

# CATALYTIC ACTIVITY OF COBALT AND MOLYBDENUM-CONTAINING Y-TYPE ZEOLITES IN THIOPHENE CONVERSION

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## ABSTRACT

The hydrodesulphurization (HDS) of thiophene on NaY and CaHY zeolites containing 0.7 and 2 wt % cobalt and 7 wt % molybdenum has been studied at atmospheric pressure.

The surface of the samples has been characterized by chemical analysis, I.R. and diffuse reflectance spectra.

It is shown that the conditions of preparation determine the overall activity and selectivity in HDS of thiophene on zeolites.

The silicium and cobaltsilicium heteropoly molybdates (Si HPM and CoSi HPM) along with molybdenum oxide that are formed in the zeolites could be the precursors of the active sites for the HDS reaction.

## INTRODUCTION

The catalytic activity of zeolites containing transition metal ions in the reaction of HDS has been studied in a number of papers [1-3]. Although the activity of such zeolites is not very high, the investigation of the CoMo-containing zeolites is interesting because it allows to reveal some aspects of the complex interaction between the catalyst components and its effect on the catalytic activity.

In a previous paper [4] we have shown the existence of a strong interaction between all components in a cobalt and/or molybdenum containing Y-type zeolites and as a result Si HPM and CoSi HPM are formed.

In the present paper we investigate the effect of their preparation conditions on the catalytic properties in the thiophene conversion.

## EXPERIMENTAL

Synthetic NaY zeolite (Groz NII, USSR) with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 4.2 has been used. Also, a CaHY zeolite (degree of exchange 48 % for each of  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$ ), obtained from the initial NaY zeolite by con-

ventional ion exchange with calcium nitrate and ammonium chloride. The two initial zeolite samples differ in their acidity as determined by butylamine titration:  $\Sigma H_O = 1.4$  and  $0.35$  mmol/g for CaHY and NaY, respectively [5]. Cobalt has been introduced in these two samples by ion exchange or by impregnation with cobalt nitrate (CoN). Molybdenum has been introduced in the initial samples by impregnation with ammonium heptamolybdate (AHM). After the introduction of both components the samples are dried at  $120^\circ\text{C}$  for 4 hrs and then calcined at  $500^\circ\text{C}$  for 2 hrs. This thermal treatment was used after introduction of each component for sample № 8. The preparation conditions are given in Table 1.

Table 1

Conditions of preparation of molybdenum and cobalt-molybdenum containing zeolites

№	Zeolites	Co/Mo	Co content (mg/g)	Conditions of preparation
1	NaY	-	-	AHM*
2	NaY	0.16	6.9	1.CoN exchange.2.AHM
3	NaY	0.16	6.9	1.AHM.2.CoN impregnation
4	NaY	0.48	20.7	1.CoN exchange.2.AHM
5	CaHY	-	-	AHM
6	CaHY	0.16	6.9	1.CoN exchange.2.AHM
7	CaHY	0.16	6.9	1.AHM.2.CoN impregnation
8	CaHY	0.16	6.9	1.AHM.120°C-4h,500°C-2h CoN impregnation

\* Impregnation by ammonium heptamolybdate (AHM).

The state of the surface of the samples has been investigated by IR and diffuse reflectance spectroscopy. The spectra were recorded on an IR - 75 spectrometer ( $400-2200\text{ cm}^{-1}$ ) using pellets in KBr and on a Beekman UV 5270 (280-800 nm) with the initial zeolite as a reference.

The hydrodesulphurization of thiophene has been studied in a flow microreactor (atmospheric pressure, temperature of  $400^\circ\text{C}$ , WHSV of  $0,6\text{ h}^{-1}$ ) loaded with  $0,2\text{g}$  catalyst. The temperature is raised upto the reaction temperature within 1,5 hours in hydrogen at flow rate of  $40\text{ ml/min}$ . The activity has been expressed in molecular percent of converted into hydrocarbons thiophene or by the amount of released  $\text{H}_2\text{S}$ .

Molybdenum was extracted by treating 0,4 g of sample with 50 ml water for 24 hrs. After the extraction the samples were dried and calcined in conditions analogous to those of the sample synthesis. The content of the active components determined by atomic adsorption spectrometry.

## RESULTS

The samples obtained by using NaY zeolite show stable catalytic activity in the HDS of thiophene (Fig.1a). The conditions of preparation effect the initial activity of the samples. Similarly to the con-

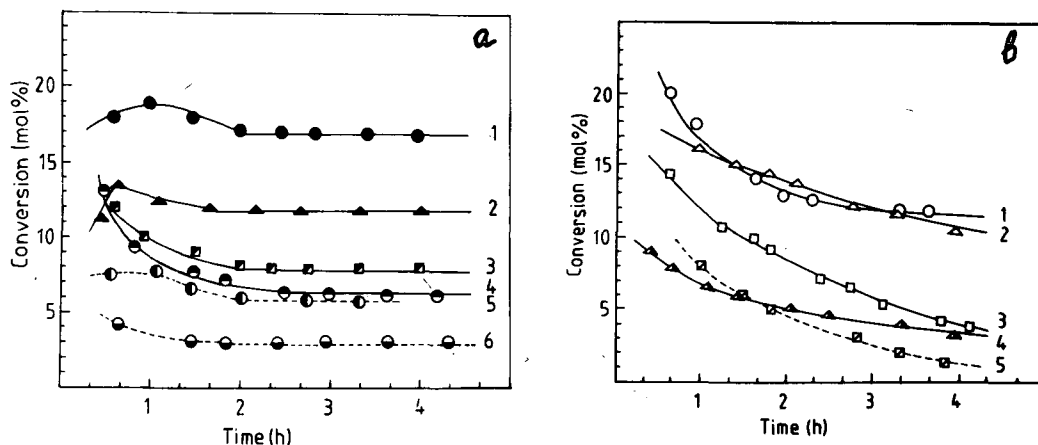


Fig.1. Thiophene conversion in  $C_4$ -products vs time for samples (see table 1) on a) NaY: 1-№ 2; 2-№ 3; 3-№ 1; 4-№ 4; 5,6-№ 2, № 4 after aqueous extraction; b) CaHY: 1-№ 8; 2-№ 7; 3-№ 6; 4-№ 5; 5-№ 6 after aqueous extraction.

ventional  $CoMo/Al_2O_3$  catalysts, cobalt also shows a synergetics effect in the case of the zeolite catalysts. The steady state conversion at a higher cobalt content (Fig.1a-4) is considerably lower. For sample №4 the activity is even lower in comparison to the activity of sample №1, which does not contain cobalt (Fig.1a-3). The aqueous extraction of the samples considerably decreases their catalytic activity (Fig.1a-5,6).

Fig 1b shows changes of the catalytic activity during the run, time for the samples prepared by using CaHY zeolite. Decreasing catalytic activity is characteristic for these samples. Here too, the conditions of preparation influence the activity. The samples, obtained by cobalt impregnation manifest higher and more stable activity (Fig.1b-1,2).

For the samples of this series,  $C_1-C_3$  hydrocarbons are revealed among products of the reaction. Even more, for samples № 5 and № 6 (Table 1) the conversion of thiophene proceeds practically as the process of hydrocracking, because the characteristic products of the reaction of HDS (butene isomers) are not observed or their quantity is very small (sample № 6).

The difference in the properties of the two types of samples in the conversion of thiophene is particularly noticeable if their activity is compared by the amount of released  $H_2S$  (Fig.2). The amount of  $H_2S$  released on NaY samples is much less and it is entirely absorbed

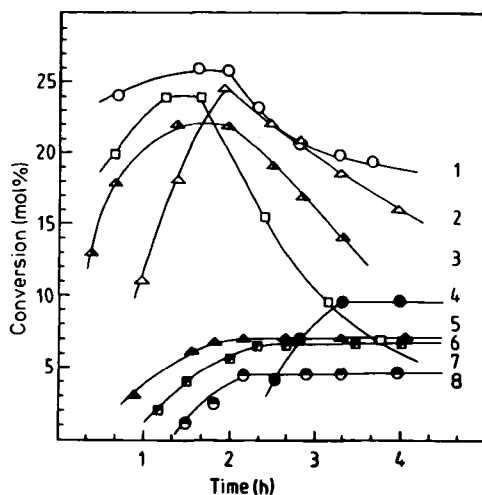


Fig 2. Thiophene conversion in  $H_2S$  vs time for samples (see table 1): 1-№ 8; 2-№ 7; 3-№ 5; 4-№ 2; 5-№ 3; 6-№ 1, 7-№ 6, 8-№ 4.

by the catalyst during the first hour of run, then its amount gradually increases (Fig.2-4,5,6,8).

In contrast, the change in the amount of  $H_2S$  released with time on the CaHY samples (Fig.2-1,2,3,7) is close to that observed on cracking catalysts [6]. A rapid increase in the amount of the released  $H_2S$  is observed for these samples and its highest value considerably exceeds the conversion of thiophene into  $C_4$ -products. However, its amount decreases with time similar to that on cracking catalysts.

The diffuse reflectance spectra of the cobalt containing samples show the presence of a cobalt triplet within the 500-630 nm character-

ric to tetrahedral cobalt [7]. The intensity of this triplet is higher in the NaY samples. The intensity increases with the increase of the cobalt content (Fig.3-1,3). However, the middle peak in the observed triplet is shifted from 570 nm to 585 nm. In our previous work [4] we related this shift to the formation of a CoSi heteropolymolybdate, where cobalt is in an octahedral surrounding.

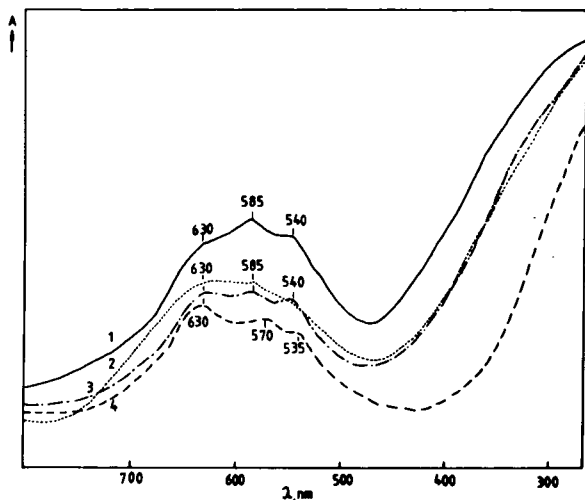


Fig.3. Diffuse reflectance spectra of samples (see table 1):  
 1-№ 4; 2-№ 6; 3-№ 2; 4- № 2 after aqueous extraction.

IR - spectra of the samples with different cobalt content are shown in Fig.4. Both of high and low cobalt contents Si HPM is formed (Fig.4-1,3).

In the spectra are revealed bands at 780, 900, 960  $\text{cm}^{-1}$  although the last band is overlapped by intensive absorption of the zeolite itself in the same range.

But in contrast to other samples obtained using NaY zeolites, after calcining of sample № 4 at 500°C, a characteristic band of  $\text{MoO}_3$  (at 860  $\text{cm}^{-1}$ ) appears, along with bands of the HPM. The second characteristic band of  $\text{MoO}_3$  at 990  $\text{cm}^{-1}$  is not observed due to intensive absorption by the zeolite. It was shown [4], that  $\text{MoO}_3$ , along with HPM is present in the samples obtained by using CaHY.

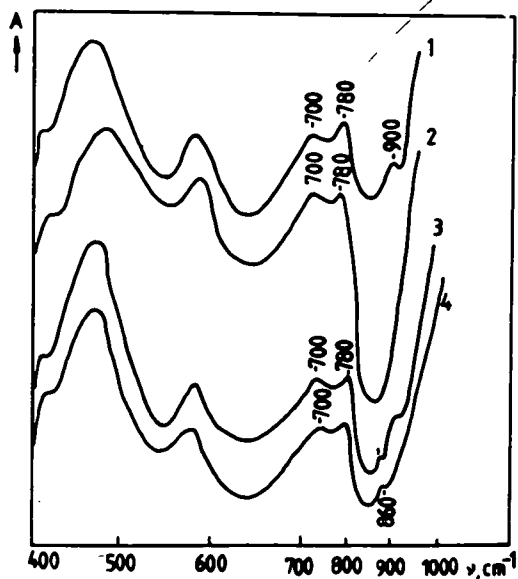


Fig.4. IR- spectra of samples (see table 1): 1- № 2; 3- № 4; 2, 4- № 2, № 4 after aqueous extraction.

#### DISCUSSION

It is known that molybdenum increases the acidity and changes the type of acid sites on the surface [8]. The heteropolycompounds formed in the zeolite also manifest acid properties [9].

Most probably the overall activity and selectivity depend on the molybdenum content and the acidity of the support.

The CaHY zeolite itself shows very low activity which decreases quickly with time.

The specific interaction between the zeolites and the components is connected with their different acidity and causes the difference in the properties of the two series of samples. Probably the higher acidity of CaHY makes the formation of  $\text{MoO}_3$  easier in samples using this carrier. Molybdenum oxide is also found in sample № 4 (on NaY), the acidity of which is probably increased due to the higher cobalt content.

The formation of large amounts of butane on some of the CaHY samples indicates that a hydrocracking processes (or possibly cracking processes without the participation of hydrogen), accompanied by polymerization of some unsaturated products. The decrease of conversion of thiophene into  $\text{C}_4$ -products and the increase in the amount of  $\text{H}_2\text{S}$  support this conclusion. The amount of  $\text{H}_2\text{S}$  released after two hours of

work for sample № 6 is three times larger than the amount of obtained  $C_4$ -products (Fig.1b-3 and Fig.3-7). The formation of coke on the samples after work is confirmed by the presence in the IR-spectra of a band at  $1595\text{ cm}^{-1}$  [10]. The last is less strongly expressed for the samples obtained from NaY.

The results show that the activity of the samples in thiophene conversion can be regulated by the order of introducing of the metal components. The activity of the samples obtained using CaHY is increased and stabilized (no matter what the intermediate thermal treatment is) if cobalt is introduced after molybdenum. It is possible that in this case cobalt influences the acid sites. The effect of the support on the activity is not so significant when cobalt is introduced by impregnation (the activity of sample № 8 is close to that of sample № 3) (Fig.1a and Fig.1b).

It should be noted that when cobalt is introduced by ion exchange the activity of the samples in the HDS reaction is higher. This is not so obvious for the samples obtained from CaHY (for example, sample № 6) due to the properties of zeolite itself.

The decrease in thiophene conversion after aqueous treatment (Fig.1a-5,6 and Fig.1b-5) correlates with the disappearance in the IR-spectra of the bands characteristic of Si HPM (Fig.4-2,4) and the preservation of bands due to  $MoO_3$ . The shift of the band at 585 nm (it was related [4] to the presence of CoSi HPM in CoMo-containing zeolites) to 570 nm in the diffuse reflectance spectra is a result of the aqueous treatment. The shift is accompanied by a decrease in the intensity of the absorption band at 300 nm which is due to the presence of  $Mo^{6+}(OH)$  (Fig.3). It should be also noted that the aqueous extracts of samples № 2 and № 6 (with ion exchanged cobalt) do not contain cobalt, while about 40% of molybdenum was extracted. The results obtained allow to suggest that the soluble in water Si HPM and CoSi HPM are the precursors of the catalytically active sites in the thiophene hydrodesulfurization.

The preservation of some activity by the samples after aqueous treatment shows that  $MoO_3$  as well as some other unidentified molybdenum compounds could be also precursors of the active sites in thiophene conversion.

The observed correlation between the presence of Si HPM in the zeolites and the catalytic activity is similar to that when  $SiO_2$  is used as a support instead of Y type zeolites [11]. Most probably the precursors of the catalytically active sites are the same on both types of support. The activity of the samples using  $SiO_2$  as a support is

higher than that of the samples supported on Y type zeolites. For example the conversion of thiophene on our sample № 2 is 17% while it is 25% on the sample having the same cobalt and molybdenum content but using  $\text{SiO}_2$  as a support. This could be explained by the higher concentration of heteropoly compounds in the latter, since 80% of the total amount of molybdenum on  $\text{SiO}_2$  is in the form of HPM [11]. This quantity is only 30% for the zeolite sample.

## CONCLUSIONS

The observed catalytic conversion of thiophene on the two series of samples shows the strongly expressed bifunctional character of the catalysts, when CaHY is used as a support. The catalytic activity is more steady for samples obtained from NaY zeolites.

The catalytic activity of the zeolite catalysts can be regulated by the order of introducing of the metal components. Cobalt, introduced by ionexchange, leads to an increase in the hydrodesulphurisation activity.

Si HPM and CoSi HPM, along with  $\text{MoO}_3$  could be precursors of catalytically active sites in thiophene conversion on Mo and CoMo-containing zeolite catalysts.

## REFERENCES

1. Visotskii, A.V., Chuikova, N.A., Lipovich, V.G., *Kinet. Catal.* 18, 1345 (1977).
2. Vrinat, M.L., Gachet, C.G., de Mourques, L., *Catalysis by Zeolites*. Elsevier, Amsterdam, 1980, p.219.
3. Kovacheva, P., Davidova, N., Shopov, D., *Zeolites*. 3, 92 (1983).
4. Spozhakina, A., Kostova, N., Damyanova, S., Shopov, D., *React. Kinet. Catal. Lett.*, in press.
5. Spozhakina, A., Popova, Z., Dimitrov, Ch., *Neftechimia*, 22, 64 (1982).
6. Mashkina, A.V., *Heterogeneous catalysis in chemistry of sulfur organic compounds*, Nauka, Novosibirsk, 1977, p.111.
7. Egerton, T.A., Hagan, A., Stone, F.S., Vickerman, J.C., *J.Chem. Soc., Faraday Trans. I.* 68, 723 (1972).
8. Ratnasamy, P., Fripiat, J.J., *J.Chem. Soc., Faraday. I.* 66, 2897 (1970).
9. Misono, M., *Proc. Climax Fourth Int. Conference on the Chemistry and Uses of Molybdenum*. Climax Molybdenum Company, Ann Arbor, Michigan, 1982, p. 289.



10. Eisenbach, D., Gallei, E., J. Catal. 56, 377 (1978).
11. Spozhakina, A., Kostova, N., Uhchnovskii, I., Shopov, D., Uhrieva, T., Applied Catalysis, in press.