

**EFFECT OF PIPERIDINE ADDITION IN SULFIDATION
OF CoMo/Al₂O₃ CATALYSTS ON THEIR ACTIVITY
AND SELECTIVITY IN THIOPHENE HYDRODESULFURIZATION**

Chavdar D. VLADOV^a, Lachezar A. PETROV^a, Cao Anh DUNG^b and Bles YTUA^a

^a *Institute of Kinetics and Catalysis,
Bulgarian Academy of Sciences, ul. acad. G. Bonchev, Sofia 1113, Bulgaria*

^b *Institute of Organic Chemistry,
Vietnamese Academy of Sciences, Hanoi, Vietnam*

Received July 9, 1992
Accepted September 2, 1992

Dedicated to Dr Miloš Kraus on the occasion of his 65th birthday.

The effect of piperidine on a commercial Co/Mo/Al₂O₃ catalyst upon its sulfidation and during thiophene hydrodesulfurization has been studied. The experiments were carried out under atmospheric pressure. Upon sulfidation of the catalyst in the presence of nitrogen-containing compound, a reversible deactivation of hydrodesulfurization active sites and/or an irreversible deactivation of the hydrogenation and isomerization active sites were observed.

CoMo/Al₂O₃ hydrodesulfurization (HDS) catalysts have found wide application in modern oil processing industry. In addition to the composition, structure, support, and preparation method, of particular importance for the activity and selectivity of these catalysts is the process of their activation, i.e. their transformation from the oxide to sulfidic form. Plenty of data exist in the literature concerning the influence of reduction and sulfidation conditions on the formation of sulfide structures and active sites in the catalysts and their catalytic properties¹⁻⁴. Most authors have established, as a general tendency, that the catalytic activity of CoMo/Al₂O₃ in HDS reactions is enhanced by increasing sulfur content of the catalyst^{2,3,5}.

The effect of nitrogen-containing compounds present in oil fractions on the catalytic activity and selectivity of Co/Mo/Al₂O₃ is also of considerable interest. It was found that nitrogen-containing entities, for which the adsorption through the N atom is unhindered, cause enhanced poisoning of the hydrodesulfurization active sites under operating conditions in HDS^{6,7}. However, the effect of the admixtures of nitrogen-containing compounds in the sulfidation agent on catalyst activation is still insufficiently studied. This is important problem from practical point of view, because during the sulfidation of the catalysts in industrial units high concentration of nitrogen-contain-

ning compounds in the processed oil fractions can play negative role on catalyst performance. Investigation of this influence was the aim of the present work.

EXPERIMENTAL

All the experimental runs were carried out with a commercial CoMo/Al₂O₃ catalyst, AKM products in Russia, which contained 3 wt.% CoO and 11 wt.% MoO₃. Its BET area, pore volume and mean pore radius were 200 m² g⁻¹, 0.35 cm³ g⁻¹ and 2.5 nm, respectively. Hydrogen, argon and thiophene were purified in the same way as described in a previous paper⁵. Piperidine (99% purity) was supplied by Aldrich.

Thiophene HDS was performed using a stainless-steel flow-circulation system. The reactor was loaded with 1 g of the catalyst of 0.2 – 0.6 mm pellet size, to avoid diffusional retardation of the reaction. All the experiments were conducted under atmospheric pressure in the 325 – 425 °C temperature region and with hydrogen : thiophene gas ratio of 10 : 1. The rate of thiophene decomposition (mol g⁻¹ h⁻¹) was used to evaluate the activity of the catalyst in HDS. Product selectivities were expressed as a ratio between the rate of formation of a certain product and the rate of thiophene decomposition.

Experimental runs were carried out in the following way. The catalyst bed was dried in a stream of argon at 120 °C for 1 h followed by activation in two steps. The first one was the reduction of the catalyst at 400 °C for 2 h in a stream of hydrogen. After that, a mixture of hydrogen and thiophene or that of hydrogen and 1% solution of piperidine in thiophene was admitted to the reactor at the working temperature. The catalyst sulfidation was taken as complete at a given temperature when the rate of thiophene decomposition equaled to that of hydrogen sulfide formation. Activities and selectivities of the catalyst were measured after its sulfidation by thiophene or by 1% thiophene solution of piperidine in the reaction of HDS of thiophene in absence and presence of piperidine. Analysis of the reaction products was made on a gas chromatograph connected to the apparatus via six-way valve. The analytical method and apparatus are described in detail elsewhere⁸.

RESULTS AND DISCUSSION

Figure 1 shows time dependence of the rate of thiophene decomposition at different temperatures in the absence of piperidine on the catalyst activated in the absence of piperidine. It is seen that, regardless of temperature, after about 10 h operation, the catalyst was completely sulfided and its activity and selectivity was constant for a long period of time (more than 50 h). Under industrial conditions (20 atm pressure and high excess of hydrogen), the catalyst keeps constant activity for more than one year. This indicates that the possible changes of catalytic properties observed during measurements in the presence of piperidine should be attributed to the interaction of piperidine with the catalyst.

Figure 2 shows time dependence of the rate of thiophene decomposition at 375 °C after sulfidation of the catalyst in the absence of piperidine (curve 1) and after the sulfidation by 1% solution of piperidine in thiophene (curve 2). The arrow on curve 2 marks the moment of changing the initial reaction mixture containing thiophene and piperidine to pure thiophene. Curve 3 describes the case when thiophene decomposition was carried out in the presence of piperidine after catalyst sulfidation by a mixture of thiophene and piperidine. It is seen that the rate of thiophene decomposition is about

two times slower in the presence of piperidine, both during the catalyst activation and HDS compared to the rate observed in the absence of piperidine. The HDS rate was almost constant for about 16 h, than it slowly decreased. This result is in agreement with the previously found slight decrease in the catalytic activity with increasing piperidine content⁹. On the other hand, upon passing thiophene over the catalyst sample activated in the presence of piperidine, its activity started to increase after about 4 h operation, and after about 20 h it reached the values found for the catalyst activated only by thiophene. Similar behaviour was found for the whole temperature range investigated. At the lower temperatures, however, relative decrease in the HDS rate was found to be considerable and the initial activity could be restored after removing piperidine from the reaction mixture only after much longer time. For example, at 325 °C the activity decrease was about 70% and the initial activity was restored after 36 h of operation in the absence of piperidine.

It is of primary importance to clarify the role of nitrogen-containing compounds in the HDS process and their effect on selectivity of the reaction. Table I presents selectivity data on butane, 1-butene, *cis*-2-butene, and *trans*-2-butene in the presence and absence of piperidine during activation of the catalyst and during thiophene HDS. It is seen that the selectivity to butane formation for the same composition of the reaction mixture in the activation and HDS reaction increases on raising the temperature. Under operating conditions, at one and the same temperature, the presence of piperidine leads to a considerable decrease in butane selectivity. This selectivity is also lower after removing piperidine from the reaction mixture.

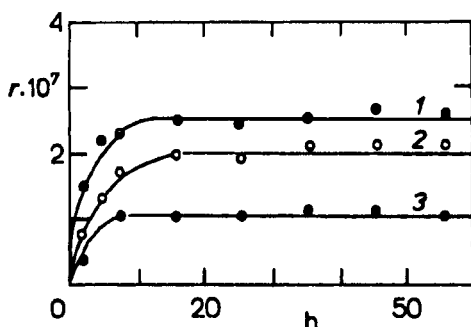


FIG. 1

Dependence of the rate r ($\text{mol g}^{-1} \text{h}^{-1}$) of thiophene decomposition on catalyst operation time t (h) in the absence of piperidine at different temperatures: 1 425, 2 375, and 3 325 °C

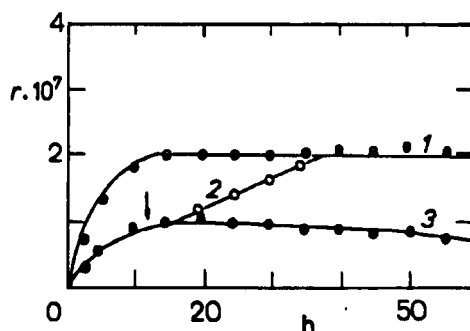


FIG. 2

Dependence of the rate r ($\text{mol g}^{-1} \text{h}^{-1}$) of thiophene decomposition at 375 °C on catalyst operation time t (h): 1 in the absence of piperidine, 2 after the catalyst sulfidation by 1% solution of piperidine in thiophene and 3 after the catalyst sulfidation by 1% solution of piperidine in thiophene and for the catalyst working under HDS conditions in the presence of the said mixture

In the absence of piperidine, the selectivity to 1-butene formation decreases with increasing temperature. At the same temperature, the presence of piperidine, even only during catalyst activation, gives rise to increased selectivity. Removing of piperidine from the solution does not result in any significant change of the selectivity. Changes of selectivities in *cis*-2-butene and *trans*-2-butene formation with temperature or in the presence of piperidine during sulfidation and/or in HDS were of similar nature.

Different effect of piperidine on the rate of HDS and on the rates of hydrogenation and isomerization confirmed the presence of at least two types of active sites on the CoMo/Al₂O₃ catalyst surface. This is in agreement with suggestions made earlier in other studies of the HDS process⁵.

Most authors who have studied the mechanism of thiophene hydrodesulfurization under atmospheric pressure suggest that the first step of the reaction is the hydrogenolysis of thiophene to butadiene¹⁰⁻¹². Butadiene thus formed is further hydrogenated to 1-butene on another type of sites. Finally, 1-butene is hydrogenated to butane or isomerized to 2-butenes. The results obtained in the present study indicate that the presence of piperidine during catalyst sulfidation leads to a competitive adsorption between sulfur- and nitrogen-containing molecules. Furthermore, the sulfur displaces completely the adsorbed nitrogen-containing species from the sites on which thiophene is dissociatively adsorbed. Thus, on removing piperidine from the reaction mixture, the

TABLE I
Product selectivity of thiophene HDS after catalyst sulfidations in the presence and absence of piperidine

Temperature °C	Time on stream, h	Sulfi- dation ^a	HDS	Selectivity			
				butane	1-butene	<i>trans</i> -2- butene	<i>cis</i> -2- butene
325	40	T	T	0.24	0.14	0.37	0.25
	40	T + P	T + P	0.15	0.15	0.40	0.28
	40	T + P	T	0.22	0.17	0.36	0.27
375	40	T	T	0.28	0.12	0.34	0.23
	40	T + P	T + P	0.22	0.13	0.37	0.27
	40	T + P	T	0.24	0.13	0.36	0.27
425	40	T	T	0.33	0.11	0.32	0.22
	40	T + P	T + P	0.24	0.13	0.36	0.26
	40	T + P	T	0.26	0.14	0.35	0.24

^a T Thiophene, P piperidine.

HDS activity is restored. Concerning the sites on which butadiene is hydrogenated and/or isomerized, it seems likely that nitrogen-containing species are irreversibly adsorbed via their nitrogen atom, which is the reason for the irreversible changes in catalyst selectivity.

The results obtained suggest that under industrial conditions special precautions should be taken to use oil fractions with low content of nitrogen compounds during HDS catalyst activation. This will improve the catalyst's performance.

REFERENCES

1. Ripperger W., Saum W.: *J. Less-Common Met.* **54**, 353 (1977).
2. De Beer V. H. J., Bevelander C., Van Sint Fiet T. H. M., Werter P. G. A. J., Amberg C. H.: *J. Catal.* **43**, 68 (1976).
3. Hargreaves A. E., Ross J. R. H.: *J. Catal.* **56**, 363 (1979).
4. Peter R., Peroutková V., Beránek L.: *Chem. Prum.* **31**, 345 (1981).
5. Petrov L., Vladov Ch., Shopov D., Friebová V., Beránek L.: *Collect. Czech. Chem. Commun.* **48**, 691 (1983).
6. Massoth F. E., Miciukiewicz J.: *J. Catal.* **375**, 110 (1986).
7. Drahorádová A., Vít Z., Zdražil M.: *Fuel* **455**, 71 (1992).
8. Petrov L., Vladov Ch., Shopov D. in: *Heterogeneous Catalysis. Proc. 4th Int. Symp. Varna 1979* (D. Shopov, A. Andreev, A. Palazov and L. Petrov, Eds), Part 2, p. 303. Publishing House Bulg. Acad. Sci., Sofia 1979.
9. Yang J., Massoth F. E.: *Appl. Catal.* **215**, 34 (1987).
10. Owens P., Amberg C.: *Adv. Chem. Ser.* **182**, 33 (1961).
11. Lipsch J. M. J., Schuit G. C.: *J. Catal.* **179**, 15 (1979).
12. Petrov L., Vladov Ch., Shopov D.: *Bull. Soc. Chim. Belg.* **643**, 96 (1987).