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The CoO–MoO_3–Al_2O_3 Catalyst. IV. Pulse and Continuous Flow Experiments and Catalyst Promotion by Cobalt, Nickel, Zinc, and Manganese

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The activities of MoO_3–Al_2O_3 catalysts promoted with various amounts of cobalt, nickel, zinc, and manganese have been determined in pulse and continuous flow experiments for the hydrodesulphurization of thiophene at atmospheric pressure and 400°C. The initial activities of a MoO_3–Al_2O_3 and a CoO–MoO_3–Al_2O_3 catalyst as inferred from pulse experiments are equal. Continuous flow experiments for all catalysts show that the activity decays rapidly and approaches a steady-state level that depends on the promoter and its concentration. Maximum steady-state activity levels are attained for each of the promoter ions at different metal-to-molybdenum ratios. Some models are discussed in an attempt to explain the experimental results.

A preliminary investigation of hydrogenation activity of the above-mentioned catalysts is reported. With increasing promoter content a minimum for the initial hydrogenation activity is found. Hydrocarbon saturation at the steady-state is comparatively insensitive to the nature of the promoter ion, which may be associated with the sulphiding of the surface.

INTRODUCTION

The present paper forms the fourth in a series dealing with investigations aimed at understanding the catalytic hydrodesulphurization over CoO–MoO_3–γ–Al_2O_3 catalysts. It is especially concerned with attempts to understand the action of Co as a promoter and to prove the necessity of a highly dispersed state of MoO_3 in the catalyst prior to reduction.

As to the first point let us recall three earlier sets of papers. Richardson (*1*), from magnetic data on catalysts with varying ratios of Co/Mo before and after reduction, concluded that it was necessary to assume an "active cobalt–molybdenum complex" (not reducible). Depending on the Co concentration and the pretreatment of the catalyst, varying amounts of Co^{2+} become incorporated in the γ-Al_2O_3 carrier in a situation as encountered in $CoAl_2O_4$ (Co^{2+} in a tetrahedral environment), in which situation it is inactive. No suggestion was given as to the nature of the active complex.

Almost simultaneously, two series of papers by Lipsch and Schuit (*2*–*4*) and Ashley and Mitchell (*5*, *6*) appeared. In both cases the catalyst prior to reduction was investigated by spectroscopic (uv, vis, and ir) and magnetic measurements. Lipsch took great care to study the various possible structures ascribed to $CoMoO_4$. On the basis of an industrial catalyst he concluded that cobalt molybdates were absent in this catalyst and that Co^{2+} was almost entirely present in a tetrahedral environment similar to that encountered in

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$CoAl_2O_4$. The MoO_3 was assumed to be present as a monomolecular layer with Mo^{6+} in an octahedral environment. Pulse experiments failed to show a promoter effect of Co^{2+}, and neither did sulphiding of the catalyst influence the activity of a prereduced sample. The conclusions of Ashley and Mitchell as to the catalyst structure were similar; $CoMoO_4$ was not present. However, they found that a considerable part of the Co^{2+} was present in an octahedral environment, but preferred to view Mo^{6+} as being tetrahedrally coordinated. From poisoning experiments on a prereduced and sulphided catalyst, Desikan and Amberg (*7*) had come to the conclusion that two types of sites or functions are present on the catalyst surface, *viz.*, A-sites, strongly electrophilic and mainly responsible for olefinic hydrogenation, and B-sites, less electrophilic and the important active agents for the desulphurization. It is noteworthy that Mitchell (*8*) also proposed the necessity for different types of sites, i.e., hydrogenation/ isomerization sites connected with the presence of Co^{2+}, and other sites more directly concerned with the desulphurization.

Following Lipsch's structural proposal we decided to examine the activities of $CoO–MoO_3–Al_2O_3$ and $MoO_3–Al_2O_3$ catalysts in experiments that are less remote from the actual technical experiments than his own pulse method. As a compromise we investigated catalytic activities in continuous flow experiments, but still at atmospheric pressure and with thiophene as the model compound. Both the supposedly beneficial influence of Co^{2+} and the necessity for a dispersed state of the Mo compound had to be reexamined by this technique.

During the investigation the need arose for the study of the influence of other cations as promoters. The promoter metals were selected with regard to their preferred coordination when incorporated in γ-Al_2O_3. According to Romeyn (*9*), Co^{2+} and Zn^{2+} have a preference for tetrahedral sites, Ni^{2+} prefers octahedral sites, and Mn^{2+} has no preference. Greenwald *et al.* (*10*) consider on the basis of X-ray intensity and magnetic measurements that in $CoAl_2O_4$ about 75% of the Co^{2+} ions are in tetrahedral interstices, the precise distribution depending on the method of preparation and subsequent heat treatment of the samples.

In the literature several studies are reported concerning the effect of the hydrodesulphurization activity of molybdenum catalysts, with and without a support, promoted by transition metal ions other than cobalt. Beuther *et al.* (*11*), measuring the desulphurization of a light gas oil over catalysts prepared by double impregnation on alumina, found the following sequence in decreasing order of promotion: Co, Ni, Pd, and Fe.

The addition of iron to a $MoO_3–Al_2O_3$ catalyst caused only a very small increase in activity. In a recent paper, Ahuja *et al.* (*12*) measured thiophene desulphurization on $CoO–MoO_3$ and $NiO–MoO_3$ catalysts deposited on γ-Al_2O_3 and SiO_2. They found that the cobalt-promoted catalysts were slightly more active than those containing nickel. The investigation of Kolboe and Amberg (*13*) on the hydrodesulphurization of thiophene indicates, however, that different catalyst activities may reflect different surface areas rather than different chemical compositions. Various MoS_2 catalysts as well as presulfided $CoO–MoO_3–Al_2O_3$ and Cr_2O_3 had very similar activities expressed as reaction rates per unit surface area.

Considering these different points of view we studied and compared the hydrodesulphurization activity of four MoO_3–γ-Al_2O_3 catalyst series containing different amounts of CoO, ZnO, NiO, and MnO.

EXPERIMENTAL

A diagram of the apparatus used for continuous flow experiments is given in Fig. 1. Hydrogen gas is introduced through tube I. The flow is regulated by pressure regulator (a) and needle valve (b) and is measured by manometer (c) and flowmeter (d). After purification via a B.T.S. catalyst (e) and molecular sieves (f), hydrogen is saturated with thiophene. To do this, H_2 is led through two vessels containing thiophene (g and h), the first one

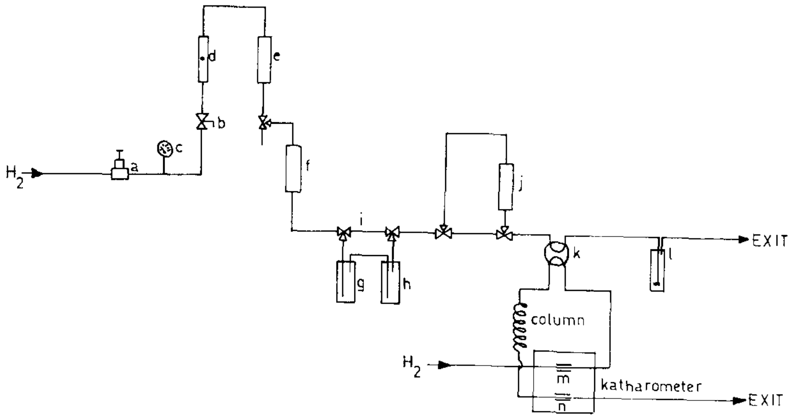

FIG. 1. Diagram of the continuous-flow apparatus.

having a temperature between 40 and 50°C and the second one being maintained at a constant temperature of 16°C. The vapor pressure of thiophene at 16°C is 52 mm Hg (*14*). This corresponds to a thiophene content in the hydrogen gas of about 6% by volume, the accuracy being 2% in the amount of thiophene. Operating without thiophene, for instance, for prereduction it is possible to use a bypass (i). After passing the tube reactor (j) with an i. d. of 8 mm, the gas is led to a loop in the sample valve (k) and via a trap (l) to the exit. The part of the gas tube between the reactor and sample valve is heated (100°C) in order to prevent condensation of thiophene in the tube. To analyze the reaction products, the gas samples (1.3 cm^3) are led [by means of valve (k)] into a glc column and the measuring channel (n) of a katharometer. The column is a 5.5-m long tube with an i. d. of 4 mm, filled with gaschrom (50–60 mesh) impregnated with 15 wt % of 1-octadecene. Tungsten coated with teflon is used as the reference and measuring wire of the katharometer. Column and katharometer were held at 30°C. The carrier gas, hydrogen, passing successively through the reference channel (m), column, and measuring channel, had an inlet pressure of 1.7 atm and its flow rate was 60 cm^3/min. The gas flow rate through the reactor was 57 cm^3/min (space velocity 14,500–17,000 hr^{-1}).

The apparatus used for pulse experiments is similar to the continuous flow apparatus described above in Fig. 1. The hydrogen carrier gas stream was first led to the reference channel (m) of the katharometer and then passed successively through the sample valve (k), reactor (j), glc column, measuring channel (n), and the exit. The flow rate, thiophene content in the hydrogen gas, and sample size were the same as for the continuous flow experiments. In order to prevent chemical attack by sulphur compounds, both the continuous flow and pulse apparatus were made of stainless steel except for the reactors which were made of quartz glass.

All the experiments were carried out at a temperature of 400°C and atmospheric pressure. For both the continuous flow and pulse experiments fresh portions of 180 mg of powdered catalyst were used. Before weighing, the catalyst was dried 1 hr at 500°C. Before starting the experiments, H_2 was led through the thiophene containers for 0.5 hr and the catalyst was reduced with pure hydrogen during 1.5 hr at 400°C. The reaction products found were: H_2S, butene-1, *n*-butane, *trans*- and *cis*-butene-2, thiophene, and furthermore, negligibly small quantities of methane, ethane, ethene, propane, propene, and isobutane.

The activities in continuous flow experiments are expressed in percentage converted thiophene. The conversion of thiophene is calculated from the quantities of thiophene, H_2S, and C_4-hydrocarbons. The differences between the three conversion curves are probably attributable to sys-

TABLE 1
KETJEN $CoO-MoO_3$ CATALYSTS SUPPORTED ON γ-Al_2O_3

Weight percentages		Surface area m^2g^{-1}
CoO	MoO_3	
0	12	227
1	12	188
2	12	201
3	12	199
4	12	217
5	12	177
6	12	192

tematic errors made on measuring the peak areas of the chromatogram and to coke-formation on the catalyst surface. The activities in pulse experiments are expressed in C_4-units. These units were obtained by multiplying the paper weights of the thiophene, H_2S, and C_4-hydrocarbon peaks with correction factors of 0.80, 1.94, and 1.0, respectively. The Ketjen prepared catalysts are given in Table 1.

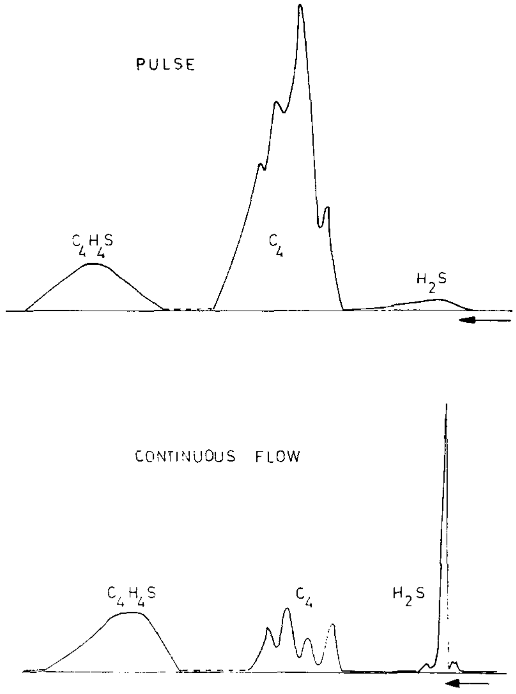

FIG. 2. Gaschromatogram of reaction products. Conditions: column 5.5 m × 4 mm, 15% 1-octadecene on Gaschrom 50 × 60 mesh, 60 $cm^3\ min^{-1}$ NTP H_2, 30°C, katharometer detection.

RESULTS

Pulse Versus Continuous Flow

An essential point in comparing the activities of the various catalysts is the method of testing. Two methods are compared: continuous feeding of the reactants to the catalysts (continuous flow), and pulsing small amounts of the reactants in a constant stream of H_2 flowing through the catalyst (pulse method). Two catalysts were compared: the Ketjenfine $CoO-MoO_3-Al_2O_3$, containing 4 wt % CoO and 12 wt % MoO_3, and a sample of $MoO_3-Al_2O_3$ supplied by Ketjen and supposedly similar, except for the absence of cobalt.

Figure 2 shows the glc diagram obtained for the pulse method and the continuous-flow method. The results for the continuous flow are relatively simple to interpret apart from the discrepancy between thiophene converted and products obtained alluded to earlier. This is not so, however, for the pulse experiments. For instance, the amounts of H_2S formed during the reaction are far less than those of the C_4-fractions. H_2S therefore appears to remain adsorbed on the catalyst. Since the discrepancies can be ascribed to "adsorption," it is interesting to see what happens if a series of pulses is fed to the catalysts (see Fig. 3). The amounts of thiophene recovered remain constant during a series of pulses. This indicates that at the most only a very small part of the thiophene is strongly adsorbed on the catalyst and that we have to do here with real thiophene conversion.

The following observations can be made from the pulse experiments:

(a) The amount of C_4-hydrocarbons remains constant and similar for $CoO-MoO_3-Al_2O_3$ and $MoO_3-Al_2O_3$. Hydrogenation is substantially complete for both catalyst systems: the first pulses produce almost exclusively butane and small traces of the butenes. Somewhat larger amounts of the butenes (about

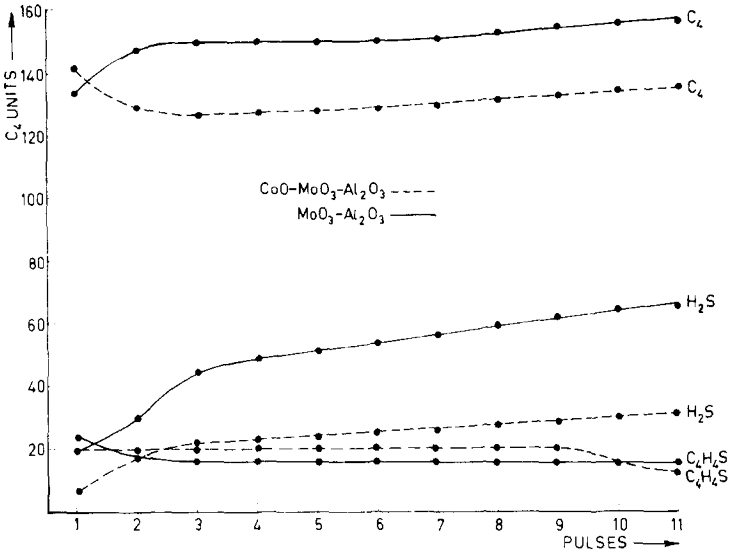

FIG. 3. Thiophene desulphurization as a function of the number of pulses. Conditions: 180 mg catalyst, 1.5 hr reduced in hydrogen at 400°C, 1.3 cm³ hydrogen with 6 vol % thiophene pulses, 400°C.

20% of total C_4) are formed after a succession of pulses.

(b) The amount of thiophene remains constant and equal for the two catalyst systems.

(c) H_2S steadily increases and this increase is faster for $MoO_3-Al_2O_3$.

The results for the thiophene conversion in continuous flow are given in Fig. 4.

Dispersion of MoO_3 *Over the Carrier Surface*

The conclusion of Lipsch and Schuit (*3*) (from reflectance measurements) and of Russell and Stokes (*15*, *16*) (from dehydrocyclization activity measurements) that active MoO_3 is dispersed over the surface of the catalyst, was checked under continuous flow conditions. Compounds and

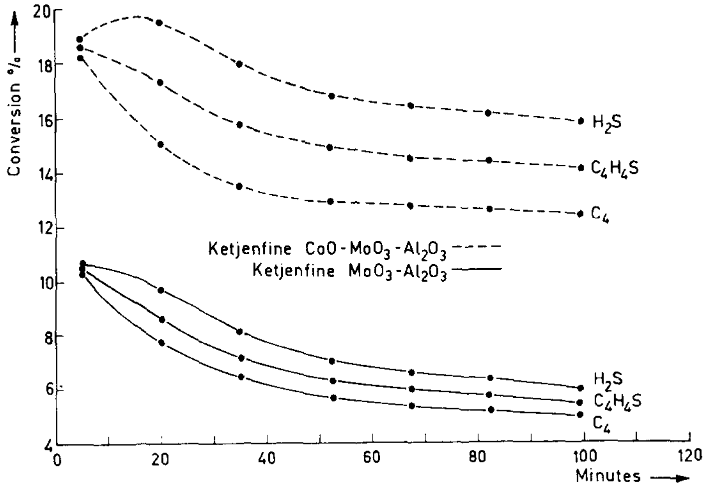

FIG. 4. Thiophene desulphurization as a function of run time. Conditions: 180 mg catalyst, 1.5 hr reduced in hydrogen at 400°C, 57 cm³ min⁻¹ NTP H_2 with 6 vol % thiophene, 400°C.

catalysts tested were: γ-Al_2O_3 Ketjen CK 300, MoO_3, a mixture of 12 wt % MoO_3 and 88 wt % γ-Al_2O_3, and a mixture with the same composition calcined 16 hr at 500°C. The specific surface area of the latter catalyst was 150 m^2/g.

The activity of γ-Al_2O_3 was found to be zero, which is in accordance with the results of Richardson (*1*). In Fig. 5(A), the conversion is plotted against the run time for pure MoO_3 and the uncalcined MoO_3–Al_2O_3 mixture. For comparison we have plotted in this figure a conversion for pure MoO_3 which is obtained after multiplying the "real" conversion (conversion found) for this compound by a factor of 0.123, which is the weight-fraction of MoO_3 in the mixture. Both catalysts had nearly the same activity on this basis. Figure 5(B) shows that after calcination of 500°C for 16 hr the conversion of the MoO_3–Al_2O_3 mixture had increased from 0.4 to 6% thiophene. As can be seen from Figs. 4 and 5(B) the commercial MoO_3–Al_2O_3 catalyst had the same activity as the calcined mixture (laboratory-prepared MoO_3–Al_2O_3 catalyst).

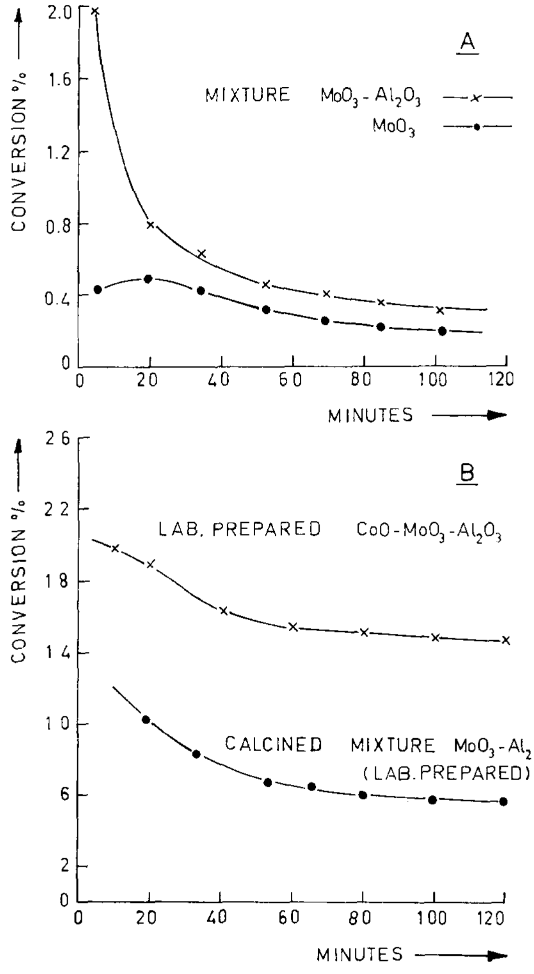

FIG. 5. Thiophene desulphurization based on the amount of thiophene converted. Conditions: see Fig. 4.

The Significance of Cobalt

As Fig. 4 shows, CoO–MoO_3–Al_2O_3 is twice as active as MoO_3–Al_2O_3 under continuous flow conditions. The activity of $CoAl_2O_4$ was found to be zero. In order to investigate the role of cobalt we prepared a CoO–MoO_3–Al_2O_3 catalyst from the calcined MoO_3–Al_2O_3 mixture. The following procedure was used. The laboratory-prepared MoO_3–Al_2O_3 catalyst was impregnated with an aqueous solution of cobalt nitrate. After evaporation the mixture of cobalt nitrate and MoO_3–Al_2O_3 was calcined for 12 hr at 750°C. The composition of the catalyst obtained was 4 wt % CoO, 12 wt % MoO_3, and 84 wt % γ-Al_2O_3, and its specific surface area was 153 m^2/g. After reduction, the activity of this catalyst was measured in a continuous flow reactor. Except at the very beginning of the reaction, no significant difference in activity was found between this CoO–MoO–Al_2O_3 catalyst and the commercial one, although the specific surface area of the latter is higher, 217 m^2/g [Figs. 4 and 5(B)].

In order to find out whether there is a relation between the amount of cobalt and hydrodesulphurization activity, catalysts containing wt 12% of MoO_3 and different amounts of cobalt were examined. Their composition and specific surface area are mentioned above, in table 1. In Fig. 6 the percentage CoO is plotted against the conversion of thiophene calculated from the amounts of thiophene, H_2S, and C_4-hydrocarbons analyzed after 100 min of reaction.

The conversion over the catalysts increases with the CoO content up to 4 wt % CoO (atomic ratio of Co/Mo:0.67) and

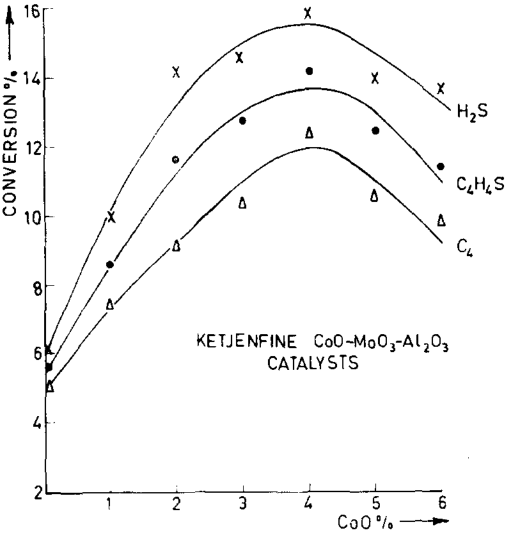

FIG. 6. Thiophene desulphurization at a run time of 100 min., as a function of the CoO content in weight percentages. Conditions: see Fig. 4.

decreases at higher weight percentages. As can be seen in Fig. 7, the production of H_2S for catalysts with a CoO content between 2–6 wt % reaches a maximum after a reaction time of 20 min. This is presumably due to the sulphidation of the catalysts in combination with the normally expected decrease in thiophene conversion. With catalysts containing less than 2 wt % CoO we have not observed this phenomenon. Because of the low thiophene conversion, though, the initial ratio of H_2S/MoO_3 for this catalyst is lower than for those which contain more CoO. This is in agreement with the H_2S production found for the calcined MoO_3-Al_2O_3 mixture and the H_2S produced in pulse experiments. From these results the conclusion can be derived that both the steady-state activity and sulphidation of the catalyst are influenced by Co.

The Effect of Nickel, Zinc, or Manganese Promoters in Comparison with Cobalt

The catalysts were prepared in a somewhat different way from the CoO-MoO$_3$-Al$_2$O$_3$ catalyst mentioned above. As carrier material we used a Ketjen H.D.S. base γ-Al_2O_3 in the powder form. This alumina was impregnated in two stages respectively with aqueous solutions of ammonium paramolybdate and promoter metal nitrate of the desired concentration. After each impregnation the incipiently wetted catalysts

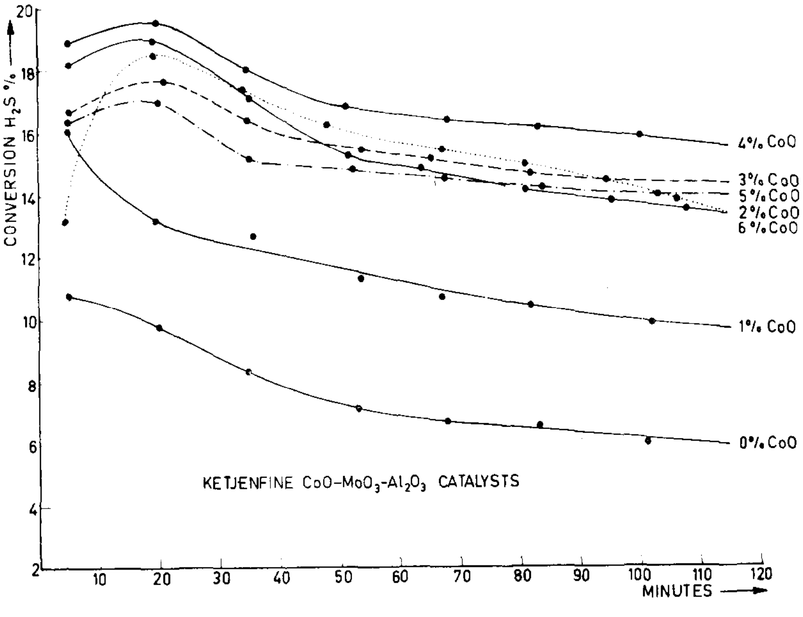

FIG. 7. Thiophene desulphurization based on the amount of H_2S produced, as a function of run time. Conditions: see Fig. 4.

TABLE 2

Promoter Oxide Content and Surface Area of the $MeO-MoO_3-Al_2O_3$ Catalysts Containing 12 wt % MoO_3

MeO wt %	Surface area m^2/g	MeO wt %	Surface area m^2/g
0 CoO	259	0 ZnO	197
1.7 CoO	251	2.2 ZnO	190
2.8 CoO	249	4.0 ZnO	186
4.1 CoO	243	6.3 ZnO	186
5.7 CoO	231	7.7 ZnO	174
0 NiO	227	0 MnO	227
2.0 NiO	191	2.0 MnO	205
4.0 NiO	185	4.0 MnO	203
5.8 NiO	189	5.5 MnO	193

were dried during 12 hr at 110°C and calcined for 2 hr at 600°C in air. The samples were tested under continuous flow conditions as described above, the only difference being the flow rate which was 143 cm^3 NTP H_2/min. Table 2 shows the specific surface area and promoter oxide content of the $MeO-MoO_3-Al_2O_3$ catalysts all containing 12 wt % of MoO_3.

In order to compare the promoter effect of the different metals we calculated the reaction rate constant k based on the percentage of thiophene converted under steady-state conditions, assuming that the reaction is first order in thiophene (*1*, *18*, *19*).

A plot of Δk, the difference between the reaction rate constant for the $MoO_3-Al_2O_3$ and the $MeO-MoO_3-Al_2O_3$ catalysts versus the Me/Mo atomic ratio, is given in Fig. 8. It shows that the effect of promoter addition is positive and only slightly dependent on the nature of the metal for samples with a Me^{2+}/Mo ratio less than 0.30. At this ratio, the optimum composition for the $MnO-MoO_3-Al_2O_3$ catalyst is found with a Δk value of 1.2. A similar value is found for the nickel-containing catalyst series, although in that case the maximum activity lies at the Ni/Mo ratio 0.59. The cobalt and zinc-containing catalysts show also an optimum composition (Co/Mo = 0.66, Zn/Mo = 0.92), but the Δk value is significantly higher than for the nickel and manganese catalyst series.

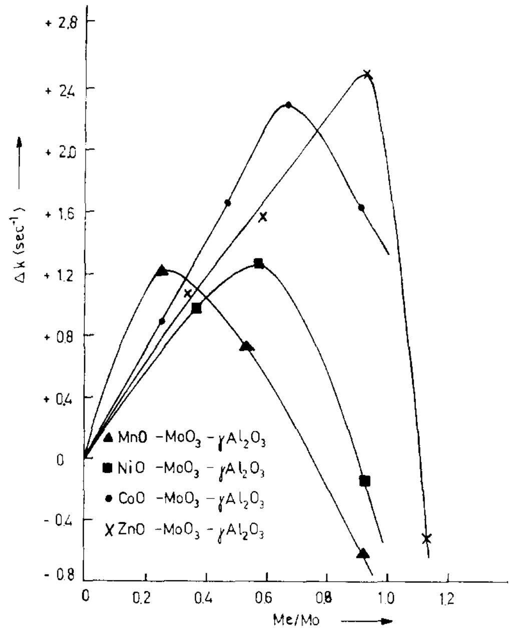

Fig. 8. Thiophene desulphurization as a function of the Me/Mo atomic ratio. Conditions: 180 mg catalyst, 1.5 hr reduced in hydrogen at 400°C, 143 cm^3 min^{-1} NTP H_2 with 6 vol % thiophene, 400°C.

A special feature of the $ZnO-MoO_3-Al_2O_3$ series is the rapid activity or Δk decrease at Zn/Mo ratios higher than 0.92. The thiophene conversion of the catalyst with the highest zinc content Zn/Mo = 1.12 is found to be even lower than the conversion of the $MoO_3-Al_2O_3$ catalyst. This is also the case for the catalysts with the highest nickel and manganese content tested. The optimum Co/Mo ratio found for the laboratory prepared $CoO-MoO_3-Al_2O_3$ catalysts mentioned here is similar to that reported above for the commercial Ketjen catalysts.

Effect of Promoter on Pulse Hydrogenation Activity. Initial Experiments

The reaction products found in our thiophene desulphurization experiments are H_2S, butane, and the three *n*-butenes. Butadiene was never found, which means that the butadiene content is lower than 1%. In Fig. 9 it is shown that the hydrogenation activity of a $MoO_3-Al_2O_3$ catalyst containing up to 4 wt % of zinc oxide is lower

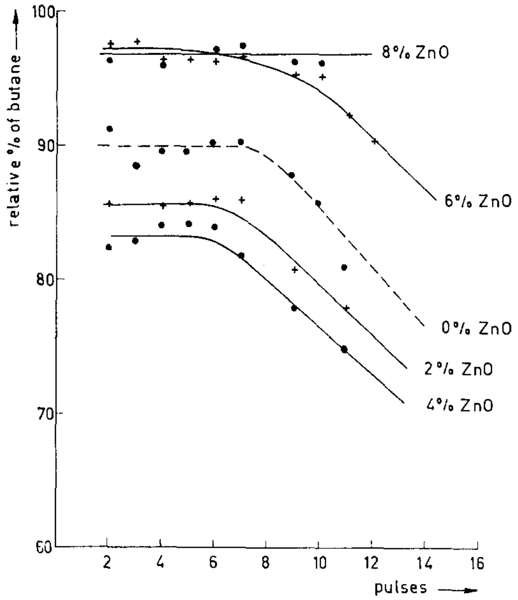

FIG. 9. Relative percent of butane in $ZnO–MoO_3–Al_2O_3$ catalysts with several weight percentages of MeO as function of number of pulses for thiophene desulphurization. Conditions: 180 mg catalyst, 1.5 hr reduced in hydrogen at 400°C, 1.3 cm^3 hydrogen with 6 vol % thiophene pulses, 400°C.

than that of the $MoO_3–Al_2O_3$ catalyst, to rise above this $MoO_3–Al_2O_3$ catalyst at high percentages. By replacing zinc by cobalt, manganese, or nickel a similar picture is obtained.

Hydrogenation Activity in Continuous Flow Experiments

The hydrogenation activities for the oxidic catalysts (reduced) at a steady-state level of thiophene desulphurization under the conditions applied here always lie between 10 and 14% of butane saturation.

By comparing pulse and continuous flow results we notice that in the initial period of the reaction most of the C_4 is converted to butane, while when reaching the steady-state merely *n*-butenes are formed. This means that there is a strong decrease in hydrogenation activity from C_4-olefins to butane; an even lower conversion to butane is reached when a $CoO–MoO_3–Al_2O_3$ catalyst is presulfided.

Similar to Owens and Amberg (*20*) and Metcalfe (*18*) we found the 1-butene concentration to be in excess of equilibrium, while the *trans*-2/*cis*-2 ratio lies close to it.

DISCUSSION

The foregoing results represent an attempt to throw further light on the role of promoters in $MoO_3–Al_2O_3$ catalysts for desulphurization as well as hydrogenation reactions.

Figure 4 allows comparison between a 12 wt % MoO_3 on γ-Al_2O_3 catalyst with and without CoO. In the pulse experiments demonstrated in Figs. 2 and 3, the results obtained were similar to those given by Lipsch and Schuit (*4*). If one were to judge from pulse experiments alone, where it is apparent that the addition of Co to an $MoO_3–Al_2O_3$ catalyst produces no significant increase in hydrodesulphurization, one would come to the conclusion that no new desulphurization sites had been created, nor existing ones modified. (It should be emphasized that this is pertinent to oxidic systems only, since insufficient sulphur is produced to sulphide anything but a minute fraction of the surface.) However, as can be seen in Fig. 4, a marked difference shows up under steady-state conditions. By comparing the results of both experimental techniques, one is led to assume that cobalt serves only to stabilize the catalyst. This can be argued, if one accepts that extrapolation to zero time in the flow experiment approaches the initial pulse conditions, i.e., equal conversion in the 70–80% range, over both catalysts. One might have expected the $CoO–MoO_3–Al_2O_3$ to give higher conversions initially, if the promoting effect of Co had occurred through a mechanism other than catalyst stabilization.

Several new features emerge on examination of changes in cobalt concentration. The steady-state activities which are approached at approximately 80 min of reaction time (see Fig. 4) differ by a factor of 2 or more in going from 0 to 4 wt % CoO. When examined as a function of Co content, a continuous improvement in the steady-state activity can be observed between 0 and 4 wt % CoO, followed by a drop towards higher CoO contents. Attainment of the steady-state implies that the catalyst surface has become sulphided during the preliminary period. If this were the only factor operative during activation, curves such as presented in Fig. 7 would have to show an initial increase in H_2S yield with time, as less and less H_2S is required for surface conditioning; this would then be followed by an asymptotic approach to the steady-state. Clearly, however, most of the curves in Fig. 7 show a maximum at about 20 min or earlier. This must be presumed to be due to at least one additional factor, namely poisoning through buildup of reaction products on the catalysts, which in turn reduces the amount of H_2S produced by thiophene hydrogenolysis.

The role of Co in converting the catalyst from an oxidic to a sulphidic state cannot be explained in a simple manner. When comparing the H_2S-uptake of a catalyst containing 0 and 4% CoO (pulse experiments, Fig. 3), it becomes clear that the presence of CoO increases the amount of sulphur captured by the catalyst. Similarly the rate of sulphur-uptake appears from Fig. 7 to depend markedly on the amount of CoO present. A simple experiment concerning the morphology of the catalyst was thought to be of interest, especially in connection with the earlier work of Lipsch *et al.* (*3*) on the dispersion of MoO_3 on Al_2O_3. These authors had concluded from diffuse reflection measurements that MoO_3 in a MoO_3–Al_2O_3 and CoO–MoO_3–Al_2O_3 catalyst was far more finely dispersed than could be accounted for by assuming a simple mixture of Al_2O_3 and MoO_3. They therefore postulated that MoO_3 is monomolecularly dispersed on the alumina surface by a reaction such as:

$$\text{solid } Al_2O_3\text{–}OH + \underset{\text{(gaseous)}}{H_2MoO_4} \rightarrow \text{solid } Al_2O_3\text{–}O\text{–}MoO_3\text{–}H + H_2O.$$

Our present experiments (see Fig. 5) show that as a consequence of heating a mixture of MoO_3 and Al_2O_3, the steady-state level of conversion of the catalyst is greatly enhanced in good agreement with Lipsch's prediction. We therefore conclude that the origin of the hydrodesulphurization activity of the oxidic forms of the molybdenum/alumina catalysts both with and without cobalt resides in this highly dispersed state of molybdenum ions on the alumina surface.

Preliminary Experiments with Different Promoter Ions (Co, Zn, Hi, Mn)

The results of a comparison of the effect of adding Co, Ni, Mn or Zn ions to the MoO_3–alumina catalyst are demonstrated in Fig. 8. Although no definitive interpretation can be made from these data, a number of interesting features arise and point to the direction in which further investigations have to be made.

At the outset it should be emphasized that all catalysts in this series, regardless of type of promoter ion or its concentration, were prepared initially in the same manner (2 hr, 600°C for calcination, and 1.5 hr, 400°C for reduction). Moreover, all data refer to a partly sulphided state attained by desulphurization of thiophene on an initially oxidic, reduced catalyst. It is noteworthy that we found no significant changes in the relative order of activities after sulphiding. At first sight it seems surprising to find so little apparent difference in the rate of increase of activity with ion concentration in the ascending branches of the curves. A possible explanation of this could be based on the work of Lo Jacono, Schiavello, and Cimino (*23*). These authors have shown that a sample of NiO on γ-Al_2O_3 corresponding to our first point on the NiO–MoO_3–Al_2O_3 curve (Fig. 8) contains 10% of its Ni^{2+} ions in the tetrahedrally coordinated form. With increasing total Ni content more and more of the tetrahedral surface sites become occupied until the process is completed, or nearly completed, at about 4 wt % of NiO. This can be seen to correspond approximately with the maximum in our graph number 8. It is therefore tempting to ascribe the rapid decrease following this maximum to poisoning by excess oxide. In terms also of the work of Lo Jacono *et al.* (*23*), one could understand the initial rise in all four curves as originating merely from tetrahedral site occupation by our four promoter ions. The exact mechanism, of course, by which such an occupation increases the catalytic activity is not at all clearly understood. Evidence cited earlier pointed towards catalyst stabilization as constituting at least one factor in the process. Our model is predicated on the assumption that for all these ions, the mechanism is the same, viz. a change in the state of the molybdenum on the alumina surface, which in turn could influence the initial sulphiding process. Marked differences between the four ions appear only at the succeeding stage of the activity curves (Fig. 8). This is then followed by a sharp drop in activity similar to that exhibited by the Ni curve referred to earlier. If the above model of tetrahedral surface site occupation were to be the only process taking place during the second impregnation, then one would expect the maxima to fall on the same Me/Mo ratio in all four cases. The data of Krischner *et al.* (*24*) show clearly that interaction with the bulk lattice of the γ-Al_2O_3 cannot be disregarded. In a comparison between ZnO and NiO reacting with γ-Al_2O_3 at 600°C to form the respective spinels, ZnO proved to be the faster reactant. This is in agreement with Stone and Tilley's (*25*) earlier determination of activation energies of 88 and 103 kcal/mol, respectively, for the formation of Zn and Ni spinels above 1000°C. Similarly, the doping of our γ-Al_2O_3 lattice can be expected to have been more extensive with ZnO than with NiO during the relatively short calcination time of 2 hr. While we were not able to find pertinent comparisons for Co and Mn in the literature, the above gives us at least one possible explanation for the relative positions of the maxima on the concentration axis.

In view of the above solubility phenomena, an interpretation of specific activities at maximum for the different ions becomes inevitably more complicated. In addition, the steady-state is based on a partly sulphided solid. For instance, to account for the promoter effect of Co^{2+} one would have to think of an interaction of Co with, possibly transfer to, the newly formed MoS_2. It is known that sulphides can incorporate metal atoms in their layer structure; Jellinek (*26*) and Voorhoeve *et al.* (*27*) have both briefly discussed this effect. Furthermore, Lo Jacono *et al.* (*28*) have demonstrated the presence of reduced states of cobalt (Co^+ and Co^0) in sulphided CoO–MoO_3–Al_2O_3 catalysts. It is therefore possible to expect the involvement of such reduced states in our promoter action. Thereby a difficulty could arise if, in order to attain the sulphided steady-state, Co^{2+} had to be transferred from a cobalt aluminate surface spinel with its highly stable tetrahedral coordination. On the other hand, Lo Jacono, Schiavello, and Cimino (*23*) have also shown that in a γ-Al_2O_3 surface, octahedrally and tetrahedrally coordinated nickel spinels may coexist. The octahedral Ni–O bonds are weaker and may be reduced more easily. A similar mechanism might be invoked for all four promoter ions.

Finally we wish to report some initial attempts further to elucidate the nature of the catalytic sites. These involved the desulphurization of thiophene pulses starting with catalysts fully reduced, but not sulphided. An analysis of C_4 saturation, expressed as percent butane formed, was found to be of particular interest. Thus Fig. 9 clearly shows the behavior of zinc-promoted catalysts, which was exhibited also by the other promoter ions, although not to such a marked extent. A decrease of percent butane in the lower concentration range of promoter ions was followed by an increase in the higher range. It will be remembered that this stands in an inverse relationship to desulphurization activity, albeit on a partly sulphided catalyst. Although it is obviously too early to attempt an interpretation, any proposed model must fit both the desulphurization and hydrogenation data. The model proposed above, in which the zinc ions at the lower concentration occupy tetrahedral alumina sites, will be one possibility which we intend to test. The resulting lowering of the acidity of the alumina surface could then be advanced as the reason for the retardation of olefin hydrogenation. Moreover, the increase in hydrogenation activity in the concentration range above the desulphurization maximum could then be ascribed to buildup of metal oxide as such on the surface. It is well known that the reduced oxides and sulfides of at least three of our promoter ions (zinc, cobalt, and nickel) are active olefin hydrogenation catalysts.

A comparison between the four promoter ions at an oxide concentration of 4 wt % shows that hydrocarbon saturation is comparatively insensitive to the nature of the promoter ion under steady-state conditions. In the experiments referred to here, all the hydrogenation activities lie between 10 and 14%. This lack of discrimination is thought to be associated with the sulphiding of the surface. Experiments presently under way are designed to show the effect of presulphiding on desulphurization and hydrogenation. Indications so far are that a presulphided CoO–MoO_3–Al_2O_3 catalyst exhibits olefin saturation which is slightly higher than that of the last-mentioned group of catalyst. Its desulphurization activity has twice the value of these catalysts, which, as will be recalled, had been merely reduced but not sulphided prior to the activity test.

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