Hydrodesulfurization of thiophene on the CoMo/Al₂O₃ catalyst modified by coking pretreatment

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The activity of a commercial CoMo/Al2O3 catalyst was examined in the reaction of thiophene hydrodesulphurization. The catalytic measurements were performed in a gradientless flow circulating system at atmospheric pressure. It was found that preliminary coking of the catalyst lead to a considerable decrease of its hydrodesulphurization activity while the selectivity to butane increases. It is also found that the catalyst coking pretreatment reduces its surface, and the formation of monolayer coke and dendrites is observed. It's possible at special conditions of catalyst coking, to increase the selectivity and therefore output of some products in the reaction.

Keywords: activity; Cobalt-molybdenum/alumina; catalyst; coking pretreatment; thiophene hydrodesulphurization

INTRODUCTION

The main reasons for the deactivation of Co-Mo/Al2O3 catalysts are the coke formation, the adsorption of the nitrogen containing compounds and heavy metals on their surface [1]. A broad area in the literature is also devoted to the question of the influence of coke on the physico-chemical properties of the heterogeneous catalytic systems including Co-Mo catalysts [2]. During the formation of coke part of the active centers of catalysts are blocked and their activities decreases. The study of the mechanism of the formation of coke becomes complicated owing to the fact that, the precursors of coke can be reagents, intermediates and the products of the reaction. The effect of coke on the selectivity of these catalysts is not well elucidated and carbonaceous deposit influence differently sites on the catalytic surface [3]. In some cases it can be shown that the reduction of the general activity of the catalyst is beneficial to its selectivity. The coking pretreatment of catalyst is one of method to study the influence of coke formation on their physico-chemical properties. Such pretreatment of heterogeneous catalysts use various types of coking agent like anthracene, naphthalene and cyclohexene [4], phenanthrene [5], toluene [6], butene [7],

butadiene [8], propene and toluene [9], acetylene [10]. The present work studies the effect of coking on the catalytic properties of CoMo/Al2O3 hydrotreating catalysts, using toluene as a coking agent.

EXPERIMENTAL

Catalyst

An alumina supported cobalt-molybdenum industrial catalyst 5AKM, (Russian product) was used for all the experiments. The composition of active parts of catalyst in wt.% is CoO 4 % , MoO3 13 % , Fe2O3 0,13 %.

Catalytic activity measurements

The catalytic activity was measured at atmospheric pressure in a metal flow-circulating gradientless system connected directly to a gas chromatograph by means of a 6-way valve. The circulating contour was kept at a constant temperature of 110°C [15]. Thiophene hydrodesulphurization was used as a model reaction. All runs were carried out in the 200 – 425 °C range with excess hydrogen. The hydrogen–thiophene volumetric ratio at the reactor inlet was 30:1. The thiophene Gas Hourly Space Velocity (GHSV) was 33.5 h-1. The temperature in the reactor was maintained within ± 1.0°C accuracy. Product selectivities were estimated as a ratio between the

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reaction rate of production of the corresponding product and the sum of the reaction rates of all products.

Experimental confirmation that the reaction proceeded in the kinetic region was obtained by carrying out experiments with differently sized catalyst grains and by calculating Weisz's criterion [16] which was less than 1.

The reactor was loaded with 1 g of catalyst of 0.1 mm size. Thiophene was introduced into the reactor with a Gilson 302 pump. Hydrogen was admitted within 1% accuracy using a Matheson electronic mass flow controller.

The catalyst activation of samples were treated in a routine way prior to the activity measurements. The procedure involved drying for 1 h at 120°C in a flow of purified hydrogen at rate of 60 ml.h-1. After that the temperature was slowly raised to 400° C and the catalyst is reduced at the same temperature for 2 h. Catalyst sulphidisation was performed at 400° C for 2 h using a hydrogen-hydrogen sulfide gas mixture (9:1) at a flow rate of 70 ml.h-1.

After activation the hydrogen sulfide flow was stopped and the temperature was lowered to the operating range for 1 h. After this preliminary operation the activity measurements were started.

Coking pretreatment of catalyst

Different tests were providing preliminary to find optimal conditions of coking. Various liquid toluene flows (1.2, 2.4 and 3.6 ml.h^{-1}) were used at different coking times (2, 3, 4 and 20h). Regarding the requirements of the equipment and the proceeding conditions of HDS reaction, the optimal toluene flow selected for precoking was 1.2 ml.h^{-1}.

Coking was carried out in the same reactor after the activation of catalyst. The coking agent used was toluene. The conditions of catalyst coking are as follows: reaction temperature = 450°C; feed rate of toluene = 1, 2 ml.h^{-1}. The process proceeds in a flow of Ar at a flow rate of 1700 ml.h^{-1}. Before introducing toluene, the catalyst is flushed with Argon for 15 min.

Analytical methods

The reaction products were analyzed using online gas chromatograph (Tsvet 104) equipped with a thermal conductivity detector and six ports sampling valve. Reaction products were separated using two columns one for the analysis of thiophene at a column temperature of 110°C (2 m long column packed with 10% Carbowax 1500 on Chromosorb W) The second column (8 m long, packed with 20% oxidipropionitrile on Diatomite C) was used to analyze hydrogen sulphide and C4 hydrocarbons, at

15 °C. Hydrogen was used as a carrier gas at a rate of 40 ml min-1 [17].

Electron spin resonance (ESR) spectra were recorded on a Brucker 200 D instrument at room temperature in the 0-5000 G range. All the spectra were acquired under similar conditions.

RESULTS AND DISCUSSION

For quantitative measurement of deposited coke ESR technique were used. Figure 1 shows the Electron Spin Resonance (ESR) spectra of the standard activated carbon and of the coke in the catalyst (curves 1 and 2).
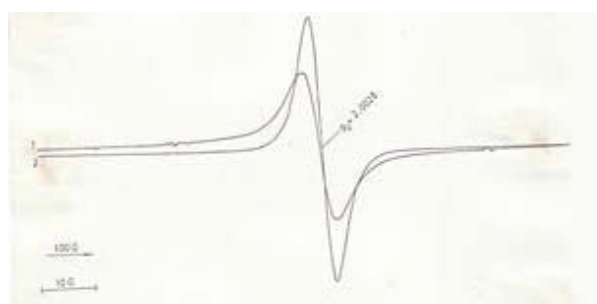
Fig. 1. ESR signal of standard activated carbon and of coke on the catalyst

Figure 2 presents the number of paramagnetic particles formed versus coking time. The curve has three different regions. The initial coking process starts slowly and after 1.5 h it is accelerated substantially until 5th h. Up to 5 h the curve grows as a straight line to 20h. The explanation of this behavior of the catalyst is following. In the first two hours a few coking centers are formed on the catalyst surface of the fresh catalyst. After reaching some critical value of the formed coking centers period a fast deposition of coke on those centers proceeds in the second period. In the third period formation of new coking centers on the less active catalyst centers followed by deposition of additional coke on them is evident.
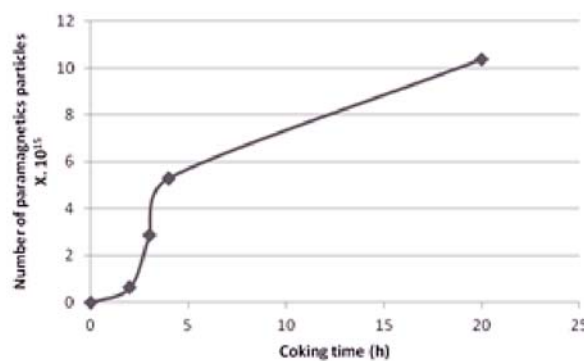
Fig. 2. Number of paramagnetic particles formed versus coking time

Figure 3 presents the dependence of the rate of thiophene decomposition at 350°C on the number of

paramagnetic particles formed on the catalyst surface at different coking time. The reduction in the activity of the catalyst is almost proportional to the increase in the number of paramagnetic particles. This dependence has also three divisions, which correspond to divisions in the curve on Figure 2. In the first period of time a linear fast decrease of the reaction rate is observed because most active catalyst active centers are blocked. In the second period reaction rate is constant which means that the coke is deposited on initially formed coking centers. After multi layers coke deposit was formed in the third period steady decrease of reaction rate was observed due to constant rate of blocking the less active surface active centers.
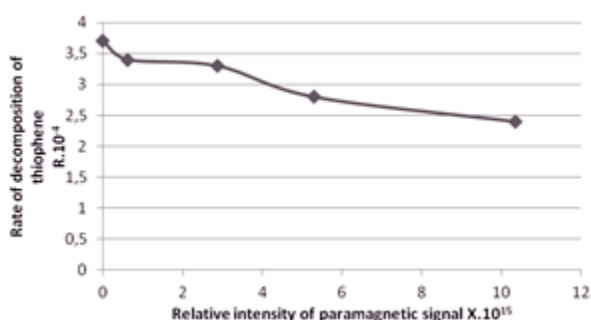

Fig. 3. Dependence of the rate of decomposition of thiophene with the relative intensity of paramagnetic signal (relative quantity of coke)

Figure 4, shows the dependence of the rate of decomposition of thiophene on temperature for fresh and coked catalyst for 3 h with $2{,}87.10^{15}$ paramagnetic particles deposited. For the two samples the dependence has the same character. This clearly indicates that the mechanism of the process does not change after the coking of catalyst. With the increase in temperature, the rate of decomposition of thiophene increases. For all temperatures studied, fresh catalyst's activity is 15 % higher than the coked sample.
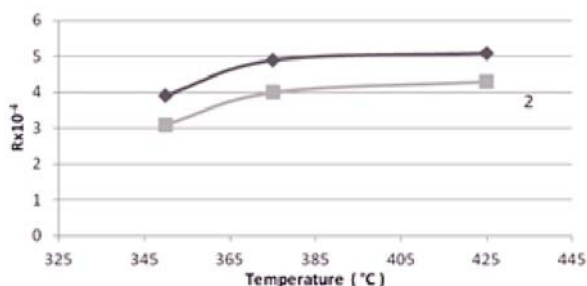
Fig. 4. Dependence of the rate of decomposition of thiophene with temperature of reaction. 1 - fresh catalyst, 2 - coked catalyst for 3 hours

To have an idea about the way in which deposited coke is located on the surface of the catalyst, we have measured its specific surface at different period of coking. Figure 5 presents the dependence of the surface area of the catalyst from quantity of coke deposited defined by the intensity of the signal g=2.004.
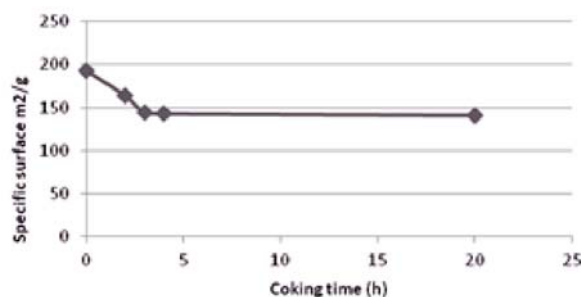
Fig. 5: Surface area of the catalysts coked at different time

It is seen that specific surface area decreases quickly at the beginning of coking process until approximately the third hour corresponding to $2{,}87.10^{15}$ paramagnetic particles. With the increase in the quantity of coke after 20 h of coking, there is very small changes of the surface area of the catalyst, nevertheless there is an increased in the quantity of coke deposited on its surface. The results presented on figure 2 confirms the suggestion of monolayer-multilayer growth of coke on the catalyst surface [11]. The rate of thiophene decomposition is reduced by coke deactivation. On figure 5 the specific surface is practically unchanged up to 5 h. Probably multilayer coke is formed and not occupied all catalyst surface [12]. The influence of this coke is not sensitive on the specific surface.

Table 1 shows the selectivity of each product in the reaction at various temperatures for catalyst coked for 3h and for fresh sample. It can be seen that, at the same temperature the butane selectivity of coked catalyst is higher than that of the fresh sample. With the increasing of temperature the butane selectivity of both samples grows, however at the same degree of thiophene conversion carried at low temperature, the butane selectivity of the coked sample is higher than that of the fresh sample. The higher butane selectivity of coked catalyst compared to that of the fresh sample shows that, under the conditions of our tests, coking has little influence on the hydrogenation sites. This behavior can be explained by the observations reported in [13, 14]. The formation of coke on the catalyst surface not concerns all its surface. Part of catalyst sites preserve its activity.

Table 1. Selectivities on the different hydrocarbon reaction products during the HDS of thiophene decomposition on catalyst coked for 3h and for fresh catalyst

Catalyst	T °C	Butane	1-butene	Trans-2-butene	Cis-2-butene
Fresh	350	0,31	0,12	0,32	0,2
Coked		0,43	0,08	0,29	0,18
Fresh	375	0,33	0,17	0,3	0,2
Coked		0,55	0,08	0,2	0,14
Fresh	425	0,42	0,15	0,25	0,17
Coked		0,71	0,05	0,12	0,09

Other studies show that the formation of coke on the surface of Co-Mo/Al₂O₃ catalysts does not influence the process of adsorption and desorption of the reagents and the products on the virgin surface of catalyst [14]. Our results confirms the existence of several types of active centers, which are influenced by the formation of coke obtained during the reaction of hydrogenation.

The selectivity of butylene-1 of coked catalyst is smaller than that of fresh catalyst at the same temperature of reaction. That is in line with the observation of high hydrogenation rate on coked catalysts. With the increase of the temperature, the selectivity of the fresh sample increases whereas that of the coked sample decreases. The higher butene-1 selectivity of fresh catalyst can be explained by the high temperature dependence of the activity of the active sites of hydrodesulfurization on temperature compared to those of hydrogenation and isomerization active sites. The low butylene-1 selectivity of coked catalyst shows that, after coking the rate of butane-1 rate formation is significantly reduced due to decrease of rate of decomposition of thiophene compared to that of hydrogenation and isomerization reactions.

After coking, the cis-2-butylene and trans-2-butylene selectivities decrease which shows that, coking led also to partial deactivation of the isomerization centers. The selectivities of these products decrease with the increase in the temperature, which is a proof that the rate of conversion of butylene-1 into butane increases more quickly than its isomerization to cis-2-butylene and trans-2-butylene.

CONCLUSION

On the basis of the results obtained, following conclusions can be made:

There are three periods of coking of hydrodesulfurization CoMo/Al₂O₃ catalyst in which catalyst deactivation is proceeding by different mechanisms.

Most of deposited coke forms multi-layer coke coverage of the surface, mainly during second and third period of coking.

The three types of active centers: hydrodesulphurization, hydrogenation and isomerization, are deactivated in different way during catalyst coking. The centers of hydrodesulphurization and isomerization are not very sensitive to coke while the centers of hydrogenation are more sensitive. That gives the possibility, by a partial deactivation of the catalyst to influence on its selectivity and respectively on the output of the various products of the reaction.

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ХИДРООЧИСТКА НА ТИОФЕН ВЪРХУ CoMo/Al$_2$O$_3$ КАТАЛИЗАТОР, МОДИФИЦИРАН ЧРЕЗ ПРЕДВАРИТЕЛНА КОКСУВАЩА ОБРАБОТКА

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(Резюме)

Активността на търговски CoMo/Al$_2$O$_3$ катализатор бе изследвана в реакцията на хидроочистка на тиофен. Каталитичните измервания се извършваха в циркулираща безградиентна система при атмосферно налягане. Установено бе, че предварително коксуване на катализатора води до значително намаляване на активността му, докато селективността по отношение на бутана се увеличава. Установено бе също така, че предварителното третиране на катализатора чрез коксуване намалява неговата повърхност и се наблюдава образуването на монослой от кокс и дендрити. Възможно е при специални условия на коксуване на катализатора да увеличи селективността и следователно добива на някои продукти на реакцията.