Hydrodesulphurization of Thiophene over Co, Mo and CoMo /γ-Al_2O_3 Catalysts

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The hydrodesulphurization (HDS) of thiophene was performed on monometallic catalysts Co/γ-Al_2O_3, Mo/γ-Al_2O_3 and bimetallic CoMo/γ-Al_2O_3. Experiments were carried out on a fixed bed catalytic reactor at 175-300°C, 30-60 atm, thiophene volume hourly space velocities of $1h^{-1}$- $4h^{-1}$ and molar ratio hydrogen/thiophene of 60/1. The thiophene conversion on the bimetallic CoMo/γ-Al_2O_3 catalyst was higher than on Co/γ-Al_2O_3 or Mo/γ-Al_2O_3.

Keywords: thiophene, hydrodesulphurization,catalyst acidity, Co, Mo, γ-Al_2O_3

The availability of conventional crude oil is continuously deacreasing because of the depletion of worldwide reserves, resulting a growing dependence on high heavy feedstocks. The conversion of lower-grade feedstocks to liquid products is causing an increase in the total sulfur content in refined products. Therefore refiners have to continue to remove substantial portions of sulfur from the lighter products; however, residua and heavy crude oil poses a particularly difficult problem. Sulfur, even in extremely low concentrations, has detrimental effects on process catalysts in the catalytic reforming units that are subsequently used to produce high-octane naphtha as a blend stock for gasoline manufacture [1]

Typically, the sulfur is removed by a hydrodesulfurization process, which is usually carried out through a catalyzed reaction with hydrogen at moderate to high temperature and pressure. The sulfur atom in sulfur compounds is reduced to hydrogen sulfide (H_2S) which is then catalytically air oxidized to elemental sulfur. Depending on the hydrocarbon type and degree of desulfurization, hydrodesulfurization may occur at 200-425°C and 10-20bar hydrogen [2]. The organosulfur compounds like mercaptans, sulfides, disulfides, thiophene derivatives, and benzothiophene derivatives - usually are converted to hydrocarbons [3].

Thiophene is frequently chosen as representative of the sulfur compounds in light feedstocks. Altough there have been reported many works on hydrodesulphurization of thiophene, the hydrodesulphurization of thiophene is extremely complex and has not been fully resolved.

The most important industrial catalysts for hydrodesulfurization consists of CoMo sulfides dispersed on a highly porous ã-alumina (γ-Al_2O_3) [4, 5]. Apart from the catalyst type involved, optimal process configurations to minimize the suppression of hydrogen sulfide on the catalyst activity are important. The hydrogen sulfide produced from sulfur compounds with higher reactivity in the early stage of desulfurization negatively influences the hydrodesulfurization of less reactive sulfur compounds.

Some noble metale catalysts showed an excelent activity in desulphurization [6] but they are expensive, so the developing of increasingly active CoMo /γ-Al_2O_3 catalysts is a goal.

The objective of this work was to prepare and characterize high activity CoMo /γ-Al_2O_3 catalysts for desulphurization process and to test their activity in a high-pressure fixed bed reactor. The optimal process configuration was determined by evaluating the thiophene conversion at different values of temperature, pressure and liquid hourly space velocity.

Experimental part

Catalyst preparation

The catalysts support is high purity aluminium oxide (γ-Al_2O_3)- granules in cylindrical form, prepared from commercial pseudoboehmite, which was kneaded in the presence of nitric acid and extruded with a 1 mm nozzle. The support was calcinated at 550°C resulting γ-Al_2O_3 [7, 8].

The catalysts were prepared by pore filling method. The catalytic precursors were aquous solution of ammonium molybdate heptahydrate and cobalt nitrate. After impregnation at room temperature, the wet cylinders were dried at 120°C for 4 h and calcinated at 450°C for 2 h [9].

Catalyst characterization

Catalyst characterization was performed by determining the acid strength, textural characteristics and by termogravimetric analyses. The acid strength distribution of the active center has been determined by the method of thermal desorption of diethyl-amine on a DuPont Instruments Thermal Analyst 2000/2100 coupled with a module 951 Thermogravimetric Analizer. Textural characteristics of the catalysts (surface area, pore volume, average pore diameter, pore-size-distribution) were determined on a Autosorb 1 Quantacrome.

Reaction tests

HDS of thiophene over Co, Mo and CoMo/γ-Al_2O_3 supported catalyst, was performed in a fixed bed reactor. A 30cm^3 amount of catalyst was placed in the middle of the reactor and the top and the bottom of the reactor were

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filled with inert glass beads. The installation is described in a previous work [9]. The feedstock consisted of thiophene and hexane as a solvent, with thiophene concentration of 0.6 wt%, was introduced by a metering pump. The experiments were carried out in the following experimental conditions: temperature (T): ranging from 175 to 300°C, pressure (p) from 30 barr to 60 barr and the liquid hourly space velocity (LHSV) from $1h^{-1}$ to $4h^{-1}$.

The composition of the reaction mixture was performed by gas chromatography (Varian 3800) coupled with mass spectrometry (Varian 4000), equipped with Agilent VF-5ms capillary column. The carrier gas was He, the oven temperature 175°C (16°C/min) and the injector temperature 155°C.

Results and discussions

The stength of acid sites and total acidity

Diethylamine thermodesorption curves of the catalysts, from 20 to 800°C, are shown in figure 1. The three zones are assigned to weak, medium, and strong acidities. The weak acidic centers are obtained in the first region which ranges from 160 to 300°C, the medium acidic centers are in the second region from 300 to 440°C and the strong acidic centers are in the last region from 440 to 580°C.

The monometallic catalyst Mo/g-Al_2O_3 have a close content of weak acidic centers with bimetallic catalyst Co-Mo/γ-Al_2O_3. The monometallic catalyst Co/γ-Al_2O_3 have a lower content of weak acidic centers than previous catalysts. The medium and strong acidic centers of the two monometallic catalysts are about half that of bimetallic catalyst Co-Mo/γ-Al_2O_3. It can be seen that the Mo catalyst has a higher total acidity than the Co catalyst (fig. 2). The results show that the acidity of the catalysts deacrease as follows: CoMo/γ-Al_2O_3> Mo/γ-Al_2O_3> Co/γ-Al_2O_3 and the total concentration of acidic centers is 1.1 mEq/g for CoMo/γ-Al_2O_3, 0.737 mEq/g for Mo/γ-Al_2O_3 and 0.522 mEq/g for Co/γ-Al_2O_3.

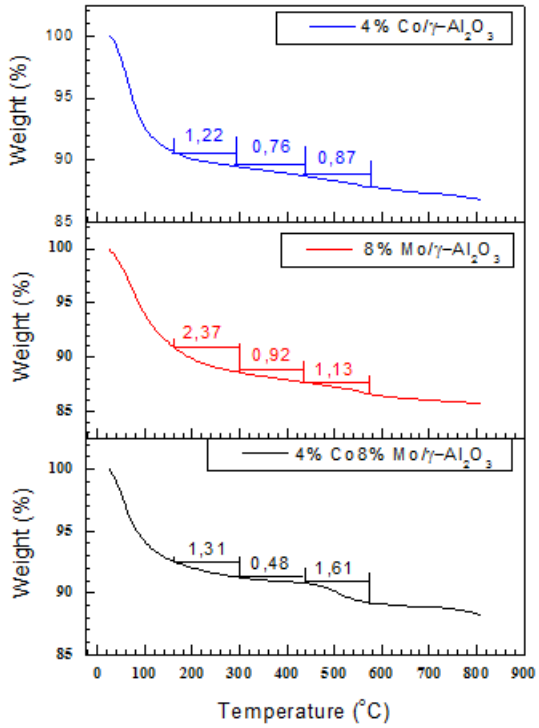

Fig. 1. Diethylamine thermodesorption curve of the catalysts

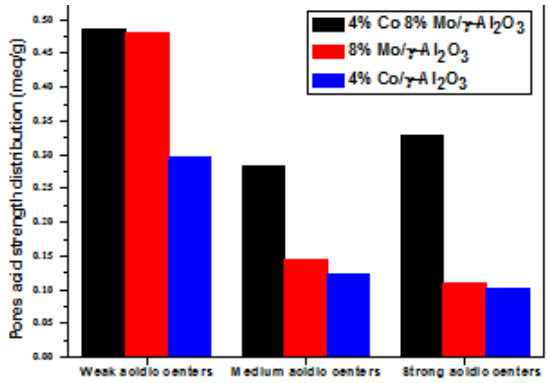

Fig. 2. Pores acid strength distribution of the catalysts

Textural characteristics

The textural properties (BET surface area, pore volume and average pore diameter) of the catalysts are summarized in table 1. The mesopore size distribution of the catalyst is between 2 and 10 nm (fig. 3).

Table 1

TEXTURAL PROPERTIES OF THE CATALYSTS

Catalyst	S_{BET}, m^2/g	Pore volume, cm^3/g	Average pore diameter, nm
Co/γ–Al_2O_3	268.577	0.441	5.859
Mo/γ–Al_2O_3	241.672	0.289	4.837
CoMo/γ–Al_2O_3	140.181	0.164	3.268

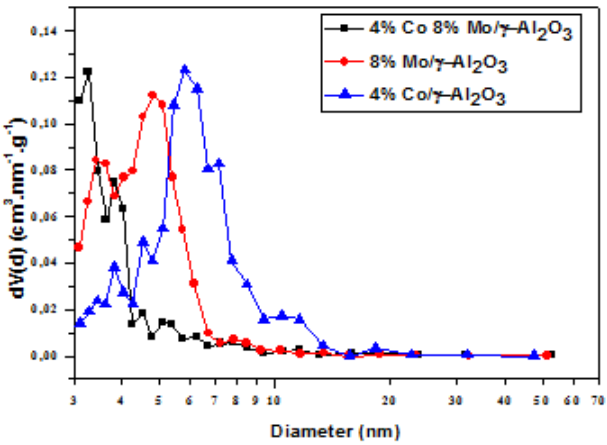

Fig. 3. Pore size distributions of the catalysts

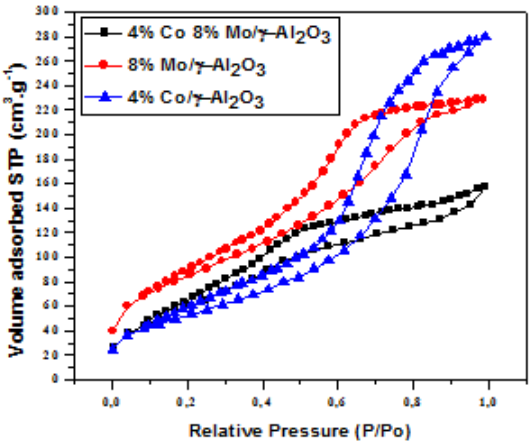

Fig. 4. The isotherm of nitrogen adsorption / desorbtion on the catalyst

The catalyst exhibits isotherms of classical IV type (fig. 4), specific to mesoporous solids. The hysteresis, indicates that all the catalysts have cilindrical pores [10].

Hydrodesulphurization of thiophene

Figure 5 shows the possible reaction pathways for the catalyzed hydrodesulfurization of thiophene [11]. The main reaction products observed during thiophene conversion

were 1-butene, cis- and trans- butene and traces of tetrahydrothiophene and dihydrothiophene were detected [11].

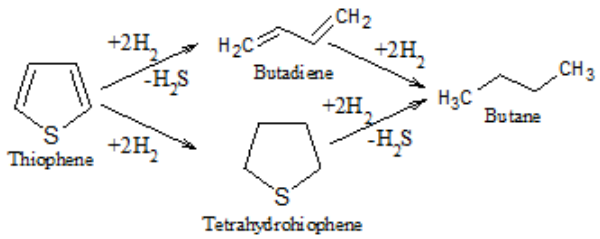

Fig.5. Thiophene hydrodesulpurization pathway

The conversion of thiophene was defined as a ratio of the weight of reacted thiophene to the weight of fed thiophene.

Effect of reaction temperature

In the range of 175-300°C, 30 bar and LHSV of $1h^{-1}$ (fig.6) the results indicate that the reaction temperature is an important factor for the hydrodesulphurization of thiophene. The highest thiophene conversion, was achieved over CoMo/γ-Al_2O_3 catalyst. The thiophene conversion over this catalyst at 175°C was 25.6% and at 300°C was 89.7%. Mo/γ-Al_2O_3 exhibited an activity close to that of the Co-Mo catalyst at a lower temperature that diminished with increasing temperature. This decrease in activity may be due to the blocking of the pores with the olefin condensation products formed by desulphurisation on acid moieties of Mo oxide at higher temperature. In the absence of cobalt there is no hydrogenation of the unsaturated products resulting from desulphurisation on Mo trioxide acid centers. Thus, it can be shown that thiophene desulphurisation precedes the hydrogenation of the olefinic groups. Also, the lower activity of the Co catalyst is due to a lower concentration of strong acid centers (the acidity of the alumina support is lower than the Mo trioxide).

The main characteristic of the catalysts that influence the hydrodesulpurization activity, is the acidity not the textural properties. The catalysts have the pore diameters from 3-5 nm and the maximum molecular size of the thiophene is 4.5 A (from geometry optimized at BHandHLYP/6-311G) [12]. Although CoMo/γ-Al_2O_3 has the lowest specific BET area, it exhibits the highest hydrodesulphurization activity due to a high concentration of acidic centers, of 1.1 mEq/g.

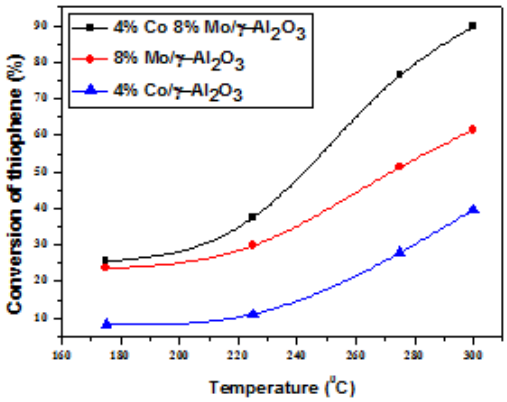

Fig. 6. Influence of reaction temperature on thiophene hydrodesulphurization over Co/g-Al_2O_3 , Mo/γ-Al_2O_3 and CoMo/γ-Al_2O_3 catalyst (p=30 bar, LHSV=1 h^{-1})

Effect of reaction pressure

For HDS of thiophene dependance on hydrogen pressure, the reaction pressure were varied at 300°C of reaction temperature and with the constant contact time, LHSV=$1h^{-1}$.

Figure 8 shows that the reaction pressure, influences less the conversion of thiophene than temperature does, over all catalysts. At 300°C, the conversion of thiophene over CoMo/γAl_2O_3 increase from 89.7% to 99.3%, at pressure from 30 bar to 60 bar. The difference between the activity of the three catalysts is more evident, the bimetallic catalyst having a higher activity than the monometallic ones due to the presence of both the acidic and metallic catalytic centers at an optimal concentration. Also, the Mo catalyst has a higher activity than Co catalyst, the low concentration of its strong acidic acids decreasing the risk of oligomerization of the olefins formed in the desulfurization step.

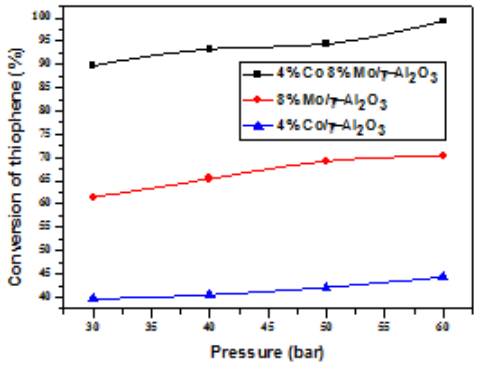

Fig. 7. Influence of pressure on thiophene HDS over Co/g-Al_2O_3 , Mo/g-Al_2O_3 and CoMo/g-Al_2O_3 catalyst (T=300°C, LHSV=1 h^{-1})

Effect of LHSV

The LHSV effect on HDS conversion was studied in the range of $1h^{-1}$ - $4\ h^{-1}$, by keeping temperature and pressure constant, respectively 300°C and 60 bar. At constant temperature and pressure, the conversion of thiophene decreased as the LHSV increased as shown in figure 8. The results are in agreement with other studies for thiophene HDS [13-15]. The tendency of LHSV decreasing is favorable to the conversion of HDS, since the residence time of reactants increases with LHSV decreases. In this case too, the differences in activity between bimetallic and monometallic catalysts remain. The increase in turbulence did not favor the solubilization of the condensation products which closed some of the pores so that the Mo catalyst activity was lower than that of the bimetallic irrespective of the contact time. As processing capacity is related to LHSV the economical demand in industry prefers relatively high LHSV in commercial hydrotreating industry operation such as 1-2.5 h^{-1}[16].

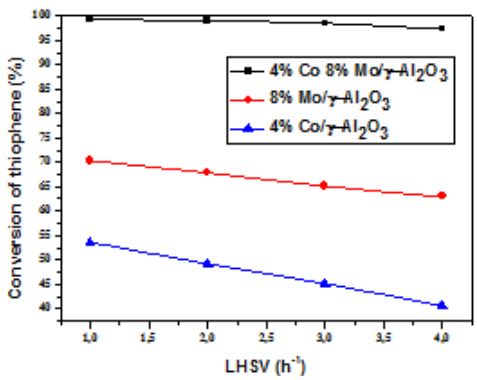

Fig. 8. Influence of LSHV on thiophene HDS over Co/g-Al_2O_3 , Mo/g-Al_2O_3 and CoMo/g-Al_2O_3 catalyst. (T=300°C, p=60 bar)

Conclusions

The hydrodesulpurization of thiophene over Co, Mo and CoMo/g-Al_2O_3 catalysts has been studied under various temperature, pressure and LHSV conditions. The results show that the reaction takes place in two steps, the first being the desulphurisation and the second the hydrogenation of the formed olefins.

A low concentration of acidic catalytic centers with high acidity (MoO_3) reduces the rate of desulphurisation and implicitly the performance of the process, and a low concentration of catalytic metallic centers (Co) diminishes the activity of the catalyst due to the partial blocking of the pores with the condensation products of the olefins formed in the desulfurization step.

Selecting an optimal impregnation method and an optimal atomic ratio between the two metals, to ensure the presence of an optimal neighborhood between the two types of catalytic centers, will allow the increasing of the catalyst activity.

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