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Temperature programmed desorption studies on hydrodesulfurization catalysts

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The temperature programmed-desorption (TPD) of butane, butene, butadiene and thiophene over a series of Co–Mo/γ-Al_2O_3 catalysts with varying Co to Mo ratio has been investigated. The TPD of butane, butene and butadiene over catalysts containing no Co showed a single desorption profile while incorporation of Co created an additional site without significantly affecting desorption from the original site. The TPD of thiophene over a series of catalysts with varying Co content showed identical desorption temperature as well as heat of desorption. It was concluded that thiophene was adsorbed on the "Mo–S" component of the catalyst and was unaffected by the presence of Co.

Keywords: Hydrodesulfurization catalysts; temperature programmed desorption

1. Introduction

The hydrodesulfurization (HDS) process over Co promoted Mo/γ-Al_2O_3 catalysts is one of the most extensively investigated catalytic processes. The role of Co, however, still remains enigmatic – both in terms of its structural and electronic relation to the "Mo–S" component as well as its role in the promotion of the HDS reaction [1–6].

In the active Co–Mo/γ-Al_2O_3 catalyst, both Mo and Co are present in the sulfided form and the Mo atoms are present in an environment very similar to that in the bulk MoS_2 [7–9]. The relation of the sulfidized Co to any known bulk stoichiometric phase is, however, doubtful. It has been proposed that Co atoms are adsorbed on the edges of MoS_2 forming a new so-called "Co–Mo–S" structure [4,10–12]. The HDS activity is supposed to reside in this phase although it is not clear whether the Co atoms modify the neighbouring active Mo sites or are themselves the new active sites. It has been suggested that in the presence of Co, there is an increase in the electron density on the Mo atoms [13] which in turn results in a

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stronger activation of adsorbed thiophene and hence a weakening of the C–S bond [14].

In this paper we report the results of the temperature programmed desorption (TPD) of thiophene over a series of Co–Mo/γ-Al_2O_3 catalysts with varying Co/(Co + Mo) ratio. It was hoped that the study would give information on how the nature and strength of interaction as well as the multiplicity of thiophene adsorption sites varied with change in Co concentration. As part of the study, we have also investigated the desorption of the C_4 hydrocarbons, butane, butene and butadiene over these catalysts.

2. Experimental

Materials. A series of Co–Mo/γ-Al_2O_3 catalysts with varying Co to Co + Mo ratio were prepared by successive pore volume impregnation. In keeping with earlier established procedures [15], the total metal to support ratio was kept at 12% and the catalysts are labelled by the ratio Co/(Co + Mo) normalized to the base 12. The catalysts were sulfided in situ in the TPD reactor prior to the TPD experiments. Thiophene was purified by distilling under dry N_2 and stored over sodium sulfate.

Temperature programmed desorption (TPD). The TPD experiments were done in an inert gas (He) flow reactor with a mass spectrometer as the detector using a modified GC-MSD system, HP5890-5970 (details in ref. [6]). In a typical TPD run 5–10 mg of the catalyst was placed in a thin walled stainless steel tube. The tube occupied the same position as the column in the GC oven and was connected to either a He or H_2 gas cylinder via an injection port using the gas plumbing provided in the GC.

The catalysts were reduced in situ in flowing H_2 at 673 K and sulfided by multiple injections of thiophene (10–15 pulses of 2 µl each). The flow was then switched to He which was used as the carrier gas. For TPD studies of butane, butene and butadiene, 10 µl (STP) of the gas was injected using a gas syringe with the catalyst maintained at 300 K, while for the thiophene experiments 2 µl was injected with the oven temperature at 373 K. For all TPD runs, the heating rate was 10 K/min with the maximum temperature, 673 K. The He flow rate was maintained at 20 ml/min.

The heats of desorption (ΔH_{des}) were obtained by curve fitting the theoretical expression for a first order desorption with readsorption process to the experimental desorption profiles. The theoretical expressions for such a process are [6]

$$-\frac{d\theta}{dT_N} = \left(\frac{\theta}{1-\theta}\right)(1-\theta_m)^2 E_m \exp\left[-E_m\left(1-\frac{1}{T_N}\right)\right] \qquad (1)$$

and

$$C_N = \left(\frac{\theta}{1-\theta}\right)\frac{(1-\theta_m)}{\theta_m}\exp\left[E_m\left(1-\frac{1}{T_N}\right)\right], \tag{2}$$

where θ is the coverage at the given temperature, θ_m is the coverage at the desorption maximum (T_m), $E_m = \Delta H_{des}/RT_m$ and C_N and T_N are the gas phase concentration and temperature normalized with respect to their values at the desorption maximum.

The desorption parameters for the experimental data were determined from the calculated profiles which gave the best "least squares fit". Both ΔH_{des} as well as the initial coverage θ_i, were treated as variables for the fit.

3. Results and discussion

3.1. TPD OF C_4 HYDROCARBONS

3.1.1. Butane

The TPD of butane (fig. 1a) shows a single desorption profile with peak maximum at 345 K. Since butane was poorly adsorbed, the counts were low and hence the estimates for the heat of desorption have a large uncertainty. Nevertheless the best fit was obtained with heat of desorption 13.5 kcal/mol (the fit is the solid line in fig. 1a).

The TPD of butane from sulfidized 3 : 12 Co–Mo/γ-Al_2O_3 catalyst is shown in fig. 1c. Two peaks are observed with T_m at 350 and 396 K respectively. The heats of desorption were obtained by the following deconvolution procedure. The left hand side of the desorption profile was first fitted. The best fit was obtained with the heat of desorption, $\Delta H_{des} = 14.0$ kcal/mol. The calculated profile was then subtracted from the experimental data and a heat of desorption obtained by curve fitting to the residual profile. The best fit for the residual spectra was for a ΔH_{des} of 16.0 kcal/mol. The overall fit (the sum of the two individual profiles, $\Delta H_{des} = 14.0$ and 16.0 kcal/mol) is shown as the solid line in fig. 1c.

A comparison of the TPD profiles of butane from Co–Mo/γ-Al_2O_3 and Mo/γ-Al_2O_3 shows that the incorporation of Co creates a new site for butane adsorption. At the same time the site on the "Mo–S" component of the catalyst is unaffected. This is reflected in the fact that both the peak temperatures as well as the heat of desorption for the first peak in fig. 1c are the same as that for butane desorption from Mo/γ-Al_2O_3 (fig. 1a).

3.1.2. Butene

The desorption profile for 1-butene from Mo/γ-Al_2O_3 catalyst shows a single peak with T_m at 364 K (fig. 1b). The calculated heat of desorption is 14.7 kcal/mol. The TPD of butene from 3 : 12 Co–Mo/γ-Al_2O_3 catalyst (fig. 1d) has two peak maxima, 390 and 487 K, with heats of desorption 17.0 and 29.0 kcal/mol respec-

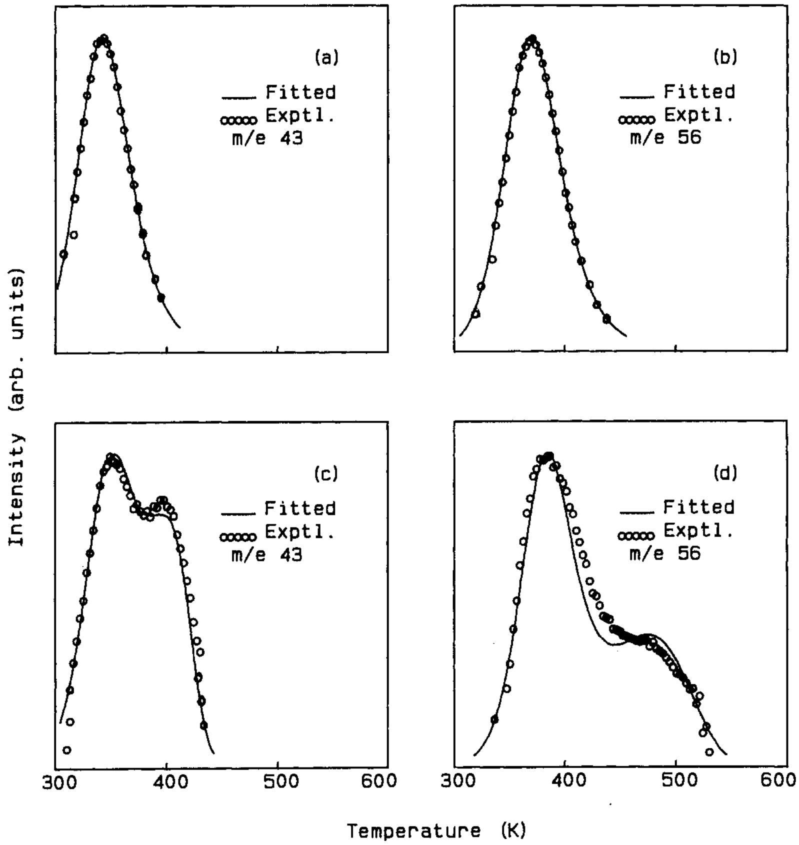

Fig. 1. The experimental and fitted desorption profiles for the TPD of (a) butane (*m/e* 43) and (b) butene (*m/e* 56) from sulfided Mo/γ-Al_2O_3. (c) and (d) are the TPD profiles for butane and butene from 3 : 12 Co–Mo/γ-Al_2O_3 catalyst. For all the profiles $\theta_i = 1$.

tively. Comparison with the desorption profile of 1-butene from Mo/γ-Al_2O_3 (fig. 1b) shows that, as in the case of butane adsorption, the incorporation of Co makes new sites available for adsorption. The position of the first peak in fig. 1d is at a slightly higher temperature compared to that of butene TPD from the 0 : 12 catalyst. Thus, the presence of Co affects the original butene adsorption sites on the "Mo–S" component of the catalyst.

3.1.3. Butadiene

Compared to butane and butene, butadiene is more strongly adsorbed on Mo/γ-Al_2O_3. The TPD profile, fig. 2a, shows a single peak at 368 K with heat of desorption $\Delta H_{des} = 16.0$ kcal/mol.

The thermal desorption of butadiene from 3 : 12 catalyst shows two features (fig. 2b), although the one appearing at higher temperature is not well defined. The

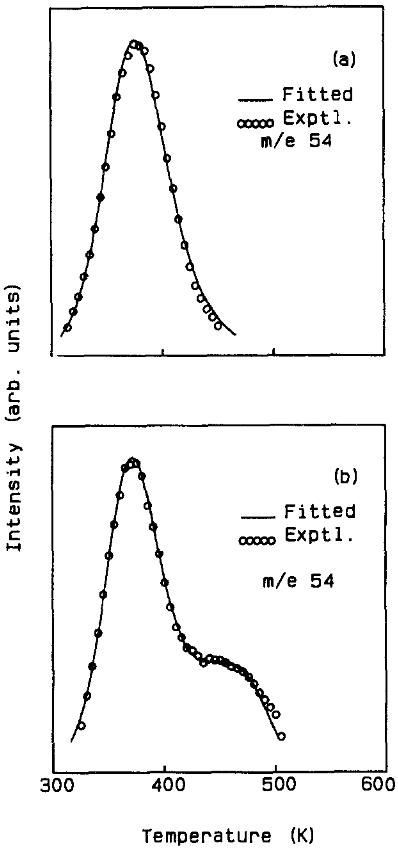

Fig. 2. TPD profiles of butadiene (*m*/*e* 54) from sulfided (a) Mo/γ-Al_2O_3 and (b) Co–Mo/γ-Al_2O_3.

best fit was obtained using two desorption profiles. The first profile has its maximum at 370 K with heat of desorption 15.0 kcal/mol while the second has its maximum at 468 K with a ΔH_{des} of 18.5 kcal/mol. The position and ΔH_{des} for the first peak are comparable to that for butadiene desorption from Mo/γ-Al_2O_3.

The results of the fit for the three adsorbates are summarized in tables 1 and 2. The adsorption of these simple C_4 hydrocarbons on sulfidized Mo/γ-Al_2O_3 shows the anticipated trend. The strength of adsorption, as reflected in T_m and the heats of desorption (table 1), increases with the degree of unsaturation of the hydrocarbon.

Table 1
Kinetic parameters from the TPD of C_4 hydrocarbons from Mo/γ-Al_2O_3

Hydrocarbon	T_m (K)	ΔH_{des} (kcal/mol)
butane	345	13.5
butene	364	14.7
butadiene	368	16.0

Table 2
Kinetic parameters from the TPD of C_4 hydrocarbons from 3 : 12 Co–Mo/γ-Al_2O_3

Hydrocarbon	T_m (K)	ΔH_{des} (kcal/mol)
butane	350	14.0
	396	16.0
butene	390	17.0
	487	29.0
butadiene	370	15.0
	468	18.5

A comparison of the desorption profiles and parameters for all three adsorbates shows that the incorporation of Co makes a new site available for adsorption. At the same time, for butane and butadiene, the site on Mo or rather the "Mo–S" component remains essentially unaffected. In the case of butene, the slight increase in the peak temperature as well as ΔH_{des} show that the original sites are altered by the presence of Co.

3.2. TPD OF THIOPHENE

TPD profiles for thiophene from sulfided Co–Mo/γ-Al_2O_3 are shown in fig. 3. No other species apart from thiophene was detected. This was confirmed by moni-

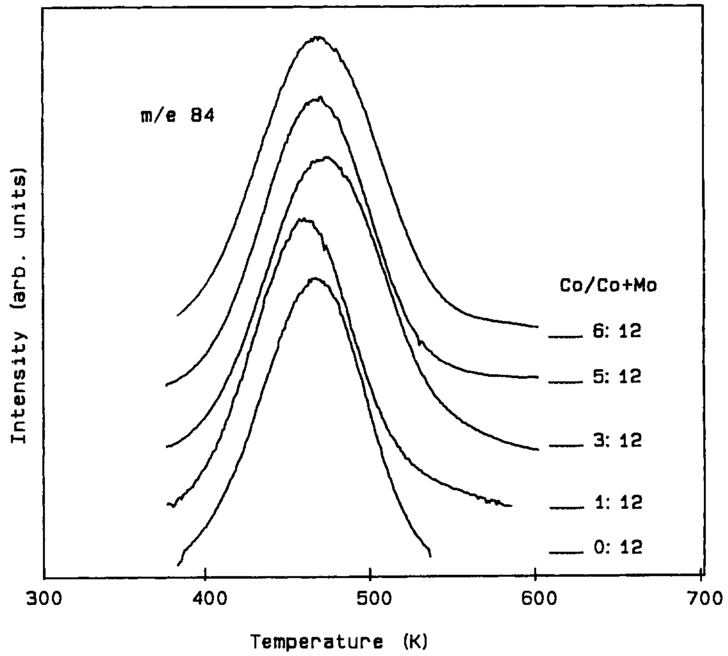

Fig. 3. TPD profiles of thiophene (m/e 84) from Co–Mo/γ-Al_2O_3 catalysts for various Co/(Co + Mo) ratios.

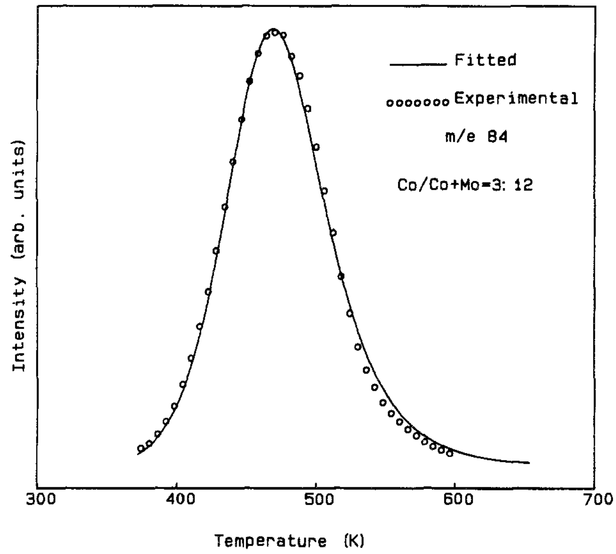

Fig. 4. The experimental and calculated desorption profiles for thiophene desorption from the 3 : 12 sulfided catalyst. The fit was for first order desorption with readsorption with ΔH_{des} of 23.7 kcal/mol.

toring all masses up to m/e 200. The profiles shown in fig. 3 are for m/e 84, the most abundant fragment of thiophene.

The kinetic parameters for the desorption were obtained by curve fitting. A representative fit is shown in fig. 4. The peak temperatures and heats of desorption are summarized in table 3.

It may be seen from fig. 3 and table 3 that neither the desorption profiles nor kinetic parameters change very much with increasing Co content. There is a small shift to higher temperatures and a marginal broadening of the profiles on going from the 0 : 12 to 3 : 12 concentrations. For Co concentrations above 3 : 12, the changes are within experimental error.

This situation is in contrast to the one encountered earlier for the desorption of C_4 hydrocarbons, where it has been observed that the incorporation of Co gave rise to a new adsorption site. In the case of thiophene adsorption, the introduction of

Table 3
Kinetic parameters derived from the TPD of thiophene from Co–Mo/γ-Al_2O_3 catalysts

Co/(Co + Mo) ratio	T_m (K)	ΔH_{des} (kcal/mol)
0 : 12	466	23.4
1 : 12	460	23.4
3 : 12	470	23.7
5 : 12	465	23.5
6 : 12	467	23.4

Co does not create any new site and the original sites which are on the "Mo–S" component of the catalyst, are only marginally modified.

It is known from earlier microscopic studies [4] that introduction of Co changes the morphology of the MoS_2 crystallites to a "rag-like" structure in which there is a large exposure of edge atoms as compared to basal plane atoms. A possible reason for the small shifts and narrowing of the desorption profiles with increasing Co content would be the greater availability of thiophene adsorption sites on the edges of the MoS_2 crystallites with a consequent decrease in the basal plane sites.

The results of the present TPD studies are in agreement with the earlier IR spectroscopic studies of thiophene adsorbed on HDS catalysts [16] which showed that the presence of Co does not cause any major change in the vibrational spectra of the adsorbed molecules. The spectra had been interpreted to show that when Co is present, the π-coordination was preferred over the σ-coordination. The above interpretation could also account for the shift and narrowing of profiles with increasing Co content. The arguments of the last two paragraphs are in no contradiction since it is possible that "edge" and "basal" plane sites prefer different coordination geometries.

In the section 1, it had been mentioned that a possible promotional role of Co was in the "activation" of thiophene molecules by modifying the sites of adsorption. The present TPD results disagree with such a model.

Activation of the thiophene – weakening of the C–S bond – would arise as a consequence of the formation of a chemisorptive bond by the back donation from the surface to the antibonding $2b_1$ MO of thiophene. The stronger the chemisorptive bond, the larger the activation [14]. If the role of Co is indeed a larger activation of the adsorbed thiophene, it should be reflected in a larger heat of desorption of thiophene, from catalysts containing Co as compared to catalysts with no Co. The present TPD results show, however, that the heat of desorption for thiophene is not appreciably affected by the incorporation of Co in the catalyst. This suggests that the promotional role of Co is probably different.

4. Conclusions

The desorptions of butane, butene, butadiene and thiophene have been studied over a series of sulfided Co–Mo/γ-Al_2O_3 catalysts with Co/(Co + Mo) ratio varying from 0 : 12 to 6 : 12. The main conclusions are summarized below.

(1) The TPD of butane, butene and butadiene over catalysts containing no Co showed a single desorption profile with the heat of desorption increasing with the degree of unsaturation of the hydrocarbon. (2) Incorporation of Co creates a new site for the adsorption of hydrocarbons without significantly affecting the original site on the "Mo–S" component of the catalyst. (3) The TPD of thiophene over a series of catalysts with varying Co content showed identical desorption temperatures as well as heats of desorption. It was concluded that thiophene was

adsorbed on the "Mo–S" component of the catalyst and was unaffected by the presence of Co.

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