Catalysis Letters 6 (1990) 157–162

INVESTIGATION OF THE PROMOTION EFFECT ON THE SULFIDE SULFUR MOBILITY AND ON THE CATALYTIC ACTIVITY OF HYDROTREATING $Co/Mo/Al_2O_3$ CATALYSTS USING ^{35}S

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Received 13 April 1990; accepted 16 July 1990

Hydrotreatment, hydrodesulfurization, catalysis, sulfide catalysts, promoter effect, radioisotope, sulfur mobility, catalytic activity, thiophene, cobalt, molybdenum, alumina

Using ^{35}S the effect of sulfur in $Co/Mo/Al_2O_3$ catalysts on catalytic activity has been studied. A linear dependency between the amount of sulfur capable of participating in the formation of H_2S and the catalytic activity has been established. It has been shown that with increasing the Co content, the overall amount of sulfide sulfur in the catalyst changes negligibly, while the amount of mobile sulfur increases linearly. It has been found that the promoter effects on the two groups of active sites that determine the sulfide sulfur mobility are different.

1. Introduction

Previously thiophene hydrogenolysis on the commercial $Co/Mo/Al_2O_3$ (ACM) catalyst and MoS_2 was studied [1]. It was shown that the formation of H_2S during thiophene hydrogenolysis proceeds with the participation of sulfur catalyst. In this process about 40% of the sulfur participates on the catalyst. We called it “mobile sulfur”. Furthermore, this mobile sulfur is diverse and contains at least two kinds of active sites (AS) differing in rates of the H_2S formation. Those kinds may be called “rapid” and “slow” AS. Various considerations about the possible nature of the AS were put forward. The nature of “slow” AS was proposed to be connected with MoS_2 crystallites strongly interacting with Al_2O_3. Cobalt introduction diminishes the interaction of MoS_2 crystallites with the support, which in turn results in the increase of the sulfur mobility. Such crystallites form “rapid” AS.

It was of interest to carry out thiophene hydrogenolysis on various molybdenum-alumina (AM) catalyst samples which differed in cobalt content to study the effect of the promoter on catalyst sulfur mobility and catalytic activity. The investigation was performed using ^{35}S.

2. Experimental

The following catalyst samples have been used: a. 12% MoO_3/Al_2O_3; b. (12% MoO_3, 1% CoO)/Al_2O_3; c. (12% MoO_3, 2% CoO)/Al_2O_3; d. (12% MoO_3, 4% CoO)/Al_2O_3.

These samples were prepared by wet impregnation of alumina with aqueous solutions of the appropriate concentration of ammonium heptamolybdate and cobalt nitrate, drying at 110 ° C followed by calcinating at 550 ° C, both for 3 h.

To prepare ^{35}S labelled catalyst, elementary sulfur (^{35}S) with molar radioactivity (MR) 1.2 GBk/mol was used as the sulfiding agent. Sulfidation of catalysts (initially in oxide form) by elementary sulfur was carried out in stainless steel 21 cm^3 microautoclave (H_2, 6 MPa, 360 ° C, 1 h). After sulfidation in the course of which some of the sulfur was transformed into H_2S, the gas from the autoclave was bubbled through a solution of $Cd(CH_3COOH)_2$. The sediment CdS obtained was used afterwards to determine the specific radioactivity (SR) of the initial sulfur. In order to remove the free sulfur and adsorbed H_2S from the catalyst, after sulfidation the samples were subjected to a He stream at 360 ° C for 1 h. The sulfur amounts on the catalyst samples were measured by using the ratio of their SR to that of CdS. The latter was considered to be equal to elementary sulfur SR (evaluated to 1 mg sulfur).

Thiophene hydrogenolysis was carried out in a pulse microcatalytic apparatus (100 mg of the catalyst, H_2 stream, 20 cm^3/min velocity, 360 ° C) using radiochromatographic analysis of products as in [1].

3. Results and discussions

According to elemental analysis and radiometric data, the sulfur content of the catalyst samples used corresponded to their stoichiometric content of MoS_2 and Co_9S_8. In carrying out thiophene hydrogenolysis on these catalysts, we have found that on each sample used, the sulfide sulfur has been transferred to H_2S, similarly to what was observed previously on the commercial ACM catalyst [1].

Fig. 1 shows the dependence of the H_2S MR on the amounts of H_2S formed during thiophene hydrogenolysis over samples which differed in Co contents. With the increase in the amount of thiophene converted both the catalyst radioactivity and H_2S MR simultaneously decreased. The total sulfur amount in the catalyst sample and the catalytic activity of the latter remained constant during the experiment.

Mathematic treatment of the data obtained allowed us to approximate the curves on fig. 1 as a superposition of two different exponential functions (table 1).

It can be seen that the equations are similar to those obtained previously in [1] for the commercial ACM catalyst:

$$\alpha = 74.1 \exp(-1.76x) + 25.9 \exp(-0.20x) \qquad (5)$$

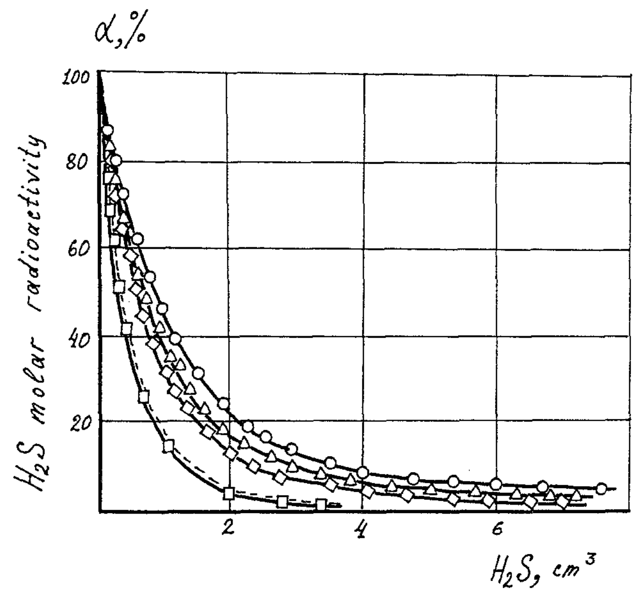

Fig. 1. Change of H_2S MR during thiophene hydrogenolysis (360 °C, 100 mg cat., H_2,) on the following labeled ^{35}S catalysts: ○-(4% CoO, 12% MoO_3)/Al_2O_3; △-(2% CoO, 12% MoO_3)/Al_2O_3 ◇-(1% CoO, 12% MoO_3)/Al_2O_3; □-(0% CoO, 12% MoO_3)/Al_2O_3; — — — unsupported MoS_2.

but differ in exponents. Comparing the curve for the promoted AM catalyst and unsupported MoS_2 (fig. 1) one can notice that they are fairly close. However, while the latter is described by the following simple exponential equation [1]:

$$\alpha = 100 \exp(-1.63x) \tag{6}$$

the curve for the supported unpromoted AM catalyst can be represented as the sum of two exponential functions. This factor exhibits some difference in AS of MoS_2 phase. On the unsupported MoS_2 during the hydrogenolysis process the conversion decreases with the increase of the amount of converted thiophene, whereas for the supported catalyst it remains practically constant.

Table 2 shows the effect of the promoter on the catalytic activity and sulfide sulfur mobility in ACM catalysts. One can see the increase of the mobile sulfur amount and of the catalytic activity on thiophene conversion with the increase of

Table 1
Change of H_2S molar radioactivity (α) in course of thiophene hydrogenolysis on Co/Mo/Al_2O_3 catalysts with different Co content

% CoO	H_2S MR change	σ, %
0	$\alpha = 81.40 \exp(-1.81x) + 18.60 \exp(-1.58x)$	±2.27 (1)
1	$\alpha = 83.96 \exp(-1.32x) + 16.04 \exp(-0.32x)$	±2.15 (2)
2	$\alpha = 82.39 \exp(-1.16x) + 17.61 \exp(-0.27x)$	±2.35 (3)
4	$\alpha = 89.07 \exp(-0.89x) + 10.94 \exp(-0.17x)$	±3.70 (4)

where x is the amount of H_2S formed [cm^3]

Table 2
Results of radioisotope investigation of sulfide Co/Mo/Al_2O_3 catalysts with different Co content (100 mg catalyst, 12% MoO_3, 360 °C, H_2 pulses of thiophene 3 μl)

CoO (%wt)	$\frac{Co}{Mo+Co}$	Thiophene conv. (γ, %)	*S* mobile [mg]	$\frac{S_{mob.}}{S_{tot.}}$ (%)	*S* rapid (mg)	*S* slow (mg)	*S* rapid (%)	*S* slow (%)
0	0	30.1	0.810	15.3	0.642	0.168	79.3	20.7
1	0.089	54.4	1.620	28.4	0.907	0.713	56.0	44.0
2	0.164	54.3	1.964	31.6	1.015	0.949	51.7	48.3
4	0.282	74.2	2.331	34.8	1.433	0.898	61.5	38.5

Co content in the catalyst. Besides, the conversion and mobile sulfur amounts are directly proportional (fig. 2). These results agree with the hydrodesulfurization mechanism offered in [2] because they allow us to conclude that catalyst activity is determined by the sulfide sulfur ability to leave the catalyst in the form of H_2S. This conclusion does not correlate with traditional schemes on the desulfurization mechanism. According to the traditional schemes, the catalytic activity depends on the rate of the cleavage of C-S bond on the thiophene molecule adsorbed on anionic vacancy (the rate controlling step) [3], and not on the rate of cleavage of Z-SH bond on the step of H_2S formation. Although the latter proves to be essential for the reaction mechanism, it is completely absent in traditional schemes.

The results obtained allow us to establish not only the dependency of the total amount of mobile sulfur on the promotor content but also the promotor effect on

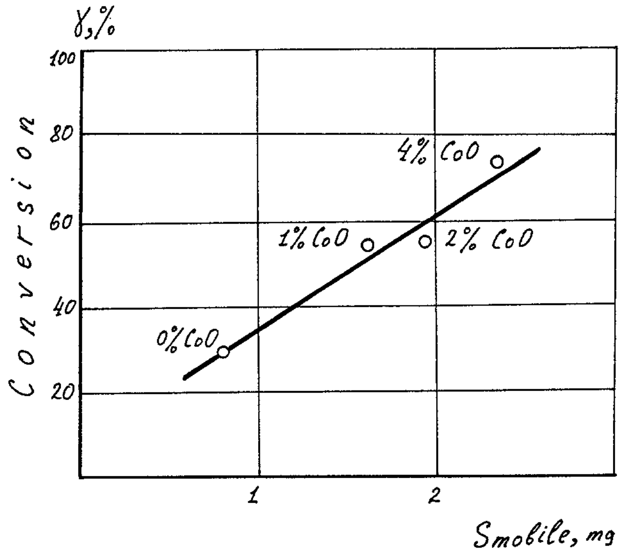

Fig. 2. Thiophene conversion dependency on the mobile sulfur content on AM and ACM catalysts with different degree of Co promotion.

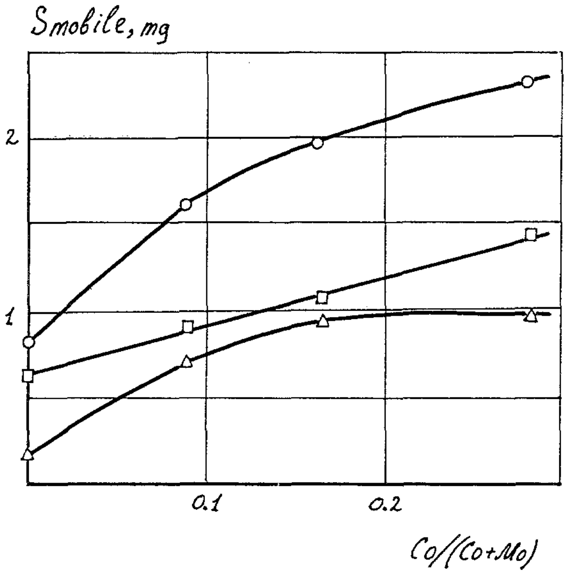

Fig. 3. The mobile sulfur amounts as a function of Co content on "rapid" (□), "slow" (▽) sites and total ones (○).

sulfide sulfur mobility on each type of site. As one can see in fig. 3, the increase of mobile sulfur amount on the catalyst depending on $r = \mathrm{Co}/(\mathrm{Co} + \mathrm{Mo})$ is determined by the sum of constituent contributions for the two types of AS. It should be noted that while the increase of mobile sulfur amount on "rapid" AS is of a linear character, for the "slow" sites the initially increasing amount of mobile sulfur is flat already at $r \approx 0.16$ and does not noticeably effect the total amount of mobile sulfur on the catalyst. These dependencies indicate that the promoter affects the growth of the "rapid" sites number to a greater degree.

References

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