THE EFFECT OF PROMOTERS ON MOLYBDENUM CATALYSTS AS USED IN HYDROGENATION.

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In the hydrogenation-cracking * of coals, tars and similar materials, a noteworthy feature is the outstanding position as catalysts of molybdenum compounds, and in particular, of molybdenum sulphide. It has been suggested that the trisulphide is the active catalyst—the catalyst losing its activity as the trisulphide decomposes into the disulphide and sulphur. On the other hand, from the work of Parravano and Malquori [1] on the vapour pressure of sulphur from molybdenum trisulphide, it would appear that, under the normal conditions of hydrogenation experiments, the trisulphide would be completely unstable, and would be converted almost instantaneously to the disulphide.

In the beginning of this work attempts were made to confirm the results of Parravano and Malquori, using a dynamic method based on Knudson's effusion method as developed by Egerton,[2] and also a static method, similar in principle to that of Parravano and Malquori, but using the quartz spring balance of Bakr and McBain [3] to determine the change in weight due to the decomposition or formation of the trisulphide.

The results of these experiments indicated, however, that at the temperatures investigated (about 300° C.) molybdenum trisulphide does not

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* *i.e.* treatment with hydrogen at high pressures (about 200 atmos.) and at temperatures of 350°-500° C.

[1] *Atti. Accad. Linc.*, 1928 (vi.), **7**, 109.

[2] *Proc. Roy. Soc. A*, 1923, **103**, 469.

[3] *J.A.C.S.*, 1927, **49**, 1157.

exhibit a constant dissociation pressure of sulphur, for although at any given temperature it may appear to do so for a fixed ratio of molybdenum to sulphur, the dissociation pressure decreases with the decrease in the amount of sulphur present. This result, suggestive of the formation of a continuous solid solution of MoS_2 in MoS_3, is not necessarily in disagreement with that of Parravano and Malquori,[1] since they did not attempt to investigate the change in vapour pressure with change in the Mo/S ratio, and it does confirm the earlier conclusion, which has since been supported by direct experiment, by several workers, that under the ordinary conditions of hydrogenation-cracking molybdenum trisulphide is unstable.

X-ray diagrams of the molybdenum trisulphide before and after several hours' heating, showed that in addition to the chemical change represented by the conversion to the disulphide, there was also a marked change in the physical structure of the catalyst. The original trisulphide was extremely micro-crystalline, almost amorphous in character, whereas the heated material had a much larger particle size and gave an X-ray diagram similar to that of molybdenite (MoS_2). It will be shown later that the increase in particle size, with the consequent decrease in surface area, was accompanied by a decrease in catalytic activity.

These results furthermore suggested that a possible method of increasing the activity of molybdenum sulphide catalysts would be the introduction of promoter atoms, whose function would be to diminish the rate of sintering of the molybdenum sulphide. In the remainder of this paper a description is given of investigations which have been carried out to determine the general effect of promoters on the catalytic activity of molybdenum compounds.

Experiments with Promoted Catalysts.

The efficiencies of the catalysts were tested by measuring their activity in the conversion of phenol to benzene by hydrogen at atmospheric pressure. This reaction was chosen as being one of the reactions involved in the technical process for the hydrogenation-cracking of low-temperature tar, for which process molybdenum catalysts are more especially used.

Experimental Method.

Cylinder hydrogen, stored in a graduated holder, was passed through a purifier (heated palladium-coated copper for the removal of traces of oxygen) and a phosphorus pentoxide drying tube. The purified and dried gas passed through a capillary flow-meter, and then bubbled through a carburettor consisting of two wash-bottles in series containing phenol, and maintained at a constant temperature (generally 85·0° C.) by an electrically heated air bath. The mixture of phenol vapour and hydrogen then entered the reaction tube, which was heated by an electric furnace. The tubing between the phenol bubbler and the reaction furnace was maintained at about 200° C. in order to avoid condensation of the phenol, and to form a preheater. The tube containing the catalyst was constructed so that while fresh batches of catalyst could easily be inserted or removed, the position of the catalyst in the furnace was always the same. The temperature of the reaction tube was measured by a calibrated platinum-platinum-rhodium thermocouple.

The products of the reaction, consisting of benzene and water, together with any unchanged phenol, were condensed in a U-tube, cooled with liquid air. The U-tube was connected to the catalyst tube by a ground joint sealed with a layer of tin-foil, so that it could be removed, and the ends closed with stoppers for the weighing and analysis of the total product.

In carrying out an experiment, the apparatus was run under the desired experimental conditions for thirty-five minutes before the U-tube was fitted into position. The product was collected over a further period of one hour, the U-tube then removed and weighed. The product was washed out into a 100 c.c. graduated flask with successive washings of 10 per cent. caustic soda, followed by distilled water, the caustic soda ensuring the complete removal of the unchanged phenol. The solution was made up to 100 c.c. and aliquot portions then taken for determination of the unchanged phenol by the potassium bromate method.[4] The accuracy of the method and the solutions used was tested by analysing a solution containing a known weight of pure phenol.

The percentage of phenol in the product thus obtained was then converted to the percentage based on the original phenol by correcting for the increase in weight of condensible material caused by the reaction,

$$C_6H_5OH + H_2 \rightarrow C_6H_6 + H_2O.$$

At the reaction temperatures used, very little conversion of benzene to cyclohexane could take place, so that errors due to the increase of weight of liquid product caused by this reaction may be safely ignored.

In order, as far as possible, to eliminate the deterioration of the catalyst by the deposition on the surface of high-boiling polymerisation products, the molecular proportion of hydrogen to phenol was maintained at about 50 : 1. Under these conditions the reaction can be treated as one of first order :

i.e. $$-\frac{dx}{dt} = kx \qquad (x = \text{concentration of phenol}),$$

from which

$$kt = \log_e \frac{a}{a - x} \qquad (a = \text{initial concentration of phenol})$$

and since α = percentage of phenol unconverted = x/a

$$kt = \log_e \frac{1}{1 - \alpha}.$$

In the experiments described below, for any one series, the throughputs of the hydrogen and phenol were constant, *i.e.* t is constant, and we have (for any given series)

$$k_1 = \log_{10} \frac{1}{1 - \alpha} . \qquad . \quad . \quad . \quad . \quad (1)$$

From the change in k_1 with temperature, values of the apparent energy of activation for different catalysts can be calculated.

Results.

The first series of experiments was carried out with a molybdenum trisulphide catalyst, prepared by precipitation from a solution of ammonium thiomolybdate by dilute sulphuric acid. The catalyst was compressed into small pellets and 1·35 gm. of catalyst inserted in the reaction chamber. A throughput of phenol of 0·3 gm. per hour was used with a reaction temperature of 350° C. The results are shown in Fig. 1, where the efficiency of the catalyst, as measured by the percentage of phenol converted, is shown plotted against the total time of heating of the catalyst. The rapid decrease in activity is evident.

In the investigation of promoters, the substances first tried were silica and chromium and aluminium oxides, but these substances tended to decrease rather than increase the activity. It was found, however, that the catalytic activity of molybdenum sulphide was markedly enhanced by the co-precipitation, with the molybdenum trisulphide, of ammonium phosphomolybdate, and later experiments showed that ammonium phosphomolybdate itself gave a highly active catalyst.

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[4] Treadwell and Hall, *Analytical Methods*, 5th edn., Vol. 2, p. 695.

Experiments with Catalysts prepared from Heteropoly-Compounds of Molybdenum.*

In view of the results obtained with the catalyst prepared from ammonium phosphomolybdate, a series of catalysts was prepared from heteropoly-acids of molybdenum, both of the 12 acid and 6 acid groups, with the promoter atom as the central atom of the complex anion. In actual practice, the ammonium salt of the heteropoly acid was always prepared, and this was heated in hydrogen for six hours at 480° C., when the heteropoly acid was decomposed, and a catalyst consisting either of the mixed oxides of molybdenum and the promoting atom or of molybdenum dioxide and the promoting atom itself obtained. By this treatment, each catalyst was subjected to a fairly drastic and identical sintering process before testing its activity and the catalysts with high initial but transient activities were deactivated.

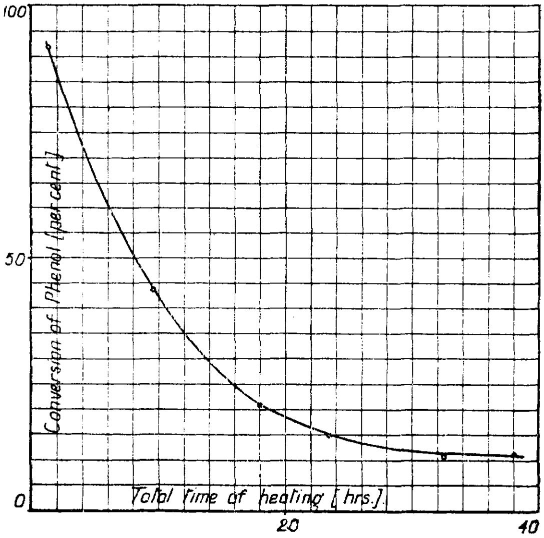

FIG. 1.

Some preliminary experiments were first carried out, with 0·45 gm. catalyst and a throughput of phenol of 0·35-0·4 gm. per hour at a reaction temperature of 350° C. A brief summary of the results obtained is given below.

TABLE I.

Catalyst.	Promoter.	Activity (per cent. conversion of Phenol).
Mo oxide	Unpromoted	24·0
,,	P	95·0 (mean of two experiments)
,,	Si	78·5
,,	Th	18·3
,,	Sn	14·1
Mo oxide V oxide	P	51·9

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* Ammonium phosphomolybdate is the ammonium salt of one of a numerous series of heteropoly-acids of molybdenum. These complex acids and their salts can be divided into two classes according to whether there are twelve or six molybdenum atoms grouped around the central atom of the complex, and can be represented by the following formulæ.[5]

1. 12 acid $R_n[X.(Mo_2O_7)_6]$ $X = P, Si, As, Th, Sn$, etc.
2. 6 acid $R_n[M.(MoO_4)_6]$ $M = Cu, Ni, Cr, Co$, etc.
$R = H, NH_4, K$, etc.

More recently Keggin and Illingworth [6] have shown by X-ray examination that the formula for phosphomolybdic acid (and possibly, therefore, of the other twelve acids) is of the type $H_{12}P(Mo_{12}O_{40})$, but the main classification of these compounds is not affected by this slight modification.

[5] Abegg, *Auerbach, Handbuch der anorg. Chem.*, Vol. 4, Part 1. second half, p. 977.

[6] *J.C.S.*, 1935, **1**, 578.

All these promoted molybdenum oxide catalysts were prepared from heteropoly-compounds of the first group, *i.e.* with 12 molybdenum atoms to each promoter atom. The unpromoted molybdenum oxide catalyst was prepared from ammonium molybdate and the mixed molybdenum oxide-vanadium oxide catalyst with phosphorus as promoter was obtained from the mixed phosphorus heteropoly compound of molybdenum and vanadium, prepared by the method described by Gibbs,[7] and according to him of the formula

$$8(NH_4)_2O . P_2O_5 . 8V_2O_5 . 14MoO_3 . 50H_2O.$$

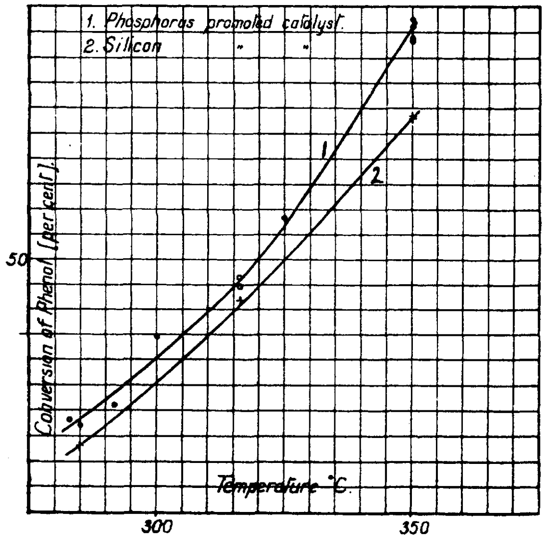

FIG. 2.

The results for the phosphorus and silicon promoted catalysts over a range of temperature of 280°-350° C. are shown in Fig. 2. The results for the phosphorus promoted catalyst were obtained from experiments with two separate batches of catalysts.

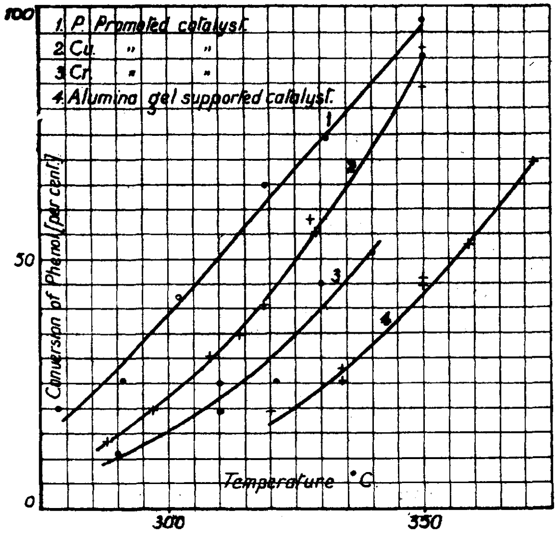

FIG. 3.

The investigation was then extended to the catalysts prepared from the second group of heteropoly compounds. In view of some erratic results obtained when using only 0·45 gm. of catalyst, it was decided to increase the weight of catalyst to 0·85 gm. with a thoroughput of phenol of 0·4 gm. per hour. For comparison, the experiments with phosphorus-promoted and the unpromoted molybdenum oxide catalyst were repeated, using the increased weight of catalyst. At 350° C. the conversion with unpromoted molybdenum oxide was 28·3 per cent. The results obtained over a range of temperature of 280°-350° C. with phosphorus, chromium and copper-promoted catalysts

[7] *Amer. Chem. J.*, 1884, **5**, 391.

are shown in Fig. 3, together with a series of results obtained over a slightly more extended range of temperatures for a supported catalyst. This catalyst was similar to that used at the Fuel Research Station in the technical high-pressure hydrogenation process,[8] and was prepared by impregnating alumina gel with ammonium molybdate so that the catalyst contained 25 per cent. by weight of ammonium molybdate. In order to maintain standard conditions of preparation of the catalysts used in these experiments, the " unpreheated " catalyst [8] was used, *i.e.* the process of ignition in air at 500° C. which is carried out in preparing the catalyst for the technical process, was omitted. Experiments showed that this ignition, while it enhanced the activity of the catalyst for high-pressure hydrogenation, had very little effect on the activity for the reduction of phenol at atmospheric pressure, as carried out in these experiments.

The chromium and copper-promoted catalysts were prepared from compounds of the second group, *i.e.* with six molybdenum atoms to each promoted atom. An analogous nickel compound was also prepared, but the catalyst thus obtained had an extremely variable activity, so the results are not given in detail here ; in general, the results for the nickel-promoted catalyst were similar to those for the copper-promoted catalyst.

The activity-temperature curve for each catalyst was obtained with a single batch of catalyst without revivification, and it was found that during the series of experiments a slight deterioration of the catalyst took place. The catalyst could be restored to its initial activity by heating in hydrogen, the deterioration was therefore presumably due to the deposition on the catalyst surface of high-boiling products formed during the reaction. This deterioration is responsible for the slight spread of the experimental results shown in the curves, since on repeating a determination at any given temperature later in a series, a somewhat lower conversion was obtained.

From a comparison of the results both with unpromoted molybdenum oxide and the phosphorus-promoted catalyst, at the two different weights of catalyst, *i.e.* with different throughputs per gm. catalyst, it is clear that the conversion of phenol does not increase so rapidly as would be expected with the increase in time of contact. Thus the kinetics of this reaction are not as simple as indicated by equation (1), and therefore any values of the activation energy must be treated with some reserve. Calculations of the heat of activation have been made for several catalysts, and it was found that there was surprisingly little variation, all the values obtained being about 25,000 calories. This point will be discussed later.

Some experiments were also carried out with copper-promoted catalysts containing varying proportions of copper to molybdenum. Following the principle of preparing promoted catalysts if possible from chemical compounds rather than from physical mixtures, two catalysts with one copper atom to one and two molybdenum atoms respectively, were prepared[9] from the compounds $Cu\ MoO_4 . 2NH_3 . H_2O$, and $(NH_4)_2\ Cu(MoO_4)_2\ 2NH_3$. A catalyst containing four molybdenum atoms to each copper atom was prepared by mixing in the requisite proportions, solutions of ammonium molybdate and copper nitrate and evaporating to dryness. The results obtained at 350° C. are given below, using 0·85 gm. catalyst.

TABLE II.

No. of Mo atoms per Cu atom .	1	2	4	6 (from Fig. 3)
Per cent. conversion of phenol	56·0	18·6	2·6	88·0

It will be seen that the catalyst obtained from the heteropoly-compound containing six molybdenum atoms to each copper atom is easily the most active, and so a more complete investigation of the other catalysts was not attempted.

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[8] King and Cawley, *Fuel Research Tech. Paper* (1935), No. 41. 4.
[9] Briggs, *J. Chem. Soc* , 1904, **85**, 672.

Determination of Surface Areas.

Since the activity of any given catalyst must be controlled both by the specific activity of the surface, and the total area of the catalyst, it was decided to make some measurements of the respective surface areas of the catalysts employed above. It is well known that the actual quantative determination of the area of any adsorbent surface is difficult, since it depends on, among other factors, the accessibility of the surface to the substance used to measure the area, but it was felt that some estimate of the relative values for these catalysts might be obtained by determining their adsorptive capacities for a gas, such as carbon dioxide, the adsorption of which would be expected to be mainly of the Van der Waals type, under given conditions of temperature and pressure.

Accordingly, determinations were made of the volume of carbon dioxide adsorbed by the catalysts at 0° C. and atmospheric pressure. The apparatus consisted of a small bulb, containing the catalyst, immersed in melting ice in a Dewar flask, and connected to (*a*) a pumping system consisting of a mercury diffusion pump, backed by a Cenco " Hyvac " oil pump, (*b*) a McLeod gauge, and (*c*) a calibrated gas burette, which served both as the burette for measuring the volume of gas admitted and as the pressure manometer. The total volume of the adsorption apparatus, exclusive of the gas burette (and the pumping system and McLeod gauge, which were cut off from the adsorption apparatus proper except when evacuating) was 7·50 c.c., so that the adsorption capacity of catalysts with low surface areas could be evaluated with fair accuracy. Before the determination of the adsorptive capacity was carried out, the catalyst (which had been previously heated in hydrogen at 480° C.) was heated in vacuo at 480° C. for two hours. The results were obtained on Table III.

TABLE III.

Promoter.	Ratio : No. of Mo Atoms / No. of Promoter Atoms	Adsorption (c.c. Co_2 per gm. Catalyst).
P . .	12	4·7
Cu . .	6	2·5
Cu . .	4	0·3
Cu . .	2	0·2
Cu . .	1	1·1
Cr . .	6	2·8
Th . .	12	1·55
Sn . .	12	ca 2·5
Unpromoted MoO_2 .	—	0·3
MoO_2 supported on alumina gel	—	9·7

An approximate value only is given for the tin catalyst, since it was found impossible to get a constant result for this catalyst.

It is clear, however, that neglecting minor differences, the catalysts can be divided into two main classes.

(*a*) Those with adsorptive capacitities about 0·3, including the unpromoted molybdenum dioxide catalyst, and two of the copper promoted catalysts ; and

(*b*) Those with areas of 1·2-5, which include those active in the hydrogenation of phenol, and in addition the tin (which through its value is somewhat erratic undoubtedly had a fairly high adsorptive capacity) and thorium-promoted catalysts, which in spite of having a much larger apparent area than the unpromoted molybdenum oxide catalyst, are less efficient catalytically. The alumina-gel supported catalyst has by far the greatest surface, this in view of its comparatively low activity, suggests that although the method of preparation of this catalyst is designed to cover the alumina gel surface completely with molybdenum oxide, this has not been realised, and the molybdenum oxide is concentrated on certain portions only of the surface.

X-ray Examination of Catalysts.

As stated in the earlier part of this paper, X-ray examinations of the sulphide catalyst were made before and after heating, and similar examinations have been made of the oxide catalysts, in all cases after they had been subjected to the normal treatment of six hours heating in hydrogen at 480° C. The catalysts were mounted on fine glass fibres, and powder photographs taken using the copper Kα line (wave-length 1·54 Å.).

The results obtained can be summarised briefly as follows :—

(1) The phosphorus-promoted catalyst has an extremely micro-crystalline structure, giving an X-ray diagram consisting only of a diffuse halo (d = 2·4 Å.), so that its structure cannot be identified. The silica-promoted catalyst has a somewhat better developed crystalline structure, and the thorium catalyst is even more crystalline. The main lines of the X-ray diagrams in both cases correspond to those of molybdenum dioxide.

(2) The X-ray diagrams for the catalysts prepared from the heteropoly compounds of the second group (*i.e.* Cu, Cr and Ni—promoted catalysts) show well defined crystalline structures. The X-ray diagrams for these catalysts also corresponded within experimental error, both in spacings and intensities, to that for the molybdenum dioxide catalyst prepared from ammonium molybdate. A representative selection of the spacings (d) and the intensities of the lines of this diagram are given below, together with the data calculated for molybdenum dioxide.[10] The intensities were calculated, using the appropriate formula,[11] the parameter u in the structure factor [10] being taken as 0·3. Absorption effects were ignored ; they would tend to reduce the intensity of the reflections for the planes with the larger spacings.

TABLE IV.

(Obs.).		(Calc.).		
d(Å).	Intensity.	d(Å).	Intensity.	
3·43	VS	3·44	10	(110)
2·45	VS	2·43 2·42	7·6	(200) (011)
2·14	W	2·17 2·165	0·5	(210) (111)
1·73	VS	1·72 1·715	6·6	(220) (211)
1·54	W	1·54	1·4	(310)

With the possible exception of the copper-promoted catalyst, it has not been possible to identify lines due to the promoters, but these lines would only be faint, and on the other hand, it is possible that the absence of the lines is due to the formation of solid solutions of the promoter in the molybdenum dioxide, the consequent distortion of the lattice being within the experimental error of the determination of film spacings.

(3) With the series of copper-promoted catalysts containing different proportions of copper, the X-ray diagrams are similar in that the main structure is that of molybdenum dioxide, but as the proportion of copper is increased new lines appear, the spacings of which agree with those calculated for copper.

(4) Samples of the phosphorus, chromium and silicon promoted catalysts were re-sintered in hydrogen at 700° C. and their X-ray diagrams taken. They show in each case that the molybdenum dioxide had been completely reduced to molybdenum.

The diagrams show also that the phosphorus and silicon-promoted catalysts had become much more crystalline in character as a result of the resintering process.

(5) The alumina gel supported catalyst gave an X-ray diagram exactly similar to that of pure molybdenum dioxide, the support, as would be

[10] Wyckoff, *The Structure of Crystals*, p. 238 ;

[11] *International Tables for determination of Crystal Structure.*

expected, showing no crystalline structure, while the molybdenum dioxide was completely crystalline.

Discussion.

A review of the data on catalytic activities and the values of the adsorptive capacities shows that a large surface area is necessary for a highly active catalyst. In the case of the phosphorus promoted catalyst (and to a lesser extent the silicon-promoted catalyst) the molybdenum dioxide is maintained in a nearly colloidal or amorphous state by the presence of the promoter atom, which furthermore confers a high degree of stability on this finely divided state, since it is only destroyed under conditions which lead to the complete reduction of the molybdenum dioxide to molybdenum.

On the other hand, the copper, chromium and nickel-promoted catalysts, have a well-developed crystalline structure, the original heteropoly compounds from which they are prepared being themselves crystalline. Nevertheless they are active catalysts, and have large surface areas, and it must be assumed that in the preparation of the catalysts by the decomposition of the crystalline heteropoly compound, the crystals develop a large internal area, and are not easily recrystallised to a denser form with lower surface area. Since the unpromoted catalyst is prepared in a similar way, by the decomposition of crystalline ammonium molybdate, the lower surface area and catalytic activity must be accounted for by the fact that any large internal area formed in this case is more easily destroyed on heating, by recrystallisation.

It must be noted, however, that while a large surface area is necessary in order to obtain a highly active catalyst it is possible to effect an increase in the total specific surface of the catalyst without increasing the catalytic activity. There are two promoted catalysts with fairly high surface areas, where the catalytic activity has been depressed by the addition of the "promoter," *i.e.* the tin and thorium-promoted catalysts.

The X-ray diagrams shows that (except in the case of phosphorus, where the catalyst structure cannot be identified) the main structure of all the catalysts is that of molybdenum dioxide itself. In the series of copper-promoted catalysts, as the copper content increases new lines appear, the spacings of which agree with those calculated for copper. These results are not in agreement with the observations made in the technical literature on the use of heteropoly-compounds as hydrogenation catalysts,[12] where it is stated that "care is taken that the said grouping" (*i.e.* that of the heteropoly-acid) "is not destroyed," whereas the results in this paper show that active catalysts can be obtained with systems where no trace of the original heteropoly-acid grouping is left—further, from the observations made in this work, it is doubtful whether such grouping could survive the conditions of hydrogenation experiments.

It has been shown earlier that the kinetics of the catalytic reduction of phenol are not as simple as that represented by equation (1). Further study of the reaction is necessary to elucidate it completely, but these experiments suggest that a possible explanation of the abnormalities observed is that some inhibition of the reaction by the products takes place (compare Aicher, Myddleton and Walker).[13] It has been shown also that there are no striking differences in the apparent energy of activation for the different catalysts, this may also be a consequence of

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[12] *Brit. Pat.* 371, 833.

[13] *J.S.C.I.*, 1935, **54**, 313T.

the more complex nature of the reaction, and might be due to the fact that the energy of activation is determined by a process, such as the evaporation of the products from the catalyst surface, which has the same or similar energy for all the catalysts.

Recent work by Griffith[14] has indicated that in the preparation of promoted catalysts by admixture of the catalyst and promoter, the concentration of the latter has a critical value, which may be similar for different promoters for the same reaction, but which varies according to the reaction used. Unfortunately, it is not possible to make a complete comparison of the catalyst-promoter ratios with those used in this work. And, on the other hand,while the preparation of the catalyst from the heteropoly-compound of molybdenum and the promoting atom of necessity does not permit of variation in the composition of the catalyst in order to prepare one of the critical composition, it has been shown above to be an extremely efficient method of promotion.

Summary.

1. Under the ordinary conditions of hydrogenation experiments molybdenum trisulphide is converted to the disulphide, and also becomes more crystalline in character with a consequent loss in catalytic activity.

2. Attempts were made to inhibit the sintering by the addition of promoters, using the hydrogenation of phenol to benzene as a measure of the activity of the catalyst. It was found that ammonium phosphomolybdate was a good promoter, and later, that it gave a highly active catalyst. A series of experiments are then described using catalysts prepared from a series of heteropoly compounds of molybdenum. It is shown that phosphorus, silicon, copper, nickel and chromium enhance the activity of the catalyst, tin and thorium depress it.

3. Determinations of the adsorptive capacities of the catalysts for Co_2 have been made. They show that while a high surface area is essential for an active catalyst, tin and thorium increase the area of the catalyst, but depress the activity.

4. X-ray diagrams have been obtained of the catalysts. The catalysts have the structure of molybdenum dioxide. In the phosphorus promoted catalyst the effect of the promoter is to maintain a micro-crystalline structure of the catalyst; the other catalysts have a well-developed crystalline structure.

The writer, who is a member of the research staff of the Department of Scientific and Industrial Research, carried out this work in the Department of Colloid Science, Cambridge, under the direction of Professor E. K. Rideal.

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[14] Griffith and Hill, *Proc. Roy. Soc. A*, 1935, **148**, 193; Griffith, *Nature*, 1936, **137**, 538; Griffith, *Trans. Faraday Soc.*, 1937, **33**, 405.