

365. Methanol Decomposition on Partially Oxidised Copper Metal. Part I.

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A method of activating copper foil, wire, or film for the dehydrogenation of methanol has been devised and investigated. Copper could be activated by limited oxidation at 900 or 300°, whereby an oxide-on-metal substrate was produced which would decompose methanol vapour at about 6 cm. pressure at 300°. In a static system, lightly oxidised catalysts produced hydrogen and carbon dioxide as major products; more extensively oxidised catalysts gave a poisoned reaction, with hydrogen, carbon dioxide and water as major products, and formaldehyde as a minor product. When reduction of the copper oxide was complete, the decomposition ceased. The reaction involved was dehydrogenation not dehydration, and experiments showed that the water-gas shift may account for some of the observations. The reaction kinetics were in accord with a reaction poisoned by products. The decomposition has also been studied with oxygen-18 incorporated in the catalysts. The carbon dioxide produced was enriched in oxygen-18 beyond the value to be expected from $\text{CO} + \text{Cu}^{18}\text{O} = \text{CO}^{18}\text{O} + \text{Cu}$. This enrichment can be interpreted in terms of the water-gas equilibrium and carbon monoxide oxidation by way of a CO_2 surface complex, or exchange with the catalyst. The nature of the oxide catalyst is discussed and the reactions are related to the expected semiconductivity of the oxide. It is suggested that a parallel exists between these catalysts and copper powder catalysts which are prepared, and made active towards this reaction, by alternate oxidation and reduction techniques, and which lose their activity after methanol decomposition has taken place upon them.

IN the catalytic thermal decomposition of alcohols, it is generally supposed that dehydrogenation takes place on metal surfaces while, on oxide surfaces, dehydration is predominant.¹ Thus copper has been regarded as a dehydrogenating catalyst, and methanol decomposition has been considered as taking place in two stages:²



The extent of reaction (2) has been shown to depend upon temperature.² Sabatier and Reid³ indicated that the temperature at which the secondary reaction became important depended upon the method of preparation of the catalyst, in particular upon the temperature at which the reduced copper powder catalyst was prepared from copper oxide. Palmer and Constable⁴ similarly concluded that the rate of decomposition of alcohols on supported, reduced, copper powders depended upon the temperature of reduction of the oxide. Frolich *et al.*,⁵ who studied the decomposition of methanol on reduced copper powder, and Kawamoto,⁶ who studied the decomposition of isopropyl and s-butyl alcohols, found that the rate of decomposition depended upon the precipitation temperature and precipitating agent used. Ghosh and Chakravarty⁷ and Ghosh and Bakshi^{8,9} used reduced copper supported on pumice, in similar studies.

¹ Sabatier and Mailhe, *Ann. Chim. Phys.*, 1910, **20**, 289, 341.

² Rideal and Taylor, "Catalysis in Theory and Practice," MacMillan, London, 1919, p. 127.

³ Sabatier and Reid, "Catalysis in Organic Chemistry," Van Nostrand, New York, 1922, p. 654.

⁴ Palmer, *Proc. Roy. Soc.*, 1920—21, *A*, **98**, 13; 1921, *A*, **99**, 412; 1922, *A*, **101**, 175; Constable, *ibid.*, 1925, *A*, **108**, 355; 1925, *A*, **107**, 270, 279; 1927, *A*, **113**, 254; Constable and Palmer, *ibid.*, 1924, *A*, **106**, 250; 1925, *A*, **107**, 255.

⁵ Frolich, Fenske, and Quiggle, *J. Amer. Chem. Soc.*, 1929, **51**, 61; Frolich, Fenske, and Hurd, *ibid.*, p. 187.

⁶ Kawamoto, *Bull. Chem. Soc. Japan*, 1961, **34**, 795, 799.

⁷ Ghosh and Chakravarty, *J. Indian Chem. Soc.*, 1925, **2**, 142.

⁸ Ghosh and Bakshi, *J. Indian Chem. Soc.*, 1926, **3**, 415.

⁹ Ghosh and Bakshi, *J. Indian Chem. Soc.*, 1929, **6**, 749.

In every case, it was necessary to activate the copper surface, or to prepare the copper by reduction of the oxide for varying lengths of time, and at various temperatures. The activity of these catalysts was not maintained, and it was necessary to "reactivate" the surface, usually by alternate oxidation and reduction. Ghosh and Bakshi,⁸ however, found that activity was maintained provided that thoria or ceria was present to act as a "promoter." Russian workers¹⁰ found that self-poisoning of copper catalysts was avoided if 12% of manganese was present. Taylor¹¹ suggested that self-poisoning was due to a geometric factor. He concluded that the active centres were peaks on the surface of the copper, where the atoms were only lightly bound, thus providing a high degree of bond unsaturation. The heat of catalytic reaction was supposed to reduce the height of these peaks, and consequently the activity of the surface. Bulk copper is inactive towards methanol decomposition; thus Palmer's¹² pure electrolytic copper, and the copper foil of Schwab and Theophilides,¹³ produced no decomposition at 500°. Schwab and Theophilides concluded that reaction took place on active centres which exist in abundance only on topochemically prepared metals, and meagrely on compact ones. Recently, Balandin and Tetenyi¹⁴ studied the decomposition of alcohols, again on reduced copper powders, and concluded that hydrogen was chemisorbed on the surface during the dehydrogenation process. On the other hand, Beeck¹⁵ could find no evidence for hydrogen chemisorption on evaporated films of copper. Such results indicate a basic difference between copper metal obtained from reduced copper oxide, and the copper metal of evaporated films. This difference appears to be reflected in the catalytic dehydrogenation of methanol, where the reaction occurs on reduced copper powder catalysts but not on pure electrolytic copper or copper foil. This difference could be ascribed to surface-area differences, powders having areas of a few m.²/g. while the copper foil of Schwab and Theophilides had a geometric area of 50 cm.². A more complex series of reactions than was previously supposed is probably taking place. Dehydrogenation might not be expected on pure copper, since there are no vacant *d* orbitals to provide sites for electron-transfer during adsorption. Studies of this reaction on copper-nickel alloys¹⁶ indicate that the activation energy for the reaction becomes high with alloys of high copper content. In this Paper we have attempted to study the factors which bring about the activation of copper metal towards methanol decomposition, to identify the products formed, and to study the mechanism and poisoning of the reaction. Our first experiments substantiated the fact that copper powders, prepared by reduction of copper oxide with hydrogen, catalyse the decomposition of methanol, but are eventually poisoned or inactivated. We found that bulk copper metal, in the form of wire or foil, would not catalyse this reaction even at 500°. Pretreatments were used in an attempt to activate the wire or foil. Chemical cleaning by solution methods, or refluxing in boiling methanol, followed by baking out at 10⁻⁵ mm., had no effect. The method used to activate copper powders, namely alternate oxidation and reduction, would not impart activity to wire or foil. Such a pretreatment would therefore appear to be specific to copper powder catalysts. Finally, a pretreatment of foil or wire was found which imparted catalytic activity to the metal such that a vigorous decomposition of methanol took place, even when the geometric surface area of a 10 g. catalyst was only 38 cm.². A coil of copper wire, or a piece of foil, was heated in an air-gas flame to 800–900° for 30 sec., and then quenched in cold methanol. The copper oxide formed was reduced, leaving a fresh copper surface protected by methanol. After being baked out in a high vacuum, this wire or foil would catalyse the decomposition of methanol vapour at 300°.

¹⁰ Kotelkov, *Trudy Saratov Sel'stokhoz Inst.*, 1957, **10**, 382 (*Chem. Abs.*, 1960, 12,756).

¹¹ Taylor, *J. Phys. Chem.*, 1926, **30**, 145.

¹² Palmer, *Proc. Roy. Soc.*, 1920–21, **A**, **98**, 13.

¹³ Schwab and Theophilides, *J. Phys. Chem.*, 1946, **50**, 427.

¹⁴ Balandin and Tetenyi, *Russ. J. Phys. Chem.*, 1961, **35**, 28.

¹⁵ Beeck, *Discuss. Faraday Soc.*, 1950, **8**, 118.

¹⁶ Dowden and Reynolds, *Discuss. Faraday Soc.*, 1950, **8**, 184.

Flame-quenched Catalysts.—These were prepared as described from 10 g. of 18 s.w.g. wire, and the wire was quickly transferred to a reaction vessel connected to a circulating pump in a vacuum apparatus. The vessel was evacuated and baked out at 500° to 10^{-5} mm. Methanol vapour, to a pressure of 5 cm., was admitted and the vessel was heated to 300° . Vigorous decomposition of the methanol took place (Fig. 1, A_1). Assuming that the reaction $\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2$ occurred, a three-fold increase in pressure should have been observed. The total pressure increment was less than this. After reaction, the

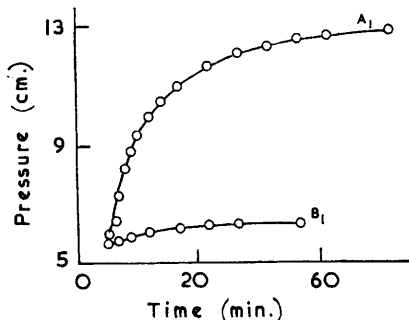


FIG. 1. Methanol decomposition on flame-quenched copper wire catalysts at 300° . Initial pressure = 5 cm. A_1 , normal reaction; B_1 , poisoned. Geometric area 38 cm.^2 .

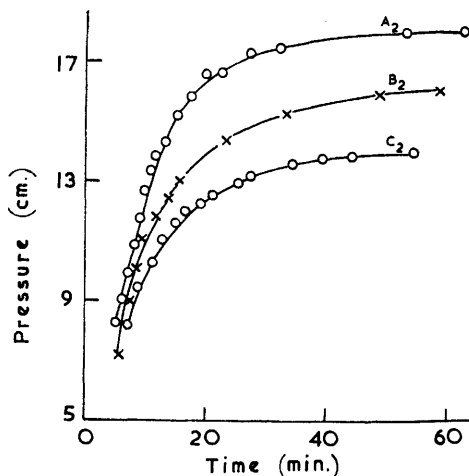


FIG. 2. Methanol decomposition on three flame-quenched copper wire catalysts at 300° . Initial pressure = 6 cm. Geometric area 38 cm.^2 .

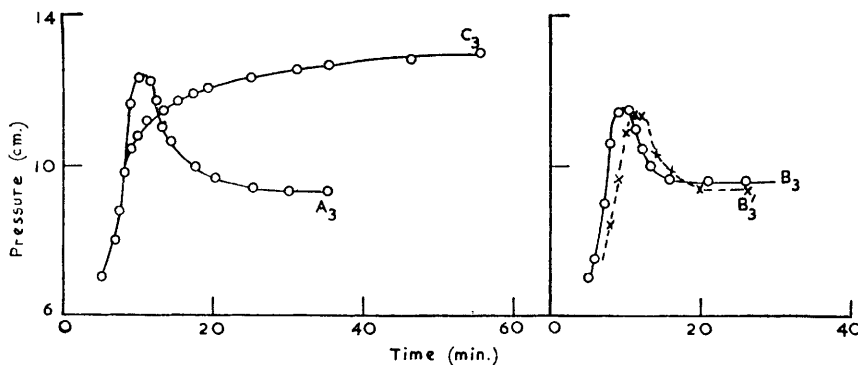


FIG. 3. Methanol decomposition on furnace-quenched copper foil catalysts at 300° . Initial pressure = 6 cm. Preheated at 900° in air for A_3 , 1 hr.; B_3 , 1 min.; C_3 , 5 sec. B_3' , interconversion catalyst. Geometric area 24 cm.^2 .

catalyst was baked out to 10^{-5} mm. to remove products. More methanol was admitted at $20^{\circ}/5 \text{ cm.}$, and the catalyst heated to 300° ; no decomposition was observed (Fig. 1, B_1). The reaction was therefore self-poisoned or self-inhibited. When fresh copper wire, or the "poisoned" catalyst, was pretreated using the flame-quenching technique, then its activity returned (Fig. 2, A_2 , B_2 , and C_2). The results shown in Fig. 2 were obtained from wires, apparently pretreated in the same manner, with the same geometric areas; considerable variation is evident. When an attempt was made to repeat the reactions on them, these wires were found to be inactive. There was, therefore, some activating agent

present, and the questions to be answered were whether the quenching process was important with regard to activation or whether another factor was involved during the heating of the catalyst. Accordingly, an experiment was conducted in which a wire catalyst was flame-treated but, instead of being quenched, it was allowed to cool in air, the resulting oxide layer being reduced in the vacuum apparatus by hydrogen. This catalyst was completely inactive. Thus, flame treatment and reduction did not activate the surface.

Furnace-quenched Catalysts.—To control time of heating and temperature closely, foils of area 24 cm.², 0.1 mm. thick, were suspended in a furnace and heated in air to 900°, for chosen periods of time, followed by immediate quenching in cold methanol. Methanol decompositions at 300° on foils heated for 1 hr., 1 min., and 5 sec. are shown in Fig. 3, A₃, B₃, and C₃, respectively. The whole interior of catalyst A₃ had been oxidised, making the foil brittle, and only the surface coating had been reduced to copper. A₃ showed unusual behaviour, *viz.*, a rapid increase in pressure to a maximum, followed by a decrease to a steady value after about 30 min. This was accompanied by the appearance of condensation within the circulation system, which could not be attributed to methanol, as its initial pressure was several cm. below saturated vapour pressure; it was assumed at this stage that the condensate was water. B₃ (1 min. heating of foil) showed a decrease in peak height, but when the time of heating was reduced to 5 sec., curve C₃, resulted. Condensation again accompanied this reaction, and, although the time of heating was short, some oxide still lay beneath the surface coating of copper after quenching. It was suspected that water was produced by reduction of copper oxide, present in the catalyst, by hydrogen from the dehydrogenation process, and that this water was causing a partial poisoning of the catalyst. Where a large quantity of oxide was present (A₃), water production was rapid, the dehydrogenation reaction was completely poisoned, and the remaining hydrogen continued to react with the oxide to produce water. Since the vapour pressure of water at 25° is 1.25 cm., it condensed in the circulating system, was effectively removed, and the pressure fell until all the hydrogen was consumed. Water is a poison for a similar reaction, the dehydrogenation of ethanol.¹⁷ For extensive reaction, one needs to avoid sufficient oxide being present in the catalyst to produce water vapour to poison the reaction. Two poisoning processes can now be distinguished: (a) that caused by water vapour; and (b) the self-poisoning or self-inhibition produced during a methanol reaction on a flame-quenched catalyst. To avoid production of oxide in the catalysts, foils were heated to 900° in nitrogen, followed by quenching in methanol. No activity could be imparted to the foils using this technique. This points to the importance of oxygen in these catalysts.

Interconversion of Catalysts.—This proved to be possible. When flame-quenched catalysts were reheated in the high-temperature furnace in air for either 1 min. or 5 sec., then, in the former case, a reaction type corresponding to B₃ was obtained and, in the latter case, a reaction type corresponding to C₃, rather than the typical flame-quenched reaction A₂, was obtained. Repetition of reaction on the catalysts showed that interconversion was possible. Thus, a second reaction, on a foil prepared by furnace heating at 900° for 1 hr., gave the result shown as B₃' (Fig. 3); this is similar to B₃, except for the reduced peak height. A second reaction on catalysts B₃ (Fig. 3) gave C₄ (Fig. 4) where the behaviour was similar to C₃ (Fig. 3), *i.e.*, continual rise in pressure, no peak, and no condensation. Repeat reactions on C₃ (Fig. 3) were not effective (Fig. 4, B₄); evidently the first reaction had removed all the necessary activating oxygen. Similar results were obtained using copper wires, and there was no reason for drawing a distinction between foil and wire.

Since oxygen was so important, reactions were attempted on flame-oxidised copper wire without preliminary reduction (Fig. 5, D₅). The reaction was similar to that from an oxidised wire quenched in methanol (Fig. 5, C₅), except that the oxide catalyst was more active. At the end of the reaction, the catalyst was reduced to a bright copper colour,

¹⁷ Armstrong and Hilditch, *Proc. Roy. Soc.*, 1920, A, 97, 262.

and an attempt at further reaction showed that it was inactive. The effect of partial reduction by hydrogen of an oxide catalyst is shown in Fig. 5, A₅; the catalytic activity was diminished. We deduce from these experiments that the quenching process was unimportant, provided that a small amount of oxide was left in the wire. The presence of this oxygen activated the catalysts. Oxygen removal meant inactivation of the catalysts, and explained the "self-poisoning" aspect exhibited by many of the reactions described above. Beyond a critical amount of oxygen a poisoning or inhibiting mechanism occurred; this was accompanied by the appearance of water as a product, which may be the catalyst poison. Such a reaction will be referred to as "poisoned."

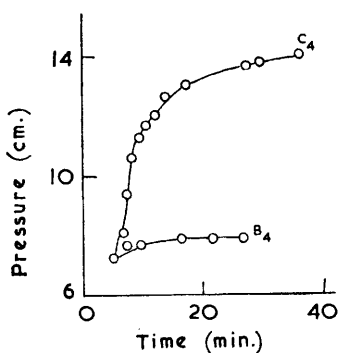


FIG. 4. Interconversion of catalysts for methanol decomposition at 300°. Initial pressure = 6 cm. B₃ (Fig. 3) after reaction gives C₄. C₃ (Fig. 3) after reaction gives B₄, poisoned.

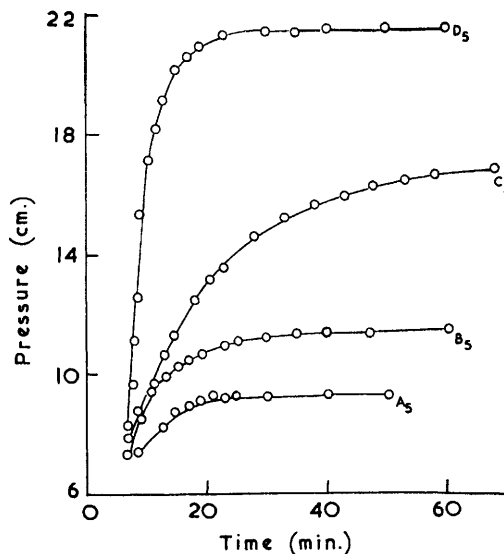


FIG. 5. Methanol decomposition on (10g.) copper wire catalysts at 300°; oxide on wires produced by oxidation in air at 900°. Initial pressure of methanol vapour = 6 cm. A₅, partially reduced by hydrogen containing 0.7 mg. of oxygen. B₅, partially reduced by methanol vapour containing 3.4 mg. of oxygen. C₅, unreduced flame-quenched wire containing 30.0 mg. of oxygen. D₅, unreduced oxide on copper wire containing 30.0 mg. of oxygen.

Gravimetric Experiments.—Gravimetric experiments were feasible, for 30–40 mg. of oxygen might be present on a 10-g. wire catalyst. After activation, the wires gained in weight; after reaction, they returned to their original weights. The initial reaction rate increased slightly with oxide concentration (Fig. 5, A₅, B₅, and C₅) and, when the oxide had been reduced, the reaction stopped, excess of methanol being present. The wire giving A₅ was prepared by *partial* reduction with hydrogen, and that giving B₅ by partial reduction with methanol vapour. C₅ and D₅ are anomalous, in that both wires contained 30 mg. of oxygen but D₅ had the higher reaction rate. Flame-quenched wires prepared in an identical manner showed regularity in behaviour. Flame-quenched wire catalysts were prepared with 7.4, 10.4, and 16.4 mg. of oxygen present on 50 g. of copper. Fig. 6 shows the results; initial rates are about equal, but the extent of reaction varies with the oxygen content of the catalyst.

Low-temperature Oxidation Experiments.—Controlled oxidation of copper in the vacuum system was followed by means of change of oxygen pressure. At 300° and 60 cm. pressure,

30 mg. were taken up in 4 hr. After (30 g.) wires of the same geometric surface area had been baked out to 10^{-5} mm. pressure, they were oxidised to contain *ca.* 10, 20, and 30 mg. of oxygen. Methanol decompositions at 300° are shown in Fig. 7, A₇, B₇, and C₇, respectively. They may be compared with a typical result from a flame-quenched wire, *i.e.*, high-temperature-preparation catalyst, Fig. 7, D₇. In Fig. 5, it was seen that the mode of preparation of the oxide wire, D₅, produced a catalyst having greater activity than the flame-quenched wire C₅. Fig. 7, however, shows that low-temperature oxidation of copper wire produced a catalyst having lower activity than a typical flame-quenched wire, D₇. There appears to be a small increase in initial rate with oxygen content. The initial rate for D₇ is higher and reaction appears to proceed to a greater extent. This shows that the temperature of preparation of the wire catalysts is as important as the quantity of oxide present. In contrast (Fig. 5), the unreduced oxide wire showed greater activity than the quenched wire, but both were high-temperature-preparation catalysts.

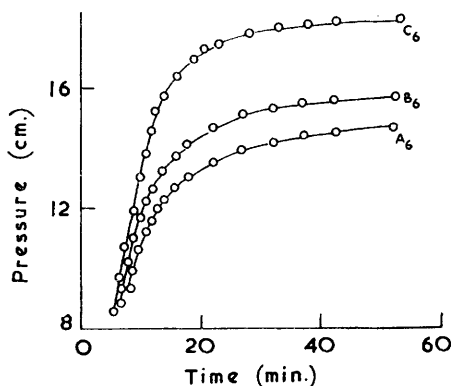


FIG. 6. Methanol decomposition on (50 g.) flame-quenched copper wire catalysts. Initial pressure of methanol vapour = 7 cm. A₆, 7.4 mg. of oxygen. B₆, 10.4 mg. of oxygen. C₆, 16.5 mg. of oxygen. Geometric area 180 cm.^2

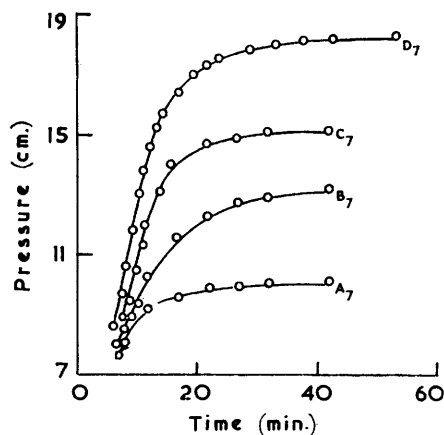


FIG. 7. Methanol decomposition at 300° on (30 g.) copper wires, oxidised at 300° in oxygen. Initial pressure of methanol vapour = 7 cm. A₇, 10.8 mg. of oxygen. B₇, 23.8 mg. of oxygen. C₇, 33.5 mg. of oxygen. D₇, flame-quenched catalyst containing 16.5 mg. of oxygen. Area of A₇, B₇, C₇, 115 cm.^2 , D₇, 180 cm.^2 .

Another feature observed with low-temperature-preparation catalysts was the appearance of water, as was the case with furnace-quenched high-temperature-preparation catalysts.

Summary.—Pure copper wire would not catalyse the decomposition of methanol vapour. If the wire was oxidised to a limited extent at high temperature (900°), then it would catalyse the decomposition such that there was a steady rise in pressure to a maximum value. The initial rate and the extent of this pressure rise were dependent upon the quantity of oxide present in the wire (cf. Fig. 6). Beyond a certain limit of oxidation at 900° , the nature of the reaction changed such that, although there was still a steady rise in pressure, condensation, assumed for the present to be water, accompanied the reaction (cf. Fig. 3, C₃). Further oxidation of the catalyst at 900° again changed the reaction type, there being a rise and fall of pressure, accompanied again by condensation (cf. Fig. 3, A₃ and B₃). If the catalyst was oxidised at low temperature (300°), there was a steady rise in pressure accompanied by condensation (cf. Fig. 7). The initial rate and the extent of this pressure rise were again dependent upon oxide concentration, but were always much less than those obtained from the high-temperature-preparation catalysts, where no condensation occurred. Inhibited reactions, where condensation was observed

to occur, we will call "poisoned" reactions. Thus the nature of the decomposition reaction depended upon the method of preparation of the catalyst. No difference in area (B.E.T. method) could be detected between a copper wire and a flame-quenched copper wire catalyst of the same geometric area.

Copper Film Catalysts.—The inactivity of unoxidised copper wire might be ascribed to small surface areas. Reactions have therefore been examined on copper films made by direct evaporation from a filament on to a glass vessel immersed in liquid nitrogen. There is evidence¹⁵ that, at this temperature, porous films are obtained and, although warming the catalyst may cause sintering, any reaction observed would indicate that pure copper, of large enough surface area, would catalyse the decomposition of methanol. Attempted reaction at 300° gave a negative result. When this film was baked out and oxidised at 300° with pure oxygen at 60 cm. pressure, followed by evacuation, activity was imparted to the catalyst, the reaction type being similar to that from wires oxidised at low temperatures (Fig. 8, A₈). When such an oxide film was partially reduced by hydrogen, a decrease in the extent of methanol decomposition was noted (Fig. 8, B₈).

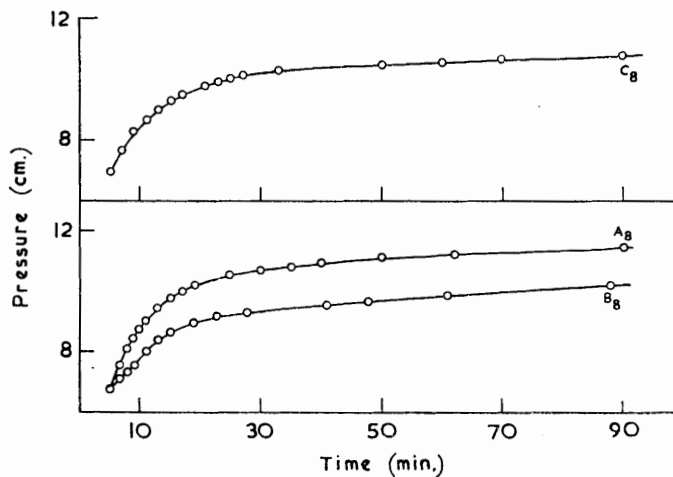


FIG. 8. Methanol decomposition at 300° on evaporated copper films. Initial pressure of methanol vapour = 6 cm. A₈, copper film oxidised in oxygen at 300°. B₈, oxide film partially reduced by hydrogen. C₈, copper metal deposited on a copper oxide film.

The problem exists as to whether reaction was taking place on copper metal or on copper oxide, and it was decided to deposit an evaporated film on top of an oxidised film, to find out whether such a system would still be active. A copper film was oxidised at 300° for several hours and, after removal of oxide from the copper filaments, a second copper film was deposited on top of the first oxide film, at liquid-air temperature. This was warmed to room temperature (sintering should then occur and the oxide film might be protected from direct reaction with methanol). When a reaction was attempted at 300°, the result compared favourably with that for an oxide film (Fig. 8, C₈); at the end of the experiment, the oxide had been reduced to copper. It would seem, therefore, that reaction with methanol can take place on a copper metal surface activated by oxide situated within the metal lattice, but the possibility that copper films are still porous at 300° must not be neglected.

Water-gas Reaction.—The analytical results for a flame-quenched catalyst show that water was never formed in any appreciable quantity, and that, although it may have been formed by reduction of the oxide with hydrogen, it was probably removed by the water-gas shift to give carbon dioxide and more hydrogen.

Studies of the water-gas equilibrium¹⁸ indicate that at 300° the equilibrium $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ will lie largely to the right. $\text{CO}:\text{CO}_2$ ratios reported vary from 0.05 to 0.10. Several water-gas experiments were attempted on our catalysts. Water and carbon dioxide were estimated by freezing at -78 and -195° , respectively, and observing the changes in pressure. On a typical (50 g.) flame-quenched catalyst containing 24.2 mg. oxygen, carbon monoxide at 6.03 cm. pressure was heated to 300° for one hour in the presence of a large excess of water. The pressure fell to 0.275 cm. and 18.7 mg. of oxygen were removed from the catalyst either by carbon monoxide or hydrogen reduction. The result corresponded to 95.5% conversion to carbon dioxide, *i.e.*, closely akin to a water-gas equilibrium. For simple carbon monoxide reduction, one might have expected 100% conversion. When an unoxidised copper wire was used, or when no catalyst was present, conversion of carbon monoxide into dioxide was never greater than 15%.

In another experiment on a (50 g.) flame-quenched catalyst the following results were obtained: before reaction at 300°, there were present H_2O , 2.1 mg., CO , 41.9 mg., O_2 on catalyst, 12 mg.; after reaction at 300°, there remained H_2O , 0.85 mg., CO , 18.7 mg., O_2 on catalyst, 0.0 mg., CO_2 , 35.5 mg. The 23.2 mg. of monoxide consumed should react stoichiometrically with 13.25 mg. of oxygen but only 12 mg. (O) were available from the catalyst. Thus, 1.25 mg. (O) had to be accounted for. 1.25 mg. of water had reacted, which provided a source of 1.1 mg. of oxygen. Thus all the oxygen was accounted for. If complete reduction of copper oxide with hydrogen is assumed, then 12 mg. of oxygen \equiv 13.5 mg. of water, and total water possible in system = 13.5 + 2.1 mg. = 15.6 mg. Assuming 95% water-gas equilibrium, water remaining = 0.8 mg. The experimental result was 0.85 mg. of water.

It was concluded that the water-gas reaction could take place, but the possibility of direct reduction by carbon monoxide of the oxide on the catalyst was not excluded. Thus carbon monoxide present in such a system would always be removed by one or other of these processes.

Decomposition Products.—With regard to dehydrogenation, one might expect hydrogen, formaldehyde, and carbon monoxide from $\text{CH}_3\text{OH} \rightarrow \text{H}_2 + \text{HCHO}$ and $\text{HCHO} \rightarrow \text{H}_2 + \text{CO}$. In addition, Ghosh and Chakravarty⁷ found methane and carbon dioxide, which probably arose from $2\text{CO} + 2\text{H}_2 \rightarrow \text{CO}_2 + \text{CH}_4$. As copper oxide was present in the catalysts, dehydration products could also be important; thus dimethyl ether and water were possible products from $2\text{CH}_3\cdot\text{OH} \rightarrow \text{CH}_3\cdot\text{O}\cdot\text{CH}_3 + \text{H}_2\text{O}$. Kemball *et al.*,¹⁹ who studied desorption products of ethanol on cupric oxide and found only carbon dioxide and water, suggested a thermodynamically feasible combustion reaction which, when paralleled to methanol decomposition, would become: $\text{CH}_3\cdot\text{OH} + 3\text{CuO} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 3\text{Cu}$. It was necessary, therefore, to search for eight possible products: hydrogen, carbon monoxide, carbon dioxide, formaldehyde, water, methanol, methane, and dimethyl ether.

Condensate. The condensates from methanol reactions on a flame-quenched wire and on two furnace-quenched wires (cf. Fig. 3) were collected at -195° . The samples were examined in the infrared region, with a Unicam S.P. 100 prism grating monochromator, by enclosing a drop between two quartz plates. In the case of the flame-quenched catalyst, no condensible product remained when the cold trap was warmed to room temperature. With both furnace-quenched catalysts, however, the spectrum revealed large quantities of water which masked other products. The absorption for water was checked by using synthetic mixtures of water and methanol. The condensation noted during these reactions was thus due, at least in part, to water. This could be titrated with Karl Fischer reagent (precautions were taken as regards blank titrations and entry of spurious water from the atmosphere).

¹⁸ De Boer, "The Mechanism of Heterogeneous Catalysis," Elsevier, New York, 1960, p. 36; Latimer and Hildebrand, "Reference Book of Inorganic Chemistry," Macmillan, New York, 1940, p. 269; Emmett, "Catalysis," Vol. 4, Reinhold, New York, 1956, p. 11.

¹⁹ Kemball, Darby, and Wheeler, *J.*, 1960, 332.

Volatile products. Provided that water and methanol could be removed from the products, and this could be done at -60° , then infrared spectral analysis could be applied to the remaining gases. Several flame-quenched wires were prepared containing *ca.* 10 mg. of oxygen (limited high-temperature catalyst), and methanol reaction at 300° was effected upon them. These were the conditions for avoiding the appearance of water condensation during a reaction. The products were separated, and titration with Karl Fischer reagent showed less than 1% water. An infrared spectrum of the non-condensable fraction, with a Perkin-Elmer-13 double-beam spectrophotometer, was compared with synthetic mixtures. Carbon dioxide was an important constituent, and carbon monoxide and formaldehyde were present to a small but undetermined extent. A fourth constituent, which did not absorb in the infrared region, was assumed, for the present, to be hydrogen.

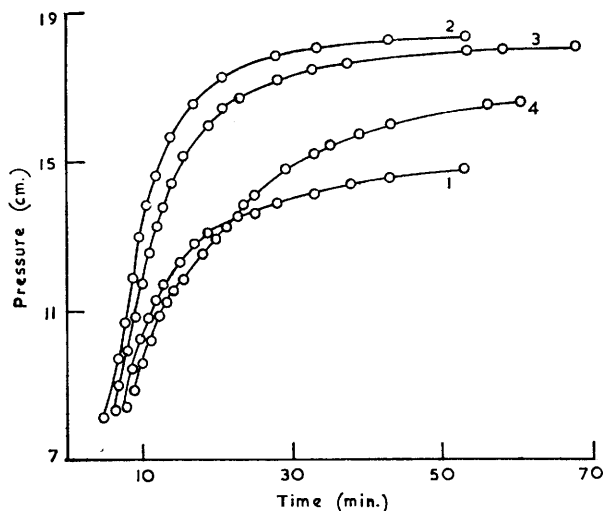


FIG. 9. Methanol decomposition at 300° on 50 g. flame-quenched copper wires. Initial pressure of methanol vapour = 7 cm. 1, 7.4 mg. of oxygen. 2, 16.5 mg. of oxygen. 3, 18.8 mg. of oxygen. 4, 40.4 mg. of oxygen.

We are indebted to Messrs. British Hydrocarbon Chemicals Ltd. for gas-chromatographic analysis which confirmed this. There was no evidence for methane or dimethyl ether. Thus the major products obtained from methanol reaction on a limited high-temperature-preparation catalyst are carbon dioxide and hydrogen.

Quantitative analysis of products. Four (50 g.) flame-quenched wire catalysts were prepared, containing 7.4, 16.5, 18.8, and 40.4 mg. of oxygen. Their geometrical area was 180 cm^2 , the thickness of the oxide²⁰ probably varying from 6×10^{-5} to 3×10^{-4} cm. The results of methanol reactions at 300° (Fig. 9) show a maximum at 16.5 mg. of oxygen; at 40.4 mg. of oxygen, the partial poisoning mechanism developed. In every case, the copper oxide was reduced to copper. A separation was made at -105° at which temperature formaldehyde has a vapour pressure of 1 mm. and carbon dioxide 10 cm., into: (a) hydrogen, carbon monoxide, and carbon dioxide; (b) methanol water, and formaldehyde. Water was estimated by Karl Fischer reagent, and formaldehyde by colorimetry, chromotropic acid being used.²¹ Since the carbon monoxide concentrations were small, it was possible to make the analysis by examining the variation, with temperature, of the pressure of the original mixture. By cooling the mixture from -78 to -105° , the range over which the vapour pressure of dimethyl ether decreases from 6 cm. to

²⁰ Rönquist and Fischmeister, *J. Inst. Metals*, 1960—61, 89, 65.

²¹ Bricker and Johnstone, *Anal. Chem.*, 1945, 17, 400.

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1 mm., the presence of this gas would have been detected. None was ever detected. Carbon dioxide was estimated by cooling to -195° , and the remaining gas was taken to be hydrogen. The results are given in Table 1. The $H_2:CO_2$ ratio is about two for

TABLE 1.

	Catalyst No.				
	1	5	2	3	4
Mode of Preparation	FQ	LT	FQ	FQ	FQ
Oxygen (mg.) on 50 g. catalyst	7.4	13.5	16.5	18.8	40.4
$H_2:CO_2$ in product (molar ratio)	3.45	1.66	2.05	2.06	1.17
H_2O , as percentage of possible yield	0	15.7	1.43	1.48	38.2
% MeOH reacted	68.5	53.5	84.5	84.7	82.9
HCHO, as percentage of possible yield	0.38	4.65	1.06	0.37	0.12

FQ, Flame-quenched catalyst. LT, Catalyst prepared by oxidising copper at 300° in oxygen.

catalysts 2 and 3, where water production is negligible. For catalysts 4 and 5, water is a major product and the ratio is less than two.

The results are summarised in Table 2.

TABLE 2.

Catalyst preparation		Reaction type	Products	
Temperature	Extent of oxidation		Major	Minor
900°	Limited	Steady rise in pressure	CO_2, H_2	
900	Extensive	Steady rise in pressure to a maximum, then fall to a steady value	CO_2, H_2, H_2O	
300	Limited	Steady rise in pressure	CO_2, H_2, H_2O	HCHO

Experiments with Oxygen-18.—Since oxygen plays a key role in the activation of copper, catalysts labelled with oxygen-18 were prepared, with the object of elucidating the reaction mechanism. Low-temperature oxidations, as before, and high-temperature oxidations, by electrical-resistance heating of wire spirals, were performed in the presence of oxygen gas enriched with oxygen-18. The extent of oxidation was measured by use of pressure changes. Four catalysts were prepared as described in the caption to Fig. 10. Calibration samples containing carbon [^{18}O]dioxide were also prepared. Methanol reactions at 300° gave the results shown in Fig. 10. A_{10} and B_{10} showed the typical reaction of limited high-temperature-preparation catalysts, cf. D_5 (Fig. 5) and Fig. 6. C_{10} gave a "poisoned" reaction comparable with A_3 or B_3 (Fig. 3). An attempt was made to terminate reaction C_{10} shortly after the maximum had been reached, as extensive reduction of the catalyst with hydrogen to give [^{18}O]water would lead to a water-gas shift, which would introduce oxygen-18 into the carbon [^{18}O]dioxide. Product analysis showed that this was not entirely successful. D_{10} , as expected from Fig. 7, produced a partially poisoned reaction with lower activity than the others.

TABLE 3.

Catalyst	A_{10} Limited high-temp. oxidn.	B_{10} Limited high-temp. oxidn.	C_{10} Extensive high-temp. oxidn.	D_{10} Limited low-temp. oxidn.
Oxygen (mg.)	33.5	33.5	82	13.5
$H_2:CO_2$ (molar ratio)	1.98	2.06	0.74	1.66
% H_2O	1.8	zero	49.9	15.7
% HCHO	< 0.01	< 0.01	< 0.01	4.7
% MeOH reacted	98.5	96.3	94.3	53.5
Original undiluted $^{18}O_2:^{16}O_2$ ratio, expressed as atom % $^{18}O_2$	—	4.66	4.66	3.20
Calibration $C^{18}O_2:C^{16}O_2$ ratio, expressed as atom % $C^{18}O_2$	—	2.33	2.33	1.60
$C^{18}O_2:C^{16}O_2$ ratio after experiment, expressed as atom % $C^{18}O_2$	—	2.56	3.45	2.15
Wt. of copper in g.	1.89	1.89	1.89	30.0

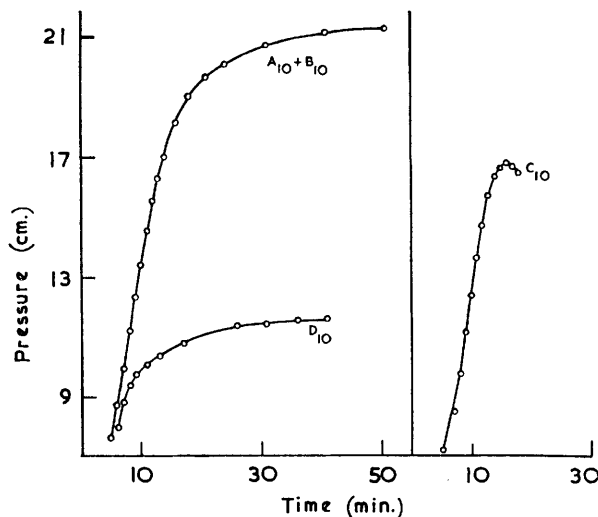


FIG. 10. Methanol decomposition on oxidised copper wire catalysts at 300°. Initial pressure of methanol vapour = 7 cm. A₁₀, oxidation at 900° in ordinary un-enriched oxygen gas of which 33.5 mg. were absorbed. B₁₀, oxidation at 900° in oxygen gas enriched with oxygen-18, with uptake of 33.5 mg.; B₁₀ is coincident with A₁₀. C₁₀, extensive oxidation at 900° in oxygen gas enriched with oxygen-18, with uptake of 82 mg. D₁₀, oxidation at 300° in oxygen gas enriched with uptake of 13.5 mg.

After reaction, the products were separated into gaseous hydrogen, carbon monoxide and carbon dioxide, and liquid methanol, water, and formaldehyde. The gases were analysed by gas chromatography, and by the freezing method. Part of the gaseous fraction was examined in a mass spectrometer for oxygen-18 enrichment in the carbon dioxide. The results are shown in Table 3. Values for unreacted methanol were calculated by difference.

DISCUSSION

Copper metal was not catalytically active in the decomposition of methanol at 300°. Only after oxidation, or oxidation and partial reduction, was it active as a dehydrogenation catalyst. We shall call the substrates catalysts, even though oxygen was removed from them; it was not removed by a straightforward solid-gas oxidation process. It is reasonable to conclude that the previously reported activity of copper powders^{4,7-9} was due to oxygen incorporation; small retention of oxygen in the copper probably gave rise to catalytic activity, and this may explain activation by alternate oxidation and reduction techniques. Since the catalyst consisted of copper oxides on copper, or of a copper-copper oxide-copper sandwich, it is necessary to comment on the likelihood of catalysis taking place on the metal. It seems unlikely²² that the semiconductor oxides could make any substantial difference to the Fermi level of electrons in the metal, in view of the limitations on the number of carriers present in an oxide. We have therefore devoted this discussion to the oxide portion of the catalysts.

The stable oxides, under our conditions at 300 and 900°, are cupric and cuprous, respectively,²³ but it is unlikely that they had reached equilibrium and perfection in structure. Tylecote²⁴ describes oxide films formed on copper as consisting of two layers, the outer of cupric oxide and the inner of cuprous oxide, above about 200°. Films formed

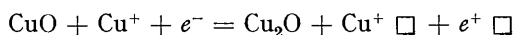
²² Block, "Actes 2me Congrès International de Catalyse (Paris, 1960)," Technip, Paris, 1961, Vol. II, p. 1644.

²³ Honjo, *J. Phys. Soc. Japan*, 1953, **8**, 113.

²⁴ Tylecote, *Metallurgia*, 1956, **53**, 191.

above 800° consist mainly of Cu₂O. Gulbransen and McMillan²⁵ found, from electron-diffraction work, that the cupric oxide content rose from a trace, after oxidation for 1 min. at 300° in oxygen at 1 atmosphere, to 100% cupric oxide, after 60 min. In their review, Rönquist and Fischmeister²⁰ suggest that copper oxidation depends on: (a) formation of a coherent cuprous oxide film; (b) oxidation of cuprous to cupric oxide, after which oxygen access is restricted; and (c) diffusion of Cu⁺ ions into the oxide, from Cu → Cu⁺ + e⁻. Low-pressure oxidation studies by O'Keeffe and Stone²⁶ lead them to think that cupric oxide can nucleate within cuprous oxide, from the aggregation of vacancies. The non-stoichiometry of oxidised copper is further illustrated by the work of Czanderna and Wieder,²⁷ who found compositions CuO_{0.67}, in which one in every four copper atoms was missing.

We conclude that our oxide films are non-stoichiometric, that oxide films on copper prepared at 300° probably contained 30–40% of cupric oxide in the oxide²⁴ for weight gains of over 1 mg. cm.⁻², and that the oxides prepared at high temperature consisted of cuprous oxide, with probably 10% of cupric oxide. At or near the interface, the amount of cupric oxide probably decreases by:²⁴



Incorporation of excess of oxygen into cuprous oxide affects its semiconducting properties. Dunwald and Wagner²⁸ established that excess of oxygen is incorporated together with the formation of Cu⁺ vacancies in cuprous oxide, each vacancy being accompanied by a positive hole. The conductivity increases, within limits, with excess of oxygen.²⁹ Smith³⁰ has shown that oxygen adsorption on cupric oxide, of composition beyond CuO_{0.7}, produces conductance and here, as in the case of cuprous oxide, the oxides are *p*-type semiconductors, the conductivity increasing with oxygen uptake. Thus the oxides used in our studies probably began their reactions as *p*-type semiconductors and contained Cu⁺, Cu²⁺, and O²⁻ ions in different amounts, with a concentration gradient of vacant cation sites and positive holes.³¹

It is suggested, on the evidence presented, that limited high-temperature oxidations, such as that for catalysts A₂ and B₂ (Fig. 2), *i.e.*, flame-quenched catalysts, produced a defect structure of cuprous oxide. Further oxidation at high temperature, *i.e.*, furnace-quenched catalysts, A₃ (Fig. 3), caused further uptake of oxygen, such that the outer layer of oxide became rich in oxygen beyond the cuprous oxide stage, tending perhaps to CuO_{0.67}. Thus a gross defect structure was produced, which gradually changed, within the interior of the catalyst to the initial defect structure. This would explain the inter-conversion of catalysts. A further methanol reaction on heavily oxidised copper reduced the oxide towards cuprous oxide, and a second reaction was then characteristic of the new degree of oxidation on the catalysts.

In the case of the catalysts prepared at 300°, *e.g.*, A₂, B₂, and C₂, this gross defect structure, tending towards cupric oxide, probably existed throughout the film.

The initial attachment of methanol to the catalyst surface is likely to be through hydrogen bonding to the O²⁻ ions, as Gale, Haber, and Stone³² deduced from calorimetry for isopropanol dehydrogenation on nickel oxide. Subsequent attachment,³³ to judge from exchange studies, involves CH₃·OH + 2* → *CH₂·OH + H*. The work of Balandin and Tetenyi,¹⁴ on the effect of variation of structure on alcohol breakdown,

²⁵ Gulbransen and McMillan, *J. Electrochem. Soc.*, 1952, **99**, 393.

²⁶ O'Keeffe and Stone, *Proc. Roy. Soc.*, 1962, *A*, **267**, 501.

²⁷ Czanderna and Wieder, *J. Phys. Chem.*, 1962, **66**, 816.

²⁸ Dunwald and Wagner, *Z. phys. Chem.*, 1933, **22b**, 212.

²⁹ Garner, Gray, and Stone, *Discuss. Faraday Soc.*, 1950, **8**, 246.

³⁰ Smith, *ref. 22*, p. 1711.

³¹ Grimley, "Chemistry of the Solid State," ed. Garner, Butterworth, London, 1955, p. 340.

³² Gale, Haber, and Stone, *J. Catalysis*, 1962, **1**, 32.

³³ Bond, "Catalysis by Metals," Academic Press, London, 1962, p. 221.

suggests that the reacting group is $>\text{CH}\cdot\text{OH}$. Methanol adsorption on a p -type semiconductor is known to diminish the conductivity of the substrate by several orders of magnitude,³⁴ and so we now examine the relationship between semiconductivity and catalysis. Hauffe predicts³⁵ that increasing the free electron concentration in a semiconductor should retard dehydrogenation and that lowering the Fermi level should encourage it. Thus our p -type semiconductors on this basis should be, and in fact are, efficient catalysts. Thus, it may be that the more oxygen there is present, after high-temperature oxidation, the better is the semiconducting property and the lower is the Fermi level. This would account for the increased rate efficiency (Figs. 6 and 7). Not only methanol is an electron donor to such a catalyst,^{34,36} so also are carbon monoxide,³⁷ hydrogen,^{34,37} and, by analogy, formaldehyde.³⁴ Thus, it might be expected that the lower is the Fermi level, the greater is the tendency of methanol to decompose into these fragments. There are several reasons why we cannot be sure about this argument. Under reducing conditions, the p -type semiconductor may be transformed to an n -type semiconductor.³⁸ Since carbon monoxide was oxidised in our system, the conversion $\text{O}^{2-} + \text{CO} \longrightarrow \text{CO}_2 + 2e^-$ donated electrons to the lattice, or it may be regarded as a reaction which reduced the Cu^{2+} concentration by $\text{Cu}^{2+} + e^- \longrightarrow \text{Cu}^+$. This change in semiconductor type has been observed by Garcia de la Banda for the chromia-catalysed dehydrogenation of isopropyl alcohol.³⁹ Furthermore, reaction may be taking place near the oxide-metal interface, where the oxide may be n -type owing to electron flow from metal to oxide.⁴⁰ Indeed, Wolkenstein⁴¹ considers that n -type semiconductors are more effective in dehydrogenation, in contrast to Hauffe's view. Dowden and his co-workers⁴² concluded, from their experiments, that isopropyl alcohol dehydrogenation was favoured by n -type semiconductors.

These differing views on the effectiveness of p - and n -type semiconductors might be reconciled as follows. Although oxygen incorporation into cuprous oxide proceeds beyond a monolayer to produce a surface rich in vacancies,⁴³ we find that the oxide is reduced and removed during methanol decomposition. Thus, although reaction started on a p -type layer in the case of the oxide catalysts, this soon disappears. The key to this problem may come from the site of the reaction, which we consider for the following reasons to be near the interface on the oxide. Taylor and Pease⁴⁴ noted an incubation period in the reduction of copper oxide by hydrogen, until red specks of copper grew in the system, and concluded that this was an interface reaction. Jones and Taylor⁴⁵ made the same observation for carbon monoxide reduction, and the auto-catalytic nature of hydrogen and carbon monoxide reduction of cuprous and cupric oxides has already been reported.⁴⁶ Yet another interface reaction has been reported by Szabo and Solymosi.⁴⁷

In the methanol decomposition, oxygen was removed from the copper oxide in forming carbon dioxide from carbon monoxide; this would set electrons free, from O^{2-} ions, which would associate with Cu^+ or Cu^{2+} ions, which would diffuse to or build up the metallic

³⁴ Bielanski, Deren, Haber, and Sloczynski, ref. 22, p. 1653.

³⁵ Hauffe, *Adv. Catalysis*, 1955, **7**, 213.

³⁶ Ljaschenko and Stepko, *Doklady Akad. Nauk S.S.S.R., Phys. Ser.*, 1952, **16**, 274.

³⁷ Garner, Gray, and Stone, *Proc. Roy. Soc.*, 1949, **A**, **197**, 294.

³⁸ Gray, ref. 22, p. 1561.

³⁹ Garcia de la Banda, *J. Catalysis*, 1962, **1**, 136.

⁴⁰ Hulig, Pickett, and MacNairn, *Acta Met.*, 1959, **7**, 11; Hulig, *ibid.*, 1956, **4**, 541.

⁴¹ Wolkenstein, *Adv. Catalysis*, 1960, **12**, 218.

⁴² Garner, Dowden, and Garcia de la Banda, *Anales. real Soc. españ. Fis. Quim., Ser. B*, 1954, **50**, 35; Also, Dowden, *J. chim. phys.*, 1954, **51**, 678.

⁴³ Garner, Stone, and Tiley, *Proc. Roy. Soc.*, 1952, **A**, **211**, 472; Jennings and Stone, *Adv. Catalysis*, 1957, **9**, 441.

⁴⁴ Taylor and Pease, *J. Amer. Chem. Soc.*, 1921, **43**, 2179.

⁴⁵ Jones and Taylor, *J. Phys. Chem.*, 1923, **27**, 623.

⁴⁶ Tatievskaya, Zhuravleva, and Chufarov, *Izvest. Akad. Nauk S.S.S.R., Otdel Tekhnol. Nauk*, 1949, **1235** (*Chem. Abs.*, 1951, **45**, 4537).

⁴⁷ Szabo and Solymosi, ref. 22, p. 1627.

phase. This could consist of freshly nucleated copper or the original metal substrate. Since Cu^+ diffusion is a slow process and yet we observe rapid appearance of copper metal, it seems likely that reaction will take place on oxide near the interface, in what may be an n -type region. In the case of the copper-copper oxide-copper sandwich catalyst, *e.g.*, flame-quenched catalysts, the interface would already be present at the beginning of the reaction and the complete decomposition may have taken place wholly on an n -type region. Further work is required to determine if an induction period exists, with reactions on oxide catalysts, until fresh copper nucleates at the surface. Present experimental techniques would mask this effect. It is also necessary to make detailed kinetic studies of the above reactions which probably display a compensating effect⁴⁸ under closely controlled conditions of oxidation. It should be possible to find out if the outermost

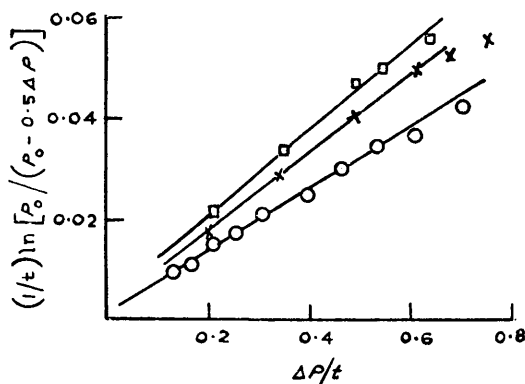
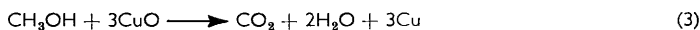


FIG. 11. Integrated rate curves for methanol decomposition at 300°. ○, from A_3 (Fig. 6). ×, from A_2 (Fig. 2). □, from 3 (Fig. 9).

copper layer, present in "sandwich" catalysts, slows the reaction rate, owing to slow diffusion of methanol to the reaction interface. This may be the explanation of the difference in reaction rates observed in Fig. 5, C_5 and D_5 , where D_5 was an oxide catalyst and C_5 a "sandwich" catalyst, both containing the same quantity of oxygen. The difference may be due to ineffective control of oxidising conditions, producing different oxidation states and Fermi levels, close to the critical value which would change the reaction. The only comments on kinetics we can make at present are as follows. This unimolecular reaction, inhibited by products, has a general kinetic equation

$$v = kKP_{\text{MeOH}} / (1 + KP_{\text{MeOH}} + KP_{\text{poison}})$$

where the symbols have their usual significance.⁴⁹ Various forms of this equation apply to the decomposition of ethanol on copper, where the poisons can be benzene, acetone, or water vapour,⁵⁰ or to the decomposition of methanol on a Fischer-Tropsch cobalt catalyst.⁵¹ Such are the kinetic equations for this reaction, which is inhibited by products, that a plot of $(1/t) \ln [P_0 / (P_0 - 0.5\Delta P)]$ against $\Delta P/t$ should be linear.⁵² Here t is the reaction time, P_0 is the initial pressure of methanol, and ΔP is the total change in pressure in the system. We have examined such plots for our reactions (Fig. 11) and find that in the last 80–90% of the reaction the plot is linear; this indicates poisoning by products. Consideration of reaction mechanism, which we have shown to exclude dehydration entirely, leads us to comment on the extent of the following reaction:¹⁹



as distinct from:



⁴⁸ Ref. 33, p. 139, and ref. therein.

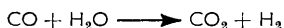
⁴⁹ Laidler, "Catalysis," ed. Emmett, Reinhold, New York, 1954, Vol. 1, p. 133.

⁵⁰ Constable, *Nature*, 1926, **117**, 230; *Proc. Cambridge Phil. Soc.*, 1926, **23**, 172; 1927, **23**, 593.

⁵¹ Darby and Kemball, *Trans. Faraday Soc.*, 1957, **53**, 832.

⁵² D. Taylor, personal communication.

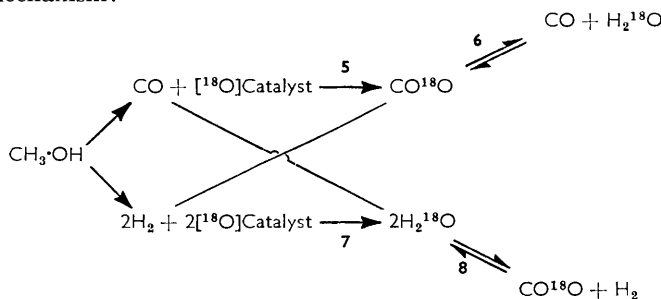
If, as in experiment 2, Table 1, no water is produced, the extent of reaction (4) could be not less than twice that of reaction (3), taking into account the water-gas shift



Thus for experiment 2, it may be calculated that dehydrogenation was the major reaction, occurring to an extent of not less than 67%. The correct quantity of oxygen was removed from the catalyst by this mechanism. For experiment 4, Table 1, where copper oxidation was extensive and water was produced, a similar calculation showed that 50% of the methanol was decomposed by dehydrogenation. Again the reactions were stoichiometrically correct, in that they removed the correct quantity of oxygen from the catalyst.

It was realised that other mechanisms could give rise to the same quantities of products. In experiment 2 it is possible that all the oxygen in the catalyst was being removed by reduction with carbon monoxide, and the total reaction was 100% dehydrogenation. In experiment 4, it might be argued that there was 100% dehydrogenation, and that both carbon monoxide and hydrogen were reducing the oxide to give carbon dioxide and water; in this case, the water-gas reaction would be unimportant.

Further insight into the mechanism comes from the tracer studies. It is possible to account for the enrichment of the carbon dioxide with oxygen-18, the increase in enrichment with the quantity of water produced, and the change in catalytic reaction type, by the following mechanism:



For lightly oxidised catalysts, *e.g.*, B₁₀, Table 3, where no water was found in the products, reaction (7) would appear to be faster than (5), allowing the water-gas shift to remove water by mechanism (8). Reaction (6) operating alone without (7) would not have altered the enrichment of carbon dioxide produced in (5). Reaction (8) would enrich the carbon dioxide beyond 2.33 atom % of oxygen-18, thus accounting for the observed 2.56 atom %. This mechanism invokes the water-gas shift, which we have shown to be possible in this system, without the need for isotope exchange⁵³ between carbon monoxide, or carbon dioxide, and cuprous [¹⁸O]oxide. We do not know, in our system, whether this process contributes to enrichments; the alternative explanation of exchange should be kept in mind also in the following argument.

For heavily oxidised catalysts, this mechanism becomes inadequate to explain the degree of enrichment of the carbon dioxide. Since water was a product with such catalysts, the water-gas shift (8) was evidently suppressed [the equilibrium for (6) lies to the left]. This suggests that carbon monoxide was failing to leave the surface, unless as the oxidised form, carbon dioxide. Since the water-gas shift was inoperative, it is necessary to seek an alternative explanation for enrichment of carbon dioxide. We think it likely that the carbon monoxide interacted with two surface atoms of enriched oxygen, through a carbonate surface-complex. Several authors^{37,54,55} have postulated such a complex in the interaction of carbon monoxide with transition-metal oxides. Kwan and

⁵³ Winter, *J.*, 1955, 2762.

⁵⁴ Garner, *J.*, 1947, 2, 1239.

⁵⁵ Hauffe, *Adv. Catalysis*, 1955, 7, 245.

Fujita⁵⁶ have also suggested such complex-formation in the chemisorption of carbon dioxide on zinc oxide. The mechanism also explains why the extent of reaction for catalyst D₁₀ was limited. Water was produced instead of hydrogen, and it condensed to give diminished pressure readings. For D₁₀, the maximum enrichment to be expected from the CO₃ complex was 2.15 atom %. The experimental value was 2.15 atom %. Thus we conclude that reaction (5) was taking place exclusively.

We would predict from this scheme that the more heavily oxidised the catalyst, the more should water production and carbon dioxide enrichment proceed concomitantly. This was observed to be the case (Table 3).

In the case of C₁₀, the degree of enrichment, 3.45 atom %, was beyond that predicted for carbonate complex-formation, 3.18 atom %. This reaction was poisoned, in that the pressure rose to a maximum and then fell to a steady value. This can be explained by assuming complete poisoning of the methanol reaction after 10 min., with the hydrogen produced reducing the catalyst oxide to water. Once methanol decomposition ceased, no further unlabelled carbon monoxide would be produced, but fully enriched water would be formed. The water-gas shift could then enrich the carbon dioxide to a considerable degree. Formaldehyde was not observed to any extent, as might have been expected from a poisoned reaction; this may be because it polymerised and was not collected. Table 3 shows as much as 94% methanol decomposition, but this may be because formaldehyde was produced and that the reaction was poisoned at this stage. No further unlabelled carbon monoxide would then have been formed. The fall in pressure in the system can be accounted for by reduction of the copper oxide with hydrogen.

The self-consistency of this scheme appears when we consider the effect of the carbonate complex on the scheme for lightly oxidised catalysts. Here (5) was thought to be slow, and this agrees with the lack of enrichment of carbon dioxide through a carbonate complex.

Self-consistency is evident when the results are considered in terms of band theory. Carbon monoxide is observed on *p*-type semiconductors as a positive species,³⁷ and hence the higher the Fermi level of the catalyst, the weaker will be the chemisorption bond between carbon monoxide and the surface, and the greater the tendency for it to react with water by the water-gas shift. Experiments with oxygen-18 showed this to be the case for lightly oxidised catalysts. We might expect the Fermi level to be lowered in the case of heavily oxidised catalysts, when carbon monoxide would become more firmly bound to the surface, and could only desorb carbon dioxide *via a carbonate surface-complex, i.e.*:



since this process involves no charge transfer from or to the catalyst. Thus any heavily oxidised catalysts have electronic properties likely to aid this mechanism, and oxygen-18 experiments confirm that this could be the case. The lower the Fermi level, the more firmly adsorbed will be the various species involved in the reaction; this may be the reason for the eventual poisoning of the reaction when the Fermi level is low enough, although the true poisoning mechanism remains obscure.

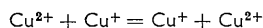
Instead of the interpretation in terms of boundary-layer or band theory, it may be more profitable to examine the reaction and poisoning mechanism on a molecular basis, as reaction occurs on single sites on the catalysts. In an evaluation of transition-metal oxides, Morin⁵⁷ pointed out the lack of overlap in the orbitals of the later 3*d* metals, and suggested that conductivity may arise from activated electron exchange between cation neighbours in different valency states. The electron-switch may also be important in catalysis, for Winfield⁵⁸ has observed that if the metal in an oxide is one which can change its valency, then usually the oxide will catalyse dehydrogenation. If we combine the idea of electron-switch and the crystal-field correlation with catalysis suggested by Dowden

⁵⁶ Kwan and Fujita, *Nature*, 1953, **171**, 705.

⁵⁷ Morin, *Bell System Tech. J.*, 1958, **37**, 1047.

⁵⁸ Winfield, "Catalysis," ed. Emmett, Reinhold, New York, 1960, Vol. 7, p. 150.

and Wells,⁵⁹ and elegantly demonstrated by Haber and Stone,⁶⁰ we may arrive at a better understanding of methanol interactions on copper oxides. One possibility is that methanol adsorption takes place after the fashion of oxygen adsorption on cuprous oxide, suggested by O'Keeffe and Stone.⁶¹ In the solid, cuprite, copper is two-co-ordinated to oxide ions. If during an adsorption of methanol, an electron-switch is possible, as might be expected on our non-stoichiometric catalyst



then the group $\text{O}^{2-}\text{-Cu}^+\text{-O}^{2-}$ can form a transition state in which cupric ions display their stable, planar fourfold co-ordination.⁶² This has the effect of tying down a positive hole and could account for diminished conductivity on methanol adsorption. The importance of the role of positive holes has been established, for example, by Hauffe⁶³ and his co-workers for the lithium oxide-nickel oxide catalysed decomposition of nitrous oxide.

The reason for the change in nature of the reaction on catalysts prepared at low temperature may be as follows. Low-temperature oxidation of copper seems likely to produce a solid with a large proportion of CuO; this has the tenorite structure in which each copper has four planar near neighbours. For this d^9 ion, adsorption may mean an unfavourable configurational change from square planar to square pyramidal. Dowden and Wells⁵⁹ suggest that this gives an unfavourable contribution of 12 kcal. per mole to the crystal-field stabilisation energy. Perhaps this renders firm chemisorption and further subsequent breakdown less likely than in the case of cuprite.

Our work allows us to comment on the technical oxidation of methanol to formaldehyde, reviewed by Dixon and Longfield.⁶⁴ When copper is used as a catalyst for the reaction of methanol and air, several possible roles are suggested for oxygen; we consider that the most important of these is the activation of the catalyst by the production of cuprous oxide. Tracer work in this laboratory by Miss Scott⁶⁵ suggests that high flow rates result in the intermediate formaldehyde being swept from the reaction zone. Further work is required on the conditions necessary for the formation of formaldehyde.

EXPERIMENTAL

The apparatus (Fig. 12) consisted of a central pumped circulating system, and catalyst vessel. The circulating pump was of a double-acting diaphragm design, the diaphragm and the ball valves being moved by electromagnets. Each movement of the diaphragm corresponded to a positive pumping stroke. The catalyst vessel used for the wire and foil experiments (CV) was attached to B10 and B29 joints. The catalyst could be placed within the vessel and supported by a glass rod thickened at one end, and the whole was fitted together prior to evacuation. The mercury manometers, M_2 , were connected to the circulating system through a gold trap and capillary tubing, to exclude mercury vapour from the catalyst vessel. Provision was made for evacuation of the circulation system to 10^{-5} mm. pressure (measured on a McLeod gauge which is not shown), and for admission of various gases either from storage bulbs or through the mercury bubbler, B1. Attached to the circulating system was the analytical section of the apparatus. Methanol vapour could be admitted to the circulating system from the methanol reservoir, MR. The methanol used was B.D.H. AnalaR grade, which had been distilled several times over AnalaR anhydrous sodium sulphate. *Ca.* 5 ml. were placed in the reservoir which was cooled to -195° and evacuated to 10^{-5} mm. pressure.

⁵⁹ Dowden and Wells, ref. 22, p. 1499.

⁶⁰ Haber and Stone, *Proc. Chem. Soc.*, 1961, 424.

⁶¹ O'Keeffe and Stone, *Proc. Roy. Soc.*, 1962, *A*, 267, 501.

⁶² Orgel, "An Introduction to Transition Metal Chemistry: Ligand Field Theory," Methuen, London, 1960, p. 57.

⁶³ Hauffe, *Adv. Catalysis*, 1955, 7, 239.

⁶⁴ Dixon and Longfield, ref. 58, p. 231.

⁶⁵ Scott, unpublished work.

High-temperature-preparation Catalysts.—Flame-quenched catalysts. 1m. lengths of 18 s.w.g. copper wire (1.2 mm. dia.), of geometrical surface area 38 cm.², were wound around glass tubing (12 mm. dia.), the wire being formed into spirals, *ca.* 6 cm. in length. Such catalysts were heated in a gas-air flame for different times, while the wire was uniformly red-hot, and then plunged into methanol. The wires were placed quickly in the vacuum system prior to "baking out" to 10⁻⁵ mm. pressure. The same procedure was adopted with copper foils, 24 cm.² copper foil being rolled into the form of a cylinder. Figs. 3 and 4 were obtained from foil catalysts, the remainder from wire catalysts. The average starting pressure of methanol used in decomposition studies was usually about 6–7 cm. The reaction temperature used was always 300°.

Furnaced-quenched catalysts. A 1 mm. tungsten wire supported the catalyst within the region heated by a Kanthal furnace to 900° (as measured by a Pt/Pt–Rh thermocouple). The catalyst could be heated in any desired gas stream, and at the end of the required period of time allowed to fall into a reservoir of methanol by rotating the tungsten wire about the B7 joint. In cases where the catalyst was heated in air, the bubbler measuring gas flow rate was removed and the bottom tap left open to permit free convection of air to take place.

Gravimetric experiments on partially reduced wires. A spiral-wound wire, 38 cm.² in area, was weighed, given the usual flame-treatment, allowed to cool in air, and reweighed to determine the extent of oxidation. The wire was then placed in the apparatus, which was flushed out

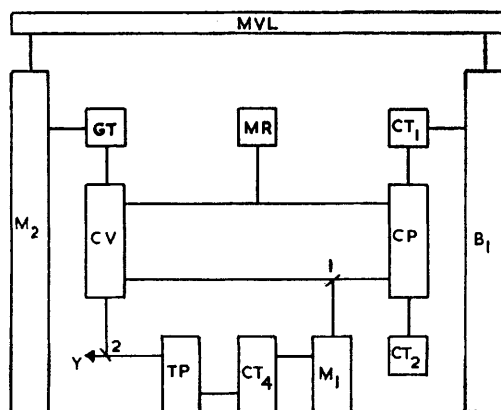


FIG. 12. B₁, mercury bubbler. CP, circulating pump. CT, cold trap. CV, catalyst vessel. GT, gold trap. M₁ and M₂, mercury manometers. MR, methanol reservoir. TP, Toepler pump. MVL, main vacuum lines. 1 and 2, three-way taps.

with hydrogen. Reduction of the wire was then commenced by heating it to 200° for a short time; this was followed by immediate evacuation of the system to terminate the reduction. The wire was then reweighed to determine the amount of oxide on it. It was replaced in the apparatus and "baked out" to 10⁻⁵ mm. pressure, prior to attempted reaction with methanol. After the reaction, the wire was again reweighed. The same general procedure was adopted in all gravimetric experiments. In the case of methanol partial reduction, the catalyst, prepared as above, was heated to 300° under a vacuum, and the tap to the methanol reservoir opened for a short time to allow methanol to flow into the hot catalyst vessel. After a few minutes the apparatus was evacuated to terminate the reduction, and the procedure continued as described above. A typical result is given below for the preparation and reaction on a flame-quenched catalyst.

Weights of copper before and after pretreatment, 49.6458 and 49.6623 g., respectively. After reaction, weight of copper = 49.6455 g. Therefore, weight of oxygen used in reaction = 16.5 mg.

Low-temperature-preparation Catalysts.—Catalyst wires of larger surface area were used in these experiments, so that a reasonable rate of oxidation could be obtained under the conditions used. 3 m. of 18 s.w.g. copper wire were lightly abraded with fine emery paper, and loose particles removed with cotton wool soaked in methanol. It was then bent into the form of three spirals fitting inside each other so that the total length of each spiral was *ca.* 5 cm. The total geometric surface area was 115 cm.². Final cleaning was effected by immersion of the wire in boiling methanol for a short time; it was then transferred to the catalyst vessel and "baked

out" to a pressure of 10^{-5} mm. The furnace was cooled, and purified oxygen was admitted into the circulating system until the pressure was 60 cm. The furnace surrounding the catalyst vessel was heated to 300° , and after an initial expansion, due to rise in temperature, the pressure fell steadily as the oxidation took place. After the required degree of oxidation had taken place, the furnace was removed and the catalyst vessel was cooled quickly by blowing cold air on to it. The decrease in oxygen pressure was then noted, and from the total volume of the system, the weight of oxygen taken up on the copper could be calculated. Catalysts containing 10.8, 23.8, and 33.5 mg. oxygen were prepared after oxidation times of 1, 2, and 4 hr., respectively. 7 cm. pressure of methanol vapour was then decomposed on these catalysts at 300° , according to Fig. 7.

Copper films. Copper films were prepared by direct evaporation in a vacuum, from electrically heated 24 s.w.g. copper wire, on to the surface of a glass catalyst vessel immersed in liquid nitrogen. These films were oxidised by use of the method described above for low-temperature-preparation catalysts, to which class these oxidised films belong. After the completion of methanol reactions on these films, the latter were estimated by dissolving them in nitric acid and titrating the resulting solution by use of the potassium iodide-sodium thio-sulphate method. In the experiment where a copper film was deposited on top of a previously oxidised one, a double-filament technique was used. The second filament was cleaned from oxide formed during the oxidation of the first film, by heating it electrically in the presence of methanol vapour to reduce the oxide, followed by ultimate heating in a vacuum. The oxide film was therefore not affected before deposition of the second film on top of it.

Analysis of Products.—Fig. 12 shows the apparatus used to isolate the gaseous products into the various fractions required for successful analysis. The general procedure adopted was as follows. At the completion of an experiment, the catalyst vessel was allowed to cool and the final pressure of the product gases noted. The mercury manometers, M_2 , were then isolated from the circulating system, and the gases in the latter allowed to expand into the analytical section of the apparatus (which was comprised of a mercury manometer, M_1 , cold trap, CT_4 , and Toepler pump, TP), through the three-way taps, 1, 2, when the new pressure reading on M_1 was noted. The mercury in the Toepler pump was at a standard fixed position during pressure measurements. The trap, CT_4 , could be cooled to any selected temperature, and the gas mixture circulated through it, by means of the Toepler pump, until no further reduction in pressure was observed. In this way, knowing the volume of the system, it was possible to estimate various gases accurately, by cooling the gas mixture successively to various temperatures. After separating off the required fraction at a chosen temperature, the remaining gases were pumped out through the three-way tap, 2, into Y (either an infrared gas cell, or a storage bulb, for gas chromatography).

The remaining condensed fraction was then isolated as follows. Methanol was distilled from the methanol reservoir, MR, into CT_4 , providing the necessary bulk solvent. Dry nitrogen was then admitted to the apparatus, up to atmospheric pressure, through the traps CT_2 cooled to -195° to remove water vapour. The three-way taps, 1 and 2, were then closed and the trap, CT_4 , was finally allowed to warm slowly to room temperature, allowing the methanol solvent and products to distil to the bottom of the trap. The trap and contents were eventually removed, the stem of the trap rinsed with 1 ml. methanol from the reservoir, and the tube stoppered ready for analysis. The traps used for CT_4 were calibrated to 0.2 ml., so that the total volume of the solution was known. A portion of this solution (0.25 ml.) was removed for analysis for formaldehyde, the chromotropic acid colorimetric method being used. The remainder of the solution was titrated with Karl Fischer reagent to determine the water present. A blank determination was also carried out on the reservoir methanol to determine its water content. On the apparatus used, an accuracy of 0.5 mg. of water was achieved. The apparatus was also tested against inadvertent admission of water vapour from the atmosphere by applying the above analytical procedure to known quantities of synthetically prepared gas mixtures admitted to the circulating system of the apparatus. The results were completely satisfactory as regards this point.

High-temperature Preparation of Catalysts containing Oxygen-18.—One yard of 24 s.w.g. copper wire (geometrical surface area, 16 cm.²) was cleaned with fine emery paper and then methanol. It was formed into a filament within the catalyst vessel and attached to two lengths of 16 s.w.g. gold wire, which in turn were connected to two silver steel terminals. This arrangement prevented oxidised copper wire adjacent to the terminals being situated outside the

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reaction zone. The copper filament was heated under a vacuum of 10^{-5} mm. Oxidation of the filament was accomplished by heating it electrically to about 900° at 5–6 cm. pressure in the presence of oxygen gas enriched with oxygen-18. The extent of oxidation was measured by means of the pressure decrease.

Low-temperature Preparation of Catalysts containing Oxygen-18.—These were prepared as described previously.

Oxygen-18.—Oxygen gas enriched with oxygen-18 was prepared by electrolysis of water enriched to the extent of 6 atom % (supplied by 20th Century Electronics Ltd.). By admission of this enriched gas to a tube containing copper powder, previously reduced with hydrogen and outgassed in a vacuum, calibration samples for oxidation were prepared. A calibration sample of oxygen-18-labelled copper oxide was prepared by heating the tube. The copper oxide was reduced under a stream of carbon monoxide (freshly prepared from sodium formate and concentrated sulphuric acid) to produce a calibration sample containing carbon [^{18}O]dioxide.

Gas Analysis for Experiments involving Oxygen-18.—After separation into two fractions, samples of the fraction containing carbon monoxide, carbon dioxide, and hydrogen were isolated for mass-spectrometric determination of the oxygen-18 enrichment of the carbon dioxide. The remainder was analysed by the freezing-value method, and by gas chromatography in a unit suitable for analysing permanent gases.

Gas Chromatography.—Two columns were used. Hydrogen and carbon monoxide were separated at 100° on a 5 ft. molecular sieve type 5A column, 30–60 mesh (retention times H_2 , 55 sec.; CO, 2.5 min.; flow rate, 75 ml./min.; positive pressure, 580 mm.; voltage on ionisation detector, 1700 v). Carbon dioxide was estimated on a 12 in. activated charcoal column, 30–60 mesh (retention time $\text{H}_2 + \text{CO}$, 1 min.; CO_2 , 2.5 min.; temperature of column, 100° ; flow rate, 150 ml./min.; positive pressure, 230 mm.; voltage on detector, 1800 v). An argon carrier was used in both cases. The detector used to estimate these gases was of the ionisation type, and incorporated a radioactive α and β ionising source. Detection was by the negative-peak method, using an ethylene bleed to provide a steady ionisation current. The steadiest background current was obtained when the ethylene was adsorbed on the column prior to admission of the gas sample. The slow desorption of the ethylene by the carrier gas then provided a steady ionisation current, which remained steady indefinitely, even when the column was removed and later replaced.

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