

# Hydrodesulfurization of Dibenzothiophene on a CoNiMo Catalyst

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*In order to evaluate the performance of CoNiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 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 (1-4h<sup>-1</sup>). The hydrodesulphurization 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 m<sup>2</sup>/g and a medium pore diameter of 4.42 nm. At high temperature of 360°C and pressure of 60bar, the CoNiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> exhibit a good activity in hydrodesulphurization, with a 100% conversion of dibenzothiophene.*

**Keywords:** hydrodesulphurization, dibenzothiophene, CoNiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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 [1-3]. 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 thioethers. Heavier petroleum fractions also contain bi- and polycyclic components with a thiophene or thiophene ring condensed with several aromatic or naphthenic cycles [4]. 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, benzothiophene and dibenzothiophene [5,6]. There are 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 [7].  $\gamma$ -Alumina, ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) is the most commonly used support for the preparation of hydrodesulfurization catalysts [8].  $\gamma$ -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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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 [9-10]. Zhang et al. [11] used the sol-gel method for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, in order to obtain NiMo catalysts for diesel hydrodesulphurisation. They used an inorganic precursor, AlCl<sub>3</sub> · 6H<sub>2</sub>O or Al(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O as the source of aluminum, polyethylene glycol (PEG 400) and NH<sub>3</sub> · H<sub>2</sub>O. Also by gel-based gel, but starting from an organic precursor, Araiza et al. synthesized  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and, for the Pt, Pd catalyst for the hydrodesulfurization studies of 4,6-dimethyldibenzothiophene [12]. Several metals demonstrated to be active in the hydrodesulfurization process, with numerous studies on transition metal sulfides [13,14]. The activities of metal sulphides (supported or not), for the hydrodesulphurization of thiophene [15,16] and benzothiophene [17] 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, ie Ru, Os, Rh, Ir [18], MoS<sub>2</sub> being the most widely used industrial catalyst.

## Experimental part

### Catalyst preparation and characterization

The CoNiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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 [19]. After each impregnation step, the catalyst was dried for 24 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 Quantacrome. The specific surface area (SSA) was calculated using the Brunauer-Emmett-Teller (BET) method for relative pressure (p/p<sub>0</sub>) ranged between 0 and 1. Pore volume (V<sub>p</sub>) were

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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  $\text{CuK}\alpha$  radiation. SEM images were collected using a FEI Inspect, S model microscope.

The physicochemical properties of catalyst 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  $2\text{h}^{-1}$  to  $4\text{h}^{-1}$ . 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 hexan) 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  $\text{CoNiMo}/\gamma\text{-Al}_2\text{O}_3$  catalyst and the pore size distribution are shown in Fig. 1. The catalyst display a type IV isotherm according to IUPAC classification and a hysteresis loop characteristic to cylindrical pores [20]. The nitrogen, begins to condense in the pores of the catalyst, at relative pressures ( $p/p_0$ ) of 0.4 when the hysteresis loop appears, and at the relative pressure ( $p/p_0$ ) 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

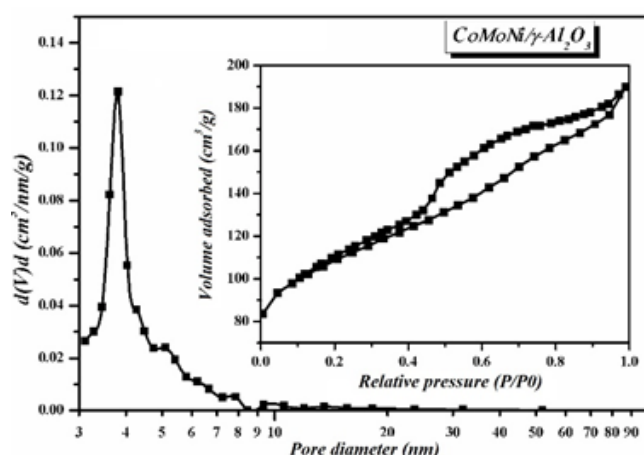


Fig. 1. Pore size distributions and adsorption-desorption isotherm of the catalyst

Tabel 1

TEXTURAL PROPERTIES OF THE CATALYST

Specific are BET ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	The mean pore diameter (nm)
163.4	0.18	4.2

of 4.2 nm, a total pore volume of  $0.18\text{ cm}^3/\text{g}$  and a surface specific surface area of  $163.4\text{ m}^2/\text{g}$ .

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  $\text{CoNiMo}/\gamma\text{-Al}_2\text{O}_3$  catalyst is  $0.621\text{ meq/g}$  with  $0.33\text{ meq/g}$  representing the concentration of weak acid sites. The concentration of medium acid sites is  $0.165\text{ meq/g}$  and the concentration of strong acidic sites is  $0.126\text{ meq/g}$  catalyst. From the analysis of the acid strength distribution, the catalyst has a low acidity.

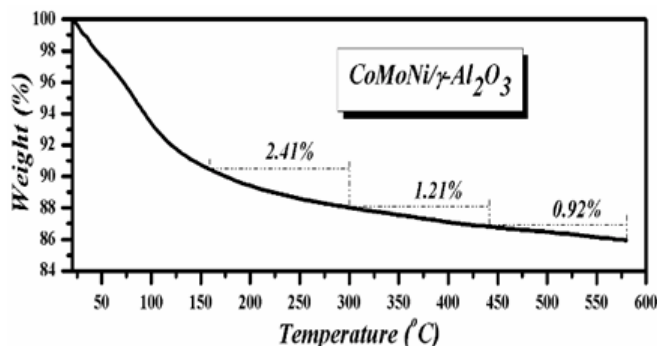


Fig. 2. Diethylamine thermodesorption curve of the catalyst

Table 2

ACID STRENGTH DISTRIBUTION OF THE CATALYST

Acidic center type	Concentration (miliechivalenți/g)
Weak	0.330
Medium	0.165
Strong	0.126
TOTAL concentration	0.621

The XRD diffractogram (Figure 3) show the characteristic peaks of alumina and MoCo confirming the presence of  $\text{CoMoOx}$ , the crystalline molybdenum oxide and nichel oxide. The X-Ray pattern shows peaks at  $2\theta = 36.7^\circ$ ;  $45.5^\circ$  and  $66.8^\circ$  which are related to crystal phase of  $\gamma\text{-Al}_2\text{O}_3$  [22-23]. As depicted in the SEM images (Figure 4), the active phases were well distributed on the alumina surface.

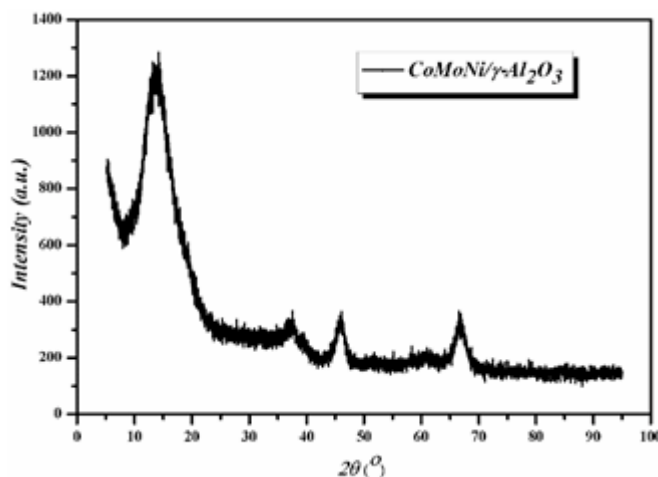


Fig. 3. XRD pattern of the catalyst

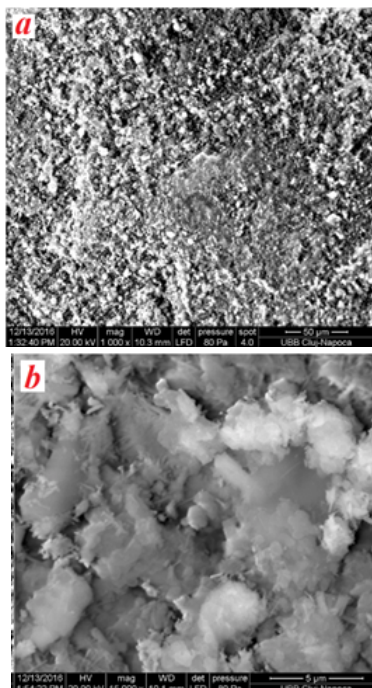


Fig.4. SEM images of the catalyst

### Hydrodesulphurization tests

From the GC-MS analysis of the reaction products there were mainly identified biphenyl, phenylcyclohexane and biciclohexil.

### Effect of reaction temperature

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

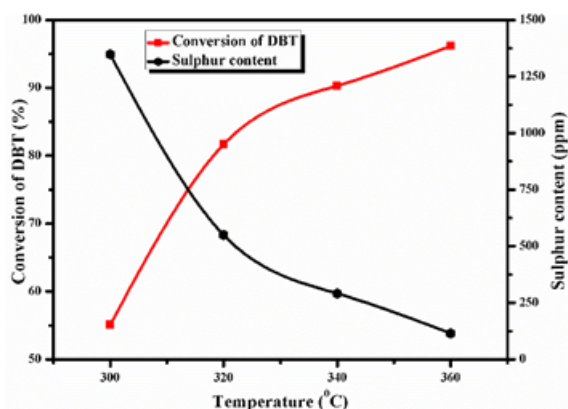


Fig.5. Influence of temperature on dibenzothiophene conversion and sulphur content, at 30 bar and LHSV  $1\text{ h}^{-1}$

The yields in the reaction products, at temperature from 300 to  $360^\circ\text{C}$ , pressure of 30 bar and LHSV of  $1\text{ h}^{-1}$  are shown in Figure 6. The yield in biphenyl was 47.62% at  $300^\circ\text{C}$  and continuously increased to 69.16% at  $360^\circ\text{C}$ . The yield in phenylcyclohexane 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  $360^\circ\text{C}$  and LHSV of  $1\text{ h}^{-1}$ , the activity of the prepared catalyst  $\text{CoNiMo}/\gamma\text{-Al}_2\text{O}_3$ , on dibenzothiophene hydrodesulphurization was improved. The conversion

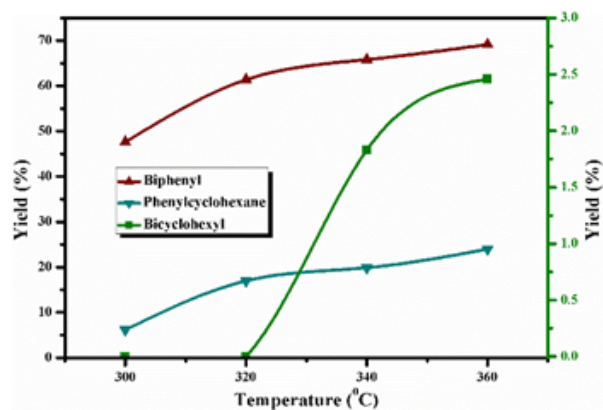


Fig. 6. Influence of temperature on the reaction products yields, at 30 bar and LHSV  $1\text{ h}^{-1}$

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 phenylcyclohexane and biciclohexil, while the yield in biphenyl decreased from 69.15% to 38.46%, for pressures from 30 bar to 60 bar (Figure 8).

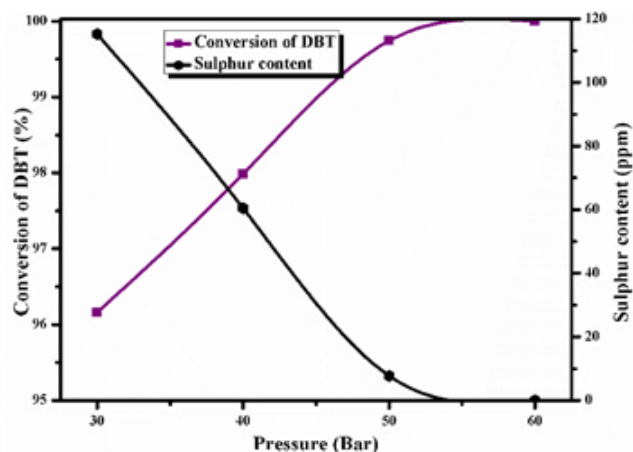


Fig. 7. Influence of pressure on dibenzothiophene conversion and sulphur content, at  $360^\circ\text{C}$  and LHSV  $1\text{ h}^{-1}$

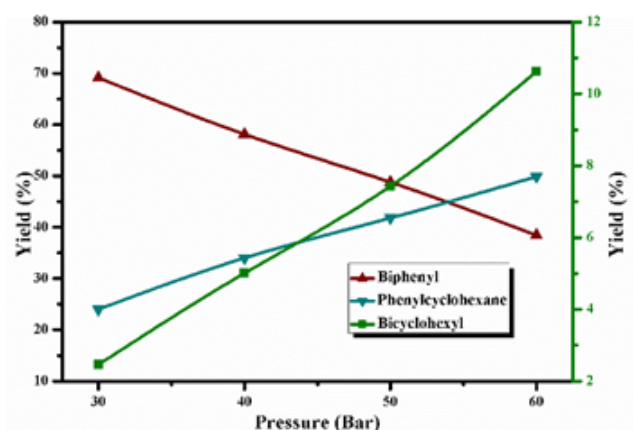


Fig. 8. Influence of pressure on the reaction products yields, at  $360^\circ\text{C}$  and LHSV  $1\text{ h}^{-1}$

### Effect of liquid hourly space velocity

Figure 9 shows the variation of benzothiophene conversion and sulphur content with liquid hourly space velocity, at  $360^\circ\text{C}$  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  $4\text{ h}^{-1}$  was 376 ppm and it was reduced to zero at  $1\text{ h}^{-1}$ .



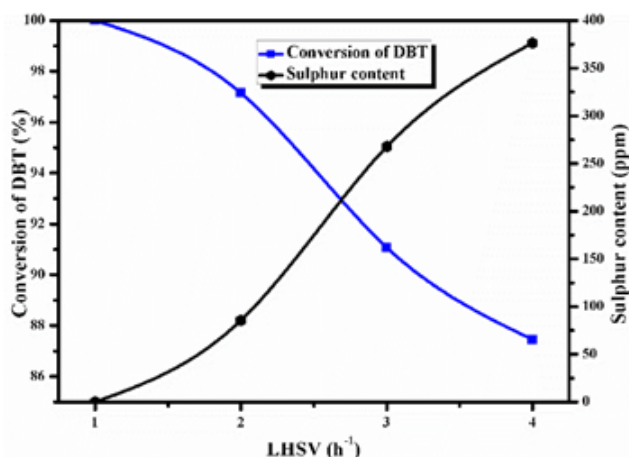


Fig. 9. Influence of liquid hourly space velocity on dibenzothiophene conversion and sulphur content, at 360°C and 60 bar

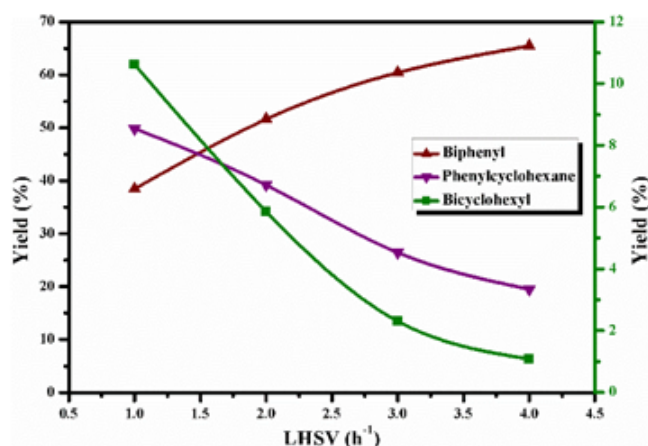


Fig. 10. Influence of liquid hourly space velocity on the reaction products yields, at 360°C and 60 bar

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 1 h<sup>-1</sup> to 4 h<sup>-1</sup>, 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 hysteresys 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 nichel 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 decreased.

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

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Hydrodesulfurarea dibenzotiofenului pe catalizator CoNiMo

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