JOURNAL OF CATALYSIS 15, 179–189 (1969)

The $CoO–MoO_3–Al_2O_3$ Catalyst

III. Catalytic Properties

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Received February 11, 1969; revised April 8, 1969

With the help of a microreactor pulse technique under chromatographic conditions, the catalytic properties of the hydrodesulfurization catalyst cobalt molybdate on alumina were investigated. Attention was given to the effect of poisoning substances. The catalyst is fully activated by reduction. Sulfidation of the catalyst does not increase its activity. A model is proposed in which thiophene is adsorbed on an anion vacancy and becomes attached with its sulfur atom to a molybdenum atom. The C–S bonds are broken by a transfer of hydrogen atoms from adjacent hydroxyl (or SH) groups. Above 220–280°C butene is hydrogenated from OH groups, but below 220–280°C it reacts directly with a H_2 molecule from the gas phase. The role of the cobalt in the catalyst remains obscure from these experiments.

INTRODUCTION

The present paper deals with a part of an investigation (*1*) concerning the structure and the catalytic properties of the hydrodesulfurization catalyst cobalt molybdate on alumina. In two former papers (*2,3*) we reported the investigation of the structure of the catalyst; it consisted of $CoAl_2O_4$ distributed throughout the bulk of the carrier alumina, and MoO_3 spread out over the alumina surface, possibly as a monomolecular layer. We shall now consider its catalytic properties. The first topic to be studied concerns activation of the catalyst. The results lead to a model for the activated catalyst which also involves proposals for the active sites. We shall in particular be interested in the hydrodesulfurization of thiophene as a representative of the most abundant class of sulfur-containing compounds. An important question in this respect is whether desulfurization and hydrogenation occur simultaneously or in separate steps. Special attention was paid to adsorption and poisoning phenomena. An attempt was made to construct a reaction mechanism based on our conclusions concerning the structure of the catalyst that explained the most important kinetic features of the reaction.

One of the first proposals for the reaction mechanism of the thiophene desulfurization was given by Griffith *et al.* (*4*). This involved two-point adsorption of thiophene. Nicholson (*5,6*), on the other hand, concluded from infrared measurements that thiophene was adsorbed on the catalyst in a four-point or flat form, i.e., the molecule is lying flat on the surface with the four carbon atoms attached to it. We discuss Nicholson's spectra in detail below and arrive at a different conclusion. Hammar (*7*) concluded from his experiments that the hydrodesulfurization of thiophene and the hydrogenation of olefins occur on different kinds of surface sites. Kirsch *et al.* (*8, 9*) considered the sulfided cobalt molybdena catalysts as exhibiting an acid type of hydrogenation activity. Hendricks *et al.* (*10*) and Blue and Spurlock (*11*) mentioned that the catalyst was not fully active until the oxides were converted to sulfides. Mann (*12*), however, activated the catalyst in a hydrogen stream at 500°C. Owens and Amberg (*13*) stated that the thiophene adsorption was inhibited by hydrogen. They concluded that the

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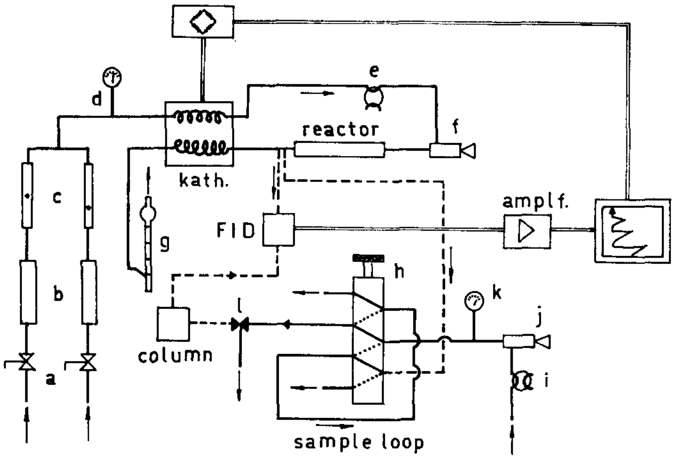

FIG. 1. Diagram of the apparatus.

primary products of the hydrodesulfurization were butadiene—although it was not found in the reaction products—and H_2S, and that C–S bond cleavage was the first step in the reaction, rather than hydrogenation of the ring. By working at very low conversion levels, Kolboe and Amberg (*14*) established that 1,3-butadiene is indeed a reaction product over cobalt moly; H_2S was supposed to inhibit the reaction. A comprehensive survey of the literature up to 1967 has been given by Mitchell (*15*). It is somewhat difficult to form a clear notion of the catalytic reaction, since many of the authors favor contradictory opinions. Therefore, it is necessary to obtain more information.

EXPERIMENTAL PROCEDURES

A microreactor pulse technique was used. The experiments were carried out at atmospheric pressure and from room temperature up to 500°C. A diagram of the apparatus is given in Fig. 1. Both H_2 and Ar could be introduced into the reactor; (a) are pressure regulators. The gases were purified in (b) with successively BTS catalyst and molecular sieves. After passing the flowmeters (c) and a manometer (d) they went to the reference channel of the katharometer (Becker). Next they passed the injection valve (e) and water cooled injection port (f) for the introduction of substances like butene and thiophene. The reactor consisted of a 1-m long stainless steel tube with an inner diameter of 2 mm and an outer diameter of 3 mm, which was "spiralized" after being filled with catalyst. The dimensions of the spiral were finally a length of about 10 cm and a diameter of about 3 cm. An electrically heated small oven was placed around the reactor. The reaction was thus carried out under chromatographic conditions, enabling adsorption phenomena to be measured. The adsorption isotherm for a certain compound can be obtained from the elution curve of that compound (*16*, *17*) [for a more detailed description see (*1*)]. To this end, 0.5% of the stream leaving the reactor went through a copper nickel capillary tube with an inner diameter of 0.25 mm directly to a flame ionization detector (FID) where the concentration profile of a pulse leaving the reactor was measured. The main stream went to the measuring channel of the katharometer and a soap film flowmeter (g).

For the analysis of the reaction products from a pulse another 0.5% of the reactor stream was led via a second capillary tube to a sample loop of 5 cm^3. After the whole pulse had left the reactor, the contents of the loop were introduced with the help of a MicroTek seven-port valve (h) into a capillary column. To reach sufficiently short injection times, a splitter (l) was used, so that only 0.25% of the carrier gas and sample entered the column. The column consisted of a 50-m long copper nickel tube with an inner diameter of 0.25 mm. It was coated with 1-octadecene. Argon was used as carrier gas. It first passed an injection valve (i) and a port (j) for introducing compounds for calibration. The pressure was 0.7 atm at (k) and the temperature of the column was held at 20°C. All parts after the reactor, with the exception of g, i, j, k and the column, were placed in an air bath held at 110°C to prevent condensation of substances in the tubes.

The following chemicals were used: catalyst (Ketjenfine) 4% CoO and 12% MoO_3 on γ alumina, sieve fraction 0.20–0.25 mm; thiophene (Merck "for synthesis"); pyridine (Merck "for chromatography"); hydrogen (Loosco 99.9% pure according to the manufacturer); helium (Loosco 99.995% pure); argon (Loosco 99.997% pure); hydrogen sulfide (Matheson "C.P."); C_1–C_4 hydrocarbons (Phillips "research grade"); BTS catalyst (BASF) activated at 150°C in H_2; and molecular sieves (Varian VacSorb) activated at 200°C.

RESULTS

Activation and Reduction of the Catalyst

The catalyst is inactive in the form as it is manufactured. To get an insight into the activation the following experiment was carried out. The reactor was filled with 0.1 g of Ketjenfine. Argon was then passed over it at a flow rate of 50 cm³ min⁻¹ NTP, while the temperature was gradually raised to 420°C. The signal, first given by the katharometer, disappeared after 2 hr indicating that no more compounds, e.g., water, desorbed from the catalyst. The argon was thereupon replaced at a certain time $t = 0$ by a hydrogen stream of 50 cm^3 min^{-1} NTP. Thiophene pulses of 1 μl were then given at various times and the reaction products analyzed. Only thiophene, butenes, and butanes were found, H_2S remaining undetected, while the quantities of other compounds were negligibly small. About 5% of the first pulse was not recovered. The subsequent pulses were completely recovered. A plot of the thiophene conversion and the produced quantities of butanes and butenes is given in Fig. 2. One can see that the catalyst is indeed activated. This is either caused by sulfidation of the catalyst by the sulfur from the converted thiophene or by reduction of the catalyst by hydrogen. To decide between the two, the experiment was repeated with a fresh portion of the catalyst, but the number of thiophene pulses was now diminished. Only the pulses indicated in Fig. 2 were given. However, the same conversions as in the first experiment were found. This clearly proves that not sulfidation but reduction activates the catalyst, because far less sulfur was available in the second experiment than in the first, whereas the amount of hydrogen remained the same. No differences in activity were found when the catalyst was pretreated during 3 hr with H_2S or H_2, indicating that it is not the sulfiding action of the H_2S that activates the catalyst but the reducing action.

Experiments with cobalt aluminate [sample PL; Ref. (*3*)] and alumina showed that

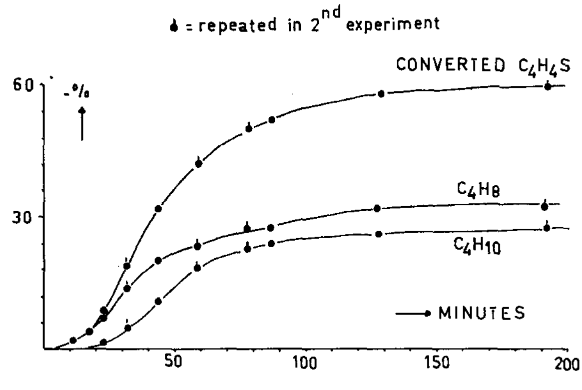

FIG. 2. Thiophene desulfurization as a function of reduction time; quantities are given as percentage carbon of 1 μl of C_4H_4S. Conditions: 0.1 g of Ketjenfine; 1 μl C_4H_4S pulses; 50 cm^3 min^{-1} NTP H_2; 420C°

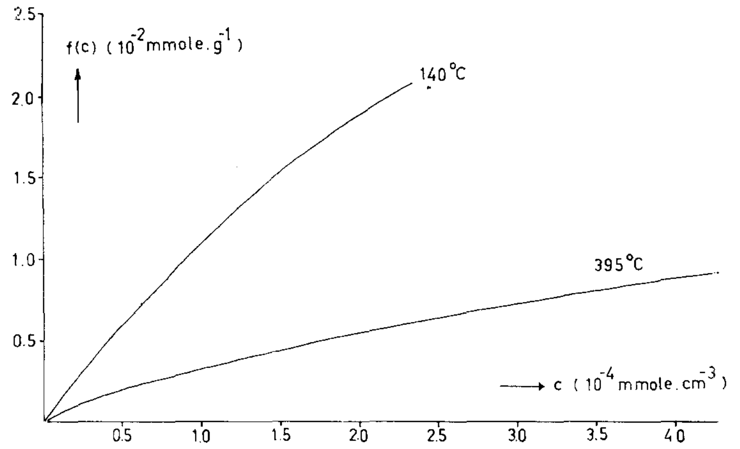

FIG. 3. Adsorption isotherms of thiophene on Ketjenfine; conditions: 2.79 g of catalyst, 4 hr reduced in H_2 at 500°C; carrier gas: argon 20 cm^3 min^{-1} NTP.

both are practically inactive for desulfurization and hydrogenation.

The reduction of the catalyst was also investigated with the help of a Stanton thermogravimetric balance. The experiments were carried out at 550°C, while a mixture of 20% H_2 and 80% N_2 at atmospheric pressure was passed over the samples. For cobalt aluminate (PL) and alumina it was found that they were not reduced. The loss in weight of Ketjenfine must, therefore, be ascribed only to a reduction of the MoO_3. The weight change correspond to the removal of 1.0–1.4 O atoms/Mo atom. This determination is rather inaccurate, owing to the relatively small weight changes and the water desorbing from the alumina. The latter is also the reason that the experiments were carried out at 550°C. At 420°C the water which was formed by the reduction desorbed so slowly that the determination became too inaccurate.

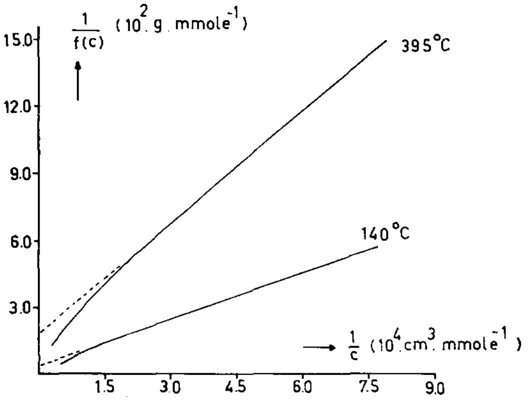

FIG. 4. Plot of the reciprocal values of Fig. 3.

The observations mentioned above are in accordance with the experiments of Mann (*12*) who activated the catalyst in H_2. They do not agree with the results of Hendricks *et al.* (*10*) and Blue and Spurlock (*11*), who stated that sulfidation is necessary. Their experiments, however, relate to industrial processes, which are performed at much higher pressures. It remains possible that at higher pressures sulfidation is indeed favorable for the catalytic activity.

Adsorption and its Inhibition by Water and Pyridine

In the chromatographic method (*16*, *17*) we have a simple means for the determination of adsorption isotherms under various circumstances. Care has to be taken, however, that the adsorbing substance does not take part in any reaction. The adsorption isotherm can then no more be determined. We found no reactions of thiophene or hydrogenation of butenes up to 400°C when using Ar as carrier gas. Only a small amount of the first two pulses on a fresh catalyst was irreversibly adsorbed. Therefore, unless otherwise stated, Ar was always used as carrier gas in the adsorption experiments.

Two typical adsorption isotherms $f(c)$ of thiophene on Ketjenfine are depicted in Fig. 3. A plot of $1/f(c)$ against $1/c$ in Fig. 4

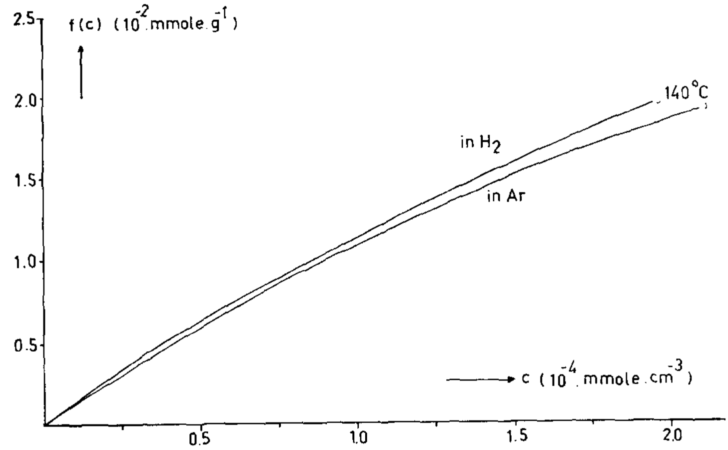

FIG. 5. Adsorption isotherms of thiophene on Ketjenfine; conditions: 2.79 g of catalyst, 4 hr reduced in H_2 at 500°C; carrier gas: H_2 or Ar 20 cm^3 min^{-1} NTP.

shows that both isotherms approximately obey the equation of the Langmuir isotherm. Extrapolation to $1/c = 0$ gives for 395°C a number of thiophene sites equal to 10^{19} sites g^{-1} and for 140°C a number of 3×10^{19} sites g^{-1}. As mentioned in the introduction, Owens and Amberg (*13*) stated that thiophene should adsorb less strongly in H_2 than in N_2. To check this we determined the adsorption isotherm in H_2 and Ar as carrier gas. However, we could not do this at higher temperatures, because of the reactions then occurring, but we determined the isotherms at 140°C where the conversions of thiophene in H_2 were negligibly small. The catalyst was first reduced during 4 hr in a hydrogen stream at 500°C. For the determination of the isotherm in H_2 the catalyst was then allowed to cool in the H_2 stream. For the determination in Ar, the catalyst was first flushed in an Ar stream during 3 hr at 500°C after the reduction. It It was then allowed to cool in the Ar stream. The isotherms are given in Fig. 5. In contradiction to the results of Owens and Amberg (*13*) hydrogen has no influence on the thiophene adsorption.

Water had a considerable effect on the thiophene adsorption, as shown in Fig. 6. Two thiophene adsorption isotherms are given obtained before and after a pulse of 20 μl of H_2O. Water was retained by the catalyst much longer than thiophene, enabling a thiophene elution curve to be determined before any water had left the column. A plot of $1/f(c)$ against $1/c$ (Fig. 7) reveals that thiophene and water adsorb competitively on Ketjenfine, indicating that

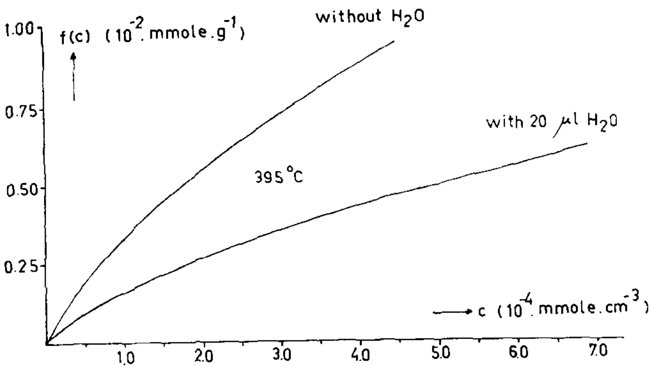

FIG. 6. Inhibition by water of the thiophene adsorption on Ketjenfine; conditions: 2.79 g catalyst, 4 hr reduced in H_2 at 500°C; carrier gas: argon 20 cm^3 min^{-1} NTP.

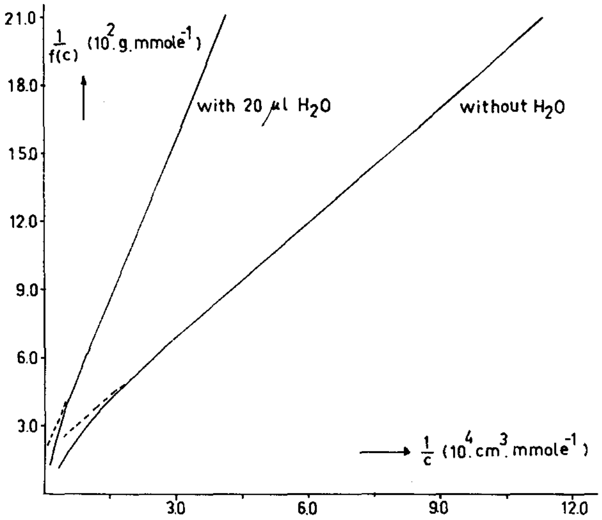

FIG. 7. Plot of the reciprocal values of Fig. 6.

the same surface sites are involved. The influence of H_2S was of the same character as the influence of H_2O. The butene adsorption was measured to be reduced by H_2O and H_2S in an even greater degree than the thiophene adsorption.

The adsorption of pyridine on the catalyst was for a considerable part of the irreversible type up to temperatures of about 400°C. As for the reversible part of the adsorption, the retention volumes were so large that many elution curves of butene and thiophene could be obtained before pyridine broke through. Pyridine had no influence on the thiophene and butene adsorption. Only when the catalyst became saturated with pyridine, did the adsorption of thiophene and butene drop.

The fact that the above-mentioned poisons have in principle the same effects on the butene and thiophene adsorption is an indication that the latter two adsorb on the same kind of surface site (site I). Another indication is that the retention time of a butene pulse was observed to decrease strongly after the introduction of a thiophene pulse. The strong irreversible adsorption of pyridine however, appears to be connected with a different type of site (site II). Pyridine appears to adsorb on both types of site although it strongly prefers site II. After having occupied these sites it is also adsorbed on site I and it is only then that inhibition of the thiophene and butene adsorption becomes noticeable. This type of adsorption appears to be reversible.

The determination of the adsorption of hydrogen was unfortunately too inaccurate for a quantitative evaluation. A few im-

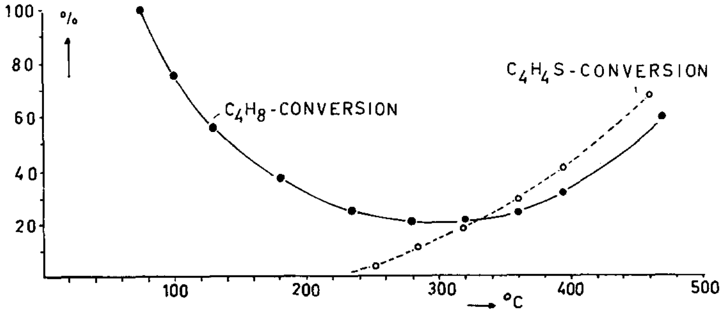

FIG. 8. Butene hydrogenation and thiophene desulfurization as a function of temperature; conditions: 2.35 g of Ketjenfine, 4 hr reduced in H_2 at 500°C; 50 cm^3 min^{-1} NTP H_2; 2 cm^3 2-butene (*trans*) and 10 μl C_4H_4S pulses.

portant phenomena were, however, observed when pulsing hydrogen in an Ar stream flowing over a reduced catalyst, that was flushed in an Ar stream at 500°C during 4 hr. No hydrogen adsorption was found from room temperature up to about 220°C. Only from 220°C on, was H_2 adsorption found to exist. It increased with increasing temperature and reached a maximum value at 550°C. At higher temperatures it decreased again. We can conclude that the H_2 adsorption is of the activated type indicating that H–H bond cleavage is involved.

The influence of the Temperature and of the Addition of Water and Pyridine on the Reaction

The dependence of the thiophene desulfurization and of the butene hydrogenation over Ketjenfine on the temperature is given in Fig. 8. No thiophene conversion was found below 210°C. For the butene hydrogenation a somewhat surprising temperature dependence was found. Especially the increase below 280°C with decreasing temperature is striking, the more so since no hydrogen adsorption was found below 220°C.

As was expected from the adsorption measurements, water had a poisoning effect on the reactions. In a typical experiment, the conversion of a 2-μl thiophene pulse at 400°C was lowered from 91 to 88% after the introduction of 3 μl of H_2O, while the ratio butane/butene in the product changed from 24/67 to 17/71. Water also lowered the hydrogenation of a butene pulse in both the high (above 220–280°C) and low (below 220–280°C) temperature ranges. The lowering of the butene hydrogenation in the high temperature range was greater than the lowering of the thiophene conversion.

The temperature had an important effect on the poisoning of the butene hydrogenation by pyridine as shown in Fig. 9. At 400°C a decrease of the butene conversion was observed after every pulse until the catalyst became saturated with pyridine (indicated by an arrow). About 6×10^{19} molecules of pyridine/g of catalyst were then irreversibly taken up. The subsequent pulses had a much smaller effect. In contrast to this, pyridine had no effect on the butene hydrogenation at 140°C. Only when the saturation point was approached did the conversion drop. As Fig. 9 shows, then about 13×10^{19} molecules g^{-1} have been taken up and the reaction is completely poisoned by the following 3×10^{19} molecules g^{-1}. As for the thiophene desulfurization, the influence of pyridine in the high temperature range was the same as found for the butene hydrogenation. The most important phenomena concerning adsorption and reaction are summarized in Table 1.

DISCUSSION

We shall begin with the discussion of Nicholson's (*5*, *6*) infrared spectra of adsorbed thiophene. He mentioned three bands: (i) A band around 3086 cm^{-1} that is observed on MoS_2 preheated at various temperatures, and on the catalyst also after heating. It is not observed, however, on a catalyst saturated with hydrogen after heating. Thiophene adsorbed on Al_2O_3 itself shows a band at 3060. (ii) A sharp band at 3005 only observed on MoS_2 at various

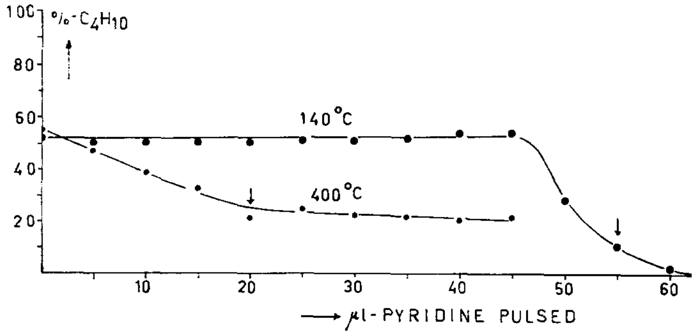

FIG. 9. Poisoning of butene hydrogenation by pyridine; conditions: 2.55 g of Ketjenfine, 4 hr reduced in H_2 at 500°C; 50 cm^3 min^{-1} NTP H_2; 2 cm^3 2-butene (*trans*) pulses.

TABLE 1
CATALYTIC PROPERTIES

	Temp[a]	Adsorption			Reaction	
		C_4H_4S	C_4H_8	H_2	C_4H_4S	C_4H_8
	HT	Yes	Yes	Yes	Yes	Yes
	LT	Yes	Yes	No	No	Yes
INHIBITION BY						
Water	HT	Yes	Yes		Yes	Yes
	LT	Yes	Yes		—	Yes
Pyridine	HT	No	No		Yes	Yes
	LT	No	No		—	No

[a] HT = high temperature range (above 220–280°C); LT = low temperature range (below 220–280°C).

temperatures. (iii) A band at 2960 observed on MoS_2 at various temperatures, also present on the catalyst but only after heating, and, finally, on the hydrogen saturated catalyst.

Nicholson assigned the C–H stretching bands as follows: 3086, either "one-point" adsorption with S as the bonding atom or physically bonded or gaseous thiophene; 3005, "two-point" adsorption, i.e., a bonding of two C atoms on one side of the thiophene ring with the surface; and 2960, "four-point" adsorption, i.e., all C atoms bonded to the surface. (It might be remarked that two-point adsorption should give rise to two bands, viz, "olefinic" and "paraffinic" C–H.)

His conclusion is that the situation causing the 2960 band is the active species and that, therefore, four-point adsorption is identical with the active intermediate. In our opinion one might just as well defend the view that the situation connected with the 3086 band is the active intermediate. It is the 3086 band that disappears on reaction with adsorbed hydrogen, while the 2960 band is far less subject to change. The assignment of a one-point adsorption to the 3086 band appears reasonable since this band is also found for gaseous thiophene and the sulfur atom is not involved in this vibration mode. This means that we believe the active intermediate to have the sulfur atom and only this atom bonded to the surface.

We can now give an explanation of the fact that reduction is necessary for the activation of the catalyst. The catalyst consisted of cobalt aluminate, alumina, and molybdenum trioxide (*3*). $CoAl_2O_4$ and Al_2O_3 were practically inactive for hydrodesulfurization and hydrogenation. This means that MoO_3 is responsible for the main part of the catalytic activity. The catalytically active intermediates must, therefore, be thiophene molecules adsorbed in the one-point form on the MoO_3. These complexes can only be formed when anion vacancies are available. The vacancies are made by reduction.

We may expect that the "independently" (*2*) bonded oxygen atoms of the MoO_3 are the ones that are removed. Hydrogen adsorption was of the activated type. The H–H bond is broken and the two H atoms are independently adsorbed very probably on oxygen atoms in the surface, so forming OH groups. Since it is unlikely that the hydrogen atoms are bonded to oxygen atoms that are linked to more than one molybdenum atom, the "independently" bonded oxygen atoms will be the agents to form bonds with the hydrogen atoms.

In view of all this we can represent the catalytically active site as depicted in Fig. 10. An oxygen atom is removed, leaving an anion vacancy, and a hydrogen molecule is adsorbed as two H atoms on adjacent O atoms, so forming two OH groups. So two conditions must be fulfilled for the catalyst to be active. Anion vacancies must be present as well as "independently" bonded oxygen atoms. The reduction of the catalyst must not, therefore, be too extensive, because many anion vacancies are then

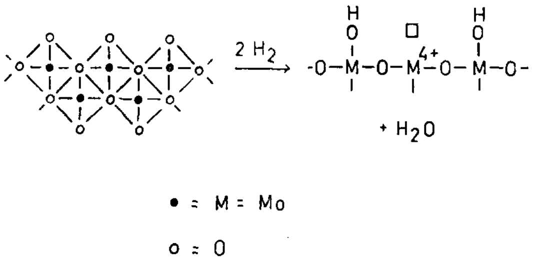

FIG. 10. Formation of the active site.

formed indeed, but too few oxygen atoms are left for the hydrogen adsorption. The reason that in the industrial processes, carried out at rather high pressures, the activation is not performed with hydrogen but with milder reducing agents such as H_2S or a mixture of H_2S and H_2, may be that H_2 alone leads to "overreduction."

The same anion vacancies that are active for the thiophene desulfurization are supposed to chemisorb butene also. So we can conclude from this that hydrodesulfurization and hydrogenation of olefins take place on the same kind of surface sites, a conclusion consistent with the fact that in the high temperature range all observations concerning adsorption and inhibition run parallel for butene hydrogenation and thiophene desulfurization. The observed inhibition of the adsorption and reactions by H_2O and H_2S can now be explained. The latter two compounds are expected to adsorb on the same anion vacancies as thiophene and butene. In view of the presumed stronger adsorptive capacity of thiophene the influence of H_2O and H_2S on the thiophene adsorption and reaction is smaller than the influence on the butene adsorption and reaction. This particular type of site then is site I. Pyridine adsorption may also occur on site I but there is present also another type: site II that is preferred by the pyridine molecule. It is well known that pyridine is strongly adsorbed on alumina and it might therefore be postulated that the strong irreversible pyridine adsorption occurs on parts of the catalyst surface that are still similar to that of free alumina. Since the irreversible pyridine adsorption considerably surpasses in magnitude the site-I type of adsorption one must then conclude that a relatively large fraction of the alumina surface is still "free" and not covered by MoO_3.

For the high temperature range we can now propose the following reaction mechanism (Fig. 11):

(a) Thiophene is adsorbed on an anion vacancy formed by reduction of the MoO_3. The sulfur atom becomes bonded to the molybdenum atom.

(b) One hydrogen atom is transferred from an adjacent OH group to the adsorbed molecule. One C–S bond is broken. This is in accordance with the literature, in which C–S bond fission is generally taken as the first step, rather than ring hydrogenation.

(c) A second hydrogen atom is transferred breaking the other C–S bond.

(d) 1,3-Butadiene desorbs, in accordance with the observations of Kolboe and Amberg (*14*). This butadiene molecule is of course hydrogenated further on other sites or may be even on the same site.

(e) The original catalytic site is restored by a reaction with two H_2 molecules and desorption of an H_2S molecule.

For the hydrogenation of butene in the high temperature range there are two alternatives; either π-adsorption of butene on the anion vacancy followed by a transfer of two hydrogen atoms to the adsorbed molecule, or a direct reaction of the olefin with a hydrogen atom from the surface and

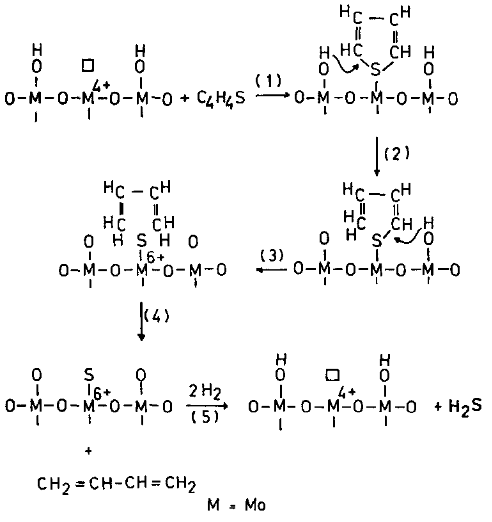

FIG. 11. Reaction mechanism for the hydrodesulfurization of thiophene.

the formation of an intermediate σ-bonded surface alkyl group. No decision between the two seems possible at this moment. When the molybdenum oxide is converted to molybdenum sulfide by sulfidation, the H atoms are not transferred from OH but from SH groups, and it might be that under certain circumstances this is favorable to the catalytic activity. However, as mentioned before, we did not observe such an increase of the activity by sulfidation during our experiments.

The next phenomenon which has to be discussed is the low temperature hydrogenation of butene. In the low temperature range no hydrogen adsorption was found below 210°C. However, it is certain that butene is adsorbed. Any reaction between hydrogen and butene is, therefore, a reaction between an adsorbed butene molecule and a gaseous hydrogen molecule. If it is accepted that the butene is adsorbed on the anion vacancies, this adsorption should then be of the π-type. The increase of the conversion with decreasing temperature can be explained from the increase of butene adsorption with decreasing temperature. A detail that so far has been left out of the discussion is the promoting influence of Co. In fact, no such influence was found in the present work. As is well-known, however, the presence of Co is of considerable importance for the functioning of a technical catalyst. We shall return to this subject in a following paper.

CONCLUSIONS

We can summarize the conclusions drawn from our experiments, together with the information from the literature, as follows. The catalyst becomes fully activated by reduction with hydrogen. In our experiments sulfidation of the catalyst did not increase its activity. It is postulated that the reduction leads to the formation of anion vacancies at the MoO_3 surface. Thiophene is attached with its sulfur atom to the Mo atom next to such a vacancy.

The C–S bonds are ruptured by a transfer of two hydrogen atoms from hydroxyl (or SH) groups in the surface. Butadiene desorbs and the original situation is restored by a reaction with hydrogen and desorption of H_2S. For the butene hydrogenation in the high temperature range either a similar reaction scheme occurs or there is a formation of σ-bonded surface alkyl groups, by direct interaction of the gaseous butene with surface hydroxyl groups. In the low temperature range the chemisorbed butene is supposed to react directly with a hydrogen molecule from the gas phase. No information could be deduced from the experiments performed as to the function of the cobalt component in the commercial catalyst.

ACKNOWLEDGMENTS

It is a pleasure to thank the "Koninklijke Zwavelzuurfabrieken v/h Ketjen N. V." for providing the catalyst. The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

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