2	3.2	-
MoO_3 (wt%)	10.0	15.5	15.5	-
NiO (wt%)	-	-	-	3.8
WO_3 (wt%)	-	-	-	24.5
Citric Acid (wt%)	-	17.4	17.4	11.0
Molar Ratio (A/(A+B))[2]	0.35	0.21	0.21	0.26

1. (Santos et al., 2019)
2. Where: A: Co or Ni; B: Mo or W.

Source: Authors.

The supported CoMo and NiW over Nb_2O_5 were prepared by wet impregnation with an aqueous solution of the precursor of CA, CoN and AHM for CoMo and CA, AM and NiN for NiW. The pH of each sample was 2.70 for the non-calcinated support, 1.38 for the CoMo/Nb_2O_5 calcined support and 1.15 for the CoMo/Nb_2O_5 calcined support.

In all samples, the wet impregnation resulted in a solid catalyst that was dried in a rotary vacuum evaporator for 1h and in the oven at 110°C for 2h. The catalyst was crushed and sieved to a size range between 250 and 315 μm and then sulfided *in situ* under H_2S/H_2 flow (10 mol% H_2S) for 10 h at 400°C and atmospheric pressure. 3-methylthiophene (98% purity) and n-heptane (>99% purity) were purchased from Sigma-Aldrich which was used without further purification. Hydrogen sulfide (1 vol% in mixture with H_2) was purchased from Air Liquide.

2.2 Characterization techniques

The specific surface area of the catalysts was measured on a Micromeritics ASAP 2000 analyzer at -196ºC. Before N_2 adsorption, the solid samples containing oxide precursors were degassed overnight under a secondary vacuum at 120°C. The specific surface area (S_{BET} in m^2/g) was calculated from the adsorption isotherm (P/P0 between 0.05 and 0.20) using the Brunauer-Emmett-Teller (BET) method. The total pore volume was calculated from the adsorbed volume of nitrogen at P/P0 equal to 0.99.

The acidity of the catalyst was measured by the NH_3-TPD technique. The samples (150 mg) were pretreated with He (30 mL/min) at 200 °C for 30 min and cooled down to 100 ºC. The ammonia adsorption was then carried out (5% NH_3 in He: 30 mL/min, for 30 min). The physisorbed ammonia was purged with He (30 mL/min) for 1 h. The desorption of NH_3 was measured from 100°C to 400°C with a rate of 5 $^{\circ}C.min^{-1}$ under the inert gas helium. The amount of desorbed NH_3 was analyzed using a TCD detector.

The decomposition temperature of the precursor as well as the stability of the support was evaluated by thermogravimetric analysis, using a thermobalance from Shimadzu model DTG-60 by heating (5mg) the sample between 25-900 °C (rate of 10 °C/min) under a nitrogen flow rate of 100 mL/min.

The crystallinity of the various samples was determined by X-ray diffraction (XRD). using Shimadzu model XRD 6100 diffractometer with a Cu-Kα tube at 40 kV and 30 mA, with a sample drawer specific for powder-like material. The diffractograms were obtained in the 2θ range between 5 and 80°, with a scanning speed of 2° min^{-1} and 0.02° step at every 0.6s.

2.3. Reaction conditions

Catalytic activity measurements were carried out in a fixed bed reactor at 250°C under a total pressure of 2 MPa with a ratio H2/feed of 360 NL/L. The sulfur model feed (0.3wt% of 3-methylthiophene), containing 1000 ppmS in n-heptane was injected in the reactor by an HPLC Gilson pump (307 series, pump's head volume: 5 cm3). The mass of catalyst used was between 200 and 300 mg. The reaction products were injected on-line using an automatic sampling valve into a Varian gas chromatograph equipped with a PONA capillary column and a flame ionization detector as in previous works (Daudin et al., 2007; Lamic et al., 2008; Naboulsi et al., 2018; Pelardy et al., 2016, 2017; Santos et al., 2019). Desulfurized products, resulting from the transformation of 3-methylthiophene are designated as HDS products corresponding also under these operating conditions to the conversion. The contact time is defined as the ratio between the total amount of feed and the mass of catalyst in the oxide form. The catalytic activity was calculated as the number of moles of HDS products formed per hour and per gram of catalyst. This parameter was calculated at a conversion lower than 30% in a differential regime.

2.4. Scientific Methodology

The scientific methodology of this work was focused on the comparative method since different catalysts have been evaluated and compared in different aspects from catalytic activity until the product distribution in a scope of laboratory research. According to Pereira et al. (2018) the nature of this study is focused on the quantitative methodology since the data have been collected from experimental results, treated and analyzed comparatively.

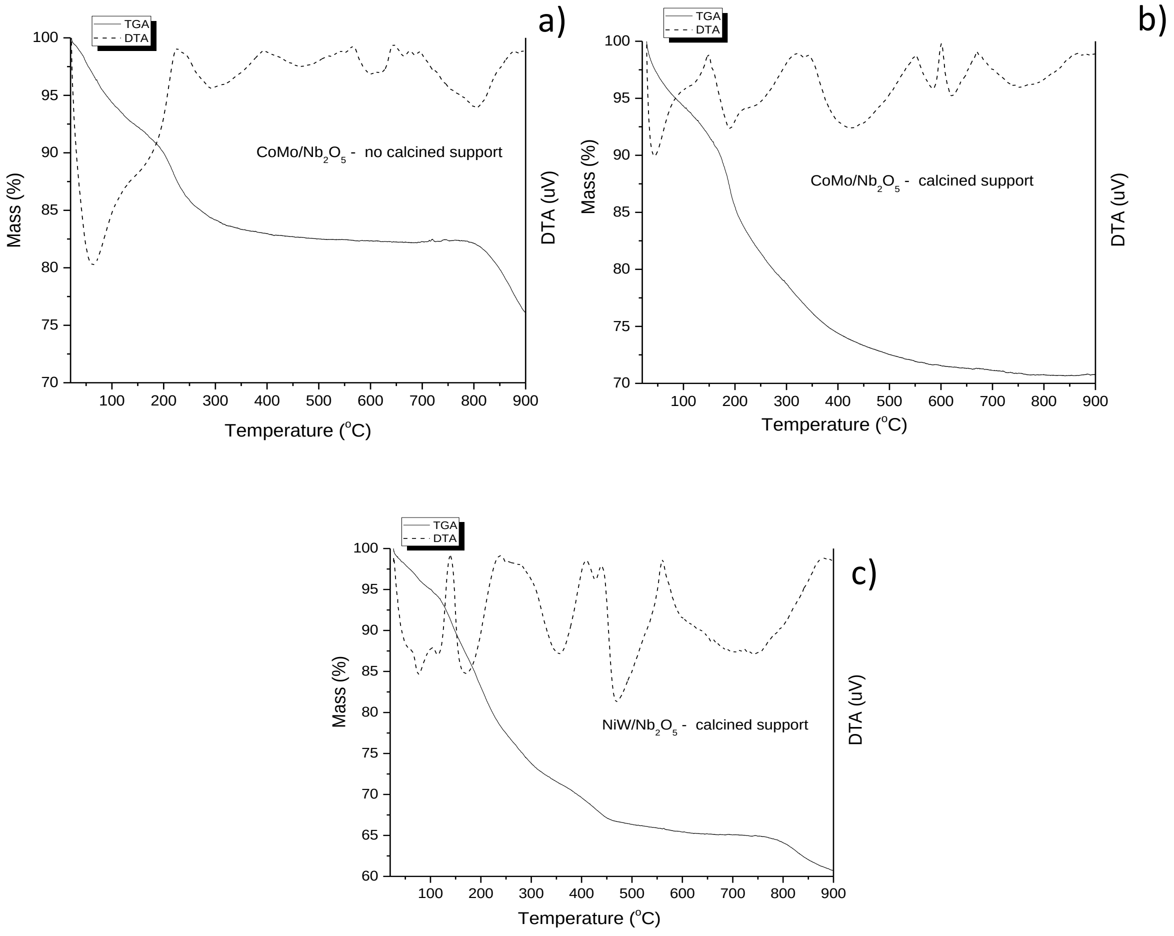
3. Results

3.1. Catalyst Characterization

The physical-chemical properties of the different catalysts CoMo/Nb_2O_5 and NiW/Nb_2O_5 were characterized by their mass loss, specific surface area, structure and acidity measured by TGA, BET, XRD and NH_3-TPD, respectively.

The thermogravimetric analysis has shown endothermic and exothermic phenomena for the three catalyst samples with and/or without a mass loss (Figure 1). The phenomena observed from room temperature up to 150ºC is attributed to mass loss due to the removal of water physically adsorbed in the oxide structure (Silva et al., 2000). The second phenomenon observed at 550ºC and 660ºC, without significant mass loss, could be correlated to the formation of crystal phase Nb_2O_5 with a pseudohexagonal structure, in accordance to the results obtained by Falk et al. (2014). Regarding the non-calcined CoMo/Nb_2O_5 catalyst it is possible to notice a peak, of exothermic nature, related to mass losses at 150ºC and 220ºC (Figure 1a) attributed to thermal decomposition of precursor salts of Co and Mo present in the metal impregnation process. Meanwhile, for the CoMo/Nb_2O_5 calcined support catalyst (Figure 1b), it was observed a thermal decomposition in different steps. Indeed, the decomposition peaks occur at 400ºC and 425ºC, with exothermic nature, corresponding to a multiple-step of decomposition for the formation of different Co and Mo oxides (Gonzalez-Cortes et al., 2014; Salazar et al., 2017). Finally, for the NiW/Nb_2O_5 catalyst (Figure 1c), an exothermic event at 350ºC, with mass loss is observed, which could be attributed to the formation of different Ni and W oxides on the niobium surface.

Figure 1. Thermogravimetric Analysis for a) CoMo/Nb_2O_5 non calcined support; b) CoMo/Nb_2O_5 calcined support; c) NiW/Nb_2O_5 calcined support.



Fonte: Authors.

The specific surface areas are very low excepted for the CoMo/Nb_2O_5 non-calcined support catalyst (29 m^2/g) (Table 2). Indeed, after the calcination step at 400°C, the specific surface area of CoMo/Nb_2O_5 and NiW/Nb_2O_5 calcined catalysts are 6 and 2 m^2/g, respectively corresponding possibly to the decomposition of precursors as shown by TGA-DTA technique. Furthermore, the loss of area could also be correspondent to the partial blocked of the pores by the presence of oxides.

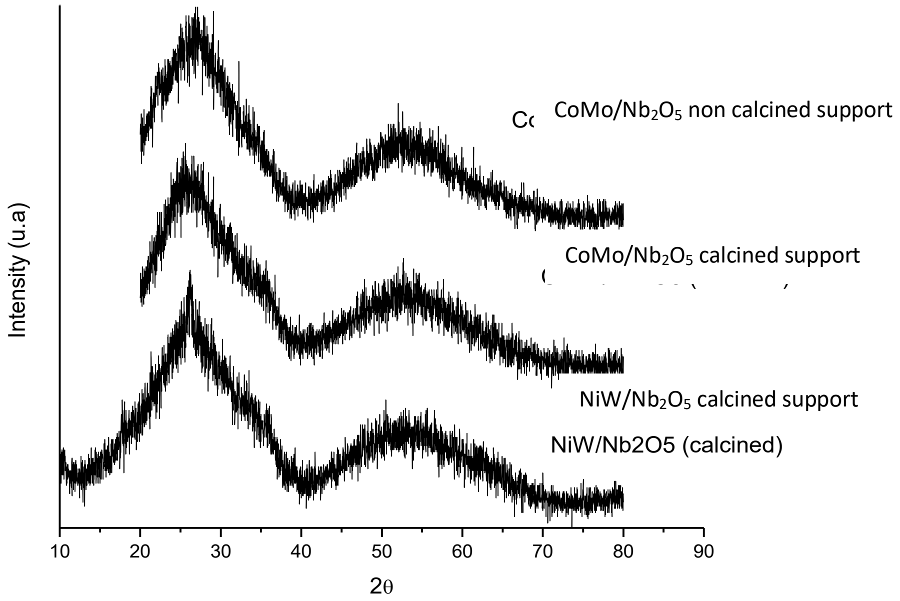
Table 2. NH_3-TPD desorption and BET surface area determined for different catalysts.

	NH3 (µmol/g)				strong/	SBET
Catalyst	Total	weak	moderate	strong	(moderate+weak) ratio	(m^2/g)
CoMo/Nb_2O_5 - non calcined support	383	173 (45%)	53 (14%)	157 (41%)	0.7	29
CoMo/Nb_2O_5 - calcined support	380	57 (15%)	105 (28%)	218 (57%)	1.3	6
NiW/Nb_2O_5 - calcined support	411	151 (37%)	177 (43%)	83 (20%)	0.3	2

Fonte: Authors.

XRD results of the non-calcined and calcined support catalysts presented an amorphous structure. In all catalyst samples, it was observed two wide peaks at 2Ø = 25º and 52º which is characteristic of a niobium amorphous phase. The intensity and shape of the peaks observed in Figure 2 suggest that there is not a defined crystallinity structure or the particles are well dispersed that they could not be noticed in the X-Ray Diffraction. Indeed, the results of these three samples are in accordance with the Nb2O5 phase observed by Santos et al. (2017). Furthermore, the patterns observed for the calcined and non-calcined CoMo/Nb2O5 have suggested that even with the support calcination step, the Nb2O5 structure has been maintained.

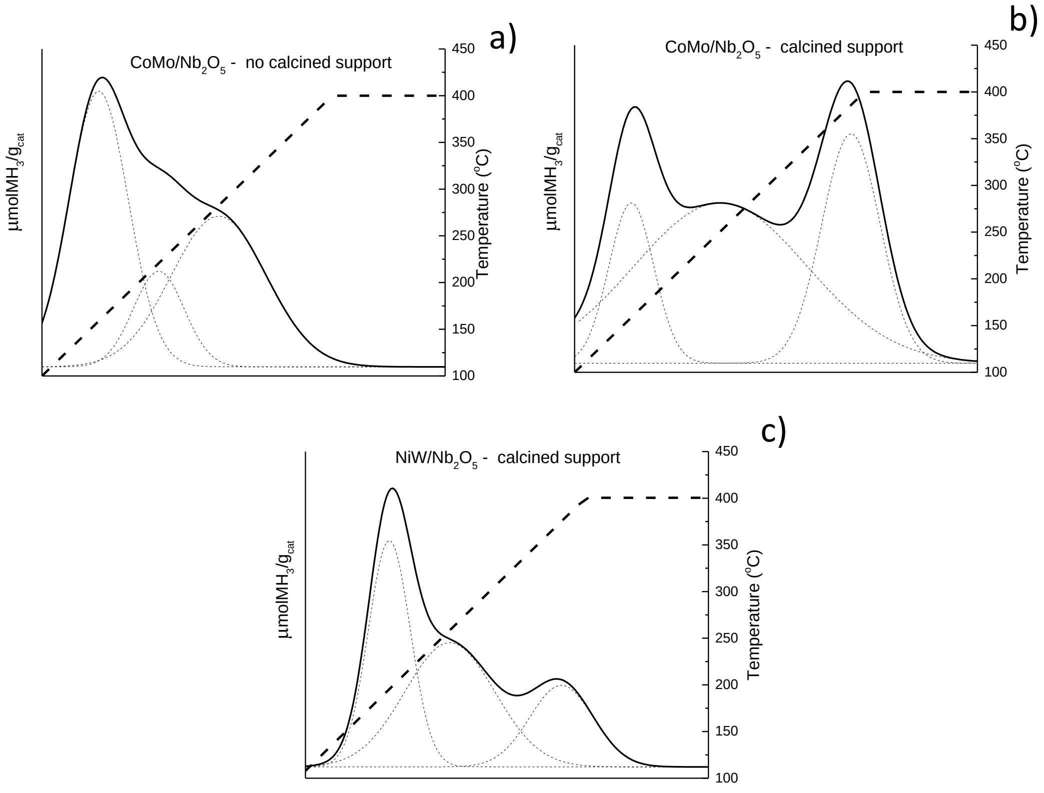
Figure 2. X-Ray Diffraction of the catalysts prepared (CoMo/Nb_2O_5 non-calcined support, CoMo/Nb_2O_5 calcined support and NiW/Nb_2O_5 calcined support).



Fonte: Authors.

Finally, the total acidity of different samples has been investigated through the NH_3-TPD. As reported in Figure 3, representing the curve of NH_3 desorption as a function of time and temperature, it can be seen that, whatsoever the catalysts, various peaks were observed corresponding to different acidity strengths. Indeed, it is noticed that for the CoMo/Nb_2O_5 non-calcined support catalyst (Figure 3a) weak and strong acid sites are predominant whereas for the CoMo/Nb_2O_5 calcined catalyst (Figure 3b) there are mainly moderate and still more relevant strong acid sites. Indeed, the literature suggests that the enhancement of temperature promotes a decrease of acidity, creating new superficial sites with different acid strengths and modifying the material properties as an ion exchanger (Kitano et al., 2012). Regarding the NiW/Nb_2O_5 catalyst (Figure 3c) there is an important predominance of weak and moderate acid sites (37 and 43%, respectively), confirming a weaker acidity of NiW in comparison with CoMo catalysts. These results and proportions of acidity strength between the catalysts are also presented in Table 2.

Figure 3. NH_3 Desorption as a function of temperature for: a) $CoMo/Nb_2O_5$ non-calcined support, b) $CoMo/Nb_2O_5$ calcined support and c) NiW/Nb_2O_5 catalysts.

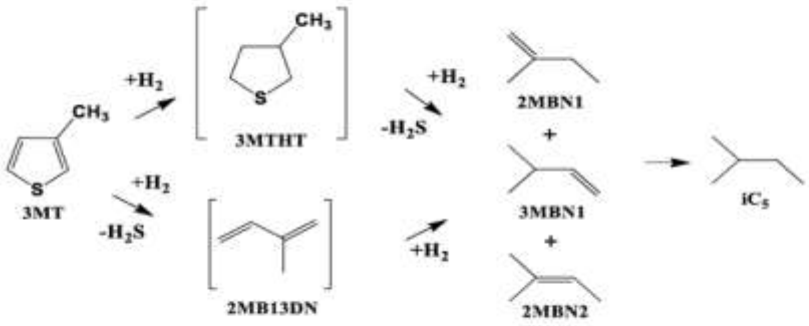


Fonte: Authors.

3.2. Transformation of 3-methylthiophene

The performance of these materials was compared for the transformation of 3-methylthiophene (3MT), used as model molecule representative of sulfur compounds present in FCC gasoline, under the following operating conditions: T = 250°C, P = 2 MPa and ratio H_2/feed = 360 NL/L. The reaction mechanism of 3MT over a $CoMo/Al_2O_3$ catalyst is presented in Figure 4 (Santos et al., 2019).

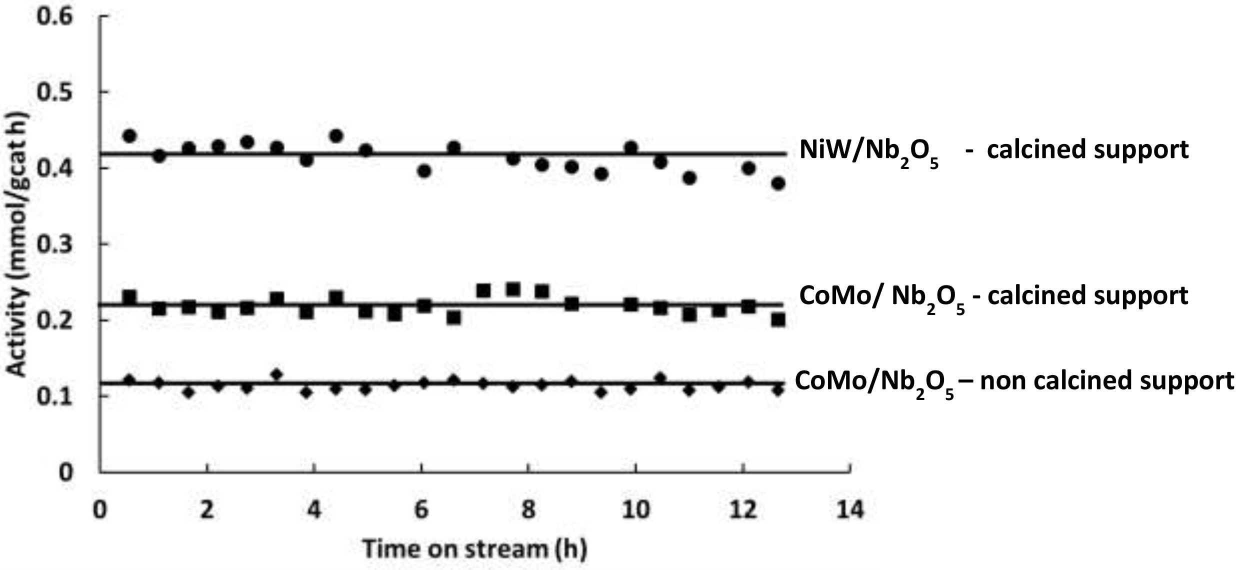
Figure 4. Reaction scheme for the transformation of 3MT. (T = 250ºC, P = 20 bar, $CoMo/Al_2O_3$, H_2/feed = 360 NL/L).



Source: Santos et al., 2019

Whatsoever the catalyst, the activity (measured at a conversion of about 30%) was stable during the time (Figure 5). The most active catalyst per gram and normalized per square meter was NiW/Nb_2O_5 followed by CoMo with calcined support and CoMo with non-calcined support. The difference observed between $CoMo/Nb_2O_5$ with the non-calcined and calcined support suggests an important role of the calcination step. Despite the higher specific surface area of the $CoMo/Nb_2O_5$ non-calcined support catalyst, it has presented a lower catalytic activity among the three catalysts evaluated and twice as low compared with $CoMo/Nb_2O_5$ calcined support. This could be explained by the fact that increasing the calcination temperature of the niobium solid, a superficial rearrangement in the hydroxyl group occurs, and water molecules could leave the molecular structure (Santos et al., 2017). It is important to notice that even though a lower activity of the $CoMo/Nb_2O_5$ non-calcined catalyst (activity for the non-calcined and calcined $CoMo/Nb_2O_5$ equal to 0.12 and 0.22 mmol/g.h, respectively), the product distribution has shown a lower pentane/pentene ratio ($iC_5/{=}C_5$), which means a lower tendency to produce hydrogenated products during the hydrotreatment reactions (Santos et al., 2017).

Figure 5. 3MT transformation as function of time on stream (T = 250 °C, P = 2 MPa, H_2/feed = 360 NL/L).



Fonte: Authors.

Furthermore, comparing the activity as well as the textural properties of the calcined CoMo/Nb_2O_5 with the commercial CoMoS/Al_2O_3 catalyst studied by Santos et al. (2019), it was observed that the niobium oxide has a lower efficiency as a support than alumina oxide (Al_2O_3) according to Table 3. This difference could be attributed to the interaction metal-support as well as the lower available surface area provided by the Nb_2O_5 support, which was confirmed by the comparison of BET results presented in Table 2. Indeed, the specific surface area of the alumina support is about 20 times higher in comparison with the Nb_2O_5 support, which leads to a better available surface area to distribute the active phase and thus enhance the catalytic activity and selectivity. Taking into account the difference in specific surface area of alumina and niobium supports, Table 3 presents the specific catalytic activity normalized per BET surface area. Therefore, the catalytic activity of prepared CoMo/Nb_2O_5 and CoMo/Al_2O_3 are 0.04 and 0.05 mmol/m^2.h, respectively, representing a difference of about 25% higher for the commercial catalyst (CoMo/Al_2O_3). However, when the NiW/Nb_2O_5 catalyst is compared to the CoMo/Al_2O_3 catalyst it is observed activities of 0.21 and 0.05 mmol/m^2.h, respectively which represents a factor 4 for the NiW/Nb_2O_5 catalyst.

The effect of the metal-promoter interaction in the catalytic activity is evidenced through the results obtained in the transformation of 3MT over NiW/Nb_2O_5 and CoMo/Nb_2O_5 catalysts since the Ni:W and Co:Mo molar ratios are similar as indicated in Table 1. Indeed, the HDS reaction occurs over the MoS_2 and WS_2 catalytic phase formed during the sulfiding process with H_2S, prior to the hydrodesulfurization reaction. Comparing the activity of NiW/Nb_2O_5 and $CoMo/Nb_2O_5$ catalysts it is possible to notice an important difference which, in the first case, the activity is equal to 0.43 mmol/g.h and the second case equal to 0.22 mmol/g.h, representing 2 times higher for the NiW than CoMo catalyst. Comparing the catalytic activity as a function of specific surface area, it is possible to notice a difference about 5 times between calcined niobium supported NiW and CoMo catalysts (0.21 and 0.04 $mmol/m^2.h$, respectively). These results suggest that the effect of Ni as a promoter of the WS_2 phase would favor the hydrogen transfer reactions more than the promotion of Co for the MoS_2. This fact could facilitate the C-S scission through a direct desulfurization reaction and thus there is a higher activity of NiW over CoMo catalyst for the hydrodesulfurization of 3MT. These results are in line with the literature where a similar behavior was observed when was studied the effect of different tungsten catalysts for the hydrodesulfurization of thiophene (Bendezú et al., 2000; González-Cortés et al., 2014). Thus, these results suggest a more efficient Ni-W-S interaction in comparison with the Co-Mo-S interaction.

Table 3. Transformation of 3MT (T = 250 ºC, P = 2 MPa, H_2/feed = 360 NL/L). iC5: isopentane, 3MB1N: 3-methylbut-1-ene, 2MB1N: 2-methylbut-1-ene, 2MB2N: 2-methylbut-2-ene, iC5/=C5: ratio isopentane/pentenes.

Catalyst	BET (m^2/g)	Activity (mmol/g.h)	Activity (mmol/ m^2.h)	Molar Yield (%)				
				iC_5	3MB1N	2MB1N	2MB2N	$iC_5/{=}C_5$
$CoMo/Al_2O_3$[1]	122	6.0	0.05	9.9	15.6	17.6	56.9	0.11
$CoMo/Nb_2O_5$ non calcined support	29	0.12	0.004	11.9	10.3	12.3	65.5	0.13
$CoMo/Nb_2O_5$ calcined support	6	0.22	0.04	19.1	4.6	14.4	61.9	0.24
NiW/Nb_2O_5 calcined support	2	0.43	0.21	11.7	4.7	17.6	65.9	0.13

1. (Santos et al., 2019) at similar operating conditions. Fonte: Authors.

According to the results present in Figure 5, it is possible to observe that even by using the chelating agent in the preparation of the catalyst CoMo/Nb_2O_5 and NiW/Nb_2O_5, it did not seem to be effective an increasing absolute of the catalytic activity above the catalytic activity obtained by a commercial CoMo/Al_2O_3 catalyst. However, by comparing the catalytic activity normalized by the specific surface area, the calcined catalysts prepared by using the chelating agent have shown a similar or even higher activity when compared with the commercial CoMo/Al_2O_3 catalyst.

4. Conclusion

The transformation of 3-methylthiophene over CoMo and NiW supported on Nb_2O_5 catalysts, under selective HDS operating conditions, has shown relevant differences in activity and product distribution. The NiW/Nb_2O_5 catalyst presented the highest activity followed by CoMo/Nb_2O_5 calcined support and finally the CoMo/Nb_2O_5 non-calcined support. However, a lower pentane/pentene ratio for the CoMo/Nb_2O_5 non-calcined support compared with CoMo/Nb_2O_5 calcined support suggests a tendency to produce a fewer hydrogenated product in a hydrotreatment process.

In the present study, it was possible to analyze the role of niobium as a support for hydrotreatment catalysts as well as its performance in the HDS of 3-methylthiophene. The catalysts analyzed have presented promising results either by its specific activity normalized per total BET (0.04 and 0.21 mmol/g.m^2 for the calcined CoMo/Nb_2O_5 and NiW/Nb_2O_5) or its HDS product distribution (iC5/=C5 ratio = 0.13 for the non calcined CoMo/Nb_2O_5 catalyst), which could lead to a low production of hydrogenated products in a hydrotreatment process.

In order to deeply understand the impact of different interactions metal-promoter as well as metal-support, future works could involve the same approach used in this study with different model sulfur species present in FCC gasoline. In this evaluation, the interaction between the different sulfur species and the catalytic active phase could be evaluated. Furthermore, a theoretical kinetic approach could also be investigated in order to understand the different reaction mechanisms involved.

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