Hydrodesulfurization of Dibenzothiophene on a CoNiMo Catalyst

RAMI DOUKEH1,2, TRAIAN JUGANARU1, ION BOLOCAN1*
1Petroleum Gas University of Ploiesti, 39 Bucuresti Blvd., 100680, Ploiesti, Romania
2National Institute for Research Development for Chemistry and Petrochemistry- ICECHIM Bucuresti , 202 Splaiul Independentei, 060021, Bucharest, Romania

In order to evaluate the performance of CoNiMo/γ-Al2O3, the hydrogenolysis of dibenzothiophene was carried out. The conversion of dibenzothiophene, the yields of the reaction products and the unconverted sulfur content, expressed in ppm, were determined, at different temperatures in the catalytic layer (300°C-360°C), pressures (40 bar-60 bar) and liquid hourly space velocity (1-4 h⁻¹). The hydrodesulfurization catalyst was characterized by: determining the textural characteristics (BET specific surface area, mean pore diameter and pore volume), the acidic strength distribution, morphological analysis (scanning electron microscopy - SEM) and by identification of the species (X-ray diffraction - XRD). The analysis of the textural characteristics results in an ordered mesoporous structure of the catalyst, with a specific area of 280 m²/g and a medium pore diameter of 4.42 nm. At high temperature of 360°C and pressure of 60 bar, the CoNiMo/γ-Al2O3 exhibit a good activity in hydrodesulfurization with a 100% conversion of dibenzothiophene.

Keywords: hydrodesulphurization, dibenzothiophene, CoNiMo/γ-Al2O3 catalyst

In many countries, stricter regulations for fuels have been introduced, with the overall tendency to be cleaner and to contain compounds which can affect the environment (sulfur compounds, nitrogen and aromatic compounds), as few as possible and in very low concentrations. In European Union, the limit concentration for sulfur is 10 ppm, since January 2009, when Euro5 type fuel has been introduced, compared to 500ppm, the concentration allowed in 1996, for Euro 2 type fuels. Petroleum fractions contain a complex mixture of sulfur compounds with different reactivity. In gasoline, are generally found mercaptans which have up to 8 carbon atoms in the molecule and acyclic and cyclic sulfides. In the middle distillates (oil and gasoline) are mainly found sulfides, thiophene and its derivatives and bicyclic thiophenes. Heavier petroleum fractions also contain bi- and poly cyclic components with a thiophene or thiophene ring condensed with several aromatic or naphthenic cycles. The type of compounds present, their reactivity, the reaction mechanism, the kinetics of hydrodesulfurization, and the factors that influence the reactivity of the sulfur compounds must be clearly known for the desulfurization process. The sulfur compounds most studied are thiols (mercaptans), thioethers (sulphides), disulfides, thiophene, benzo-thiophene and dibenzothiophene. There is a lot of possibilities for hydrodesulfurization catalysts, and their choice in refineries usually adapts to the characteristics of the petroleum fractions and to the specifications of the refined product. The most used catalysts have the active component in the form of molybdenum sulfide or tungsten, to which cobalt and nickel are added as promoters. Other possibilities are Ni-Mo, Ni-W, or Co-W rarely. γ-Alumina, γ-Al2O3, is the most commonly used support for the preparation of hydrodesulfurization catalysts. γ-Alumina crystallizes in cubic form with structural defect in which the oxygen atoms are arranged in a compact cube network and the aluminum atoms are arranged in a tetrahedral and octahedral network. In order to achieve γ-Al2O3 stoichiometry, starting from the chemical formula of a M3O4 spinel (M-metal or metal combinations), the positions for the Al atoms are not fully occupied. Vacant positions are distributed both on octahedral and tetrahedral centers. The distribution of Al atoms is dependent on the synthesis method. Zhang et al. used the sol-gel method for γ-Al2O3 support, in order to obtain NiMo catalysts for diesel hydrodesulfurisation. They used an inorganic precursor, AlCl3·6H2O or Al(NO3)3·6H2O as the source of aluminum, polyethylene glycol (PEG 400) and NH3·H2O. Also by gel-based gel, but starting from an organic precursor, Araiza et al. synthesized γ-Al2O3, and for the Pt, Pd catalyst for the hydrodesulfurization studies of 4,6-dimethyl-dibenzo-thiophene. Several metals demonstrated to be active in the hydrodesulfurization process, with numerous studies on transition metal sulfides. The activities of metal sulphides (supported or not), for the hydrodesulfurization of thiophene and benzothiophene depend on the position of the metal in the periodic system. Even though there are small differences between studies, all show that transition metals in the second and third groups have a volcano-type dependence between activity and position in the periodic system, and are generally more active than those in the first column, i.e. Ru, Os, Rh, Ir. MoS2, being the most widely used industrial catalyst.

Experimental part
Catalyst preparation and characterization
The CoNiMo/γ-Al2O3 catalyst was prepared by the incipient wetness co-impregnation using ammonium molybdate tetrahydrate, cobalt (II) nitrate hexahydrate (Sigma-Aldrich) and nickel (II) nitrate hexahydrate respectively. After each impregnation step, the catalyst was dried for 3 h and calcined for 4 h at 450 °C, with the exception of the final calcination that last 6 h. After the final calcination step, the catalyst was activated in a hydrogen stream at 450°C for 4 h. The composition of the active phase of the prepared catalyst was: 11.5% Mo, 3% Co and 2% Ni.

Textural characteristics: surface area, pore volume, average pore diameter and pore-size-distribution were determined on a Autosorb 1 Quantachrome. The specific surface area (SSA) was calculated using the Brunauer-Emmett-Teller (BET) method for relative pressure (p/p0) ranged between 0 and 1. Pore volume (Vp) were...
determined by nitrogen adsorption at a relative pressure of 0.99 and pore size distributions from the branch isotherms adsorption by Barrett-Joyner-Halenda (BJH) method were also taken into account. 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 Analyzer. XRD measurements were carried out with a Bruker D8 Advance X-ray equipment using CuKα radiation. SEM images were collected using a FEI Inspect, S model microscope.

The physicochemical properties of catalysts are characterized and correlated with the observed hydrodesulfurization activities of dibenzothiophene.

Dibenzothiophene hydrodesulphurisation tests

Hydrodesulphurization of dibenzothiophene was performed in a high-pressure fixed-bed continuous reactor at pressures (p) ranging from 40 bar to 60 bar, temperatures (T) of 300 to 360°C and liquid hourly space velocity (LHSV) from 2h⁻¹ to 4h⁻¹. The feed consisted of a solution of 1.73 % wt of dibenzothiophene (Aldrich, 99%) in hexane (Sigma-Aldrich, 99%). Prior to the activity test, the catalyst was sulfided using a 1% dimethyldisulphide solution (in hexane) at 350°C and 5 bar. The samples were collected and analyzed by gas chromatography equipped with mass spectrometer CP-3800 Triple Quad Agilent Technologies, on a DB-5 column.

Results and discussions

Catalyst characterization

The nitrogen adsorption–desorption isotherms for the CoNiMo/γ-Al₂O₃ catalyst and the pore size distribution are shown in Fig. 1. The catalyst display a type IV isotherm according to IUPAC classification and a hysteresys loop characteristic to cylindrical pores [20]. The nitrogen, begins to condense in the pores of the catalyst, at relative pressures (p/p₀) of 0.4 when the hysteresis loop appears, and at the relative pressure (p/p₀) of 1, the pores are completely filled with the condensed liquid. From the analysis of the textural data (Table 1 and Figure 1), it is observed that the catalyst has a uniform pore size distribution, with an mean diameter of 4.2 nm, a total pore volume of 0.18 cm³/g and a surface specific surface area of 163.4 m²/g.

Diethylamine thermodesorption curve of the catalyst is shown in Figure 2. (160-300°C-concentration of weak acidic centers, 300°C-440°C-concentration of centers with medium acidity, 450-580°C-concentration of centers with high acidity) [21]. On the basis of the thermodesorption curve of the catalyst, it was calculated the strength of acid sites and total acidity (Table 2). The total acidity of the CoNiMo/γ-Al₂O₃ catalyst is 0.621 meq/g with 0.33 meq/g representing the concentration of weak acid sites. The concentration of medium acid sites is 0.165 meq/g and the concentration of strong acidic sites is 0.126 meq/g catalyst. From the analysis of the acid strength distribution, the catalyst has a low acidity.

![Fig. 1. Pore size distributions and adsorption desorption isotherm of the catalyst](image1.png)

**Table 1**

| Property          | Value          |
|-------------------|----------------|
| Specific area BET (m²/g) | 163.4          |
| Pore volume (cm³/g)    | 0.18           |
| The mean pore diameter (nm) | 4.2            |

![Fig. 2. Diethylamine thermodesorption curve of the catalyst](image2.png)

**Table 2**

| Acidic center type | Concentration (mequiv/g) |
|--------------------|--------------------------|
| Weak               | 0.330                    |
| Medium             | 0.193                    |
| Strong             | 0.126                    |
| TOTAL concentration| 0.621                    |

The XRD diffractogram (Figure 3) show the characteristic peaks of alumina and MoCo confirming the presence of CoMoOₓ, the crystalline molybdenum oxide and nickel oxide. The X-Ray pattern shows peaks at 2θ= 36.7°; 45.5° and 66.8° which are related to crystal phase of γ-Al₂O₃ [22-23]. As depicted in the SEM images (Figure 4), the active phases were well distributed on the alumina surface.

![Fig. 3. XRD pattern of the catalyst](image3.png)
Hydrodesulphurization tests
From the GC-MS analysis of the reaction products there were mainly identified biphenyl, phenylciclohexane and biciclohexil.

Effect of reaction temperature
The dibenzothiophene conversion values and sulphur contents achieved at 30 bar and LHSV of 1 h\(^{-1}\), at different temperatures, are shown in Figure 5. It is clear the beneficial effect of temperature on the catalyst activity. At 300°C the benzothiophene conversion was 55.07% and achieved 96.16% at 360°C. The initial sulphur content in the feed was 3000 ppm and decreased after hydrodesulphurization process to 1347 ppm at 300°C and to 115 ppm at 360°C.

The yields in the reaction products, at temperature from 300 to 360°C, pressure of 30 bar and LHSV of 1 h\(^{-1}\) are shown in Figure 6. The yield in biphenyl was 47.62% at 300°C and continuously increased to 69.16% at 360°C. The yield in phenylciclohexane also increased with temperature from 6.14 to 19.87%.

Effect of pressure
Increasing the pressure from 30 bar to 60 bar, at constant temperature of 360 °C and LHSV of 1 h\(^{-1}\), the activity of the prepared catalyst CoNiMo/γ-Al\(_2\)O\(_3\), on dibenzothiophene hydrodesulfurization was improved. The conversion increased from 96.16% at 30 bar to 100% at 60 bar and the sulphur content was reduced to zero at 60 bar (Figure 7). An increased pressure favors the formation of phenylciclohexan and biciclohexil, while the yield in biphenyl decreased from 69.16% to 38.46%, for pressures from 30 bar to 60 bar (Figure 8).

Effect of liquid hourly space velocity
Figure 9 shows the variation of benzothiophene conversion and sulphur content with liquid hourly space velocity, at 360 °C and a pressure of 60 bar. As expected, at higher LHSV, because of shorter contact time between raw material and catalyst, the conversion of benzothiophene decreased. The sulphur content at 4 h\(^{-1}\) was 376 ppm and it was reduced to zero at 1h\(^{-1}\).
The formation of bicyclohexyl and phenylcyclohexane is negatively influenced by LHSV. The yield in bicyclohexyl decreased from 10.7% to 1% when LHSV increased from 1h⁻¹ to 4h⁻¹, and the yield in phenylcyclohexane decreased from 49.87 to 19.52%.

Conclusions

The catalyst display a type IV isotherm according to IUPAC classification and a hysteresis loop characteristic to cylindrical pores. The catalyst has a low acidity, the total acidity being 0.621 meq/g from which the concentration of weak acid sites was 0.33 meq/g.

The XRD diffractogram show the characteristic peaks of alumina and MoCo confirming the presence of CoMoOₓ, the crystalline molybdenum oxide and nickel oxide. The reaction products there were biphenyl, phenylcyclohexane and bicyclohexyl.

The yield in phenylcyclohexane and bicyclohexane increases with temperature after a slower slope than the yield in biphenyl.

An increased pressure favors the formation of phenylcyclohexane and bicyclohexyl, while the yield in biphenyl deacreased.

The formation of bicyclohexyl and phenylcyclohexane is negatively influenced by LHSV.

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