JOURNAL OF CATALYSIS **86**, 55–66 (1984)

Adsorption and Catalytic Properties of Co–Mo–Al_2O_3 Catalysts and of Their Components in Thiophene Hydrodesulfurization Reaction

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Received August 5, 1982; revised April 26, 1983

The catalytic activities of Co–Mo–Al_2O_3 catalysts and of their components in the thiophene hydrodesulfurization reaction (HDS) were studied by a flow circulation technique. Catalysts in the oxidic form with $CoMoO_4$ as the main phase are shown to possess the highest activity for the thiophene HDS reaction. Adsorption of H_2, thiophene, and of their mixture on sulfided $CoMoO_4$ and technical Co–Mo–Al_2O_3 catalysts was investigated by TPD. H_2 is adsorbed both molecularily and dissociatively on the catalysts studied, while thiophene is molecularily adsorbed. Desorption activation energies for the different H_2 and thiophene forms were measured. The thiophene HDS reaction involves high-temperature forms of adsorbed thiophene, while hydrogenation of unsaturated hydrocarbons (butenes) involves high-temperature forms of adsorbed hydrogen. A scheme of the thiophene HDS reaction on sulfided $CoMoO_4$ and technical Co–Mo–Al_2O_3 catalysts is suggested on the basis of the results obtained.

INTRODUCTION

The thermodesorption technique has been widely used for the study of gas and catalyst surface interaction, since valuable data are obtained on interaction energy, composition, structure of surface forms, and their contribution to catalytic processes (*1*, *2*).

Numerous workers (*3–10*) studied the thiophene HDS reaction on Co–Mo–Al_2O_3 catalysts, for thiophene and its derivatives belong to a sulfur compound type which is least readily removed by HDS of petroleum stocks. But previous studies were carried out either in a flow system without considering diffusive effects (*4*, *5*) or in a pulse mode (*3*). Studies (*11*, *12*) on the thiophene HDS reaction showed that hydrogenation is preceded by C–S bond splitting. Based on the reaction scheme suggested, butadiene is the main intermediate reaction product which hydrogenates to butenes and butane (*13–17*).

The catalytic activities of Co–Mo–Al_2O_3 catalysts were studied by a flow circulation technique; the adsorption of H_2 and of thiophene on sulfided $CoMoO_4$ and technical Co–Mo–Al_2O_3 catalysts by a thermodesorption technique (TPD).

METHODS

Al_2O_3–CoO, Al_2O_3–MoO_3, and Al_2O_3–CoO–MoO_3 catalyst samples were prepared by impregnating γ-Al_2O_3 support with heated solutions of $(NH_4)_6MoO_7O_{24} \cdot 4H_2O$ and $Co(NO_3)_2 \cdot 6H_2O \cdot$ CoO–MoO_3 catalyst was prepared by coprecipitation of $(NH_4)_6Mo_7O_{24}$ and $Co(NO_3)_2$ solutions. Precipitation was carried out at 363°K at pH 6–6.5. The solutions were then evaporated, dried at 423°K and calcined at 873°K for 6 h. The impregnated catalysts were pretreated in the same manner. Before measuring the catalytic activity, the catalysts were presulfurized with H_2–H_2S (20% H_2S) at 673°K for 3–4 h (*18*). An open recirculation system was used to measure the catalytic activity; the measurements were carried out at atmospheric pressure in the temperature range 523–593°K. The rate of formation of C_4 hydrocarbons was taken as a measure of catalytic activity at a constant degree of conversion (a = 50%) at 563°K

0021-9517/84 $3.00

which was obtained by choosing a suitable amount of catalyst Ten percent by volume of thiophene in cyclohexane solution served as a model compound Cyclohexane suffered no conversion in the reaction conditions The mean rates of thiophene conversion were determined by the following equation

$$W_y(W_{z_1}, W_{z_2}) = \frac{q^0_{C_4H_4S}}{100 \quad t \quad S} \qquad y(z_1, z_2), \text{ mol/m}^2 \quad \text{s},$$

where $W_y(W_{z_1}, W_{z_2})$ are the mean rates of conversion of thiophene to n-butane, *trans*-butene, and *cis*-butene, respectively, $y(z_1, z_2)$ denote the degree of conversion of thiophene to n-butane, *trans*-butene, and *cis*-butene, respectively, $q^0_{C_4H_4S}$ is the original amount of thiophene (moles), S is the total surface of the catalyst loaded to the reactor (square meters), t is the time (seconds)

Analysis of reaction products was obtained by a gas chromatographic technique, TCD serving as detector Thiophene analysis was performed with a column (3 m × 3 mm i d) packed with SE-30 on Chromaton at 383°K C_4 hydrocarbon analysis was accomplished with a column (12 m) packed with Al_2O_3, H_2 served as carrier gas

The sample sulfur content was determined by the Schoniger method, titration was carried out by the Wagner technique (*19*) Catalyst sulfidation level was calculated as total conversion of Co and Mo oxidic species to the corresponding Co and Mo sulfides

Thiophene and H_2 adsorption studies were made with a thermodesorption unit whereby the sample was evacuated at 10^{-4}–10^{-5} Torr (1 Torr = 133 3 N/m^{-2}) and chromatographic analysis of the desorption products was performed The carrier-gas rate in all runs was 0 83 ml/s, the temperature being programmed from 293 to 873°K (0 225°K/s) The maximum temperature, to which the catalyst samples were exposed, did not exceed 873°K in order to preclude undesirable phase conversions and caking of catalyst samples

For adsorption measurements, a catalyst sample was placed in a quartz reactor and evacuated at 873°K to 10^{-4}–10^{-5} Torr After the reactor was cooled to the adsorption temperature (T_{ads}), H_2 or thiophene was admitted into the unit, and adsorption was continued for 1 h, here after the gas phase was pumped at T_{ads}, the catalyst sample was cooled approximately to 293°K, and the carrier gas Ar was admitted into the unit On stabilization of the operational parameters, the temperature-programmed heating of the sample was initiated, a TPD curve was obtained and desorption products were analyzed Adsorption of H_2, thiophene, and of their mixture was carried out at 298, 373, 473, and 573°K Kinetic parameters were determined based on the desorption rate as a function of temperature at a constant heating rate (calculation was made employing one TPD curve) (*20*)

Desorption activation energies for different forms of H_2 and thiophene were determined by the Polyani-Wigner equation (*21*)

$$-\frac{dQ_s}{d\tau} = \nu Q_s^n \exp(-E/RT),$$

where Q denotes the fractional amount of gas adsorbed on the catalyst surface, τ, time, ν, frequency factor, n, desorption order, E, desorption activation energy Approximate integration of this equation gives the following relationship for the desorption process at linear temperature increase with constant rate β

$$\text{first order} \quad \ln\frac{\ln(Q_{so}/Q_s)}{T^2} = \ln \nu R/\beta E - E/RT,$$

$$\text{second order} \quad \ln\frac{1/Q_s - 1/Q_{so}}{T^2} = \ln \nu R/\beta E - E/RT$$

RESULTS AND DISCUSSION

Catalytic Activity of Co–Mo–Al_2O_3 Catalysts

A study was made of 12 Co–Mo–Al_2O_3 catalyst samples of different composition,

TABLE 1

Catalytic Properties of Co–Mo–Al_2O_3 Catalysts and of Their Components in Thiophene HDS Reaction

	Catalyst	S, (m^2/g)		Sulfidation level (%)	W × 10^7 mol/m^2 s (563°K)				Selectivity at 563°K, %		
		Before the reaction	After the reaction		C_4H_{10}	C_4H_8		Total	C_4H_{10}	*trans*-C_4H_8	*cis*-C_4H_8
						trans	*cis*				
	Al_2O_3	188	175	—	—	—	—	—	—	—	—
1	CoO (Co_3O_4)	4 3	4 4	9 31	0 196	1 672	0 810	2 678	7 32	62 43	30 25
2	MoO_3	4 5	6 3	10 57	1 560	2 180	1 110	4 850	32 16	44 95	22 89
3	Al_2O_3 MoO_3 = 1 1	43	38	19 91	0 459	0 500	0 201	1 160	39 57	43 10	17 33
4	Al_2O_3 CoO = 1 1	79	80	55 44	0 183	0 402	0 193	0 779	23 49	51 60	24 90
5	CoO MoO_3 = 1 1	6 0	6 1	24 00	0 560	5 420	2 530	8 510	6 58	63 69	29 73
6	Al_2O_3 CoO MoO_3 = 1 1 1	10 3	7 0	69 30	1 420	12 728	6 237	20 385	6 97	62 44	30 59
7	Al_2O_3 CoO MoO_3 = 2 1 1	70	67	68 77	0 538	3 538	1 616	5 722	9 40	62 36	28 24
8	80% Al_2O_3 + 20% (CoO MoO_3 = 2 1)	134	115	71 94	0 331	1 813	0 864	3 008	11 0	60 27	28 73
9	80% Al_2O_3 + 20% (CoO MoO_3 = 1 1)	130	106	81 78	0 424	2 731	1 262	4 417	9 60	61 83	28 57
10	80% Al_2O_3 + 20% (CoO MoO_3 = 1 2)	140	123	54 65	0 360	0 020	0 950	3 330	10 81	60 66	28 53
11	Al_2O_3–CoO–MoO_3 (technical)	145	138	62 54	0 334	1 640	0 727	2 701	12 36	60 70	26 94

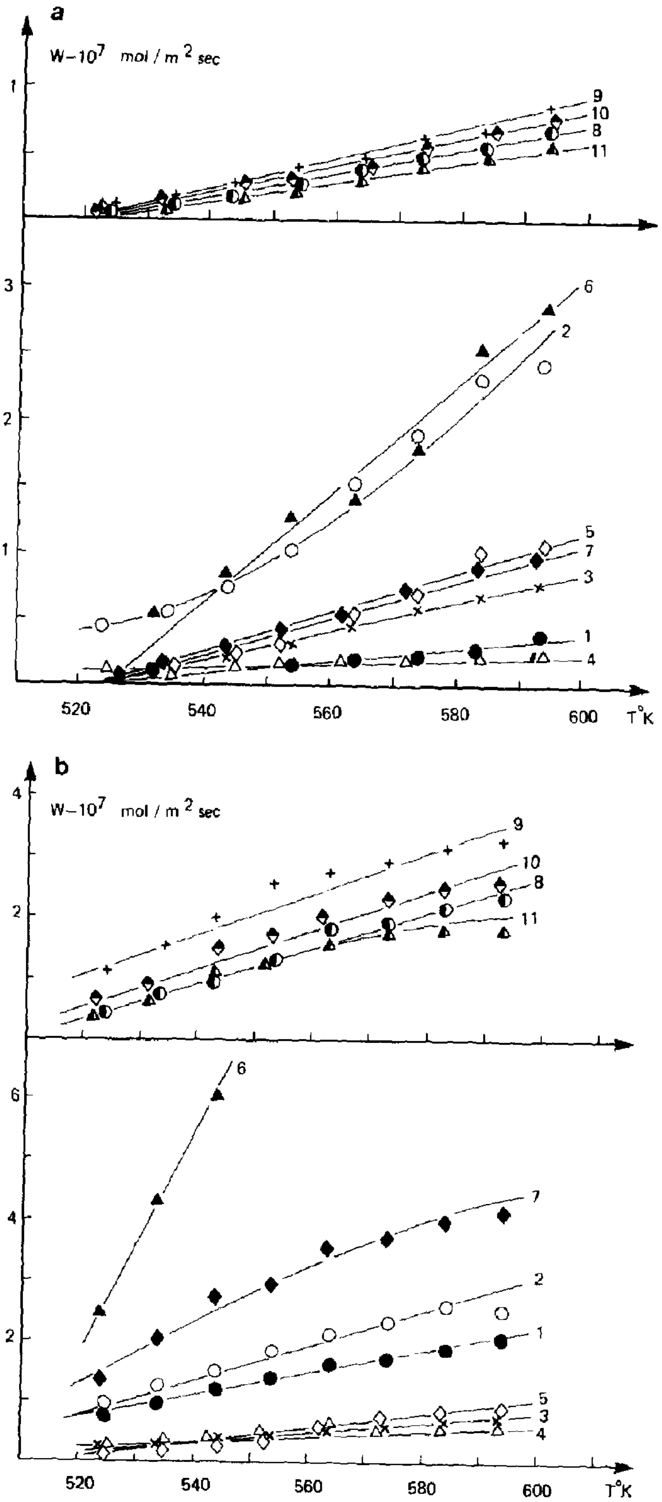


FIG 1 n-Butane (a), *trans*-butene (b), and *cis*-butene (c) formation rate and total rate of thiophene HDS reaction (d) on Co–Mo–Al_2O_3 catalysts as a function of temperature (curve indexes correspond to those of the samples in the table)

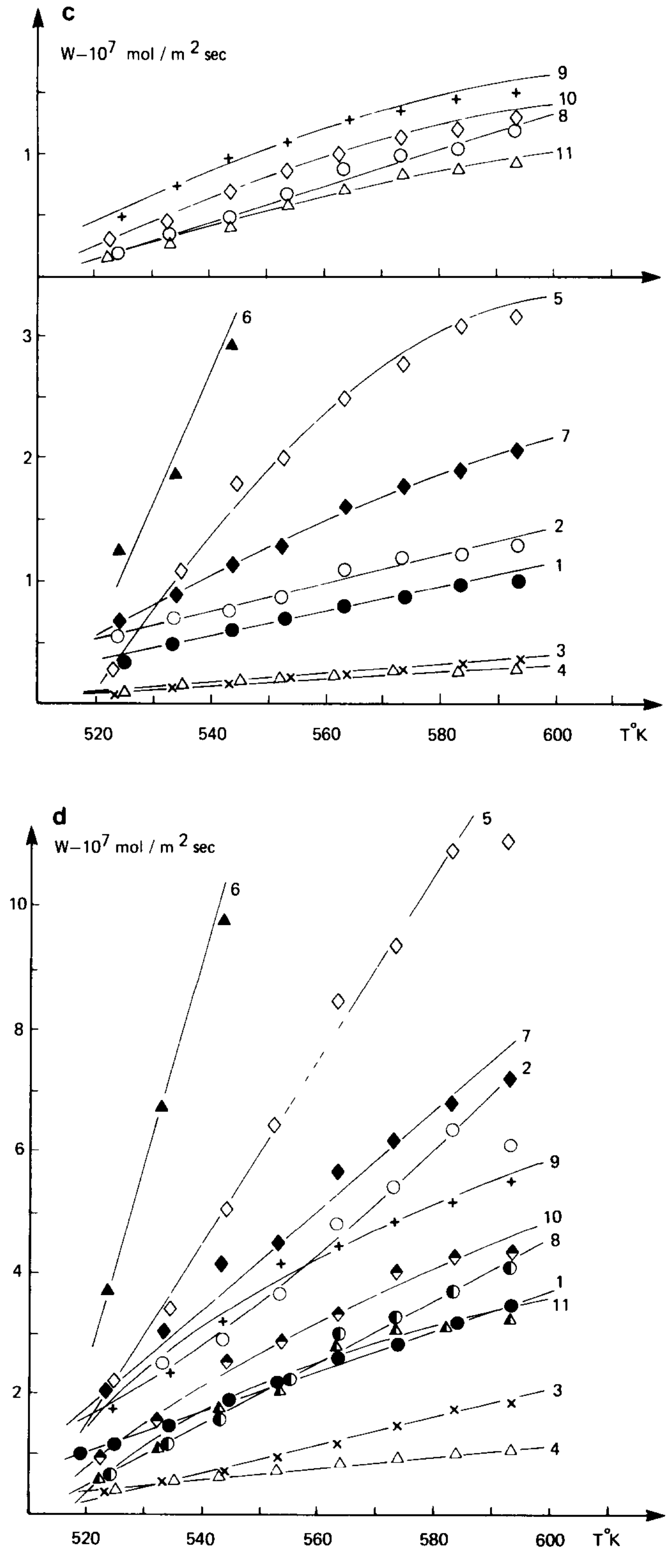


FIG 1—*Continued*

including individual Co, Mo, and Al oxides The main characteristics of Co–Mo–Al_2O_3 catalyst activity are presented in Table 1 n-Butane, *trans*- and *cis*-butenes were found among the thiophene HDS reaction products C_1–C_3 hydrocarbons appeared among the reaction products if the reaction was carried out above 623°K

Different periods of time were found to be required for the catalysts to achieve a steady state in the thiophene HDS reaction, particularly long periods (15–20 h) were necessary for individual Co and Mo oxides Short periods of time (2 to 3 h) were required for binary catalysts to achieve a steady state and still shorter periods—for Co–Mo–Al_2O_3 catalysts Initial activity of individual Co and Mo oxides was considerably higher than at steady state, while binary and Co–Mo–Al_2O_3 catalysts demonstrated an insignificant decrease in HDS activity with time

Among individual oxides, MoO_3 showed the highest activity for the thiophene HDS reaction (see Table 1 and Fig 1d), MoO_3 catalyst activity was nearly twice as large as that of Co oxide After the reaction the same samples contained considerably less sulfur than was necessary for Co and Mo oxides full conversion to the corresponding sulfides Physical and chemical analysis data (ir spectroscopy, thermal and X-ray phase analysis) showed the presence of Co and Mo sulfides, MoO_2 as well as metallic Co (*22*)

No significant change was observed in the thiophene HDS rate in the presence of equimolar amounts of Co and Mo supported on Al_2O_3 as compared to individual oxides (see samples 3 and 4 in Table 1) At the same time, the said catalyst samples (Co-containing in particular) demonstrated an increase in their sulfidation level Among binary catalysts, sample 5, whose original unsulfided form is $CoMoO_4$, showed the greatest activity (see Fig 1d) (*23*) In the presence of this catalyst, the HDS reaction rate was considerably greater than in the presence of individual Co and Mo oxides (8 51 × 10^{-7} mol/m^2 s at 563°K), it did not correspond to the sum of conversions for the components Such an increase in the HDS reaction rate cannot apparently be explained by the increase alone in the amount of sulfide species, since their concentration only slightly exceeds the total concentration of individual compounds It is reasonable to suggest that in the HDS reaction $CoMoO_4$ forms a compound whose activity is considerably greater than that of CO and Mo sulfides This compound might be $CoMoO_xS_y$ which makes the main contribution to the thiophene HDS process

If $CoMoO_4$ is supported on Al_2O_3, its reduction in the thiophene HDS reaction proceeds less readily, which should result in oxisulfide level growth As can be seen from Table 1 and Fig 1d, catalyst sample 6 does show a considerable increase in HDS activity, the thiophene HDS reaction rate is 20 385 × 10^{-7} mol/m^2 s The sulfidation level of this sample is considerably greater than that of $CoMoO_4$

Reported data (*24*) suggest that Mo^{3+} ions located at MoS_2 crystallite edges are responsible for the HDS reaction Incorporation of Co^{2+} ions into MoS_2 crystallites results in concentration growth of such active sites According to data (*14*), interaction between MoS_2 and Co_9S_8 in sulfided catalysts is promoted by Al_2O_3 support, the latter also displaying a considerable synergetic effect Physical and chemical analysis data permit the suggestion that the principal components exist on Al_2O_3 support surface in the form of microcrystallites or clusters, $Al_2(MoO_4)_3$ being a nucleus surrounded by $CoMoO_4$ and MoO_3 (*22*) On the basis of the results obtained, it seems valid to conclude that the active components of CoMo–Al_2O_3 catalysts are represented by oxisulfide compounds formed by $CoMoO_4$ in the HDS process Al_2O_3 support acts as stabilizer for these sulfided compounds, while Co is involved in the formation of $CoMoO_4$ whose activity is considerably higher than that of MoO_3 (*25*)

To verify this suggestion, a study was made of several catalyst samples of a composition similar to that of technical Co–Mo–Al_2O_3 catalysts with respect to the total concentrations of Co and Mo oxides but with varying CoO MoO_3 ratios (see Table 1, samples 8–10) Among these samples, the highest catalytic activity was shown by sample 9 (CoO MoO_3 = 1 1) Samples 8, 10, and 11 and Co–Mo–Al_2O_3 technical catalyst sample (all of them containing excess of CoO or MoO_3) demonstrated a lower catalytic activity (see Fig 1d)

Special reference should be made to the highly selectivity for n-butane of MoO_3, Al_2O_3 MoO_3 = 1 1 and CoO–Al_2O_3 catalyst samples (Fig 1a) a close similarity is observed among all the other catalyst samples as regards their activity for n-butane, *trans*- and *cis*-butenes, their selectivity for butenes is high and that for n-butane is low (Figs 1a–c)

It should be noted that neither butadiene nor 1-butene were found among reaction productions A study (*14*) was made of the thiophene HDS reaction on Co–Mo–Al_2O_3 catalyst samples at low conversions (a = 0 5%), butadiene and 1-butene content in reaction products was shown to decrease rapidly with conversion level growth ($a \geq$ 1%) No butadiene was found when the thiophene HDS reaction was carried out on Cr catalysts at high hydrogen thiophene ratios (*11*)

Hydrogen Thermodesorption

Hydrogen TPD curves obtained in a flow of Ar show several peaks representing various forms of adsorbed H_2 (Figs 2 and 3) Adsorption of H_2 in sulfided $CoMoO_4$ catalyst occurs in five forms (Fig 2) At T_{ads} of 298°K H_2 adsorption occurs only in three forms, form I appears on TPD curves in the range of 323–873°K at the temperature of peak maximum (T_{max}) of 443°K, form II appears in the range of 523–873°K at T_{max} of 823°K, form III appears in an isothermal desorption mode at 873°K As T_{ads} rises to 373°K, the amount of H_2 adsorbed in form III decreases, and form IV appears, T_{max} of the latter being observed at 803°K Form V of adsorbed H_2 appears at $T_{ads} \geq$ 473°K, T_{max} of form V is shifted to the high-temperature region due to an increase of T_{ads}

Chromatographic analysis of desorption products showed that forms I, II, IV, and V contain only H_2, while form III contains also H_2S The desorption activation energies for the various forms of H_2 are as follows (kJ/mol) 25 1 (form I), 36 0 (form II), 33 5 (form IV), 35 6 and 41 8 at T_{ads} of 473 and 573°K, respectively (form V) (*26*)

As is seen in Fig 2, the location of T_{max} of form I is not affected by the change in the temperature of H_2 adsorption The first order of desorption observed suggests that H_2 of form I is adsorbed in a molecular state For the other high-temperature forms of adsorbed H_2, changes in T_{ads} result in shifting of T_{max}, the second order of desorption observed suggests that H_2 is adsorbed in an atomic state in these forms The presence of H_2S in the desorption products of high-temperature form III can probably be attributed to the fact that H_2 of form III is adsorbed on S atoms of the catalyst, which results in the formation of H–S groups desorbing as H_2S

Hydrogen adsorption on sulfided Co–Mo–Al_2O_3 catalysts occurs in four forms

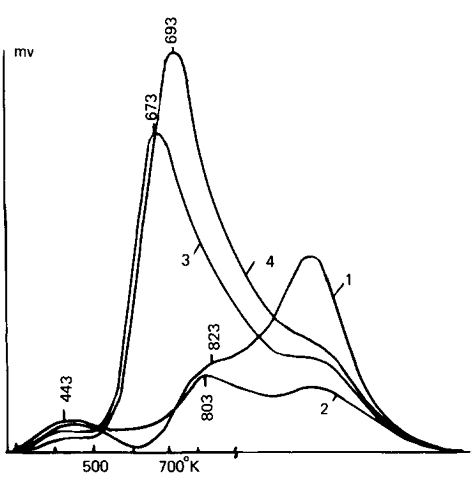


FIG 2 TD curves of hydrogen adsorbed on sulfided $CoMoO_4$ catalyst at 298 (1), 373 (2), 473 (3), and 573°K (4)

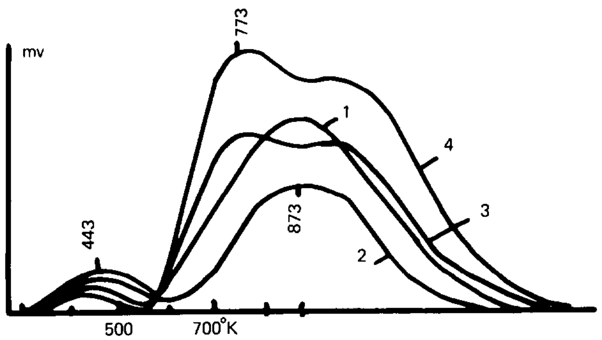


FIG 3 TD curves of hydrogen adsorbed on Co–Mo–Al_2O_3 catalyst at 298 (1), 373 (2), 473 (3), and 573°K (4)

(Fig 3) At T_{ads} of 298 and 373°K H_2 adsorption occurs only in two forms, form I appears on TPD curves in the range of 323–523°K at T_{max} of 443°K and form II—in the range of 573–873°K

At $T_{ads} \geq$ 473°K form II disappears and hydrogen TPD curves show two new forms form III (T_{max} of 773°K) and form IV, desorption of H_2 in the latter occurring in an isothermal desorption mode at 873°K

High-temperature trailing edge, appearing on TPD curves in an isothermal desorption mode, may be due to the presence within this form of states characterized by higher values of desorption activation energy or by H_2 dissolution in the catalyst on heating

Calculated activation energies for H_2 desorption are as follows (kJ/mol) 34 7 (form I) and 83 3 (form II, see Table 2) Attempts at calculating activation energies for forms III and IV of H_2 desorption proved unsuccessful due to poor peak resolution The desorption products of form IV were found to contain H_2S, all the other forms containing only H_2

Thiophene adsorption occurs on sulfided $CoMoO_4$ catalyst in four forms (Fig 4) At T_{ads} of 298°K thiophene adsorption occurs only in three forms at T_{max} of 443°K (form I) and 683°K (form II), form III appearing in TPD curves in an isothermal desorption mode at 873°K As T_{ads} rises to 573°K, the amount of thiophene adsorbed in form I decreases and that in form II increases, then the amount of thiophene adsorbed in form II is observed to drop, and at $T_{ads} \geq$ 473°K form IV appears on TPD curves with T_{max} of 723°K As is seen from Fig 4, the change in the degree of catalyst surface coverage by adsorbed thiophene causes no change in T_{max} This result is in favor of thiophene being adsorbed molecularily in all the forms (*2*) Desorption products of these forms were found to contain thiophene, n-butane and butenes, as was reported elsewhere

TABLE 2

Desorption Activation Energies for the Various Forms of Adsorbed Hydrogen

Catalyst	E_a (kJ/mol)				
	Form I	Form II	Form III	Form IV	Form V
CoO MoO_3 = 1 1	25 1 T_{max} = 443°K T_{ads} = 298°K	36 0 T_{max} = 823°K T_{ads} = 298°K	—	33 5 T_{max} = 803°K T_{ads} = 298°K	35 6 T_{max} = 673°K T_{ads} = 473°K
CoO–MoO_3–Al_2O_3	34 7 T_{max} = 443°K T_{ads} = 298°K	83 3 T_{max} = 773°K T_{ads} = 298°K	—	—	41 8 T_{max} = 693°K T_{ads} = 573°K

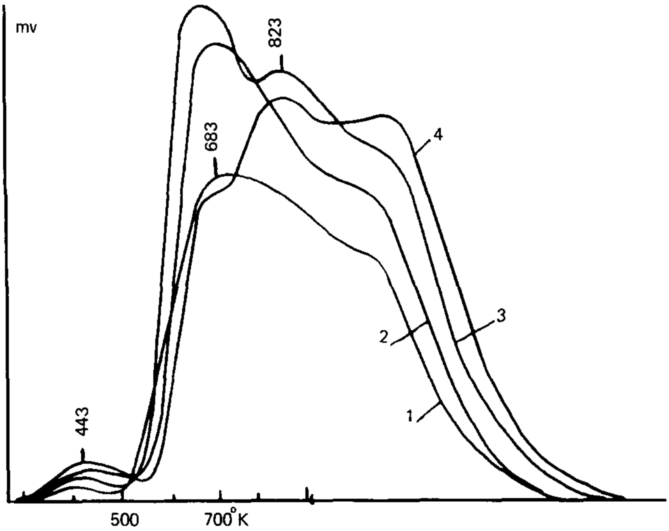


FIG 4 TD curves of thiophene adsorbed on CoMoO$_4$ catalyst at 298 (1), 373 (2), 473 (3), and 573°K (4)

(*17*) As T_{ads} rises from 298 to 573°K, the activation energy value for form I of thiophene desorption changes from 20 9 to 28 0 kJ/mol Attempts at calculating desorption activation energies for the other forms of adsorbed thiophene proved unsuccessful due to their almost complete overlapping on TPD curves

Thiophene adsorption on sulfided Co–Mo–Al$_2$O$_3$ catalyst occurs in two forms (Fig 5) Form I of thiophene adsorption appears on TPD curves in the range of 323–473°K at T_{max} of 423°K, form II in the range of 523–873°K at T_{max} of 753°K and at thiophene T_{ads} of 298°K From these results, T_{max} values are concluded to be independent of the degree of catalyst surface coverage The first order desorption observed shows that thiophene adsorption on the sample surface occurs in a molecular form As T_{ads} increases, thiophene desorption activation energies increase from 18 0 to 27 6

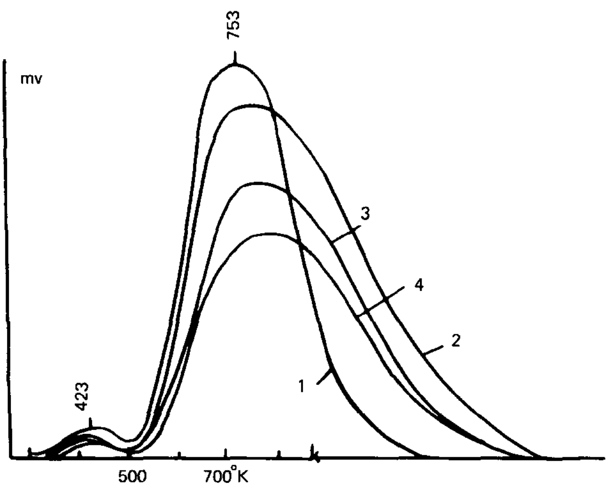


FIG 5 TD curves of thiophene adsorbed on Co–Mo–Al$_2$O$_3$ catalyst at 298 (1), 373 (2), 473 (3), and 573°K (4)

kJ/mol for high-temperature form II (Table 3)

Thiophene Thermodesorption from the Catalyst Surface Pretreated with Hydrogen

To determine the contribution of the various forms of adsorbed H_2 to the thiophene HDS, thiophene adsorption was carried out, employing a catalyst pretreated with H_2 at T_{ads} of 473 or 573°K Figure 6 demonstrates a considerable dissimilarity existing between thiophene TPD curves with H_2 preadsorption on sulfided $CoMoO_4$ catalyst and TPD curves of thiophene and H_2 Four forms of thiophene thermodesorption with H_2 preadsorption on $CoMoO_4$ catalyst are observed at T_{ads} of 473°K and T_{max} of 423, 623, and 793°K for forms I, II, and III, respectively, form IV appearing on TPD curves in an isothermal desorption mode at 873°K Chromatographic analysis of desorption products showed that low-temperature form I contains H_2 and thiophene, form II—mainly butenes and form III—butane High-temperature form IV contains considerable amounts of H_2S As T_{ads} increases from 473 to 573°K, amounts of thiophene adsorbed in these forms (form III in particular) are observed to increase on TPD curves (Fig 6)

Three forms are observed on thiophene TPD curves with H_2 preadsorption on technical $Co–Mo–Al_2O_3$ catalyst (Fig 7) with T_{max} of 423 and 693°K for forms I and II, respectively, form III appearing in an isothermal desorption mode at 873°K Analysis of the various forms by chromatographic techniques showed that low-temperature form I contained only H_2 and thiophene, while forms II and III contained thiophene hydrogenolysis products The presence of butenes in forms II and III can be accounted for by the interaction of

TABLE 3

Desorption Activation Energies for the Various Forms of Adsorbed Thiophene

Catalyst	E_a (kJ/mol)		
	Form I	Form II	Form III
$CoO\ MoO_3 = 1\ 1$	20 9 $T_{max} = 443°K$ $T_{ads} = 298°K$	—	—
	28 0 $T_{max} = 443°K$ $T_{ads} = 573°K$		
$CoO–MoO_3–Al_2O_3$	18 0 $T_{max} = 423°K$ $T_{ads} = 298°K$	30 5 $T_{max} = 753°K$ $T_{ads} = 423°K$	
	27 6 $T_{max} = 423°K$ $T_{ads} = 573°K$	41 8 $T_{max} = 753°K$ $T_{ads} = 573°K$	

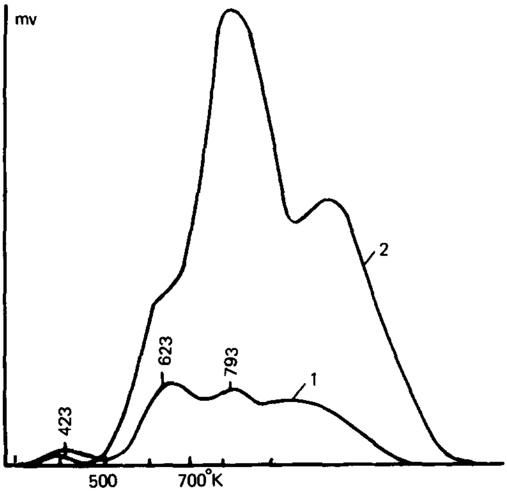


FIG 6 TD curves of thiophene with preadsorption of hydrogen, adsorbed on $CoMoO_4$ catalyst at 473 (1) and 573°K (2)

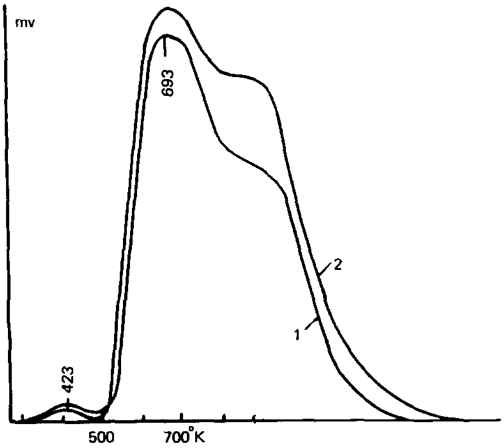


FIG 7 TD curves of thiophene with preadsorption of hydrogen, adsorbed on $Co–Mo–Al_2O_3$ catalyst at 473 (1) and 573°K (2)

thiophene and H_2 adsorbed on the catalyst, which results in the formation of butenes, capable of adsorption on the sample surface alongside the original thiophene and H_2

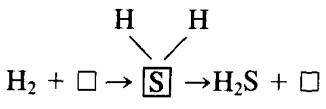
Thus H_2 adsorption on the catalysts studied can occur in three forms a molecular one which desorbs from the catalyst surface in the temperature range of 323–523°K and an atomic one which desorbs in the temperature range of 573–823°K Hydrogen, desorbing from the catalyst surface in an isothermal desorption mode at 873°K, appears to be adsorbed on S atoms of the catalyst, which may result in the formation of H–S groups, the latter being capable of forming H_2S on desorption Desorption of the said forms of H_2, adsorbed on $CoMoO_4$ catalyst at higher temperatures, occurs in the same temperature range as for the technical Co–Mo–Al_2O_3 catalyst It suggests similar energy characteristics of H_2 adsorbed on various catalysts This fact also suggests that compounds of close chemical composition are formed on the catalyst surface in the genesis process

Thiophene adsorption on sulfided $CoMoO_4$ and technical Co–Mo–Al_2O_3 catalysts occurs in a molecular form The main contribution to thiophene adsorption on these catalysts is made by high-temperature forms, thiophene adsorption on $CoMoO_4$ catalyst occurs in three forms, while that on Co–Mo–Al_2O_3 catalyst—in only one form different from the latter three The existence of the various forms of thiophene adsorption on the sulfided $CoMoO_4$ catalyst can apparently be attributed to the fact that this catalyst is a multiphase system Clusters of active components on technical Co–Mo–Al_2O_3 catalyst surface form a kind of common adsorption sites on which thiophene adsorption occurs, as a consequence, only one high-temperature form of thiohene adsorption is observed on this catalyst Comparison of thermodesorption data, obtained on adsorption of H_2, thiophene and of their mixture, allows to determine in what way they affect each other while adsorbing on the catalysts studied Simultaneous adsorption of H_2 and thiophene affects the thiophene HDS The results obtained suggest that the thiophene HDS involves high-temperature forms of thiphene which give desorption spectra with peaks at T_{max} of 683 and 823°K for $CoMoO_4$ catalyst (Fig 4) and 753°K for Co–Mo–Al_2O_3 catalyst (Fig 5) Hydrogenation of unsaturated compounds (butenes), formed in the thiophene HDS reaction, involves forms of adsorbed H_2 with T_{max} of 673°K for $CoMoO_4$ catalyst (Fig 2) and 773°K for Co–Mo–Al_2O_3 catalyst (Fig 3) The high-temperature form of H_2, desorbing in and isothermal desorption mode at 873°K, is responsible for H_2S formation

The thiophene HDS reaction mechanism on MoO_3–Al_2O_3 catalyst was studied in greater detail (*13*), H_2 adsorption on O atoms of MoO_3–Al_2O_3 catalyst was shown to be the first stage at which OH groups and anion vacancies are formed Thiophene adsorbs on these sites to form Mo–S bond, then the first and the second H atoms of OH groups migrate toward the adsorbed thiophene molecule to cause C–S bond scission Desorption of butadiene followed by hydrogenation occurs at the same or other sites

The thiophene HDS scheme described above was suggested for oxidic MoO_3–Al_2O_3 catalyst Under HDS reaction conditions, the catalyst is sulfided and reduced to give Mo sulfide and various reduced forms (*22*) OH groups are unlikely to exist on the catalyst surface under reaction conditions or else their concentration may be too low for them to play the leading role in the thiophene HDS reaction

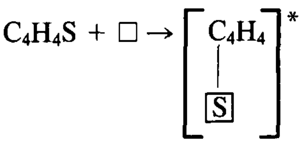
Analysis of the data obtained suggests the following scheme of the thiophene HDS reaction



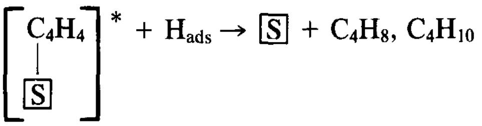
$$(1)\ H_2 + \square \rightarrow \overset{H\ \ \ H}{\overset{\diagdown\ \diagup}{\boxed{S}}} \rightarrow H_2S + \square$$

Hydrogen adsorbs rather strongly on sulfided $CoMoO_4$ and Co–Mo–Al_2O_3 catalysts

This suggests direct participation of H_2 in the catalytic process

(2)


$$C_4H_4S + \square \rightarrow \left[\begin{array}{c} C_4H_4 \\ | \\ \boxed{S} \end{array}\right]^*$$

(3)


$$\left[\begin{array}{c} C_4H_4 \\ | \\ \boxed{S} \end{array}\right]^* + H_{ads} \rightarrow \boxed{S} + C_4H_8, C_4H_{10}$$

where $\boxed{S}$ is the catalytic S ion and $\square$ a free vacancy In the presence of Al_2O_3 support, H_2 more readily interacts with thiophene on the surface of the sulfided Co–Mo–Al_2O_3 catalyst, which results in lower desorption temperatures of peaks containing thiophene HDS reaction products

ACKNOWLEDGMENTS

The authors thank Kamyanov V F for a helpful discussion

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