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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-Al_2O_3 catalyst in simultaneous hydrodesulfurization (HDS) of dibenzothiophene (DBT) and hydrogenation (HYD) of naphthalene (NT). H_2, H_2S, N_2 and H_2S (15 vol.%)/H_2, H_2S (85 vol.%)/H_2 mixtures were used as activating agents. Bimetallic RhMo/γ-Al_2O_3 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 H_2S 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.

Keywords: Rh/γ-Al_2O_3; Activating mixtures; RhMo/γ-Al_2O_3; Hydrodesulfurization; Hydrogenation

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-Al_2O_3 monometallic catalyst and the content of metals for RhMo/γ-Al_2O_3 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-Al_2O_3,

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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 m^2/g, volume and average pore diameter: 0.6 cm^3/g and 11.6 nm; total acidity = 324 μeq NH_3/g; isoelectric point = 6.7). Rh(x) catalysts were prepared using $RhCl_3 \cdot 2H_2O$ $2H_2O$ (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 ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 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 Kα 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 H_2S (15 vol.%)/H_2 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 isooctane 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%)–Lorenzian (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 Scoffield'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 H_2/liquid charge volume ratio of 500, and 0.5 g of catalyst. Before evaluation, the catalyst was dried and activated *in situ* using a N_2 flux of 100 ml/min at 393 K for 1 h; then, the flux N_2 was changed by one of the activating agents (H_2, H_2S, H_2S (15 vol.%)/H_2, H_2S (85 vol.%)/H_2 or N_2), 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 × 0.32 mm × 0.25 μm 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.