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Isomerization and cracking under HDS conditions using γ-alumina modified with boron as catalysts support

Sonia A. Giraldo, Aristóbulo Centeno *

Centro de Investigaciones en Catálisis (CICAT), Escuela de Ingeniería Química, Universidad Industrial de Santander,
carrera 27 calle 9, Bucaramanga, Colombia

Abstract

In this work, γ-alumina acidity was modified by adding different boron proportions and used as a support for CoMo and NiMo catalysts. Catalysts were tested in simultaneous reactions of dibenzothiophene (DBT) and *o*-xylene under typical hydrotreating conditions. It was found that catalysts are able to develop simultaneous hydrodesulfurization (HDS), cracking and isomerization reactions when boron was added to the alumina support. On the other hand, it was also found that capacity of catalysts to develop the $C_{aromatic}$–CH_3 bond scission directly correlates with total acidity, and this correlation is not dependent upon the active phase (CoMo or NiMo). Activity in HDS is not substantially affected when the boron content in the catalyst is low. In some cases HDS activity is enhanced. It was also shown that it is possible to obtain information concerning the behavior of catalysts for deep HDS of refractory compounds, using simple and not expensive model molecules.

Keywords: Isomerization; Boron; HDS; Acidity modification; Modified alumina

1. Introduction

Deep HDS of diesel and gasoline is necessary to comply with the new worldwide strict environmental legislations concerning sulfur content in fuels. Sulfur content in diesel is usually removed through HDS using CoMo and NiMo catalysts, but reaching its required levels using current technology and operating conditions is impossible. The ruling process should be modified by improving the design, changing process conditions or looking for more active catalysts [1–4]. The latter alternative is technically and economically the most promising one.

The molecules that must be desulfurized in order to decrease sulfur levels, as the di-alkyl-dibenzothiophens, are the most refractory to HDS [5–7]. The position of the alkyl groups plays an important role in reactivity control. The 4,6-dimethyl dibenzothiophene (4,6-DMDBT) has the lowest reaction velocity compared to the one of isomers where the alkyl substitutions are in different positions.

The limitation of sulfur adsorption on the active sites of catalysts caused by steric hindrance is the main reason for the low reactivity of this compound [2,8–11]. Its HDS route is not the typical direct desulfurization (DDS) present on CoMo/γ-Al_2O_3 catalysts [12]. Several reaction routes are possible for the HDS of 4,6-DMDBT, based on the decrease of the steric hindrance: (a) hydrogenation of one of the rings of DBT [11,13,14], which confers certain flexibility to the methyl groups [15]; (b) isomerization, which changes the position of the methyl groups from 4, 6 to 3, 7 or 2, 8 positions [16]; (c) total or partial removal of methyl groups [13,14]; and (d) cracking of the C–C bond of the thiophenic ring [13], which confers certain flexibility to the molecule in order to allow sulfur adsorption. The three latter routes are related to the acidity of the catalyst. Support also plays an important role in the reactivity in relation to both its physicochemical characteristics and its influence over the dispersion of active metals. The addition of boron and fluorine has contributed to increase dispersion and acidity of the alumina [17,18]. Boron increases DDS, interpreted as the augmentation on the Brönsted acidity of the catalyst and, thus, facilitating the migration of the methyl groups. The addition of fluorine leads to more active catalysts for 4,6-DMDBT conversion. The activity increases as

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* Corresponding author.
E-mail address: acenteno@uis.edu.co (A. Centeno).

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the fluorine content in the catalysts increases. This increasing in activity is associated with the augmentation of the isomerization capacity related to the acidity. Several zeolites have been added to the alumina to increase its acidity, expecting an augmentation in isomerization and dealkylation capacities. The HDS of the 4,6-DMDBT on CoMo and NiMo catalysts supported on alumina–oxides mixtures has been studied by Lecrenay et al. [19] showing that, when the alumina–TiO_2 mixture is used, the activity increases compared to the one obtained when only alumina is used as a support. The use of other oxides like ZrO_2 and B_2O_3 [19] increases the HDS activity, which is also related to the acidity augmentation.

It is clear that the search of new catalysts for the 4,6-DMDBT HDS should consider catalytic systems with certain acid characteristics in order to contribute to the decrease of the steric hindrance needed for the 4,6-DMDBT adsorption.

In this work, the alumina acidity was modified by boron addition. Modified alumina was used as support of CoMo and NiMo catalysts. These catalysts were tested in simultaneous DBT and *o*-dimethylbenzene reactions under typical HDT conditions in order to evaluate the catalytic behavior in HDS, isomerization and cracking. Although the literature reports HDS catalysts supported on alumina and modified with boron with contents lower than 4% [20], in this work the boron contents were higher in order to favor isomerization and cracking reactions by increasing acidity as well as to analyze its effect on HDS. The literature also shows [21–24] that boron content augmentation increases not only alumina acidity, but also its acidic force. The aim of these modifications is to establish an appropriate relation between the capacity to achieve both the $C_{aromatic}$–CH_3 bond scission and the hydrogenolysis capacity of the C–S bond that allows the desulfurization of steric hindered molecules for the adsorption. This work also aims to show that it is possible to use simple and not expensive model molecules in order to obtain information concerning the performance of catalysts to eliminate sulfur of complex molecules highly refractory to HDS.

2. Experimental

2.1. Catalysts

Two series (CoMo and NiMo) of catalysts were prepared using a gamma alumina as support (Procatalyse) (BET surface area = 230 m^2/g; volume and diameter pore average: 0.7 cm^3/g and 10 nm; total acidity = 324 μequiv. NH_3/g), modified with boron addition. Boric acid was used as B_2O_3 precursor to give to the catalysts concentrations of 4, 8, 12 and 14% (w/w) as B_2O_3. Also, two catalysts (CoMo and NiMo) supported on alumina without modification were prepared as reference catalysts.

Initially, the alumina was crashed to obtain a particle diameter between 0.3 and 0.6 mm. Afterwards, the alumina was dried at 393 K during one hour and, subsequently, dry impregnation was used to incorporate the boron. Boric acid was dissolved in a volume similar to the one of the pore volume of the alumina and warmed moderately to facilitate solubilization. The solid impregnate with the boric acid solution was dried with air flow at 393 K for 12 h and afterward calcined at 778 K during 4 h.

Dry impregnation of a solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Merck) on the modified alumina was used to prepare CoMo and NiMo catalysts, calculating 15% (w/w) as MoO_3 content in the final catalyst. Later, the cobalt ($Co(NO_3)_2\cdot 6H_2O$) or nickel ($Ni(NO_3)_2\cdot 6H_2O$) salt was added, according to each case, to give 2% (w/w) as CoO or NiO in the catalyst. Dry impregnation was used.

The reference catalysts CoMo and NiMo were prepared on alumina without modification with the same molybdenum, cobalt or nickel percentages, following the same procedure as described before.

2.2. Characterization of the catalysts

Specific area was determined by the BET method, pore volume, distribution and pore size for the BJH method. The nitrogen adsorption–desorption isotherms, were determinate using an apparatus Nova 1300 of Quantachrome.

The acidity of the catalysts was measured by TPD of ammonia after having been activated. The catalyst (0.3 g approximately) undergoes the same reduction–sulfuration procedure used to activate the catalyst for the reaction. This procedure will be described later. Once finished, the activation catalyst was cooled down, even under the activation mixture, until room temperature and subsequently N_2 was introduced during 1/2 h to eliminate residuals of the activation mixture. The catalyst was subjected again to cleaning with flow of N_2 during 15 min at 373 K, and afterward N_2 was changed for NH_3 conserving the same temperature during 15 min. Later, the catalyst was cleaned again with N_2 for 15 min, and afterward the N_2 was changed for He, always to 373 K, during 1/2 h. Then, the temperature was increased to 773 K at 10 K/min. The desorbed ammonia was retained in 100 ml of a 0.4% (w/w) boric acid solution. An aliquot of 20 ml was taken to be titrated with sulfuric acid 0.01 N in an automatic high precision titrator (Titroline).

2.3. Catalytic evaluation

The catalysts were evaluated in a 500 ml stainless steel batch reactor (Parr Instruments) at 583 K and 5 MPa. The reactive solution was formed by DBT (3%, w/w) as model molecule for HDS, *o*-dimethylbenzene (1%, w/w) as model molecule for the isomerization and cracking, hexadecane (2%, w/w) as internal standard for the chromatographic analysis, and decline as solvent. One gram of catalyst was used for evaluation.

Activation procedure: the catalyst was dried with N_2 at 393 K during 1 h. Subsequently, N_2 was changed by H_2S (15 vol.%)/H_2 mixture and temperature was raised to 673 K at 10 K/min. The catalyst was maintained at these conditions for 4 h. Once activated, the catalyst was quickly submerged into the reactive mixture avoiding all contact with air, and then the reactor was closed. The reactive mixture occupied the 3/4 of the volume of the reactor (approximately 160 ml). The air was evacuated by cycles of pressurization–depressurization with nitrogen and later with hydrogen. The mixture was heated until reaching a temperature of 633 K at 10 K/min under a hydrogen partial pressure of 0.7 MPa. Moderate agitation was used to maintain homogeneous temperature inside the reactor. After the reaction temperature was reached, the pressure was increased to 3.5 MPa with H_2 and with an agitation of 1000 rpm. The first sample was taken out at this moment, denoted as the time zero for the reaction. All the conversions reached until that moment were not considered for the calculations. Liquid samples at 45, 90, 120, 180, 240 and 300 min were taken out to be analyzed by gas chromatography using a HP 6890 chromatograph equipped with a FID detector and a HP 5 of 30 m (crosslinked 5% PH ME silicone) column. Reagents and reaction products were identified and quantified using specific patterns.

2.4. Expression of results

The pathways of the reaction of the DBT proposed by Houalla et al. [25] consider a direct desulfurization route to produce first biphenyl and then cyclohexyl benzene (CHB); they also consider another route beginning with the DBT hydrogenation of one of the rings followed by desulfurization to obtain also CHB as final product. The prospective products of the cracking of *o*-dimethylbenzene are methylbenzene and benzene, and those of the isomerization are *m* and *p*-dimethylbenzene.

The HDS activity of the catalysts, as characterized by the disappearance of BDT, is reported as a pseudo-first-order reaction with rate constant K. This is determined according to the equation used by Gevert et al. [26], valid to conversions smaller than 15%. The behavior of the catalysts for isomerization and demethylation reactions is reported as the scission of the $C_{aromatic}$–CH_3 bond of the *o*-dimethylbenzene after 5 h of reaction.

3. Results and discussion

The results for the textural characteristics and total acidity of the catalysts are presented in Table 1. This table shows that the specific decreasing area is more significant for catalysts of the NiMo series than for the CoMo series. The most drastic change in area occurs for the catalysts with low contents of B_2O_3. It is also observed in Table 1 that the total acidity directly correlates with the boron content in the catalyst. In most of the cases, NiMo supported modified alumina catalysts are more acid than the corresponding CoMo catalysts.

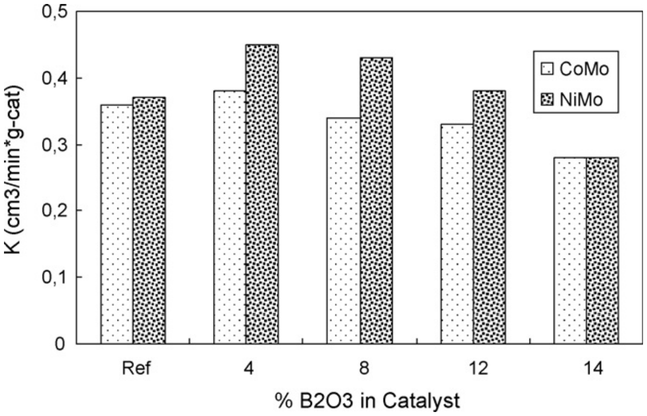

Fig. 1. Activity in HDS of CoMo and NiMo catalysts supported on modified alumina with boron.

The detected products of the HDS of DBT were CHB and biphenyl. Intermediate products were not observed.

The activity in HDS for the CoMo and NiMo catalysts is presented in Fig. 1. It is observed that in general the catalysts of the NiMo series have higher HDS activity than the ones corresponding to the CoMo series. The activity in HDS is moderately influenced by the quantity of boron on the support. The catalysts presented changes in their activity compared with the reference catalyst depending on the boron content. For the two series, the catalyst with 4% of B_2O_3 presented the maximum of activity. These results agree with other works [20,27–29] in which it is reported that alumina modified with B_2O_3 is a good support for HDS catalysts. The high activity of the catalysts supported on modified alumina with B_2O_3 can be attributed to a better dispersion of molybdenum caused by a good dispersion of boron on the alumina surface. According to some authors [27], boron increases the dispersion of the active phases and increases the force as these phases link to the alumina surface. Ramírez et al. [20] conclude that the incorporation of boron into the alumina support for CoMo catalysts diminishes the interaction between the molybdenum oxide species and alumina, increasing the reducibility of

Table 1
Textural characteristics and total acidity of CoMo and NiMo catalysts supported on modified alumina with boron

Catalyst*	Area BET (m^2/g)	Pore volume (cm^3/g)	Pore diameter (Å)	Specific acidity (μ-equiv. NH_3/g)	Acidity (μ-equiv. NH_3/m^2)
NiMo	161	0.5	115	564	3.50
NiMo(4)	116	0.5	112	940	8.10
NiMo(8)	110	0.4	113	2115	19.23
NiMo(12)	105	0.4	112	5136	48.91
NiMo(14)	104	0.4	112	6758	64.98
CoMo	133	0.5	113	583	4.38
CoMo(4)	108	0.4	114	896	8.30
CoMo(8)	106	0.4	113	2457	23.18
CoMo(12)	91	0.4	110	5387	59.20
CoMo(14)	89	0.4	112	5743	64.53

* In parenthesis nominal B_2O_3 percentage.

molybdenum in the precursors of the catalyst. The quantity of tetrahedral Co decreases, indicating that less Co is lost into the alumina matrix. These authors attribute the increase of the HDS activity to the augmentation of Co species acting as Mo promoters, resulting of the redistribution of the Co and Mo oxide species. This redistribution is caused by the decreasing of the proportion of the tetrahedral coordinated Co^{2+} and Mo^{6+} strongly interacting with alumina [24].

The electronegativity of boron (=2) is higher than the one of aluminum (=1.5); therefore, the formation of the B–OH group in the surface of the modified alumina presents higher acidity that the one of the Al–OH group. This higher acidity allows $Mo_7O_{24}{}^{6-}$ to be linked more strongly to B^{3+} than to Al^{3+}. Except for catalysts with 14% B_2O_3, which present a relatively low activity, a slight decreasing in activity for HDS is observed for both series when B_2O_3 content is higher than 4%. The decreasing in activity can be related to the decrease of the specific area as observed in Table 1. The decrease in the activity in HDS of the catalysts with high content of boron is attributed to the decrease of the surface area as well as to the reducibility degree of MoO_3. According to Chen et al. [27], molybdenum supported on γ-Al_2O_3–B_2O_3 linked particularly to the B–OH groups, is more easily sulfurated-reduced compared to the one supported on γ-Al_2O_3. Higher activities are also observed for NiMo catalysts compared to those of CoMo catalysts, as it has been found by other authors for the HDS of petroleum heavy fractions [30].

The reaction products of *o*-dimethylbenzene detected were benzene, methylbenzene, *m*-dimethylbenzene and *p*-dimethylbenzene. The distribution of these products after 5 h of reaction as a function of the B_2O_3 content in the catalyst is presented in Fig. 2 for the CoMo series and in Fig. 3 for the NiMo series. It is observed in these figures that, for both series, the quantity of those products increases as the boron content in the catalyst increases.

An appreciable change is also observed in the activity for the conversion of *o*-dimethylbenzene for catalysts with 14% of B_2O_3, being these ones the most actives in both series. For the catalysts on alumina without modification and modified with 4% of B_2O_3, the quantity of products is very low.

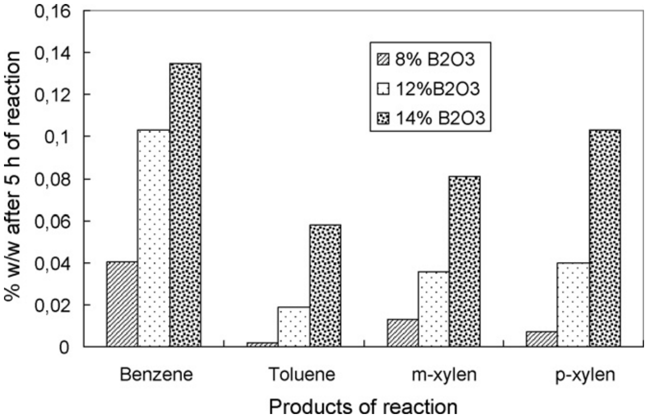

Fig. 3. Products distribution after 5 h under HDS conditions of the *o*-dimethylbenzene reaction using NiMo catalysts supported on modified alumina with boron.

In Fig. 4, the variation of the acidity is presented as a function of the B_2O_3 content for the two series of catalysts. The results show the same tendency for the two series. In Fig. 5, the scission of the methyl radical, calculated as the sum of all of the products detected by chromatography coming from a demethylation reaction, is presented as a function of the catalyst acidity, for the CoMo and NiMo series. In this figure, it is observed that total acidity correlates with the catalyst capacity to break the $C_{aromatic}$–CH_3 bond of *o*-dimethylbenzene. This correlation is approximately lineal and independent of the active phase of the catalyst.

The incorporation of boron on the alumina surface leads to catalysts that present active sites for HDS and HYD associated to molybdenum, cobalt or nickel and acid sites to catalyze the scission of the $C_{aromatic}$–CH_3 bond and isomerization reactions.

Acidity measurements confirm that the number of acid sites increases in the catalyst as the boron content increases, as observed in Fig. 4. It is observed in our results that the addition of boron leads to changes in the behavior of the CoMo and

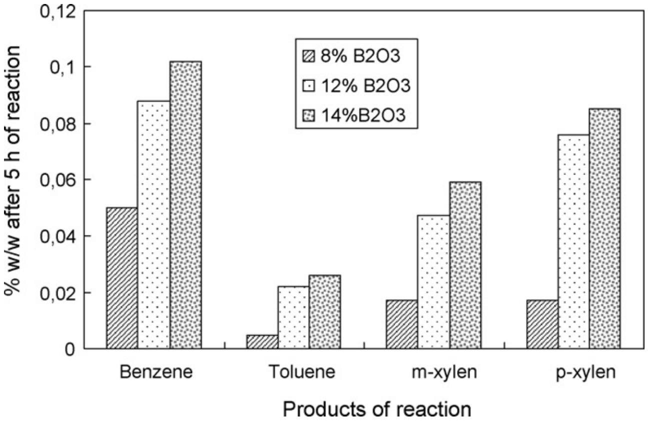

Fig. 2. Products distribution after 5 h under HDS conditions of the *o*-dimethylbenzene reaction using CoMo catalysts supported on modified alumina with boron.

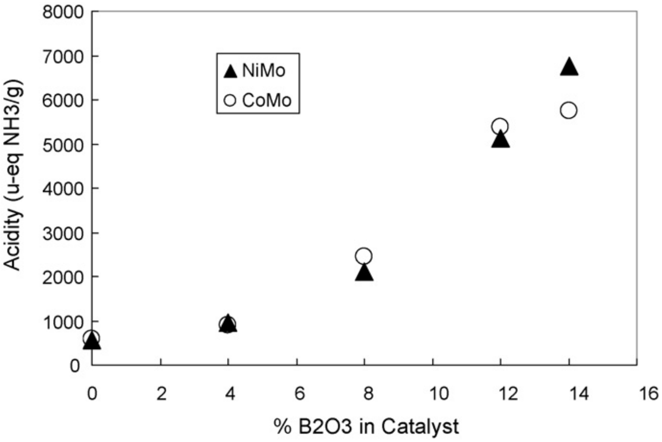

Fig. 4. Total acidity as a function of the B_2O_3 content for CoMo and NiMo catalysts supported on modified alumina.

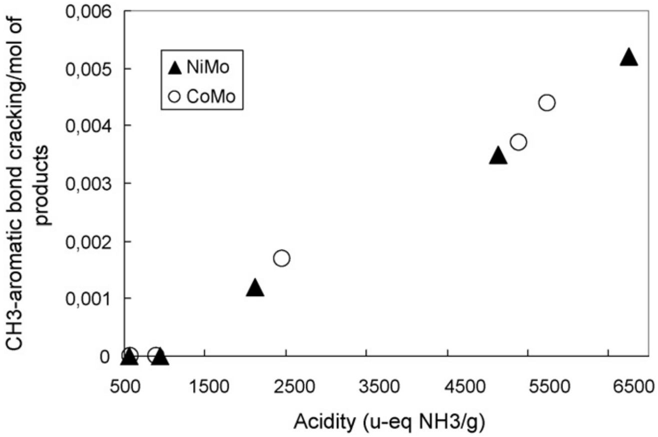

Fig. 5. Rupture of radical methyl in function of the acidity of the catalyst, for the two series of CoMo and NiMo catalysts.

NiMo catalysts. The increase of the acidity has increased the capacity of the catalysts to carry out the isomerization reactions and the $C_{aromatic}$–CH_3 bond incision compared with the reference catalysts. If the most important reaction is analyzed, in this case the catalytic cracking, it is observed that a direct correlation exists between the capacity of the catalyst for the $C_{aromatic}$–CH_3 bond scission and the acidity of this catalyst. Indeed, as observed in Fig. 5, the capacity of the catalyst for the $C_{aromatic}$–CH_3 bond scission is directly related to the total acidity, and it is independent from metals forming the active phase of the catalyst. In the case of isomerization, there is not a direct relation, which is accountable considering that steric factors are involved in this case. However, it is clear that the isomerization reaction occurs only when boron is present in the catalyst. Several authors have used boron into catalysts in order to increase the direct desulfurization (DDS) [20,31,32] and have studied the nature and intensity of the acid sites formed [21,33–35]. The correlation between the acidity nature and HDS activity was also investigated [33–35]. The results of this work indicate that the catalysts supported on alumina without modification and those supported on alumina modified with B_2O_3 content lower than 4% present activity for neither isomerization nor the catalytic scission of the $C_{aromatic}$–CH_3 bond. It is also clear that as the boron content increases in the catalyst, the isomerization capacity also increases, for the two series of catalysts studied as reported in the literature [36].

For the studied catalysts, when the concentration of B_2O_3 is at its highest (14%), these are more active for isomerization and the scission of the $C_{aromatic}$–CH_3 bond. Catani et al. [37] indicate that the modification of the γ-Al_2O_3 with boron leads to a modification of the acidity allowing the industrial use of the catalyst for the structural isomerization of light olefins as *n*-butane. Sibeijn et al. [22] have established that for B_2O_3 contents higher than 5%, the hydroxyls of the alumina are totally covered for lineal polymers of B_2O_3 connected to the alumina, with superficial hydroxyls in the borders of these polymeric structures. They have also show that the quantity of hydroxyls of boron diminishes when the B_2O_3 content increases, modifying the acid characteristics of the alumina. Flego et al. [23] have demonstrated that with boron content lower than 2%, the total number of hydroxyl groups remains constant, the acidity is stronger but the number of acid sites do not change, and at high contents, as the boron content increases, both the acidity and the acid force increase.

The literature presents some studies concerning the HDS of 4,6-DMDBT using catalysts CoMo and NiMo supported on alumina modified with boron [34,35,38,39]. The results from these studies related to the activity in HDS and the influence of acidity on this reaction go in the same direction that those presented in this work. Therefore, the validity of our results is confirmed. We think that it is possible to extrapolate the results of the performance of the catalysts in isomerization and cracking of simple molecules like *o*-xylene in HDS environments to molecules with steric hindrances. This appreciation indicates that it is possible to obtain preliminary, valid and significant information concerning the behavior of catalysts for the deep desulfurization using an adequate, easy and not expensive experiment.

4. Conclusions

It is possible to obtain information concerning the behavior of catalysts for deep HDS of refractory compounds using simple model molecules.

Catalysts CoMo and NiMo are able to develop simultaneous HDS, cracking and isomerization reactions when boron is added to the alumina support.

The capacity of the catalyst to develop the $C_{aromatic}$–CH_3 bond scission reactions is directly related to its total acidity.

The activity for HDS of the catalysts supported on modified alumina with boron is not substantially affected when the boron content in the catalyst is low; in some cases, this activity is enhanced.

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