

Comparative Study Between two Reaction Kinetic Mechanisms of Thiophene Hydrodesulphurization over CoMo / γ -Al₂O₃ Supported Catalyst

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The kinetic study of the thiophene hydrodesulphurization process was carried out for CoMo/ γ -Al₂O₃ catalyst, at temperatures between 175 and 275 °C, pressure ranged from 30 bar to 60 bar and the liquid hourly space velocity from 1 h⁻¹ to 4 h⁻¹. For the reaction mechanism, the Langmuir-Hinshelwood-Hougen-Watson model (LHHW) was used and two kinetic models were proposed: the first model, that considered that H₂ is adsorbed on a different type of active center than thiophene and the second model, that considered that the two reactants are adsorbed on the same type of active sites. The values obtained for the average relative error (ARE) and the correlation coefficient between the experimental and the calculated data (R²) indicate that the Langmuir-Hinshelwood model, describing the adsorption on two active sites, best describes the kinetics of the thiophene hydrodesulfurization reaction over CoMo/ γ -Al₂O₃ tested catalyst.

Keywords: thiophene, hydrodesulphurization, kinetic study, Co, Mo, γ -Al₂O₃

The reduction of pollutants in fuels is nowadays a major challenge in the refining industry due to the increasingly demanding environmental regulations, especially regarding sulfur levels [1]. Among several processes to obtain friendly fuels, hydrotreatment remains as the most important one to remove sulfur and other heteroatoms from petroleum fractions and heavy oils [2]. The catalytic species for hydrotreating petroleum products have been nickel molybdenum or cobalt molybdenum sulfides for many years and their superior performances have been established. Alumina has been widely applied commercially as an excellent support for such sulfides [3]. Hydrodesulfurization (HDS), the catalytic chemical process widely used to remove sulfur (S) from natural gas and from refined petroleum products, occur through two main pathways: direct desulfurization (DDS), with the cleavage of C-S bond, or hydrogenation (HYD), which involves the formation of partially hydrogenated intermediates which further react to cyclohexylbenzene and bicyclohexyl [4-6]. The model compounds most frequently used, in order to develop kinetic expressions and reaction pathways that describe the HDS process, are heteroatomic aromatics (thiophenes): thiophene, benzothiophene and dibenzothiophene. Although, as a class, these are the least reactive, they are also the most prevalent organosulfur compounds found in the heavier feedstocks currently being introduced and are therefore viewed as better analogs for the actual industrial HDS process [7]. Thiophene and DBT reacts preferentially through DDS route, whereas DMBT hydrodesulfurization occurs predominantly via HYD route [6, 8-9]. A lot of kinetic studies have been carried out for compounds such as thiophenes, benzothiophene, dibenzothiophene and alkyl-dibenzothiophenes. For these compounds, kinetic expressions of the Langmuir-Hinshelwood type (the most widely used model to explain the kinetics of heterogeneous catalytic processes) [10-11] have been developed that involve different forms of competitive and uncompetitive adsorption.

The kinetic parameters reported in the literature strongly depend on the reaction conditions and the nature of the

catalysts. This fact clearly indicates that no reliable kinetic data are available for this reaction and, therefore, kinetic studies over a broad temperature range are required.

In the present study, activity of the CoMo sulphided catalyst supported on γ -Al₂O₃ is examined in the HDS of the thiophene, in order to develop kinetic expressions and reaction pathways that describe the process, under similar conditions with those practiced in industrial operation (e.g., naphtha desulphurization: pT: 15-35 bar, T : 523-623 K) [12].

Experimental part

Characteristics of the catalyst

The CoMo hydrodesulphurization catalyst was prepared by incipient wetness co-impregnation of the γ -Al₂O₃ support and it has the characteristics demonstrated in our previous work [13]. Chemical composition, textural characteristics and total acidity are presented in table 1.

Catalytic tests were made in a stainless-steel fixed-bed reactor. An amount of 30 cm³ catalyst was placed in the middle of the reactor and (The top and the bottom of the reactor were filled each with an amount of 80 cm³ inert

Table 1
CHARACTERISTICS OF THE CoMo/ γ -Al₂O₃ [13]

Chemical composition, wt%	
Cobalt	4
Molybdenum	8
Physical properties	
Surface area, m ² /g	140.181
Pore volume, cm ³ /g	0.164
Average pore diameter, nm	3.268
Total acidity, meq/g	1.1

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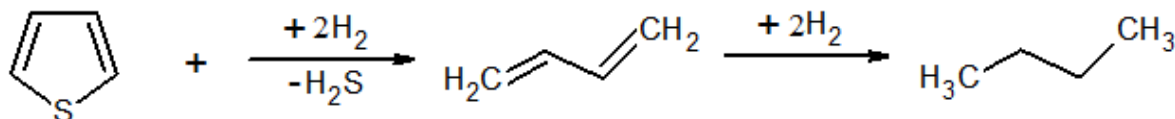


Fig.1. Reaction scheme of thiophene HDS

1 st Mechanism (H ₂ is adsorbed on a different type of active center than thiophene)	2 nd Mechanism (H ₂ and thiophene are adsorbed on the same type of active sites)
$T + \Delta \xrightleftharpoons[k'_T]{k_T} T\Delta \quad (1)$ $H_2 + 2\theta \xrightleftharpoons[k_{H_2}]{k_{H_2}} 2H\theta \quad (2)$ $T\Delta + 2H\theta \xrightarrow{k} S\Delta + B + 2\theta \quad (3)$ $S\Delta + 2H\theta \xrightleftharpoons[k_{H_2S}]{k'_{H_2S}} H_2S + \Delta + 2\theta \quad (4)$	$T + \Delta \xrightleftharpoons[k'_T]{k_T} T\Delta \quad (1')$ $H_2 + 2\Delta \xrightleftharpoons[k'_{H_2}]{k_{H_2}} 2H\Delta \quad (2')$ $T\Delta + 2H\Delta \xrightarrow{k} S\Delta + B + 2\Delta \quad (3')$ $S\Delta + 2H\Delta \xrightleftharpoons[k_{H_2S}]{k'_{H_2S}} H_2S + 3\Delta \quad (4')$
$r_3 = k \cdot \frac{K_T \cdot K_{H_2} \cdot p_T \cdot p_{H_2}}{\left(1 + K_T \cdot p_T + \frac{K_{H_2S} \cdot p_{H_2S}}{K_{H_2} \cdot p_{H_2}}\right) \cdot \left(1 + K_{H_2}^{\frac{1}{2}} \cdot p_{H_2}^{\frac{1}{2}}\right)^2} \quad (5)$	$r_3 = k \cdot \frac{K_T \cdot K_{H_2} \cdot p_T \cdot p_{H_2}}{\left(1 + K_T \cdot p_T + K_{H_2}^{\frac{1}{2}} \cdot p_{H_2}^{\frac{1}{2}} + \frac{K_{H_2S} \cdot p_{H_2S}}{K_{H_2} \cdot p_{H_2}}\right)^3} \quad (5')$

glass beads with the average diameter of 12 mm. The temperature was measured by an automatic system using three thermocouples placed in the reactor jacket. The thermocouples located at the top and bottom of the reactor were used to measure the temperature of the inert glass zones, whereas the catalyst temperature was monitored by the third thermocouple inserted in the middle of the reactor) [14]. The feedstock consisted of thiophene and hexane as a solvent, with thiophene concentration of 0.6 wt%, was introduced by a metering pump. The molar ratio of hydrogen/ thiophene was 60/1. The experiments were carried out in the following experimental conditions: temperature (T): ranging from 175 to 300°C, pressure (p) from 30 bar to 60 bar and the liquid hourly space velocity (LHSV) from 1 h⁻¹ to 4 h⁻¹ [13].

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 [14].

Kinetic studies

For the reaction mechanism, the Langmuir-Hinshelwood-Hougen-Watson model (LHHW) was used and two kinetic models were proposed: the first model, that considered that H₂ is adsorbed on a different type of active center than thiophene and the second model, that considered that the two reactants are adsorbed on the same type of active sites.

The HDS reaction mechanism is presented in figure 1. Thiophene (T) is hydrodesulfurized to give butadiene (B), which is subsequently hydrogenated to butene, followed by its HYD toward butane. The consecutive reaction scheme was generally adopted for the hydrogenolysis of

thiophene into butadiene, butene, and butane, as given in figure 1.

Arrhenius form is used to calculate the constant reaction kinetics. Arrhenius equation parameters, such as the activation energy (E_{HDS}) and pre-exponential factor (A) are determined.

$$k = A \cdot \exp\left(\frac{-E_a}{R \cdot T}\right) \quad (6)$$

where R is the universal gas constant, and T is the reaction temperature.

The temperature dependences of the rate constant and the equilibrium constants can be expressed as follows:

$$K_i = K_{0,i} \cdot \exp\left(\frac{\Delta H_i}{R \cdot T}\right) \quad i: T, H_2, H_2S \quad (7)$$

where k_i is the adsorption constants of the component (e.g. thiophene, H₂, H₂S), ΔH_i is the adsorption enthalpy for the component.

The design equation for a tubular reactor is given by Equation (8), where F_T is the molar flow rate of thiophene, m_{cat} is the mass of the catalyst in grams and r is the reaction rate.

$$-\frac{dF_T}{dm_{cat}} = r \quad r: \text{mol} \cdot \text{min}^{-1} \cdot \text{kg}^{-1} \quad (8)$$

For any position in a flow system, F_T is defined according to Equation (2), where F_{T0} is molar flow rate of thiophene into the system and x_T is the thiophene conversion.

$$F_T = F_{T0} \cdot (1 - x_T) \quad (9)$$

From Equations (8) and (9), the differential form of the design equation for a plug-flow reactor is written as:

Parameter	1 st Mechanism (H ₂ is adsorbed on a different type of active center than thiophene)	2 nd Mechanism (H ₂ and thiophene are adsorbed on the same type of active sites)
A ₀ :(mol.Kg ⁻¹ .min ⁻¹)	537.85	93.71
E:(KJ.mol ⁻¹)	49.08	37.44
K _{T0} :(bar ⁻¹)	2.36	2530.50
K _{H2S0} :(bar ⁻¹)	32.69	22.46
K _{H20} :(bar ⁻¹)	42.84	1502.30
DHK _T :(J.mol ⁻¹)	120.00	107.55
DHK _{H2S} :(J.mol ⁻¹)	969.40	753.49
DHK _{H2} :(J.mol ⁻¹)	10.18	21.81
SSE	0.0087	0.0142
Rsq	0.993	0.988
ARE	2.90	4.47

Table 2
KINETIC AND ADSORPTION PARAMETERS OF HDS OF
THIOPHENE OVER CoMo/γ-Al₂O₃

$$F_{0T} \cdot \frac{dx_T}{dm_{cat}} = r \quad (10)$$

The molar fractions of thiophene, hydrogen and hydrogen sulfide are expressed in terms of the conversion of thiophene, as follows:

$$p_T = \frac{F_{0T} \cdot (1 - x_T)}{F_{0T} \cdot (1 - x_T) + F_{0H_2} + F_s} P \quad (11)$$

$$p_{H_2} = \frac{F_{0H_2} - 2x_T \cdot F_{0T}}{F_{0T} \cdot (1 - x_T) + F_{0H_2} + F_s} P \quad (12)$$

$$p_{H_2S} = \frac{x_T \cdot F_{0T}}{F_{0T} \cdot (1 - x_T) + F_{0H_2} + F_s} P \quad (13)$$

where F_{0T} and F_{0H_2} are the molar rates of thiophene and hydrogen at the inlet of the reactor, F_s is molar rate of solvent (n-hexane). The parameters were estimated by minimizing the residual sum of squares.

$$SEE = \sum (x_{(exp)} - x_{(calc)})^2 \rightarrow \min \quad (14)$$

The average relative errors (ARE) is defined by Equation (15).

$$ARE = \frac{\sum \left| \frac{x_{(exp)} - x_{(calc)}}{x_{(exp)}} \right|}{N} \quad (15)$$

Results and discussions

The pre-exponential factor, the thiophene activation energy and the adsorption parameters are presented in table 2. The kinetic and adsorption parameters can be estimated from the experimental data.

The minor deviations of the thiophene conversion between the experimental measurements (x_{exp}) and the model predictions (x_{calc}) for all runs reveal that the two-site Langmuir-Hinshelwood model describe well the reaction kinetics of thiophene HDS over Co-Mo/γ-Al₂O₃ catalyst.

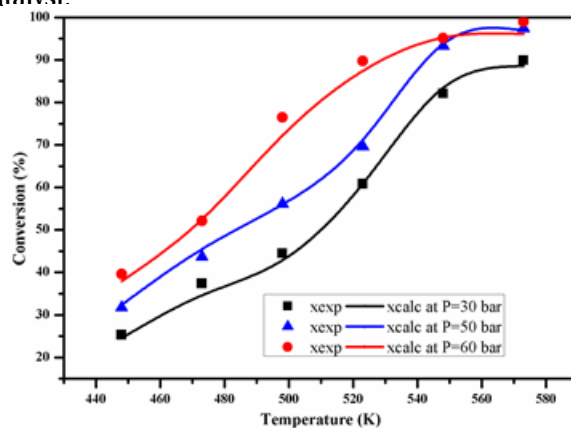


Fig.2. The experimental and calculated conversion variations with temperature, at different pressures and LHSV 1h⁻¹, for the 1st Mechanism

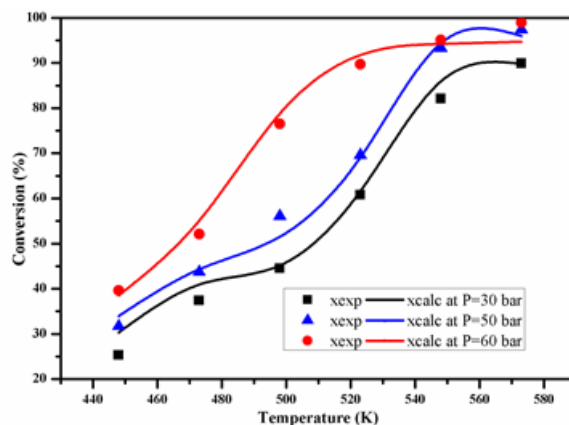


Fig.3. The experimental and calculated conversion variations with temperature, at different pressures and LHSV 1h⁻¹, for the 2nd Mechanism

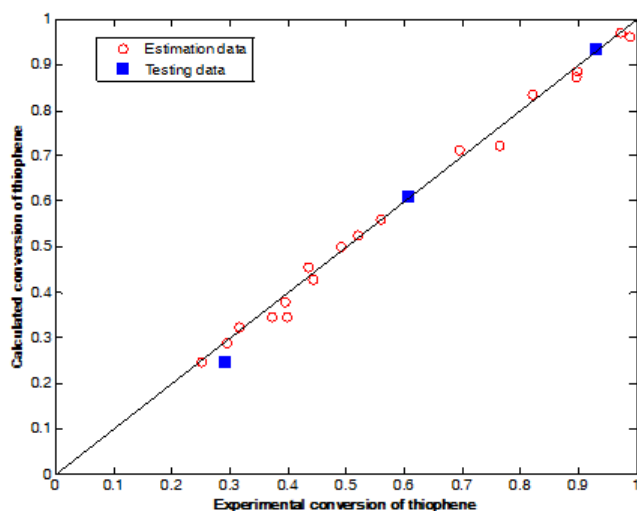


Fig.4. Calculated versus experimental thiophene conversion values for the 1st Mechanism

According to the 1st Mechanism, when H_2 is adsorbed on a different type of active center than thiophene, the activation energy is 49.08 KJ/mol and the average relative error (ARE) is 2.9. Also the coefficient between the experimental and the calculated data (R^2) has a value very close to 1 (0.993). When it is considered that H_2 and thiophene are adsorbed on the same type of active sites, the R^2 coefficient is only 0.988.

The values obtained for the two kinetic models and the correlation coefficient between the experimental and the calculated data (R^2) indicate that the Langmuir-Hinshelwood model, describing the adsorption on two active sites, best describes the kinetics of the thiophene hydrodesulfurization reaction over CoMo/ γ - Al_2O_3 tested catalyst.

Conclusions

The hydrodesulfurization of thiophene has been studied over CoMo catalyst prepared by incipient wetness co-impregnation of the γ - Al_2O_3 support. Catalytic tests were made in a stainless-steel fixed-bed reactor.

The experiments were carried out in the following experimental conditions: temperature ranging from 175°C to 300°C, pressure from 30 bar to 60 bar and the liquid hourly space velocity from 1 h⁻¹ to 4 h⁻¹.

The composition of the reaction mixture was performed by gas chromatography coupled with mass spectrometry, equipped with Agilent VF-5ms capillary column.

For the reaction mechanism, the Langmuir-Hinshelwood-Hougen-Watson model (LHHW) was used and two kinetic models were proposed: the first model, that considered that H_2 is adsorbed on a different type of active center than thiophene and the second model, that considered that the two reactants are adsorbed on the same type of active sites.

The mechanism according to which H_2 is adsorbed on a different type of active center than thiophene has a value

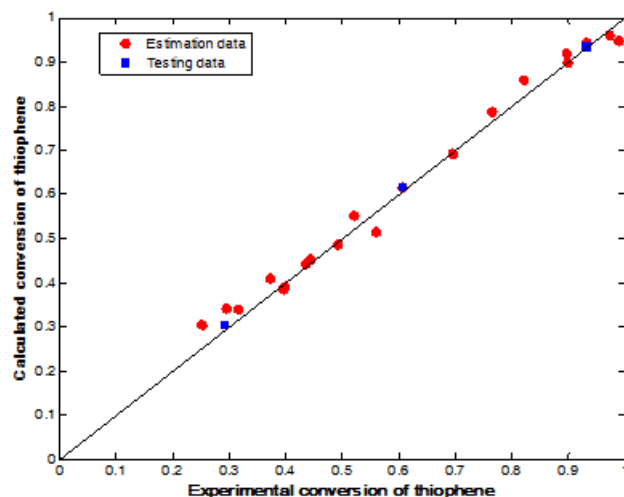


Fig.5. Calculated versus experimental thiophene conversion values for the 2nd Mechanism

of coefficient between the experimental and the calculated data very close to 1 and better represents the studied process.

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