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## MOLYBDENUM OXIDE CATALYSTS

# MOLYBDENUM OXIDE CATALYSTS FOR THE **REDUCTION OF PHENOL TO BENZENE.**

By L. A. WOODWARD AND A. T. GLOVER.

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It is known<sup>1</sup> that phenols may be reduced to the corresponding aromatic hydrocarbons by hydrogen at atmospheric pressure in the presence of suitable catalysts, including compounds of molybdenum. The behaviour of molybdenum oxide catalysts has been investigated more particularly by Bahr and Petrick 2,8 and by Kingman.4 The former workers explained the deterioration of the catalysts during use as due principally to the progressive reduction of the trioxide MoO<sub>3</sub>, which they supposed to be the active species, to form the dioxide MoO<sub>2</sub>, which they supposed to be inactive. In support of this view they found that a specimen of the dioxide, prepared by reduction of the trioxide, showed hardly any On the other hand Kingman, by X-ray examination of active activity. catalysts with and without promoters, found that they all possessed the MoO<sub>2</sub> structure. The present work was undertaken in the hope of throwing light on the apparent incompatibility of these earlier results and upon the general behaviour of molybdenum oxide catalysts in the reduction of phenol to benzene by hydrogen at atmospheric pressure.

## **Determination of Catalyst Activities.**

## Experimental.

A flow method similar to that of Kingman 4 was used, in which phenol vapour A now interloce similar to that of hingman was used, in which picture report was entrained by passing a steady stream of hydrogen through molten phenol at constant temperature, the mixture was passed over a weighed quantity of catalyst at known temperature, and the reaction products were collected and analysed. The constancy of the rate of passage of hydrogen (approx. 10 l. per hr.) was indicated by a capillary flow-meter and the stream of gas passed through  $P_2O_5$  drying-tubes and also a liquid-air trap (to remove traces of condensible matter) before entering an oil thermostat containing two spiral phenol saturators The thermostat temperature was regulated to  $75 \pm 0.1^{\circ}$  c. By a in series.

<sup>3</sup> ibid., 1933, 14, 187. <sup>4</sup> Trans. Faraday Soc., 1937, **33**, 784.

<sup>&</sup>lt;sup>1</sup> Fischer, Bahr and Petrick, Brennstoff-Chemie, 1932, 13, 45.

<sup>&</sup>lt;sup>2</sup> ibid., 1933, 14, 161.

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suitable arrangement of mercury seals, also immersed in the thermostat, the hydrogen stream could be made to pass either directly into the reaction vessel without phenol entrainment, or alternatively through the phenol saturators. The glass reaction vessel was vertical, the catalyst sample being supported near the middle on an asbestos plug resting on a suitable constriction. The vessel was heated by an electric furnace and the reaction temperature measured to  $\pm 2^{\circ}$  c. by a fine-gauge thermocouple situated within a thin glass sheath at the centre of the catalyst bed. The hydrogen entered at the top through a ground glass joint, the purpose of which will be explained below in the section dealing with the X-ray investigation of the catalysts. For the whole of its passage from thermostat to reaction vessel, the reaction mixture was electrically heated to 100° c. to prevent condensation of phenol vapour. The products issuing from the bottom of the reaction vessel were collected by passage for a measured time through two weighed receivers immersed in liquid air, condensation before reaching the receivers being prevented by electrical heating. The receivers were then re-weighed, the condensate washed out with NaOH solution and the amount of phenol present determined with standard bromate-bromide solution in the usual way.

Before undertaking activity determinations, hydrogen was passed through the phenol saturators for 24 hr., after which the condensate collected in absence of catalyst was found to be 100 % phenol. Collection was always complete in the first of the two receivers. The rate of input of phenol was about 0.38 g./hr., the variations being so small as not seriously to affect the observed values of catalyst activity.

From the equation :

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

it follows that, if W is the weight of condensate and w the weight of phenol it contains, the % conversion of phenol to benzene is given by  $\frac{\vartheta_0^*}{w}(W-w) \times 100}{w + \frac{\vartheta_0^*}{v}(W-w)}$ . The value of this expression was taken as a measure of the mean catalyst activity over the period of collection. No account was taken of the very small quantities of water that may be formed by reduction of the catalyst.

Activities of Catalysts without Preliminary Reduction.—The starting material, as for all catalysts used in the present work, was Analar molybdenum trioxide previously dried at 100° c. Preliminary experiments showed that 0.35 g.



FIG. 1.—Effect of reaction temperature on the variation of activity of MoO<sub>3</sub> catalyst with time.

was a suitable amount for test and, except where otherwise stated, this was the weight taken. In each run the catalyst was raised to the reaction temperature

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in half an hour with pure hydrogen passing. Then phenol entrainment was started and condensates collected over successive 1 hr. periods.

A series of runs was carried out with reaction temperatures of 300, 325, 365, 400 and 440° c. The results are shown graphically in Fig. 1, in which activities are plotted at the middle of the corresponding I hr. periods. To illustrate the degree of reproducibility of the determinations, the points for duplicate runs are included for one reaction temperature  $(365^{\circ} c.)$ . Results at other temperatures showed similar agreement. Some differences between duplicate runs are to be expected, owing principally to non-reproducibility of catalyst packing and slight variations of phenol input rate. They are seen, however, to be too small to cast doubt on the general shapes and relative positions of the curves.

#### Discussion.

The activity-time curves show an initial rise (probably from zero) to a maximum. This effect was not present in the work of Kingman 4 whose catalysts were subjected to preliminary reduction before test; and it received only brief mention from Bahr and Petrick.<sup>2, 3</sup> The time required to attain the maximum activity is seen to diminish regularly with increase of reaction temperature. These phenomena can best be accounted for on the view that the original molybdenum trioxide is inactive and that the activity is developed as the result of reduction, the rate of which increases with increase of temperature. The attainment of a maximum followed by a slow fall indicates that the generation of activity by reduction is opposed by a process of deterioration, probably due to thermal sintering of the active surface and cloaking by deposit of small quantities of products of high molecular weight from side-reactions. That such deposits play a part in the deterioration is shown by the observation of Bahr and Petrick that CO<sub>2</sub> was evolved when a spent catalyst was heated in air, and that a revivification of activity resulted. Our observations, however, are not in harmony with the view of these workers that the active species is the trioxide and that the reduced catalyst is The principal evidence adduced in support of their theory was inactive. that a specimen of molybdenum dioxide, prepared by complete reduction of the trioxide, was found to have hardly any activity. The significance of this evidence was further investigated by the following experiments on pre-reduction of molybdenum trioxide.

## Reduction of Molybdenum Trioxide by Hydrogen.

Reduction in absence of phenol was studied at 300, 350 and 450° c. The weight of trioxide taken for each run was 5 g., which was the largest amount that could be accommodated in the reaction vessel so as to lie wholly within the range of constant temperature of the furnace. In order to remove adsorbed water, each sample was first kept for several hours in a stream of hydrogen at  $150^{\circ}$  c., at which temperature reduction is negligible. Reduction was then allowed to proceed at the desired temperature until the rate of collection of water in the liquid-air traps became inappreciable. The times required at 300, 350 and 450° c. were respectively 120, 90 and 60 hr. The total weights of water collected were the same within 3 %, showing that practically the same stage of reduction had been attained in all three cases. All the products had the dark colour of molybdenum dioxide. The trioxide is white.

The products were cooled to room temperature and removed from the reaction vessel for analysis. In the case of the product of reduction at 450° C., exposure to the air produced no observable effect. The molybdenum content, determined gravimetrically as lead molybdate,<sup>6</sup> was found to correspond within the limits of experimental error to MoO<sub>4</sub> (theoretical, 75.0%; observed 74.65%). This result is in agreement with that of Herington and Rideal <sup>6</sup> who found that the loss of weight on reduction at 475° C. corresponds to formation of molybdenum dioxide only, though at 550 and 575° C. appreciable further reduction (presumably to molybdenum metal) occurs. It also confirms the observation of Bahr and Petrick <sup>3</sup> that reduction at 450° C. gives the dioxide quantitatively.

<sup>6</sup> See Treadwell and Hall, Analytical Chemistry (1935), Vol. II, p. 277. <sup>6</sup> Proc. Roy. Soc. A, 1945, 184, 434. As shown by the equality of the amounts of water formed, the product of reduction at 300° c. and 350° c. is likewise molybdenum dioxide; but when the samples were exposed to the air (after cooling to room temperature) they were found to be pyrophoric and glowed brightly. The percentages of molybdenum by weight in the resulting powders were found to be 69.6 for the sample reduced at 300° c. and 72.6 for that reduced at 350° c. These correspond roughly to 35 %  $MOO_2 + 65$  %  $MOO_3$  and 70 %  $MOO_2 + 30$  %  $MOO_3$  by weight respectively. After exposure to air the powders retained the dark colour of the doxide unchanged.

Activities of Pre-reduced Catalysts.—Activity-time curves for the phenolhydrogen reaction at  $350^{\circ}$  c. were determined for catalysts which had been prereduced to molybdenum dioxide at temperatures of 300, 350 and  $450^{\circ}$  c. For each run the standard weight (0.35 g.) of the trioxide was taken and the times of pre-reduction (120, 90 and 60 hr. respectively) were chosen in the light of the above results so as to ensure complete formation of molybdenum dioxide in all cases. After pre-reduction the temperature was adjusted as rapidly as possible to  $350^{\circ}$  c., whereupon phenol entrainment and hourly activity determinations were begun. The results obtained are shown in Fig. 2. A similar sample of trioxide reduced for 60 hr. at  $550^{\circ}$  c. was found to be completely inactive.



FIG. 2.—Effect of pre-reduction temperature on activity of MoO<sub>2</sub> at 350° c.



FIG. 3.—Activity at 350° c. of catalyst pre-reduced at 300° c.

The curves of Fig. 2 are essentially different in form from those of Fig. 1. The initial rise of activity from zero to a maximum, observed for the trioxide without pre-reduction, is absent. This provides strong evidence for the view expressed above that this initial rise is due to reduction of the inactive trioxide, and shows the incorrectness of the view of Bahr and Petrick that the trioxide is the active species. Furthermore, it is seen from Fig. 2 that, although all the catalysts tested had been reduced completely to molybdenum dioxide, their initial activities decrease sharply with increase of reduction temperature. Now it appears from their account that the specimen of dioxide which Bahr and Petrick found to be nearly inactive had been prepared by reduction of the trioxide at 450° c. Their observation as to its very low activity is thus in agreement with ours; but their deduction that molybdenum dioxide is always inactive is seen to be inadmissible, and the apparent inconsistency with the results of Kingman's X-ray examination of active catalysts is resolved.

Evidence is given below that the active dioxide formed at the lower temperatures differs in particle size from the almost inactive dioxide formed at  $450^{\circ}$  c.

Reference to Fig. 2 shows that, although the catalyst reduced at  $300^{\circ}$  c., has a considerably higher initial activity than that reduced at  $350^{\circ}$  c., the rate of deterioration of the former is much greater. In consequence, the activity-time curves cross after about 3 hr. working. From a practical point of view, therefore, there is clearly an optimum temperature of prereduction for the best overall catalyst performance. This can be explained on the view that the initially more active catalyst surface is either more susceptible to thermal sintering or that it enhances the small amount of side reaction and so becomes more rapidly cloaked with products of high molecular weight.

Activity of Pre-reduced Catalysts after Exposure to Air.—0.35 g. of molybdenum trioxide was reduced for 120 hr. at 300° c. and cooled to room temperature. Air was then passed through the reaction vessel and a sharp rise of temperature was observed. When this pyrophoric effect had subsided, the air stream was replaced by hydrogen, the temperature raised to 350° c. and activity determinations at once started. The activity-time curve for this catalyst is shown in Fig. 3, which for comparison also shows the curve from Fig. 2 for the corresponding catalyst pre-reduced at the same temperature but not exposed to air. An exactly analogous pair of curves was obtained for catalyst pre-reduced at 350° c.

Exposure to air is seen to cause an appreciable reduction of activity, but it is notable that the two curves of Fig. 3 are of similar form. Although by analysis the composition after exposure to air corresponded roughly to  $35 \% \text{ MOO}_2 + 65 \% \text{ MOO}_3$  instead of pure  $\text{MOO}_2$ , there is no sign of an initial rise of activity of the kind observed with molybdenum trioxide. The diminution of activity caused by exposure to air may be due to sintering of the active surface at the high temperatures of the pyrophoric effect; but apart from this it appears that the active structure, when once developed, survives the oxidation by air and does not have to be produced afresh by re-reduction of trioxide. Further light on this interesting point is provided by the X-ray investigation of these catalysts described below.

## Reaction of Catalysts with Phenol in Absence of Hydrogen.

It has been shown by Woodward and McKee<sup>7</sup> that active catalysts will react with phenol at  $350^{\circ}$  c. in absence of hydrogen and that benzene is produced. The evidence was as follows. A sample of active molybdenum oxide catalyst was thoroughly de-gassed by evacuation at  $420^{\circ}$  c., after which the temperature was lowered to  $350^{\circ}$  c. and phenol vapour admitted up to a pressure of approximately o 1 mm. Hg. The pressure was unchanged after 6 hr., showing that in any reaction that might have been occurring each molecule of phenol had been replaced by one molecule of product in the gas phase. That benzene had in fact been formed was proved by determination of the pressure-volume curve of the resulting vapour at room temperature. The curve obtained was quite different from that of phenol vapour and showed a distinct break at the saturated vapour pressure of benzene.

In the present work this reaction of catalysts with phenol in absence of hydrogen was investigated by the flow method in a manner similar to that for the activity determinations described above. A sample of catalyst that had been completely reduced at  $300^{\circ}$  c. cooled and exposed to air (pyrophoric) was raised to  $350^{\circ}$  c. in a stream of nitrogen, whereupon phenol entrainment and activity determinations were started. Reaction with phenol took place, but in order to obtain an initial activity of a suitable magnitude for measurement it was found convenient to use a larger weight of catalyst (3 g.) than in the activity determinations for the phenol-hydrogen reaction. The phenol input rate was also slightly lower (approx. 0.32 g./hr.). The results obtained are shown in Fig. 4.

7 Unpublished work.

In calculating the activities it was assumed that the oxygen of the phenol is taken up by the catalyst with production of benzene. As far as condensation of products is concerned, therefore, the reaction is  $C_6H_5OH \rightarrow C_6H_6$  and the activities (i.e. % conversions) are accordingly obtained from the expression:

$$\frac{\frac{94}{78}(W-w)\times 100}{w+\frac{94}{78}(W-w)}.$$

Owing to the different catalyst weight the scale of activities is of course different from that for the previous experiments with phenol and hydrogen.

A similar curve to that of Fig. 4 was obtained for the catalyst reduced at  $350^{\circ}$  c. and exposed to air, the initial activity being lower and the rate of fall slightly less. A catalyst reduced at  $450^{\circ}$  c. showed no measureable reaction with phenol at  $350^{\circ}$  c. in absence of hydrogen. Unreduced molybdenum trioxide was likewise without activity.

Although in the experiments of Woodward and McKee, quoted above, the catalyst was thoroughly pumped out before admission of phenol vapour, it might possibly be objected that adsorbed hydrogen from the original reduction may not have been completely removed and that the formation of benzene may have been by the ordinary reaction,

 $C_6H_5OH + H_2 \rightarrow C_6H_6 + H_2O.$ 

To account for the constancy of the pressure it would then be necessary to assume that the water remained strongly adsorbed. Such an objection appears to be inadmissible in relation to the present work, however, since the catalyst in question had been exposed to air before use, and it is most unlikely that any hydrogen remained associated with it after the consequent pyrophoric oxidation.

As stated above, the activities of Fig. 4 were calculated on the assump-



FIG. 4.—Reaction of catalyst with phenol at 350° c. in absence of hydrogen.

tion that the catalyst takes up the oxygen from the phenol molecule with formation of benzene. This finds support in the fact that the weights of the successive hourly condensates were all the same within a few per cent., although their phenol contents were so markedly different. The reaction cannot therefore have involved any serious breakdown of the phenol to gaseous products or polymerisation to involatile material remaining on the catalyst surface. It is thus reasonable to suppose that the reis simply: phenol + active catalyst  $\rightarrow$  benzene + " oxidised action catalyst." The active catalyst on the left-hand side of this equation had taken up oxygen, on exposure to air, so as to attain a composition corresponding approximately to 35% MoO<sub>2</sub> + 65% MoO<sub>3</sub> (see above). From the weight of catalyst used and the total amount of phenol converted a rough calculation shows that the uptake of oxygen from phenol was sufficient to make the final composition correspond to about 25 %  $MoO_2 + 75 \% MoO_3$ . It is remarkable that after its pyrophoric reaction with air the catalyst should still be able thus to take up oxygen from phenol at 350° c. The amounts concerned indicate that in both cases the reaction is not confined to the surface of the catalyst, but involves penetration of oxygen into the interior of the particles. Possibly the rapid fall of activity in Fig. 4 is due to the increasing slowness of this penetration with increase of the amount of oxygen taken up at the catalyst surface.

It is interesting to note that, since the "oxidised catalyst" may be reduced with hydrogen, it is possible to effect the overall reaction,  $C_6H_5OH + H_2 \rightarrow C_6H_6 + H_2O$ , in two separate stages: (i) phenol + active catalyst  $\rightarrow$  benzene + "oxidised catalyst," followed by (ii) "oxidised catalyst" + hydrogen  $\rightarrow$  water + active catalyst. It is not suggested that the catalytic reduction of phenol in presence of hydrogen necessarily proceeds by such stages, but it appears probable that the affinity of the catalysts that are active for the reduction of phenol by hydrogen will also react with phenol alone, whereas catalysts that are inactive for the phenol-hydrogen will not react with phenol.

This striking parallelism is also of interest in relation to the view of Herington and Rideal 6 that the active species in the reduction of phenol by hydrogen is not molybdenum dioxide but a thin surface layer of molybdenum metal, the presence of which they infer from the fact that appreciable reduction beyond the stage of MoO<sub>2</sub> is possible at higher temperatures. The work of these authors is concerned principally with catalysis of a quite different reaction, the aromatisation of paraffins. By comparing their results with those of Kingman<sup>4</sup> they find, for molybdenum oxide catalysts containing different promoters, that in general greater ease of reduction beyond MoO<sub>2</sub> at high temperatures is associated with lower activity for aromatisation and higher activity for phenol reduction. This they take as evidence that the catalytically active species for the two reactions are respectively molybdenum dioxide and molybdenum metal. The possibility that molybdenum dioxide is the active catalyst for phenol reduction cannot, however, be ruled out on this evidence; for if one property of this species (namely, ease of high-temperature reduction to metal) is affected by the presence of promoters, it is not unreasonable to suppose that other properties (for instance, catalytic activity for phenol reduction or aromatisation) will also be affected. The present work indeed provides evidence in support of the view that it is the dioxide that is active in the reduction of phenol by hydrogen; for it is improbable that any surface molybdenum metal would survive pyrophoric oxidation, and yet the catalytic activity is not thereby destroyed. Were it only a question of the survival of activity for the phenol-hydrogen reaction, it could be objected that the excess hydrogen might be able rapidly to reduce the oxidised molybdenum to metal again : but after the pyrophoric effect the catalyst is still active for reaction with phenol in absence of hydrogen, where such re-reduction is out of the question. Hence, if we admit the parallelism between the activities of catalysts for the reaction with phenol in absence of hydrogen and for the catalytic reduction of phenol by hydrogen, it becomes difficult to maintain the view that the active species is molybdenum metal.

#### X-Ray Examination of Catalysts.

Samples were examined by the X-ray powder method in the hope of throwing light upon the structure of the "oxidised catalyst," referred to in the preceding discussion. It should of course be borne in mind that this method gives information about the bulk structure of the catalyst particles, whereas their catalytic activity is a property of the surface. However, the quantities of oxygen taken up when active molybdenum dioxide samples are exposed to air indicate that this reaction is not confined to the surface. As capacity to take up oxygen in this manner is associated with catalytic activity, it was thought to be of interest to use the X-ray powder method of investigation.

## Experimental.

Owing to the pyrophoric character of some of the powders, specimens to be photographed were not mounted in the customary manner upon a hair, but were enclosed in thin-walled capillary tubes filled with hydrogen. The capillaries (diam. o·5 mm.; wall thickness < o·02 mm.) were made of boro-silicate glass having a high permeability to X-rays. Capillaries of Lindemann glass proved to be too fragile and collapsed on evacuation.

The following technique was adopted for transferring catalyst from reaction vessel to capillary without contact with air. A current of hydrogen was passed upwards through the reaction vessel (i.e. in the reverse direction from that during catalyst reduction or activity determination), the ground-glass joint at the top was then opened and the phenol lead-in tube replaced by a vertical tube blown out a few inches above the joint into a thin-walled bulb with a hydrogen exit at the top. After allowing sufficient time for the hydrogen stream to replace all the air, the tube above the bulb was drawn off. The reaction vessel and attached bulb-tube, filled with hydrogen, were then withdrawn from the reaction furnace and inverted, whereupon the catalyst fell into the bulb, which was drawn off. The bulb containing the catalyst was then transferred to a specially constructed vessel fitted with an internal 100-mesh sieve and tapering below to a narrow neck to which the boro-silicate capillary was attached. This vessel was evacuated and hydrogen let in to I atm. pressure, after which the bulb containing the catalyst was broken by a suitable device operated from outside without admission of air. By tapping, a sample of the catalyst powder was made to pass through the sieve and so into the capillary, which was then drawn off for mounting in the X-ray camera.

The copper K-lines were used, and for purposes of comparison photographs were first taken with specimens of pure molybdenum dioxide (prepared by complete reduction of the trioxide at  $450^{\circ}$  c.) and of pure re-sublimed trioxide. Both specimens gave well-defined diagrams. Owing to the finite sizes of specimen and source, the values of the interplanar spacings d, deduced in the usual way from the measured positions of the lines, are subject to systematic corrections known from previous work with comparable samples to range from -0.15 A. at small angles to -0.01 A. at angles near  $90^{\circ}$ . Taking these corrections into account, the d-values and relative intensities of all the lines measured (II for the dioxide and 23 for the trioxide) agreed well with the values calculated from the recorded crystal structure data for the respective compounds.<sup>8</sup>

the recorded crystal structure data for the respective compounds.<sup>8</sup> Samples of dioxide prepared by the complete reduction of the trioxide at 300° c. and 350° c. and transferred to the capillaries without contact with air were next examined. The diagrams corresponded to the  $MoO_2$  structure, but with the same exposure time as before, were less well-defined and showed only the strongest lines. This indicates that the particle size is smaller than for the inactive dioxide produced at 450° c. Diagrams were also obtained for samples of the catalysts reduced at 300° c.

Diagrams were also obtained for samples of the catalysts reduced at  $300^{\circ}$  c. and  $350^{\circ}$  c. and then exposed to air. Although by analysis these had compositions corresponding to about 65 % and 30 % molybdenum trioxide by weight respectively, both had the dark colour of the dioxide and gave diagrams showing only the strongest lines of the MoO<sub>2</sub> structure with no trace of the MoO<sub>3</sub> structure. The observed *d*-values for these samples, as deduced from the measured positions of the lines without the corrections referred to above, are given in Table I, together with the corresponding values observed for MoO<sub>3</sub>.

MoO <sub>2</sub> .			" 65 % MoO3."		" 30 % MoO3."	
h. k. l.	d (A.).	Intensity.	d (A.).	$\Delta d$ (A.).	đ (A.).	$\Delta d$ (a.).
1 1 0	3.31	strong	3.32	+ 0.04	3'34	+0.03
200 101	2.35	strong	2.39	+0.04	2.37	+0.03
2 2 0 2 I I	<b>1</b> .68	strong	1.24	+ <b>0</b> •06	1.72	+0.04
3 1 0	1.20	med ium			1.23	+0.03

 
 TABLE I.—Uncorrected Lattice Spacings of Active Catalysts after Exposure to Air.

<sup>8</sup> Wyckoff, The Structure of Crystals (2nd. Edn., 1931), p. 238; ibid. (2nd Edn. Suppl., 1935), p. 38.

Although the values of d in Table I require correction to convert them to true lattice spacings, the values for each  $(h \ h \ l)$  are comparable with one another. It is seen that the spacings for the active catalysts after exposure to air are all greater than those for pure MoO<sub>2</sub>. The differences shown in the table in the columns headed  $\Delta d$  are small, but outside the estimated limits of experimental error  $(\pm \text{ orol } A.)$  of the uncorrected d-values.

X-ray powder photographs were also taken for samples of trioxide catalyst after use for different times in the phenol-hydrogen reaction at  $350^{\circ}$  c. The same procedure was followed as in the determination of the activity curves of Fig. 1, the reaction being started without pre-reduction of the catalyst. After the desired time the catalyst was allowed to cool and was then transferred to the capillary without contact with air. Samples that had been working for 5 hr (corresponding roughly to attainment of maximum activity) and 10 hr. both showed the black colour of molybdenum dioxide, but gave normal X-ray diagrams of MoO<sub>3</sub> only. A sample after 10 hr. working at  $440^{\circ}$  c. again gave the normal MoO<sub>3</sub> diagram strongly, but the most intense lines of MoO<sub>2</sub> also appeared faintly. The *d*-values of these lines were all greater by 0.03 A. than the corresponding lines for ordinary MoO<sub>2</sub> (cf. Table I).

The X-ray diagrams show that samples of molybdenum dioxide formed by reduction at 300 and  $350^\circ$  c. have the same structure as the product of reduction at  $450^\circ$  c., but a smaller particle size. This may well be connected with the fact that the dioxide formed at the lower temperatures shows high catalytic activity, whereas that formed at  $450^\circ$  c. is almost inactive. Kingman <sup>4</sup> found that a large surface area is necessary in order that a catalyst shall be highly active.

Associated with the catalytic activity is the pyrophoric oxidation on exposure to air. Despite the large amounts of oxygen taken up, the X-ray diagrams show that the dioxide structure persists, but with an expansion of the lattice spacings. It seems probable that when the active catalyst reacts with phenol in absence of hydrogen the oxygen of the molecule is taken up by the dioxide lattice in this way.

After use for 5 or 10 hr. in the phenol-hydrogen reaction at  $350^{\circ}$  c., samples of molybdenum trioxide (not pre-reduced) showed high activities and the dark colour of the dioxide, but gave X-ray diagrams of MoO<sub>3</sub> only. The amounts of dioxide present were evidently too small to be recorded in the X-ray photographs, and the result shows that the activity is developed as soon as a thin surface layer has been reduced.

Our thanks are due to Mr. J. L. Copp for carrying out preliminary experiments, to Dr. W. Hume-Rothery for facilities and advice in connection with the X-ray investigations and to Dr. E. F. G. Herington for helpful discussion.

#### Summary.

r. When molybdenum trioxide is used as catalyst for the reduction of phenol to benzene at atmospheric pressure, the activity-time curves for temperatures from  $325^{\circ}$  to  $440^{\circ}$  c. show an initial rise from zero to a maximum, indicating that the effective catalyst is formed from the trioxide by reduction.

2. Samples of molybdenum dioxide prepared by complete reduction of the trioxide at  $300^{\circ}$  c. or  $350^{\circ}$  c. are active when tested at  $350^{\circ}$  c. Dioxide similarly prepared by reduction at  $450^{\circ}$  c. is almost inactive at  $350^{\circ}$  c. X-ray examination shows that the active samples have the smaller particle size.

shows that the active samples have the smaller particle size. 3. Active dioxide is pyrophoric, inactive dioxide is not. Considerable quantities of oxygen are taken up by active dioxide on exposure to air, but the X-ray diagram is still that of  $MoO_2$  without any  $MoO_3$  and the material remains catalytically active.

4. Active dioxide after exposure to air reacts with phenol at 350° c. in absence of hydrogen. Molybdenum trioxide and inactive dioxide do not. The reaction is apparently a removal of oxygen from the phenol molecule by the catalyst with formation of benzene. The evidence is discussed and shown to favour the view that the catalytically active species in the reduction of phenol by hydrogen is molybdenum dioxide rather than molybdenum metal possibly present on the surface.

Jesus College, Oxford.