

Behavior of catalysts with rhodium in simultaneous hydrodesulfurization and hydrogenation reactions

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Abstract

The behavior of catalysts containing rhodium was evaluated in hydrotreating (HDT) reactions at 583 K and 5 MPa. The influence of the temperature and the nature of the activating agent were analyzed for the monometallic Rh/ γ -Al₂O₃ catalyst in simultaneous hydrodesulfurization (HDS) of dibenzothiophene (DBT) and hydrogenation (HYD) of naphthalene (NT). H₂, H₂S, N₂ and H₂S (15 vol.%) / H₂, H₂S (85 vol.%) / H₂ mixtures were used as activating agents. Bimetallic RhMo/ γ -Al₂O₃ catalysts with different Rh/Mo ratios were also tested in the same reactions. Some of the catalysts were characterized by XPS. The results show that for the Rh monometallic catalyst, the H₂S present in the activating mixture leads to an increase in the selectivity to HDS. Synergy in both HDS and HYD reactions was detected for the bimetallic catalysts, and it presents a slight increase with the Rh/(Rh + Mo) atomic ratio. These results lead to speculate about the possible role of Rh in bimetallic catalysts.

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1. Introduction

The exhaustion of oil resources in the majority of oil producing countries, and especially in Colombia, has necessarily led to the processing of heavy refractory fractions of oil by conventional cleaning treatments. Additionally, requirements in almost all of the countries, especially the industrialized ones, are becoming more severe every day regarding the amount of sulfur and aromatics contained in the fuel offered in the market [1,2]. Nowadays in Colombia, theoretic levels of accepted sulfur content are of 300 ppm for gasoline and 500 ppm for diesel; however, these levels have not been attained. These conditions lead to modify the actual processes used in oil refineries in order to become more efficient in the elimination of sulfur. One of the alternatives presented to improve this situation is the development of new catalytic systems, especially those to remove sulfur from refractory molecules by HDS. Noble metals by themselves or associated to another metal have been shown to present the

appropriate characteristics for deep HDS [3–13]. Activation is one of the most important steps that influence the catalytic behavior of the HDT catalysts depending on conditions used such as temperature and activating agent [7,14–17]. During the activation step, different species are formed inside active phases, and therefore, different catalytic behaviors are present. Moreover, it has been shown that each metal or couple of metals must have a different activation protocol that leads to the best behavior in HDT reactions. A second determinant factor in the behavior of bimetallic catalysts in HDS is the content of metals [6,13,14]. With these arguments in mind and looking forward to make an experimental contribution to the understanding of the behavior of HDT catalysts containing noble metals, the aim of this study was to analyze the influence of activation conditions of the Rh/ γ -Al₂O₃ monometallic catalyst and the content of metals for RhMo/ γ -Al₂O₃ bimetallic catalysts in the HDS of DBT and HYD of NT.

2. Experimental

2.1. Preparation and characterization of catalysts

Two series of catalysts were prepared by incipient wetness impregnation supported in gamma alumina (γ -Al₂O₃),

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Procatalyse): the first series of monometallic catalysts with different wt.% of Rh (Rh(x), $0.15 \leq x \leq 2$); the second series of bimetallic catalysts with different content of metals (Rh(x)Mo(y), $0.15 \leq x \leq 2$, $y = 2, 8$ or 15). The alumina was crushed and sieved to an average particle size of 0.3–0.6 mm; then, it was dried and calcined at 773 K (superficial area BET = 220 m²/g, volume and average pore diameter: 0.6 cm³/g and 11.6 nm; total acidity = 324 μ eq NH₃/g; isoelectric point = 6.7). Rh(x) catalysts were prepared using RhCl₃·2H₂O (Sigma) as a precursor salt. An appropriate salt amount was dissolved in a water volume equal to sixfold the volume of the alumina pore and was put in contact with the latter until pH stabilization. Subsequently, the water was evaporated in a rotary evaporator (318 K and 60 rpm). Then, the solid was dried with a synthetic air flux of 100 ml/min, increasing the temperature to 393 K at a heating rate of 2 K/min; this temperature was maintained for 12 h. Finally, the calcination was performed under the same air flux, increasing the temperature at a rate of 8 K/min to 773 K; this temperature was maintained for 4 h.

Rh(x)Mo(y) catalysts were prepared by successive wet impregnations starting from aqueous solutions of each of the precursor salts. First, Mo was impregnated from an ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O, Merck) solution with the adequate concentration in order to obtain the desired metal content, then, it was dried and calcined in the same way as monometallic catalysts. Following that protocol, the Mo oxide on alumina (Mo(y)) was obtained. The Rh was wet impregnated on Mo(y), dried and calcined as explained before. Moreover, another bimetallic catalyst was prepared following the described procedure but inverting the impregnation order: first the Rh and then the Mo, Mo(8)Rh(2). The Mo and Rh for all catalysts contents were verified by atomic absorption analysis, and they were found to be near the nominal value of ± 0.3 .

2.2. X-ray photoelectron spectroscopy (XPS)

The surface composition of all the studied bimetallic catalysts was evaluated by XPS. XPS spectra were obtained by a Surface Science Instrument SSX-100 model 206 (Unité CATA de l'UCL, Belgium), with a monochromatic Al K α source (1486.6 eV), operating at 10 kV and 15 mA. The spectrometer is interfaced to a Hewlett-Packard 9000/310 computer for data acquisition and analysis. The width of the energy band analyzed was 50 eV for each individual spectrum. The energy scale of the spectrometer was calibrated in reference to the Au_{4f7/2}, whose binding energy was fixed at 83.98 eV. The positive charge developed on the surface of the samples was neutralized with a flood gun, whose energy was adjusted to 6 eV. Before analysis, all catalysts were activated with a mixture of H₂S (15 vol.%) / H₂ at 673 K using the same method as the one used before the catalytic assay. Powdered samples were pressed on stainless steel capsules, which were maintained under iso-octane until they were introduced in the equipment in order to avoid their exposure to air. Samples were degassed under a minimum vacuum of 5×10^{-7} mmHg during 12 h before the introduction in the camera for analysis. During

the analysis, the pressure did not exceed 5×10^{-8} mmHg. The correspondent signals to C_{1s}, O_{1s}, Al_{2p}, S_{2p}, Mo_{3d} and Rh_{3d} were detected for each one of the catalyst samples. The binding energy of C_{1s} line corresponding to C–H or C–C was found to be 284.8 ± 0.2 eV in all the cases. This line was checked at the beginning and at the end of the analysis of each catalyst, and a change in its position was not found. A nonlinear Shirley-type [18] baseline and an iterative least-squares fitting algorithm were used to decompose the peaks taking a Gaussian (85%)–Lorentzian (15%) distribution. Atomic concentration ratios on the surface of the catalyst were calculated as the ratios of the corresponding peak areas corrected with theoretical sensitivity factors and based on Scofield's photoionization cross sections [19].

2.3. Activation procedure and catalytic evaluation

The behavior of catalysts was evaluated with a model charge composed by 2 wt.% of DBT (Acros Organic, 99%), 3% of commercial NT, 2% of hexadecane (J.T. Baker, 100%) used as an internal standard for the analysis of the condensable product, and the remaining was commercial cyclohexane. Catalytic tests were made in a fixed bed high-pressure flow reactor at 5 MPa and 583 K, a liquid flow rate of 30 ml/h, a H₂/liquid charge volume ratio of 500, and 0.5 g of catalyst. Before evaluation, the catalyst was dried and activated *in situ* using a N₂ flux of 100 ml/min at 393 K for 1 h; then, the flux N₂ was changed by one of the activating agents (H₂, H₂S, H₂S (15 vol.%) / H₂, H₂S (85 vol.%) / H₂ or N₂), and the temperature was also changed by the selected one (583, 673 or 773 K). These conditions were maintained for 3 h at atmospheric pressure. Conditions of catalytic tests were established by preliminary tests carried out to verify the absence of diffusional limitations. Samples of the liquid charge and condensable products were taken every hour until a steady state was attained (three consecutive samples were obtained with approximately the same results). These samples were analyzed in a HP 6890 gas chromatograph equipped with a FID detector and a 30 m \times 0.32 mm \times 0.25 μ m capillary column (HP-5, Crosslinked 5% PH ME Silicone).

HDS and HYD catalytic activities are expressed both by the respective DBT (%C_{HDS}) and NT (%C_{HYD}) conversion. The selectivity to HDS (S_{HDS}) is expressed as the ratio of conversions in HDS and HYD. The intensity of synergy (%I_{HDS} or %I_{HYD}) for bimetallic catalysts is calculated as the excess of activity with respect to the sum of experimental activities of corresponding monometallic catalysts.

3. Results and discussion

3.1. Influence of the activation conditions

The catalyst Rh(2) was chosen to analyze the influence of the activation conditions on the behavior of Rh in HDT reactions. Results of the behavior at steady state of this catalyst, activated with different activating agents and at different temperatures, are presented in Table 1.

Table 1
Performance of Rh(2)/ γ -Al₂O₃ catalyst in HDT reactions at steady state when different activation conditions were used

Activating Agent	T _a (K)	%C _{HYD}	%C _{HDS}	S _{HDS}
N ₂	673	10	25	2.5
H ₂	673	17	31	1.8
H ₂ S (15 vol.)/H ₂	673	7	29	4
H ₂ S (15 vol.)/H ₂	773	1	11	11
H ₂ S (85 vol.)/H ₂	673	3	29	9.7
H ₂ S	583	7	26	3.7
H ₂ S	673	4	42	10.5
H ₂ S	773	2	21	10.5

T_a, activation temperature; S_{HDS}, selectivity to HDS; C, conversion.

In general, Table 1 shows that Rh presents low or almost none HYD capacity at HDS conditions when sulfur is present in the activating mixture; Rh(2) presents the greatest activity in HYD (17%) when reduced with H₂. However, this catalyst shows HDS activity when each of the activating mixtures was used, especially when activated with pure H₂S. The best performance in HDS occurs at 673 K (%C_{HDS} = 42%) when H₂S is used as the activating agent.

Results for the no-activation (N₂) procedure (Table 1) show that Rh is active for both HDS and HYD. Moreover, stability was observed during the reaction indicating that the oxides formed during the preparation step are stable at the reaction conditions and that they are not further transformed by the H₂S produced during the reaction. This result suggests that a transformation from the oxide phases to the sulfide ones does not exist, or if this transformation occurs, there is no additional effect on the HDS and HYD reactions. During the calcination, Rh can form oxides such as RhO, RhO₂ and Rh₂O₃ [20], the latter being the most stable. Taking this into account, it can be said that the oxide formed in larger proportion during the calcinations at 773 K was Rh₂O₃.

According to the literature [9,20,21] and to what was observed when the catalyst is activated with H₂, it can be affirmed that Rh was not totally reduced after treating Rh₂O₃ with H₂ at 673 K, presenting a combination of oxides and metal species that intervened in their catalytic properties. In this case, the catalytic system was stable during the reaction for HDS and showed a slight increase for HYD. An increment in the activities for both reactions at steady state compared with the catalyst that was not activated is also observed, but the formation of catalytic sites for HDS was the most favored. This indicates that the phases formed during reduction are either precursors of HDS active sites originated in the reaction environment or could contain active sites for the HDS.

When the catalyst is activated with different H₂S/H₂ ratios, appreciable changes were observed in the HDS activity (Table 1); the HDS is more sensitive to temperature changes than to the H₂S concentration in the activating mixture. Additionally, the HDS activity does not present changes during the reaction; it can be said that the active sites for HDS were formed during the activation step and were stable at the reaction conditions. The activity for HYD does not present significant changes outside the error margin of the reaction system, which is approximately $\pm 5\%$. It is important to note that a correlation

between the presence of H₂S and the HDS activity exists if the results of the no-activation and the reduction with H₂ are compared with those when H₂S is present in the activating mixture. This result indicates that the Rh is able to generate active sites for the HDS in sulfur-rich environments, leading to speculate that HDS active sites in phases containing Rh are sulfides of this metal and that HYD sites fundamentally correspond to metallic Rh or Rh oxides. Results presented in this work confirm the idea that when H₂S is present during activation, as well as throughout the reaction, Rh sulfides for HDS are generated, and they are stable at any of the different H₂/H₂S ratios in the reaction environment.

When the catalyst is activated with pure H₂S (Table 1), the catalytic behavior is similar to the one when it is activated with the H₂S/H₂ mixture; namely, it does not show HYD activity, but it presents a high HDS activity. This behavior indicates that the concentration of H₂S in the activating mixture plays a crucial role in the formation of adequate active phases for the HDS, favoring HDS activity when the catalyst is activated with pure H₂S. This result confirms what it has been shown before regarding the nature of the active phases and, thus, of the active sites with Rh. The presence of H₂S in the activating environment induces the formation of different types of Rh sulfides on the surface of the catalyst; these sulfides can present a defined stoichiometry. They can also present complex structures with reticular defects and form non-stoichiometric sulfides [20], which are the ones that give adequate characteristics for HDS activity. Based on the described, it can be concluded that the active phase formed on the catalyst when activated in the presence of H₂S is the same phase that the one formed when activated with H₂S/H₂ but in different proportions. The interaction between the Rh and the sulfur forms two species known as RhS₂ and Rh₂S₃. Pecoraro and Chianelli [3,4] observed that Rh₂S₃ was formed when a catalyst containing Rh was activated with H₂S or H₂S (15 vol.)/H₂ mixture at 673 K. Based on this fact, we think that the predominant active phase in this catalyst is Rh₂S₃, and according to our results this phase is stable and able to form HDS active sites.

When activated at 673 K, Rh(2) presents a stable activity in HDS from the beginning of the reaction with each of the mixtures used for its activation; this can be attributed to the fact that stable active phases for HDS are generated during this activation step. When the catalyst is activated at other temperatures (583 or 773 K) and with pure H₂S, the activity in HDS increased throughout the reaction. This result indicates that at these activation temperatures, the formed Rh compounds were not adequate for HDS, but under reaction conditions, Rh sulfides as active phases for HDS reactions are produced.

3.2. Influence of the catalyst composition

In this section, the behavior of the monometallic and bimetallic catalysts when changing their metal content is analyzed. The atomic ratios of the catalyst components measured by XPS and the nominal composition are presented in Table 2. It is observed that the ratio Rh/Mo determined by

Table 2
Atomic ratios measured by XPS between the elements of catalysts of the RhMo/ γ -Al₂O₃ system

Catalyst ^a	Atomic ratio				
	Rh/Mo (N)	Rh/Mo	Rh/Al	Mo/Al	S/Al
Rh(0.3)	–	–	0.006		0.012
Rh(0.15)Mo(2)	0.105	0.27	0.002	0.007	0.013
Rh(0.3)Mo(2)	0.21	0.46	0.004	0.008	0.028
Rh(0.5)Mo(2)	0.35	0.45	0.003	0.006	0.013
Rh(1.5)Mo(2)	1.05	1.00	0.006	0.006	0.019
Rh(0.3)Mo(15)	0.03	0.05	0.003	0.058	0.106
Rh(1.5)Mo(15)	0.14	0.12	0.005	0.046	0.091

^a The nominal content wt.% of each metal is shown in parenthesis. All catalysts were activated at 673 K and with H₂S (15 vol.%) / H₂. N, nominal.

XPS is approximately equal to the nominal ratio for catalysts with the highest Mo and Rh contents, and it is about twice the nominal ratio for catalysts with low Mo and Rh contents. This suggests an important change in the Rh dispersion based on the amount of Mo present in the catalyst. It is also possible that some part of the incorporated Mo in the first impregnation was dissolved during the Rh impregnation; however, this possibility is not probable because after the Mo impregnation the material was calcined and MoO₃ was formed. A temperature programming reduction analysis of the MoO₃/ γ -Al₂O₃, prepared in the same way as the one in this study, carried out in a previous work, shows that the MoO₃ is stable up to 860 K [22]. Furthermore, it has been experimentally proved for the PtMo/ γ -Al₂O₃ catalysts that the noble metal dispersion increases when metal contents are low. The highest platinum dispersion is obtained for the Pt(0.5)Mo(2) catalyst [13].

Table 3 presents results of the behavior of monometallic and bimetallic catalysts in the RhMo/ γ -Al₂O₃ system, activated in a standard manner (673 K and with a mixture of H₂S (15 vol.%) / H₂). From these results, it can be inferred that monometallic catalysts with Rh content <2% are more active for HDS than for HYD, and the HDS activity increases as the Rh content increases. Regarding bimetallic catalysts, a decrease in the

Table 3
Performance of Rh/ γ -Al₂O₃, Mo/ γ -Al₂O₃ and RhMo/ γ -Al₂O₃ catalysts in HDT reactions at steady state, activated at 673 K and with a H₂S (15 vol.%) / H₂ mixture

Catalyst ^a	%C _{HDS}	%C _{HYD}	S _{HDS}	%I _{HDS}	%I _{HYD}
Rh(0.15)	7	2	3.5		
Rh(0.3)	12	3	6		
Rh(0.5)	14	5	4.6		
Rh(1.5)	22	7	3.1		
Mo(15)	16	4	4		
Mo(2)	5	2	2.5		
Rh(0.15)Mo(2)	21	9	2.3	75	125
Rh(0.3)Mo(2)	34	14	2.4	100	180
Rh(0.5)Mo(2)	34	18	2	79	157
Rh(1.5)Mo(2)	47	26	2	74	189
Rh(0.3)Mo(15)	37	12	3	32	71
Rh(1.5)Mo(15)	58	26	2.2	53	136

C, conversion; I, intensity of synergy; S_{HDS}, selectivity to HDS.

^a The nominal content wt.% of each metal is shown in parenthesis.

selectivity to HDS is observed when they are compared to the monometallic ones. A synergistic effect for the two reactions, especially for HYD, is observed for these catalysts indicating that an effect associated with the interaction between the two metals exists. This synergetic effect has also been found in both systems Rh-W in HDS and HYD reactions [6] and Rh-Mo in HDS and HDN reactions [8]. Two tendencies, depending on the Mo content in the catalyst, can also be observed (Table 3). The first one corresponds to the two bimetallic catalysts with the highest Mo content (15%); they present an appreciable activity for HDS as well as for HYD, but at the same time, the values %I_{HDS} and %I_{HYD} are relatively low. The second tendency corresponds to the catalysts with low Mo content (2%), the activity values are lower than the presented for the first ones, but the synergetic effect increases as the Rh content in the catalyst increases.

Table 4 presents the catalytic performance of the Rh(2), Mo(8) and Mo(8)Rh(2) activated with pure H₂. This table shows that the Mo(8)Rh(2) catalyst is not very selective towards the HDS and presents only synergy in HYD. Additionally, a decrease in the HYD conversion and an almost constant HDS conversion were observed during the reaction, indicating that HYD sites were formed in the activation step, but they were deactivated during the reaction. These results are probably due to the presence of H₂S. However, the sites formed for HDS remained constant during the reaction. When comparing the behavior of this bimetallic catalyst with the one activated by the standard procedure (Table 3), it can be said that the presence of H₂S during the activation is necessary to develop a cooperative effect between the two phases, especially for the HDS reaction.

In Fig. 1, the intensity of synergy as a function of the Rh/(Rh + Mo) atomic ratio measured by XPS is presented for the bimetallic catalysts tested. This figure shows that when the Rh/(Rh + Mo) ratio in the catalyst increases, the intensity of synergy changes for both HYD and HDS. A mild maximum of synergy for HDS a Rh/(Rh + Mo) atomic ratio around 0.3 is observed. As it has been shown for various bimetallic systems in HDT, a maximum value for the intensity of synergy is possible [6,7,9,13,14]. This synergetic effect can be related to a higher Rh dispersion at lower Mo concentrations as suggested by the results of XPS shown in Table 2. Similar results have been found in previous studies from our laboratory for the PtMo/ γ -Al₂O₃ system [13]. It is important to note that the intensity of synergy in HYD is higher than in HDS. Taking into account the results of the activity and selectivity of monometallic catalysts and the ones presented for bimetallic

Table 4
Performance of Rh/ γ -Al₂O₃, Mo/ γ -Al₂O₃ and MoRh/ γ -Al₂O₃ catalysts in HDT reactions, activated with H₂ at 673 K

Catalyst ^a	%C _{HDS}	%C _{HYD}	S _{HDS}	%I _{HYD}
Rh(2)	31	17	1.8	–
Mo(8)	20	9	2.2	–
Mo(8)Rh(2)	51	39	1.3	50

C, conversion; I, intensity of synergy; S_{HDS}, selectivity to HDS.

^a The nominal content wt.% of each metal is shown in parenthesis.

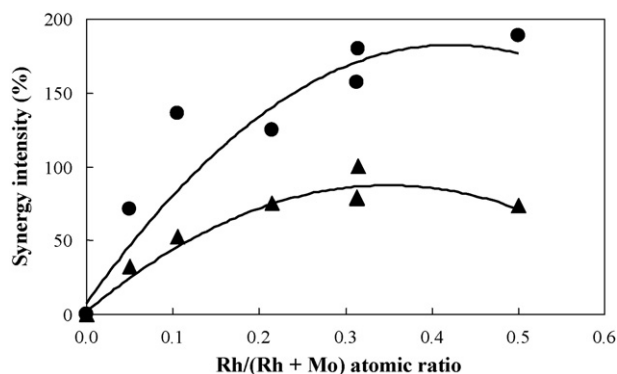


Fig. 1. Intensity of synergy as a function of the Rh/(Rh + Mo) atomic ratio measured by XPS for RhMo/ γ -Al₂O₃ bimetallic catalysts: (▲) %I_{HDS}; (●) %I_{HYD}.

catalysts, it can be speculated that the presence of Rh could be playing a significant role on the capacity of HDS of the catalyst as well as both the generation and transformation of the active sites of the Mo towards sites with more capacity for HYD.

4. Conclusions

In the activating mixture, the presence of H₂S is definitive for the selectivity to HDS of Rh/ γ -Al₂O₃ catalysts in HDS and HYD reactions. The activation with pure H₂S favors the formation of active sites for HDS and, in any proportion, inhibits the formation of active sites for HYD.

The activation temperature influences the HDS activity of Rh/ γ -Al₂O₃ catalysts, implying that a maximum exists around 673 K.

A synergetic effect was detected with RhMo/ γ -Al₂O₃ catalysts evidencing an interaction between Rh and Mo. It can be speculated that the phase containing Rh acts independently and promotes the active sites on Mo. The intensity of synergy depends on the metal content, and this intensity is related with the dispersion of both metals.

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