

**Investigations on hydrogenation of selected organic sulfur
compounds on the Ni-Mo/Al₂O₃ catalyst in terms
of natural gas desulfurization***

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Technological problems of natural gas desulfurization in syngases manufacturing plants have been discussed and the results of investigations on the activity of the model Ni-Mo/Al₂O₃ catalyst in hydrogenation of selected sulfur compounds have been presented. The HDS reaction rate is dependent on a compound structure. The hydrogenation rate on the Ni-Mo/Al₂O₃ catalyst for the given sulfur compound increases in the order: CS₂>(CH₃)₂S>C₄H₁₀S>C₂H₆S₂>C₄H₄S.

1. INTRODUCTION

Sulfur compounds are present in all fossil feedstocks such as natural gas, crude oil and coal, used both as energy carriers and substrates in the chemical industry. Desulfurization of abovementioned fossil feedstocks belongs to the important technological issues [1]. Due to its wide availability natural gas is used as a basic feedstock in the most important branches of the chemical industry. Technological predispositions and solutions of chemical plants necessitate deep purification of natural gas. Sulfur compounds belong to potent poisons of the

*This article is dedicated to Professor Dobiesław Nazimek on the occasion of his 65th birthday

catalysts used in syngases production and conversion processes that are run at manufacturing plants of ammonia, methanol, DME and liquid hydrocarbons [2]. The catalysts that are utilized in these plants (especially nickel and copper ones) are very sensitive to sulfur compounds and in their presence undergo deactivation. The recommended sulfur level for natural gas (especially for the one processed in reformers) is less than 0.02 ppmv [3]. The sulfur problem also pertains to engine fuels, where the law restrictions force the investigations on highly effective new generation technologies, so-called „ultra-deep desulfurization” [4].

The concentration of sulfur compounds in raw natural gas depends on the geographic localization of deposits and can be in a wide range. Sulfur in natural gas occurs mainly in the form of hydrogen sulfide, however, organic sulfides and disulfides, carbon disulfide or thiols as well as other compounds of a more complex structure can be also present [3]. The purification of gases, especially with a high content of sulfur compounds (raw natural gas, coal and biomass gasification products, coke oven gas), is generally performed by means of absorption methods e.g. Sulfinol process, washing with amines etc. As a result of these operations it is possible to decrease the hydrogen sulfide content below 1 ppm. From the practical viewpoint of chemical syntheses on the industrial scale natural gas requires thorough purification. With this end in view hydrogen sulfide sorption on selective sorbents preceded by hydrodesulfurization process (HDS), i.e. catalytic hydrogenation of organic sulfur compounds, is commonly used. In classical process desulfurization of natural gas is carried out in two stages: (Figure 1a):

- hydrogenation of organic sulfur compounds to H_2S on the Ni-Mo or Co-Mo catalysts at the temperature of 350–400 °C, under the pressure of 2–4 MPa with the gas hourly space velocities (GHSV) in the range of 1000–3000 h^{-1} and the concentration of supplied hydrogen in the range of 2–5% vol.



- sorption of the resulting H_2S on a zinc sorbent (ZnO).



The Co-Mo catalysts exhibit higher activity in HDS processes than the Ni-Mo catalysts, wherethrough the cobalt catalysts are preferred in processing of feedstocks containing sulfur compounds of low reactivity. What is a remarkable shortcoming of cobalt catalysts is the fact that they also catalyze the exothermic reaction of carbon oxides methanation and this can cause negative effects such

as undesirable elevation of temperature in the case of carbon oxides-containing feedstocks [5]. This is not the case for Ni-Mo catalysts and they are recommended for HDS processes of feedstocks that may contain CO_2 e.g. natural gas from local deposits.

Since a sulfide form is an active form of Ni-Mo or Co-Mo catalysts, they require initial activation in $\text{H}_2\text{S}/\text{H}_2$ stream. The operating conditions of this process have a remarkable influence on the final activity of catalysts. Its constancy is determined by maintenance of the appropriate extent of catalyst sulfidation [6-8]. In the case of feedstocks containing low amounts of organic sulfur compounds or when their concentration fluctuates in time and problems with maintaining the catalyst active form may occur, elimination of the HDS loop and utilization of a zinc-copper sorbent in the sorption loop besides the zinc sorbent may be an alternative. The zinc-copper sorbent is a bifunctional system [9]. It is characterized by the activity towards hydrogenation sufficient for conversion of low amounts of organic sulfur compounds into H_2S and concurrently it acts as an effective sorbent of the resulting H_2S [10].

In modern manufacturing plants of syngases, with a feedstock being processed in the prereforming stage [11], the utilization of low-temperature HDS catalyst and additional introduction of desulfurizer with the zinc-copper sorbent allowing for the removal of sulfur to the level below 20 ppb is an attractive processing solution. Such a configuration of the process generates technological advantages (radical simplification of the feedstock saturation stage) and also extends operating time of costly catalysts for syngases production (Figure 1b) [12].

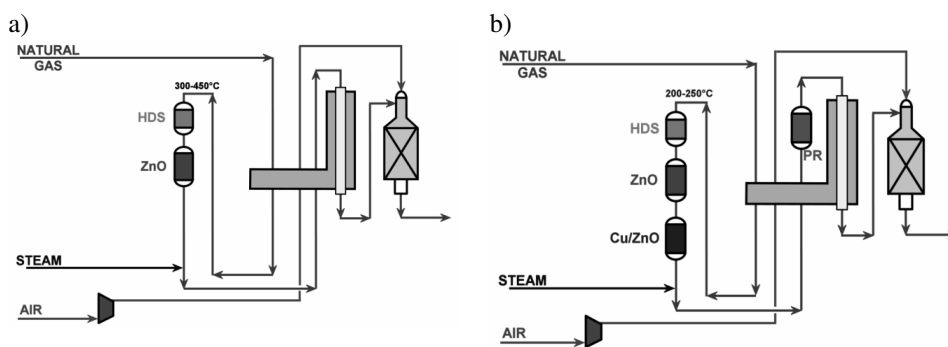


Fig. 1 Scheme of desulfurization loop in syngases manufacturing plants a) classical solution b) modern configuration.

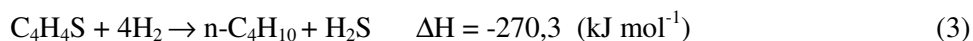
Performance and productivity of the desulfurization loop is very much dependent on the HDS catalysts properties. The ideal catalyst should be

characterized by high and constant activity per bed volume unit and correspondingly high and constant mechanical strength. The catalyst should also exhibit high activity towards hydrogenation of various sulfur compounds, which may substantially differ in reactivity [3].



Fig. 2 Commercial HDS catalysts and sorbents (INS) a) hydrodesulfurization catalyst (HDS), b) zinc-copper sorbent Cu/ZnO, c) zinc sorbent ZnO.

Model reactions are used for evaluation of catalytic properties towards hydrogenation. The literature data indicate that thiophene is usually used for this purpose (3), although it practically does not occur in natural gas.



In this work the investigations on the hydrogenation reaction rates of selected sulfur compounds on the model Ni-Mo/Al₂O₃ catalyst are presented. The knowledge of hydrogenation kinetics of various sulfur compounds is a basis for design and optimization of the scale of HDS catalyst loadings in industrial reactors.

2. MATERIALS AND METHODS

2.1. Preparation of catalysts

The Ni-Mo catalyst was prepared on Al₂O₃ carrier (INS Al₂O₃, 220 m²/g), obtained by thermal shock method [13]. The catalyst was prepared by impregnation method; first with a (NH₄)₆Mo₇O₂₄ solution and then with a Ni(NO₃)₂ *6H₂O solution. After each impregnation the catalysts were dried for 12 h at 105 °C and calcined at 500 °C for 4 hours.

2.2. Chemical content

The chemical composition of the samples was determined by means of the ICP-OES (inductively coupled plasma optical emission spectrometry) method. The measurements were done on a Varian 720-ES ICP-OES spectrometer with a horizontally oriented, axially viewed plasma, ideal for high sensitivity analyses.

2.3. Texture and specific surface area

Specific surface area and pore structure of catalysts were determined using N₂ adsorption isotherm in the temperature of liquid nitrogen with a Micromeritics ASAP 2050 Xtended Pressure sorption analyzer.

2.4. Test procedure

Before the activity measurements the samples were tentatively sulfided with hydrogen sulfide according to the previously developed methods [14]. After sulfidation procedure the catalyst was treated with a hydrogen stream saturated with selected sulfur compounds e.g. carbon disulfide, dimethyl sulfide, butanethiol, 1,2-ethanethiol, thiophene. The catalyst activity in hydrogenation reactions of sulfur compounds was compared with thiophene hydrogenation rate.

The catalysts activity measurements in hydrogenation reactions were carried out in a Zielinski-type reactor [15] under atmospheric pressure. A schematic diagram of the experimental apparatus is shown in Figure 3.

Activity measurement conditions:

- grain size 0.1-0.16 mm;
- sample weight 150 mg;
- pressure atmospheric;
- temperature 260, 300, 400 °C;
- reaction mixture flow rate 4.6 dm³/h

The analysis of hydrogen sulfide, the main hydrogenation product in exhaust gas from the reactor was performed on a Philips gas chromatograph equipped with an FPD detector.

Hydrogenation reaction rate was calculated according to the equation:

$$r = C_{\text{H}_2\text{S}} * V / m_{\text{cat.}} \text{ [Ndm}^3_{\text{H}_2\text{S}} / \text{g}_{\text{cat.}} \cdot \text{h}^{-1} \text{]} \quad (4)$$

where: C_{H₂S} – hydrogen sulfide concentration in exhaust gases, V– reaction mixture volume, m_{cat} – catalyst weight.

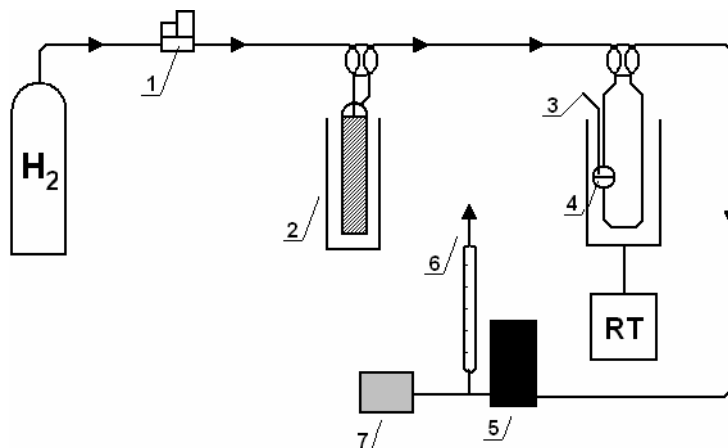


Fig. 3. Scheme of experimental installation for sulfidation and catalyst activity measurements in hydrogenation of various sulfur compounds: 1 – flow controllers, 2 – thermostated saturator, 3 – thermocouple, 4 – Zielinski reactor with catalyst sample, 5 – chromatograph, 6 – flowmeter, 7 – computer.

3. RESULTS AND DISCUSSION

The evaluation of hydrogenation rates of selected sulfur compounds (carbon disulfide, dimethyl sulfide, butanethiol, 1,2-ethanethiol, thiophene) was performed on the carrier Ni-Mo/Al₂O₃ catalyst, having characteristics shown in Table 1. The model Ni-Mo/Al₂O₃ catalyst contains 3.5% wt. NiO and 14.5% wt. MoO₃ and has the specific surface area of 188 m²/g. Dominant pore size in the range 2-50 nm indicates the mesoporous structure of the catalyst.

Figure 4 shows the comparison of hydrogenation reaction rates of organic sulfur compounds with different structure and physicochemical properties, hydrogenated on the model Ni-Mo/Al₂O₃ catalyst. The catalyst activity for carbon disulfide hydrogenation was taken as a standard.

Tab. 1 Physicochemical characteristics of the Ni-Mo catalyst.

Sample	Composition			BET surface area [m ² /g]	Pore volume BJH model [cm ³ /g]
	NiO	MoO ₃	Al ₂ O ₃		
Al ₂ O ₃	-	-	> 99	220	0.45
Ni-Mo/Al ₂ O ₃	3.5	14.5	balance	188	0.43

The hydrogenation rate for thiophene is a few times lower than that for the other sulfur compounds: CS₂>(CH₃)₂S>C₄H₁₀S>C₂H₆S₂>C₄H₄S.

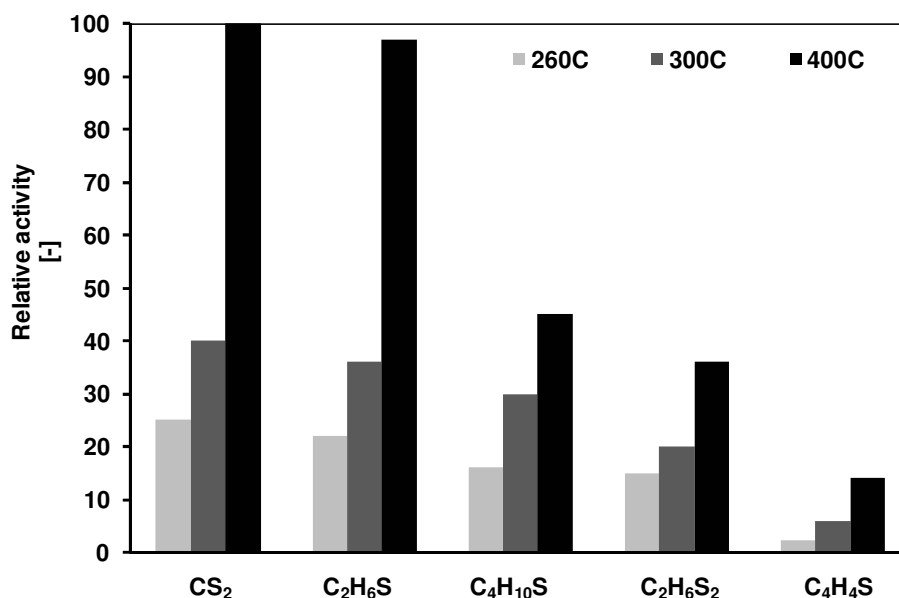


Fig. 4 Hydrogenation rates of various sulfur compounds on the Ni-Mo catalyst at temperatures 260, 300 and 400 °C.

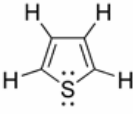
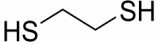
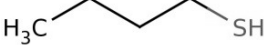
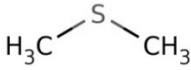
Table 2 shows the apparent activation energy for hydrogenation reaction of individual sulfur compounds.

Tab. 2. Apparent activation energy for HDS reactions on the Ni-Mo/Al₂O₃ catalyst.

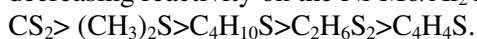
Sulfur compounds	Apparent activation energy E_a [kJ/mol]
thiophene	40.0
1,2-ethanedithiol	33.2
butanliol	31.5
dimethyl sulfide	31.0
carbon disulfide (IV)	29.5

The values of apparent activation energies for hydrogenation of sulfur compounds on the catalyst investigated depend on the compound structure and vary in the range from ca. 30 kJ/mol for linear compounds to ca. 40 kJ/mol in the case of aromatic ones (thiophene) (Table 3).

Tab. 3. Formula and properties of organic sulfur compounds.

Sulfur compounds	Formula	Hydrogenation rates
thiophene	C_4H_4S 	low
1,2-ethanedithiol	 $C_2H_4(SH)_2$	medium
butan-1-ol	 C_4H_9SH	medium
dimethyl sulfide	 $(CH_3)_2S$	high
carbon disulfide (IV)	CS_2 $S=C=S$	high

The results of kinetic investigations and the evaluation of hydrogenation activation energy allow for the following arrangement of sulfur compounds with decreasing reactivity on the Ni-Mo/Al₂O₃ catalyst:



4. CONCLUSIONS

The following conclusions can be drawn from our studies:

- there is a pronounced correlation between the type of sulfur compound and the hydrogenation rate; compounds with linear structures are more easily hydrogenated than the aromatic ones,
- the hydrogenation rate of the sulfur compounds on the Ni-Mo/Al₂O₃ catalyst decreases in the following order: $CS_2 > (CH_3)_2S > C_4H_{10}S > C_2H_6S_2 > C_4H_4S$, with the reaction rate for thiophene being a 5 times lower than for other compounds,
- at the temperature of 400 °C hydrogen disulfide and dimethyl sulfide hydrogenation rates are 5-6 times higher than for the analogous reaction with thiophene,

- Ni-Mo/Al₂O₃ catalyst show high activity towards hydrodesulfurization of sulfur compounds present in natural gas.

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