# Dimethyldisulphide Hydrodesulphurization on NiCoMo/Al<sub>2</sub>O<sub>3</sub> Catalyst

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Hydrodesulphurization of dimethyldisulphide was performed on Ni-Co-Mo / $\tilde{a}$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The catalyst was characterized by determining the adsorption isotherms, the pore size distribution and the acid strength. Experiments were carried out on a laboratory echipament in continuous system using a fixed bed catalytic reactor at 50-100°C, pressure from 10 barr to 50 barr, the liquid hourly space velocity from 1h<sup>-1</sup> to 4h<sup>-1</sup> and the molar ratio H<sub>2</sub> / dimethyldisulphide 60/1. A simplified kinetic model based on the Langmuir–Hinshelwood theory, for the dimethyldisulphide hydrodesulfurization process of dimethyldisulphide has been proposed. The results show the good accuracy of the model.

Keywords: kinetic, catalyst, hydrodesulphurization, dimethyldisulphide

Worldwide, new regulations have been adopted to reduce sulfur in motor fuels to minimize adverse effects on the environment and implicitly on health. In most developed countries the sulfur level in petrol was restricted to 10 ppm[1]. In 2005 the maximum concentration of sulfur in diesel in Europe was reduced from 350 to 50 ppm and from 2009 to 10 ppm.[2]

Sulfur is the most common element in crude oil after carbon and hydrogen. The average content of sulfur in crude oil varies between 0.03-7.9% gr. The sulfur compounds can be found in two forms: inorganic and organic. Inorganic sulfur such as elemental sulfur, H<sub>2</sub>S and pyrite can be dissolved or suspended [3] and organic sulfur is present as thiols, sulfides and thiophene compounds [4].

Hydrodesulfurization is a hydrotreatment process used to remove sulfur. The process is catalytic and the catalyst used differs according to the nature of the process (hydrofining or hydrotreating), the nature of the raw material, etc. [2]. Removing of sulfur compounds during oil refining operations to obtain different petroleum products is not a simple process and is becoming more and more difficult to achieve as the sulfur concentration decreases. The three types of fuel: diesel, gasoline and jet fuel contain various sulfur compounds. Generally, the gasoline contains mercaptans, sulfides and thiophenes, while diesel fuel contains especially benzothiophenes, dibenzothiophenes and derivatives thereof. Conventional, hydrodesulfurization is used to reduce the sulfur concentration of liquid fuels. This process requires suitable catalysts for the removal of sulfur compounds and occurs at high temperatures, for example at 450°C and at pressures of 20-40 atm. There are also disadvantages of the hydrodesulfurization process, such as high costs, but also the decrease in fuel efficiency by lowering the octane number due to saturation of aromatic or olefinic groups [5-7]

One of the recent problems for all countries is the removal of sulfur-based organic compounds from automobile fuels because they are poisonous for oxidation catalysts in the combustion emission control system and reduce their effectiveness in oxidizing carbon monoxide, hydrocarbons and organic matter volatile. One of the methods used to remove sulfur in diesel is the hydrodesulfurization process.

The selection and the usage of the various active catalysts that make it possible to obtain clean fuels with a lower sulfur content would be one way of improving fuel quality along with other aspects (the quality of the raw material subjected to desulphurisation, working conditions, changes in Diesel fuel properties, contamination during transport and delivery to consumers [7].

Catalytic hydrodesulfurization is the most widely used process that can convert organic compounds with sulfur to hydrogen sulphide and other inorganic sulphides. These technologies include conventional hydrotreatment, the use of advanced catalysts and / or reactor design, and a combination of hydrotreating processes with some additional processes such as distillation to meet fuel quality specifications. The operating conditions at which the usual hydrotreatment takes place is a hydrogen pressure of more than 2 MPa and a temperature of about 300°C. To reduce sulfur to a low content, are required more severe conditions. It is known that common desulphurisation processes have some disadvantages: they use expensive catalysts and large amounts of hydrogen and they are energy consumers [2].

Currently, desulphurization of refined streams is carried out by a catalytic hydrodesulfurization (HDS) process in fixed bed reactors. Sulfur bound in various organic species is thus transformed into H2S, which is eliminated and then converted to elemental sulfur through the Clauss process [2].

In present, the hydrodesulfurization reactors from refineries operates at moderate temperatures (300-360°C) and hydrogen pressures of 3MPa, usually on CoMo /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or NiMo /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts; the catalyst being activated by treatment with a mixture of H<sub>2</sub>S and H<sub>2</sub> [7].

Tests have highlighted the molybdenum sulfide catalyst where are located the active centers which presents different activities for the C-S hydrogenolysis reaction and hydrogenation.

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The Co-Mo catalysts are often used in the hydrodesulfurization industrial process as well as in other hydrogenation processes [8]. These Co-Mo/ $\gamma$ -alumina catalysts are relatively effective for desulphurisation but exhibiting lower activity for hydrogenation [8]. The nanocatalysts type CoMo / Al-HMS (3.4% Co and 9.4% Mo) synthesized by deposition under supercritical conditions (methanol-carbon dioxide) showed a high performance attributable to a larger and uniform dispersion of metals on a support with a larger specific area.

The deposition of coke on the catalyst surface represents the major deactivation factor of these catalysts in the hydrodesulphurisation processes of diesel. The presence of acid catalytic centers involves varoius side reactions [10] as well as coke formation. These deposits on the catalysts used for hydrodesulfurization are evidenced by <sup>13</sup>C-NMR method. The coke formed on the catalyst depends on the types of hydrocarbons contained in the feedstock [11].

The CoMo /  $\gamma$ -alumina catalysts modified by phosphorus addition have much activity for hydrodesulfurization, and maximum activity is achieved at a 1% P<sub>2</sub>O<sub>5</sub> content. A further increase in phosphorus content may reduce activity by forming CoMoO<sub>4</sub> which results in a Mo dispersion diminishing and the formation of relatively stable Co-Mo-P compounds [12].

The use of MgO as a support for Mo and CoMo catalysts allowed an improved catalyst activity of about 3.3 times greater than of the CoMo /  $\gamma$ -alumina industrial catalyst, while the selectivity for C = C linkage hydrogenation / C-S bond hydrogenolysis remained the same [13].

Catalytic hydrodesulfurization is the most commonly used technology that can convert organic compounds with sulfur in hydrogen sulphide and in other inorganic sulphides. These technologies include conventional hydrotreatment, the use of advanced catalysts and / or the design of a more efficient reactor but also a combination of hydrotreatment processes with other additional processes such as distillation, extraction, etc. To meet the fuel quality specifications. The operating conditions at which the usual hydrotreating takes place are relatively aggressive: a hydrogen pressure of more than 2 MPa and a temperature of about 300°C [2].

Thus, CoMo catalysts are preferred for HDS of unsaturated hydrocarbon streams, such as from fluidized bed catalytic cracking (FCC), while NiMo catalysts are preferred for the processing of fractions requiring mainly hydrogenation processes [14].

## **Experimental part**

#### Catalyst preparation and characterization

The materials used in this work were dimeyhldisulphide (Sigma-Aldrich), cobalt (II) nitrate hexahydrate puriss p.a.(Sigma-Aldrich), nickel (II) nitrate hexahydrate puriss p.a.(Sigma-Aldrich), ammonium heptamolybdate tetrahydrate (Sigma-Aldrich),  $\gamma$ -alumina granulated and electrolytic hydrogen purity from Linde Company. The catalysts where prepared by impregnation of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support with aqueous solutions of the precursors of catalysts (ammonium molybdate heptahydrate, cobalt and nickel nitrate), applying the method of filling the pores. After impregnation, the catalyst was dried at 120°C for 4 h and calcinated at 450°C for 6 h, followed by activation in a hydrogen stream at 450°C for 4 h. Chemical composition of catalysts used in the experimental program was determined by atomic absorption (Varian AA240FS). The metal content of catalyst is: 2% Ni, 2% Co and 11.5% Mo.

Catalyst characterization was performed by determining the textural characteristics and acid strength. Textural characteristics : surface area, pore volume, average pore diameter and pore-size-distribution were determined on a Autosorb 1 Quantacrome. 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.

# Hydrodesulphurisation of dimethyldisulphide tests

Hydrodesulphurisation of dimethyldisulphide was performed in a continuous fixed bed catalytic reactor. The volume of the catalyst was 40 cm<sup>3</sup>, placed in the middle of the reactor and the top and the bottom of the reactor were filled with inert glass beads. The feedstock consisted of dimethyldisulphide and hexane as a solvent, with dimethyldisulphide concentration of 1 wt%.

Experimental conditions were: temperature (T), ranging from 50-100°C, pressure (p) from 10 barr to 50 barr and the liquid hourly space velocity (LHSV) from  $1h^{-1}$  to  $4h^{-1}$  and the molar ratio H<sub>2</sub>/dimethyldisulphide: 60/1. The reaction product were collected under stationary regime conditions and analyzed by gas chromatography (Varian 3800) coupled with mass spectrometry (Varian 4000). The carrier gas was He, the injector temperature was 155°C and the oven temperature 175°C (16°C/min).

# **Results and discussions**

# Catalyst characterization

Diethylamine thermodesorption curve of the catalyst is shown in figure 1 (A-concentration of centers with weakly acidic, B-concentration of centers with medium acidity, Cconcentration of centers with high acidity).

On the basis of the thermodesorption curve of the catalyst, it was calculated the stength of acid sites and total acidity (fig. 2).

From figure 2 it is observed that the catalyst has a high content of weak acidic centers and a much lower concentration (less than half of the concentration of weak centers) of medium acids centers and strong acidic



Fig. 1. Diethylamine thermodesorption curve of the catalyst



11.5% Mo-2% Co-2% NI/ Al2O3

Fig. 2. Pores acid strength distribution of the catalyst



Fig. 3. The isotherm of nitrogen adsorption / desorbtion on the



centers. The total concentration of acidic centers is greater than 0.8 mEq / g).

#### Textural characteristics

Texture data was obtained by automatic recording and processing of adsorption-desorption isotherms of nitrogen. Thus adsorption-desorption isotherm is shown in figure 3 and the pore size distribution is shown in figure 4.



Fig. 5. Influence of reaction temperature on dimethyldisulphide conversion over NiCoMo/ $\gamma$ -Al<sub>2</sub>O<sub>2</sub> ( LHSV 3 h<sup>-1</sup>)

#### *Hydrodesulphurisation of dimethyldisulphide* Effect of reaction temperature

Figure 5 shows variation of dimethyldisulphide conversion, over 11.5% Mo, 2%Co, 2% Ni / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, with temperature, from 50°C to 100°C, at LHSV of 3h<sup>-1</sup> and different pressures. The reaction temperature is an important factor for the hydrodesulphurization of dimethyldisulphide, the highest dimethyldisulphide conversion, was achieved at 100°C, for all the pressures studied over NiCoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.



Fig. 6. Influence of pressure on dimethyldisulphide conversion over NiCoMo/γ-Al<sub>2</sub>O<sub>2</sub> (LHSV 2 h<sup>-1</sup>)



Fig. 7. Influence of LHSV on dimethyldisulphide conversion over NiCoMo/ $\gamma$ -Al<sub>2</sub>O<sub>2</sub> at 50 °C



Fig. 8. Influence of LHSV on dimethyldisulphide conversion over NiCoMo/ $\gamma$ - Al<sub>2</sub>O<sub>3</sub> at 20 bar

Effect of reaction pressure

The conversion of dimethyldisulphide is influenced by pressure at temperatures below 100°C.

Figure 6 shows that the reaction pressure has very low influence/ has no influence on the conversion of dimethyldisulphide at 100°C.

## Effect of liquid hourly space velocity

The LHSV effect on conversion was studied in the range of 1-4 h<sup>-1</sup>, at fixed temperature and fixed pressure. At constant temperature and pressure the dimeyhldisulphide conversion decreases with the increase of LHSV as shown in figure 7 and figure 8, because the residence time of reactants increases with LHSV decreases.

#### Kinetics

The process of desulphurisation proceeds according to the reaction:

$$H_{3}C \xrightarrow{S} CH_{3} + H - H \longrightarrow 2 H_{3}C - SH$$
 (1)

Adsorption and reaction devolve on one type of active centers according to the following mechanism:

$$DMDS + \Delta \xrightarrow[k'_{DMDS}]{k'_{DMDS}} DMDS\Delta$$
(2)

$$3H_2 + 6\Delta \xrightarrow[k'_{H2}]{k_{H2}} 6H\Delta$$
 (3)

$$DMDS\Delta + 2H\Delta \xrightarrow{k} 2CH_4 + 2S\Delta + \Delta$$
(4)

$$S\Delta + 2H\Delta \xrightarrow{k'_{H2S}} H_2S + 3\Delta$$
 (5)

Langmuir–Hinshelwood-type rate expression is used for dimethyldisulphide hydrodesulfurization:

$$r = k \frac{K_{DMDS} K_{H2}^{1/3} p_{DMDS} p_{H2}}{(1 + K_{DMDS} p_{DMDS} + \frac{K_{H2S}}{\frac{1}{K_{H2}^3} p_{H2S} + K_{H2}^{\frac{1}{6}} p_{H2}^{\frac{1}{2}})^3}$$
(1)

where *k* is the rate constant,  $K_{pMDS}$ ,  $K_{H2S}$  and  $K_{H2}$  are the adsorption constants of dimethyldisulphide and hydrogen respectively, and  $p_{pMDS}$ ,  $p_{H2}$  and  $p_{H2S}$  are the partial pressures of dimethyldisulphide, hydrogen and hydrogen sulfide, respectively.

The temperature dependences of the rate constant is expressed by Arrhenius equation:

$$k = A_0 \exp\left(-\frac{E}{RT}\right)$$
;  $Kj = K0j \exp\left(-\frac{\Delta Hadsj}{RT}\right)$  (2)

 $A_0$  is the preexponential factor of the rate constant,  $E_{HDS}$  is the hydrodesulphurization activation energy, R is the universal gas constant (8.314 J/mol·K) and T is the reaction temperature.

The hydrodesulphurization of DMDS was carried out a fixed bed reactor, consequently the mass balance for dimethyldisulphide is given by the following equation:

$$-\frac{dF_{DMDS}}{dm_{cat}} = r$$

$$F_{DMDS} = F_{DMDS0} (1 - x_{DMDS})$$
(4)
(5)

$$\frac{dx_{DMDS}}{dm_{cat}} = \frac{r}{F_{DMDS0}}$$

where *r* is the reaction rate (mols<sup>-1</sup>kg<sup>-1</sup>),  $F_{DMDS}$  is the molar rate of dimethyldisulphide (mol/s),  $F_{DMDS}$  is the molar rate of dimethyldisulphide at the inlet of the reactor (mol/s) and  $m_{cat}$  is catalyst mass (kg).

$$V_{DMDS} = \frac{F_{DMDS}^{0}(1-x)}{F_{DMDS}^{0} + F_{H2}^{0} + F_{harger}}$$
(8)

$$y_{H2} = \frac{F_{H2}^{0} - 3xF_{DMDS}^{0}}{F_{DMDS}^{0} + F_{H2}^{0} + F_{hexan}}$$
(9)

$$y_{H2S} = \frac{2xF_{DMDS}^{0}}{F_{DMDS}^{0} + F_{H2}^{0} + F_{hexan}}$$
$$p_{i} = y_{i} P$$

where:  $i = DMDS, H_a, H_aS$ 

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In order to estimate the kinetic model parameters, the least squares method was used, the method focused on choosing the parameters of the kinetic model in such<sup>10</sup> way that minimizing an objective function (model error) defined as the sum of the squares of the differences between experimentally measured molar fractions and those calculated on the basis of the proposed kinetic model.

Table 1KINETIC AND ADSORPTION PARAMETERS FORTHE PROPOSED MECHANISM

Danamatan	Value
rarameter	value
A0(molmin <sup>-1</sup> Kg <sup>-1</sup> )	5966.6031(1 +/- 0.079817)
E(kJ·mol <sup>-1</sup> )	35441.9374(1 +/- 0.0058951)
KDMDS(bar <sup>-1</sup> )	76.2471(1 +/- 0.056074)
K <sub>H2</sub> (bar <sup>-1</sup> )	107602.5027(1 +/- 0.34819)
K <sub>H2S</sub> (bar <sup>-1</sup> )	6604.9996(1 +/- 0.20659)
SSE	0.00562
ARE (%)	3.656
R <sup>2</sup>	0.9937



Fig. 9. Correlation between experimental data and model predictions for dimethyldisulphide conversions

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Fig. 10. The natural logarithm function of the reaction constant as function of 1/ T

where: ARE -the average relative errors

The values of the kinetic and adsorption parameters, are summarized in table 1.

The results show that the average relative errors (ARE) is less than 4 %, indicating the good accuracy of the model.

The correlation between experimental data and model predictions for dimethyldisulphide conversions is presented in figure 9.

As shown in figure 9, the adequacy of the model with experimental data is good.

The linearity of the natural logarithm of the reaction constant with the inverse of temperature, presented in figure 10 demonstrates the adequacy of the proposed model.

## Conclusions

Hydrodesulphurization process of dimethyldisulphide was performed on Ni-Co-Mo /  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The catalyst was characterized by determining the adsorption isotherms, the pore size distribution and the acid strength.

Hydrodesulphurization experiments were performed in continuous system at 50-100°C, pressure from 10 barr to 50 barr, the liquid hourly space velocity from  $1h^{-1}$  to  $4h^{-1}$  and the molar ratio  $H_2$  /dimethyldisulphide 60/1. A simplified kinetic model based on the Langmuir–Hinshelwood theory, for the dimethyldisulphide hydrodesulfurization process of dimethyldisulphide has been proposed. The results show the good accuracy of the model.

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