CLXIX.—*Promotion of Catalytic Reactions.   Part I.*

By Samuel Medsforth.

A.   *The Action of Hydrogen upon the Oxides of Carbon.*

IN the course of experimentation on the oxidation of methane, it became necessary to prepare large quantities of this gas, and for this purpose various methods of preparation were studied, including the well-known Sabatier reactions :

$$CO + 3H_2 = CH_4 + H_2O$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O.$$
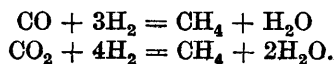
The quantities of the reacting gases in the case of carbon monoxide were those used in the Cedford process for the production of methane (*J. Gasbeleucht.*, 1911, **54**, 737), that is, one part of carbon monoxide to five parts of hydrogen. The catalyst was nickel prepared *in situ* by the reduction of the oxide from nickel nitrate deposited on pumice.

In considering the above equations, it will be observed that water is one of the end-products, and it was thought that the presence of a catalytic dehydrating agent in contact with the nickel catalyst would materially increase the velocity of the reaction. The results of preliminary experiments were sufficiently interesting to warrant further investigation.

The effectiveness of promoters in catalytic reactions is now a well-established fact; the Badische Company state that the oxides of thorium, glucinum, and zirconium are capable of functioning as promoters in the methane synthesis (D.R.-P. 2306, 1914).

Pease and Taylor (*J. Physical Chem.*, 1920, **24**, 241) define promoter action as including " all those cases in which a mixture of two or more substances is capable of producing a greater catalytic effect than can be accounted for on the supposition that each substance in the mixture acts independently and in proportion to the amount present." The maximum accelerative effect will be obtained when the number of points of contact of the promoter and catalyst exposed to the reacting substance or substances is at a maximum. On this view, therefore, it should be possible to determine the optimum catalytic effect on the velocity of a reaction by means of a series of experiments in which the proportion of promoter to the same quantity of catalyst is varied. This optimum concentration will differ with each substance and with the method of preparation. It is difficult, if not impossible, to secure uniformity of deposition of the catalyst and promoter on the surface of the carrier, and therefore too concordant results were not be expected. It was found that in addition to the surface effects, the temperature at which the catalytic effect was at a maximum differed with the substance used, having regard of course to the production of undesirable by-products. The results shown in this paper are in the majority of cases the mean of a number of determinations.

· Table I shows in column I the maximum catalytic effect produced by the use of the substances enumerated on the formation of methane from a mixture of carbon monoxide and hydrogen ($CO : H_2 = 1 : 5$ by volume), and in column II the maximum catalytic effect on the synthesis of methane from carbon dioxide and hydrogen ($CO_2 : H_2 = 1 : 6$ by volume). The figures refer in every case to the optimum concentration of promoter added to

the nickel, the quantity of which was kept constant throughout the experiments. The effect produced by nickel alone is taken as unity. The details of these experiments will be found in a later part of the paper. Columns III and IV show the increase in effect produced, taking that due to the promoter thoria as 100.

TABLE I.

Name.	Maximum effect.		Increase in catalytic effect.		Rideal and Taylor. Dehydrating properties.	
	I	II	III	IV	V.	VI.
	(CO, H_2).	(CO_2, H_2).	(CO, H_2).	(CO_2, H_2).		
Cerium oxide.........	17·7	Not det.	103·6			
Thorium ,, ...	17·1	12·8	100·0	100·0	100	D
Glucinum ,, ...	16·6	12·65	96·9	98·0	45·0	M
Chromium ,, ...	15·7	11·40	91·4	88·2	91·0	M
Aluminium ,, ...	14·3	10·45	82·6	80·1	98·5	D
Silica	12·3		70·2		84·0	M
Zirconia	8·9		49·1		45·0	M
Molybdenum oxide	6·3	2·2	32·9	10·1	23·0	M
Vanadium ,,	4·0	1·35	18·6	3·0	9·0	M
Tin ,,	No acceleration		0	0	0	
Magnesium ,,		,,	0	0	0	H
Copper		,,	0	0	0	H
Silver....................		,,	0	0	0	H
Nickel	1·0	1·0				

D = dehydrating agent; M = mixed dehydrating and dehydrogenating agent; H = hydrogenating agent only.

It was stated at the outset that the experiments were undertaken to discover the effect of the addition of a dehydrating agent to the catalyst on the velocity of the reactions given above. It is difficult to find a basis of comparison between the substances tested and the well-known catalytic dehydrating agents of a suitable type, for obviously the action of the latter will vary with each reaction investigated. Rideal and Taylor (" Catalysis in Theory and Practice," p. 288) give a list of oxides arranged in order of their dehydrating action on ethyl alcohol at 340—350°, counting the effect due to thoria as 100, and this table (column V) has been used for a first comparison. It will be seen from the table that with the striking exception of glucinum oxide there is a very fair measure of agreement between columns III and IV on the one hand and column V on the other, at all events in the general order of the oxides and metals. It can be stated therefore that the velocity of the reactions investigated can be increased by the addition of a small quantity of a suitable dehydrating agent to the nickel.

Theoretical Discussion on the Action of Promoters in the Methane Synthesis.

The study of promoters has received comparatively little attention and only a few suggestions are to be found on the possible mechanism

of their action. Catalysis itself has been regarded as a purely physical phenomenon, or as a purely chemical one, or as a combination of both. Surface conditions and surface action are of primary importance in catalytic work, but it was realised that considerations of physical phenomena (such as adsorption) alone would scarcely be sufficient to explain the precise mechanism of the reactions studied. It is not proposed therefore to discuss in this paper the physical aspects of the subject, but to indicate the probable nature of the chemical action of the various substances used as promoters.

(a) *Carbon Monoxide and Hydrogen.*—The formation of methane by the passage of a mixture of carbon monoxide and hydrogen over nickel may be explained in two ways :

1. The oxygen of the monoxide is considered to be quadrivalent and there is formed an unstable intermediate compound by the union of three molecules of hydrogen with one molecule of the monoxide, probably in combination with the catalyst (compare Sabatier and Senderens, *Ann. Chim. Phys.*, 1905, [viii], **4**, 467). The course of the reaction may be represented simply as follows :

$$Ni + CO + 3H_2 \longrightarrow \overset{Ni}{\underset{H_4COH_2}{|}}* \longrightarrow Ni + CH_4 + H_2O.$$

2. An intermediate compound of the methyl alcohol type is formed (probably *via* formaldehyde), which is dehydrated to give the residue $:CH_2$ and water, the former being immediately hydrogenated to methane (compare Bone and Davies, T., 1914, **105**, 1694) :

$$CO + 2H_2 \longrightarrow H_2C \cdot HOH \longrightarrow :CH_2 \longrightarrow CH_4.$$

In both cases, the nickel is considered to be acting as a hydrogenating catalyst and as a dehydrating agent, and its power of functioning as the latter is known to be small. Consequently, the rate of formation of methane will be comparatively low. The presence, therefore, of a suitable dehydrating agent, even in minute quantity, at the surface of the nickel will increase the velocity of the dehydration and by so doing will leave the catalyst free to do the work of hydrogenation at an enhanced rate. In other words, the function of a promoter is to relieve the catalyst of part of its work, in fact to take over work which it can do better than the catalyst itself.

With nickel and a promoter, P, present, the reaction according to the first suggested mechanism may be represented as follows :
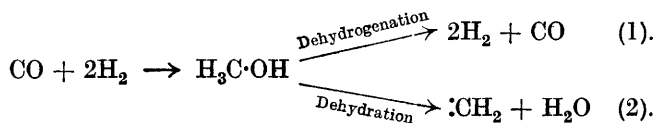
$$Ni + CO + 3H_2 \longrightarrow \overset{Ni \ \ P}{\underset{H_4C \cdot OH_2}{| \ \ |}} (II) \longrightarrow Ni + CH_4 + H_2O + P.$$
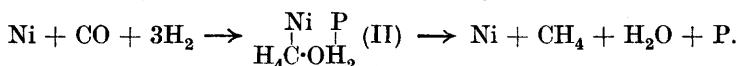
* This formula represents the " complex " supposed to be formed after the intramolecular change has taken place.

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According to this scheme, a double "complex" formation is assumed in which the promoter P combines loosely with the intermediate compound, formed by the union of the reacting gases with the catalyst. The nature of the promoter, that is, its dehydrating properties, indicate that it is attached to the remainder of the double "complex" as shown in II, that is, through the HOH group.

On this hypothesis, the activity of substances such as ceria, thoria, etc., and the inertness of others, for example, copper, silver, may be explained. The promoting power of a substance as far as these reactions are concerned becomes a function of its catalytic dehydrating effect on the intermediate compound supposed to be formed. Further, since the instability of the intermediate compound ensures rapid dehydration, a very high maximum catalytic effect is obtainable by the introduction of a powerful dehydrating agent, and Table I shows the extraordinary increase produced by such substances.
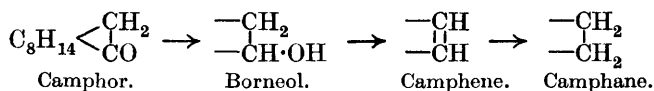
Now, in addition to the formation of methane another operation appears to take place when a mixture of carbon monoxide and hydrogen is passed over nickel. It has been shown by the author that if a mixture of one part of methyl alcohol and three of hydrogen (that is, the proportions in which these two substances would be present assuming the formation of the alcohol in the experiments described in this paper) be passed over nickel, the rate of decomposition of the alcohol into carbon monoxide and hydrogen will be far greater than that of the formation of methane. The rate of production of methane with thoria present is fourteen times that with nickel alone. These experiments would appear to show that when a mixture of carbon monoxide and hydrogen (1 : 5) is passed over nickel, rapid formation of an intermediate compound of the methyl alcohol type takes place (probably *via* formaldehyde) which is decomposable in two ways :

$$CO + 2H_2 \longrightarrow H_3C \cdot OH \begin{array}{c} \xrightarrow{\text{Dehydrogenation}} 2H_2 + CO \quad (1). \\ \xrightarrow{\text{Dehydration}} :CH_2 + H_2O \quad (2). \end{array}$$

In addition, therefore, to acting as a hydrogenating and a dehydrating catalyst, the nickel functions also as a dehydrogenating agent, so that the promoter will, by increasing the rate of dehydration, suppress the dehydrogenation and enable the nickel to hydrogenate at an enhanced rate.

Some experiments carried out by Ipatiev (*J. Russ. Phys. Chem.*

Soc., 1912, **44**, 1695) seem to support the second view of the mechanism of the reaction and the dehydration hypothesis. He found that camphor was hydrogenated in the presence of nickel oxide at 320—350° to borneol. This in turn could be dehydrated at 350—360° in the presence of alumina to camphene, which could then be hydrogenated at 240° to camphane. By using a mixture of nickel oxide and alumina in the presence of hydrogen, camphor could be converted directly to *iso*camphane at 200° or less.

$$C_8H_{14}{<}{CH_2 \atop CO} \rightarrow {-CH_2 \atop -CH{\cdot}OH} \rightarrow {-CH \atop -CH} \rightarrow {-CH_2 \atop -CH_2}$$

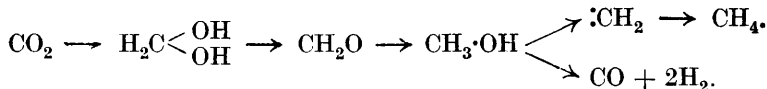| Camphor. | Borneol. | Camphene. | Camphane. |

(See Pease and Taylor, *loc. cit.*).

More information may be obtained on the mechanism of the reaction as a result of further experiments, particularly on the oxide of glucinum, as the cases in which this substance is more active than thoria or alumina are limited, generally, to the production of esters from mixtures of alcohols and acids (D.R.-P. 261878).

Selective Promotion.—It will be shown in the experimental portion of this paper that in the presence of a promoter a slightly larger percentage of carbon dioxide is obtained in the final gas than with the catalyst alone, under conditions which preclude the possibility (verified by tests) of the decomposition of the carbon monoxide to the dioxide and carbon. Carbon monoxide will react with water as follows :

$$CO + H_2O \rightleftharpoons CO_2 + H_2,$$
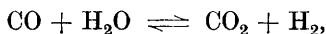
and, as is well known, promoters are capable of accelerating this reaction. The effect of various promoters has been determined and it is hoped to communicate the results in a later paper. It has been found that the velocity of this reaction at 180—280° is, with nickel alone, much smaller than that of the methane synthesis. It would appear, therefore, that when two reactions, both capable of being accelerated, take place at the same time in the presence of the same catalyst and promoter, that which is normally the slower is accelerated to a greater *comparative* degree than that which is normally the faster. Support for this statement was obtained whilst investigating the action of carbon monoxide on excess of steam in the presence of nickel, and nickel and promoters. Whilst carbon dioxide and hydrogen are the main products of the reaction, methane is also formed, the quantity of which is greater when, for example, alumina is present than when nickel alone is used. Selective promotion may be said to be operating in these two cases.

(b) *Carbon Dioxide and Hydrogen.*—The mechanism of this action may be expressed in a similar manner to that described above with carbon monoxide, namely,

$$CO_2 \longrightarrow H_2C{<}^{OH}_{OH} \longrightarrow CH_2O \longrightarrow CH_3 \cdot OH \left\langle \begin{array}{l} :CH_2 \longrightarrow CH_4. \\ CO + 2H_2. \end{array} \right.$$

This representation would explain the formation of carbon monoxide, which has been found in the exit gases by various workers, particularly where a large excess of hydrogen is not used.

Probably a simpler hydrogenation than that shown above (II) takes place, the result being a compound which is dehydrated to give the monoxide and water :

$$Ni + CO_2 + H_2 \longrightarrow Ni(HCO \cdot OH) \longrightarrow Ni + H_2O + CO.$$
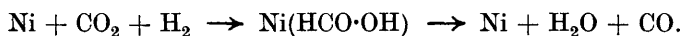
The production of methane from carbon dioxide and hydrogen appears therefore to involve two more operations than is the case with the monoxide. The catalyst takes part in an extra hydrogenation, and the promoter in a dehydration. This would account satisfactorily for the higher temperature necessary with carbon dioxide, and also for the somewhat lower accelerating effect obtained by the use of promoters.

Applications of the hypothesis outlined above will be considered after the experimental part (Section B).

EXPERIMENTAL.

Materials used.—(a) The carbon monoxide was prepared by the dehydration of formic acid with sulphuric acid and was freed from carbon dioxide by passage through a strong solution of caustic soda. The average purity throughout the experiments was 99·8 per cent. Cylinder carbon dioxide was used in the experiments involving this gas.

(b) The hydrogen was prepared electrolytically and was of a high order of purity (99·9 per cent.).

(c) The nickel used was prepared from nickel cubes (obtained by the Mond process) and contained a small proportion of iron and carbon. Comparative tests showed that these impurities were present in such small amounts as to have no influence on the results. A stock solution of nickel nitrate was made from the cubes, and finely divided nickel was obtained by the reduction of the oxide resulting from the ignition of the nitrate, deposited on pumice.

The temperature and time of reduction were varied according to the nature of the promoter, experience having shown that nickel

oxide after the addition of substances such as silica, capable of combining with it, required a higher temperature for reduction than did nickel alone or with promoters of the type of thorium oxide. In general, the reduction temperature was 330—350°,* rising to 450—470° in the case of nickel silicate.

(*d*) The substances tested for promoter action were obtained as pure as possible, but in many cases laborious purification was necessary before the results were trustworthy, chiefly owing to the presence of traces of poisonous sulphur-containing compounds. Thorium nitrate, for example, was purified both by recrystallisation and precipitation methods. In this work, with the exceptions hereafter stated, only irreducible or difficultly reducible oxides were used.

(*e*) *Pumice* (20—30 mesh), purified by boiling with concentrated hydrochloric acid, followed by the complete removal of the latter, was used as the support for the catalyst, after tests had shown that it was practically inert.

Preparation of Catalysts.—The preparation of the individual mixtures tested is noted below in Table II. Wherever possible, the following method was adopted. The pumice was added to about 10 c.c. of the mixed nitrates in solution in the desired proportions, and the mixture dried between 80° and 100° with stirring. The nitrates were then ignited at as low a temperature as possible until completely converted into the oxides.

It has been stated that precipitated alumina is much more active as a dehydrating agent than alumina prepared by the ignition of the nitrate. It was found actually that the method of preparation had only a slight influence on the activity of this substance in the methane synthesis.

Concentration of Catalyst.—In order to obtain comparative results, 1 gram of pumice was used in each experiment, and the amount of the nickel after reduction was 0·1 gram. The quantity of pumice taken was checked by measurement of the catalyst space in each experiment. The amount of promoter added varied over a wide range.

Temperature.—Carbon monoxide is decomposed more or less rapidly above 300° in the presence of nickel, and in the majority of the experiments involving this gas this temperature was not

* In view of the discussion as to the necessity of oxygen for the activation of hydrogenating catalysts (Willstätter and Waldschmidt-Leitz, *Ber.*, 1921, **53**, [*B*], 113), it is of interest to note that whilst the lower oxides of nickel were themselves quite inactive in this synthesis, there is considerable evidence to show that they act as promoters to the nickel, which alone is only slightly active.

TABLE II.

Substance +nickel.	Optimum con- centration as % of nickel.	Max. speed in c.c./min.	Temp.	Method of preparation.
Cerium oxide	4	620	270°	By ignition of nitrates.
Thorium ,, ...	10—12	600	270	,,
Glucinum ,, ...	20	580	275	,,
Chromium ,, ...	15	550	295	,,
Aluminium ,, ...	15	500	297	,,
Silica	7	430	295	By precipitation.
Zirconia	18	310	280	,,
Molybdenum oxide	12	220	292	Ex. nickel nitrate- amm. molybdate.
Vanadium ,,	7	140	298	Ex. nickel nitrate- amm. vanadate.
Tin ,,	No acceleration			
Magnesium ,,	,,			
Copper	,,			
Silver.....................	,,			
Nickel		32—35	285—290	By ignition of nitrate.

exceeded. It is to be noted, however, that the heat of reaction was sufficiently great to make temperature control a very difficult matter and the temperatures recorded below must be regarded as only approximately accurate.

Apparatus and Procedure.—The required mixture ($CO : H_2 = 1 : 5$ or $CO_2 : H_2 = 1 : 6$) was stored in an aspirator over gas-saturated, acidified water, from which it could be passed at varying speeds through a drying system and into the catalyst chamber. The latter consisted of a straight glass-tube, fused to a preheating coil disposed around it and heated in a carefully lagged air furnace, thermometers being placed both inside and outside the tube to indicate the temperature. After reduction was complete and before an experiment was commenced, the apparatus was swept out by a current of the mixed gases, and between separate experiments involving the use of the same catalyst, the latter was kept in an atmosphere of hydrogen. In addition to volume relationships, analyses of the exit gases were made and used as a further check on the accuracy of the aspirator readings.

Maximum Catalytic Effect.—In all cases, the catalytic effect of the substance under examination was measured by the maximum speed at which the gases could be passed over it, to ensure a complete or almost complete removal of the carbon monoxide or dioxide at the temperature employed. This was chosen as the most convenient point for comparison, although, of course, the space-time yield can be increased by reducing the time of contact of the gases with the catalyst within certain limits.

The optimum concentration was determined for a number of

promoters and the maximum speeds attainable at this concentration are shown in Table II. The speeds are compared with that obtained with nickel alone, that is, 32—35 c.c. per min. for 0·1 gram of catalyst on 1 gram of pumice at 285—290°. Great difficulty was experienced in estimating small alterations in speed with small changes in concentration of the promoter round and immediately beyond the optimum concentration. The figures representing the optimum concentration therefore are given to the nearest whole number and the higher speeds are accurate to about 10 c.c. per min.

In the above table those substances showing no acceleration * have been prepared by various methods and tested at different temperatures. All possible methods have not been exhausted, and it is proposed to continue experiments on these substances. The results obtained by the more detailed investigation of some of the promoters are shown in Table III.

TABLE III.

Quantity of promoter as % of Ni.	Maximum speed in c.c./min.						
	Ce_2O_3.	ThO_2.	GlO.	Al_2O_3.	Mo_3O_3.	V_2O_3.	Cu.
0·5	300	60	32	75	32	32	33
1·0	540	320	35	200	40	54	30
2·0	560	420	—	260	—	60	—
3·0	590						
4·0	620						
5·0	610	480	160	320	80	95	—
6·0						120	
7·0	600					140	
9·0		590				120	
10·0	600	600	290	450	200	110	26
12·0		600		470	220		
15·0	580	600		500	190		
16·0				490			
18·0			540				
20·0	560		580	460			
23·0			560				
50·0	470	570	420	380	110	24	
100·0		530	280				No action
200·0	380	470					
About 400		350					

The results tabulated above show that no relationship can be established between the molecular weight of a promoter and its optimum concentration. One per cent. of glucinum oxide, for example, with a molecular weight of 25, is one-ninth as effective as 1 per cent. of thorium oxide, with a molecular weight of 264, indicating that in the former case the nickel has covered the whole of the oxide, and in the latter the promoter has been deposited in part at the surface of the catalyst. With thoria and to a

* Sodium hydroxide, sodium carbonate, potassium carbonate have been shown to be ineffective as promoters in this reaction.

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lesser extent with ceria, a large, ill-defined region exists in which quite considerable changes in concentration produce no corresponding effect on the velocity. In fact, above the optimum concentration there was not with the majority of promoters that decrease in velocity expected on the assumption that the increase in concentration diminished the surface of the catalyst exposed to the action of the gases. Surface conditions are evidently very complex at these concentrations, although it is probable that to some extent the decrease in surface of the nickel is counteracted by the increase in accelerating power of the promoter.

For these reasons, the curves in Fig. 1, showing the relationship between the concentration of the promoters named and the speeds, have not been continued far beyond the optimum concentration.

Surface Covered by Promoters.—It is desirable at this stage to attempt to form an estimate—necessarily only approximate—of the probable changes in exposed surface of the catalyst due to small differences in the concentration of the promoter, particularly round the optimum concentration.

Two cases will be considered, (1) in which both catalyst and promoter are deposited on a support, (2) the catalyst is deposited on the promoter.

1. With the amounts of nickel and pumice used above, that is, $0 \cdot 1$ gram of nickel to 1 gram of pumice, or 10 per cent., it may be assumed for the purposes of the calculation that a uniform distribution has been obtained. If the quantity of promoter, for example, thoria, be taken at the optimum concentration, namely, 10—12 per cent. of the nickel (at. wt. 59), then if the whole of the thoria (mol. wt. 264) is deposited on the nickel, the surface covered by it will be approximately 1/40 that covered by the catalyst. An additional 1 per cent. of thoria will increase the surface area covered by it by 1/400 (approx.) and even with 100 per cent. of thoria present, the surface covered will be but 1/4 to 1/5 of the total.

Round the optimum concentration, therefore, marked changes in velocity with changes in concentration of promoters of high molecular weight would not be expected.

2. Different results are obtained when thoria replaces the pumice as carrier, and for the same catalyst space about five times the quantity of oxide is required. Thus assuming the nickel to be deposited entirely at the surface of the thoria, $0 \cdot 1$ gram of nickel on 5 grams of thoria, that is, 2 per cent., gives the same exposed surface of catalyst as $0 \cdot 1$ gram of nickel on 1 gram of pumice. A reduction, therefore, from $2 \cdot 0$ per cent. to $1 \cdot 8$ per cent. of nickel means a change in surface of 10 per cent., so that when the catalyst

is deposited at the surface of the promoter, small changes in the concentration of the former produce important alterations in the velocity of the reaction (compare Section B, The Incandescent Mantle).

Influence of Temperature.—Reference was made previously to the fact that nickel oxide to which chromium oxide had been added required a higher temperature of reduction than nickel oxide alone. It has been found that oxides capable of combining with nickel oxide under proper conditions, forming, for example, nickel chromate, exert their maximum catalytic effect at a higher temperature than does either nickel alone or nickel in conjunction with substances of the thoria type (see Table II). The following table shows the influence of temperature on the maximum catalytic effect of a nickel–thoria and a nickel–chromium oxide catalyst, respectively.

TABLE IV.

	Speed in c.c./min.		
Temp.	Ni–ThO_2.	Ni–Cr_2O_3.	Ni.
$295°$	590	550	32—35
280	600	220	,,
270	600	62	27
250	330	24	
200	86	Less than 10 c.c.	*ca.* 2
150	15	Not estimable	

The reduction in speed shown in the case of the nickel–chromium oxide catalyst is greater than can be accounted for by the fall in temperature : alumina, silica, molybdenum oxide displayed the same comparative inertness below 270°.*

Typical analyses of the gases produced are given in the following table.

TABLE V.

	Ni alone. Temp. 280°.		Ni–Thoria. Temp. 270°.	Ni–Thoria. Temp. 180°.
	I.	II.		
Carbon dioxide	0·4	0·6	1·2	1·3
Carbon monoxide	0·3	0·9	0·5	0·8
Methane	31·6	31·2	30·7	
Hydrogen	67·2	67·2	67·4	
Total	99·5	99·9	99·8	

Carbon Dioxide and Hydrogen.—A few experiments have been carried out with these gases and the maximum velocities obtained at the optimum concentration of promoters are given in Table VI. The temperature was 360—370° in all the experiments.

* Probably compound formation of some type is taking place below this temperature.

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TABLE VI.

Oxide.	Speed in c.c./min.	Oxide	Speed in c.c./min.
Thorium	550	Molybdenum	95
Glucinum	540	Vanadium............	58
Chromium	490	Ni alone	43
Aluminium	450		

Table VII shows in greater detail the effect of the concentration of the oxides of thorium and glucinum on the speed.

TABLE VII.

Conc. as % of Ni present.	Speed in c.c./min.		Conc. as % of Ni present.	Speed in c.c./min.	
	ThO_2.	GlO.		ThO_2.	GlO.
0·1	50		10·0	550	260
0·5	62		20·0	540	540
1·0	80	60	30·0	—	490
5·0	270	—	50·0	520	

The results have been plotted in Fig. 1. The curves for glucinum oxide given by the two oxides of carbon lie close together, whilst small quantities of thoria do not exhibit the same accelerative power in the carbon dioxide–hydrogen reaction as in that involving the lower oxide.

### B. *Applications of the Dehydration or Hydration Hypothesis.*

Promoters have been used in many catalytic reactions, and in considering the probable mechanism of their action on the diverse catalysts employed, it is necessary to deal with each reaction separately. The nature of the reacting substances, of possible intermediate compounds, and of end-products, and their action on the catalytic materials must be studied. In addition, optimum concentrations will differ with each catalyst and with the nature of the support, if any.

Action of Carbon Monoxide on Steam.

It has been stated previously that carbon monoxide reacts with steam as follows :

$$CO + H_2O \rightleftharpoons CO_2 + H_2.$$
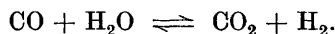
Armstrong and Hilditch (*Proc. Roy. Soc.*, 1920, [*A*], **97**, 265) have advanced the theory that the effectiveness of copper as a catalyst in this reaction is due to its power of dehydrogenating formic acid, which they conceive to be the intermediate compound formed :

$$CO + H_2O \rightarrow HCO \cdot OH \rightarrow CO_2 + H_2.$$
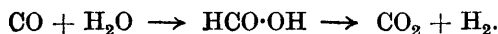
The Badische Co. have used nickel as a catalyst, and as this metal decomposes steam only slowly at a red heat, but dehydrogenates

formic acid rapidly at low temperatures, the mechanism of the process may be considered to be similar to that with copper.
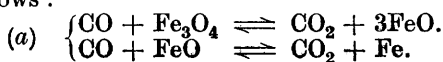
Further, the reversibility of the dehydration process in the case of ethyl alcohol in the presence of oxide catalysts has been demonstrated by Engelder, who was able to show that the alcohol–water–ethylene equilibrium could be displaced by the addition of water to the incoming alcohol (*J. Physical Chem.*, 1917, **21**, 676).
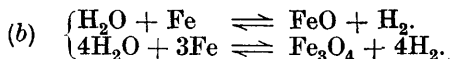
FIG. 1.

Concentration of the promoter expressed as percentage of nickel.
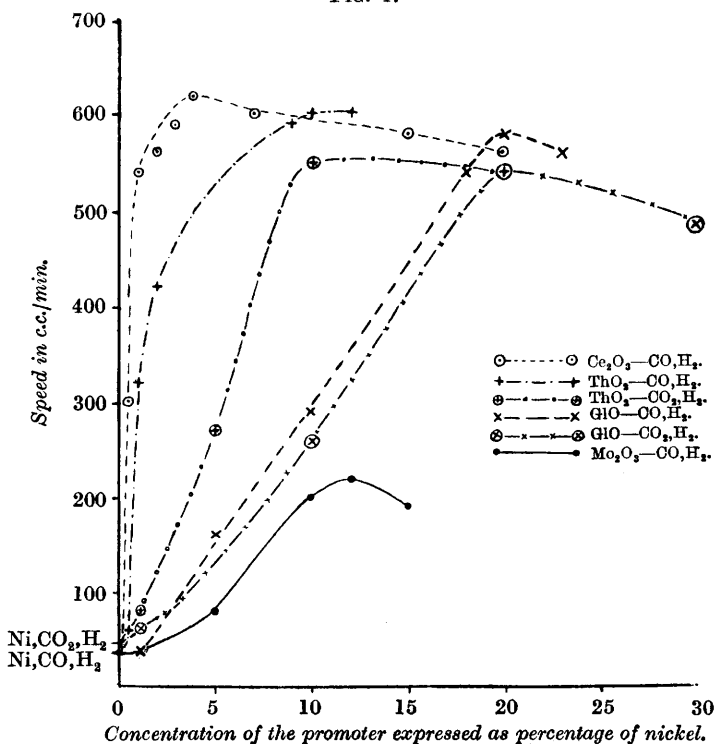
It will follow, then, from the conclusions of these authors that the presence of a hydrating agent such as alumina or thoria in contact with the catalyst, for example, nickel, will accelerate the velocity of the reaction by forming the intermediate compound, in this case formic acid, for decomposition by the catalyst.

In addition to copper, the action of iron oxide has been studied by Armstrong and Hilditch, who attribute the formation of carbon dioxide and hydrogen to alternate reduction and oxidation of the catalyst as follows :

$$(a) \quad \begin{cases} CO + Fe_3O_4 \rightleftharpoons CO_2 + 3FeO. \\ CO + FeO \rightleftharpoons CO_2 + Fe. \end{cases}$$

$$(b) \quad \begin{cases} H_2O + Fe \rightleftharpoons FeO + H_2. \\ 4H_2O + 3Fe \rightleftharpoons Fe_3O_4 + 4H_2. \end{cases}$$

The addition of promoters to the iron or iron oxide increases the velocity of this reaction to a marked extent, and among the most effective are hydrating agents and oxygen carriers. For example, with a mixture of iron oxide, chromium oxide, and thorium oxide, the velocity of this reaction is at least eight times as great as that with iron alone (compare Pease and Taylor, *loc. cit.*). On the assumption that reduction and oxidation are taking place only, the thorium oxide would appear to operate by adsorption of water vapour, thus producing a greater concentration of this gas at the surface of the catalyst. The chromium oxide may act in some way as an oxygen carrier, but more probably acts in a similar manner to thorium oxide.*

The remarkable increase in activity shown by iron in the presence of promoters, together with the known dehydrogenating action of this metal, suggests that the hydrogen is produced both through the formation of formic acid and through the reduction and oxidation of the catalyst. In any case, hydration occurs and the function of the promoter will be in part to do work—hydration— for which it is more suited than the iron.

The experiments to test these suggestions are still in an early stage, but sufficient evidence has been obtained to support the hypothesis.

Nickel and iron have been used as catalysts, and it has been found that the speed with nickel alone is greater than with iron alone at the temperature of 400—450°. The results with promoters show that the accelerative influence with iron as catalyst is proportionately far in excess of that with nickel, although the actual speeds obtained are in the reverse order. Further experiments on the effect of the addition of the same promoter to substances capable of catalysing the same reaction in varying degree are required before a general statement on this point can be made. This case must not be confused with that previously cited, in which two reactions are taking place simultaneously in the presence of the same catalyst.

It would be anticipated from the hypothesis, that a good dehydrogenating catalyst in contact with a good hydrating agent would give satisfactory results, and it is noteworthy that the majority of the catalytic materials patented by the Badische Co. for use in this reaction consists of such a mixture. The following may be

* In many oxidation experiments involving water, it has been shown that iron–thoria is more active than iron–chromium oxide; which would scarcely be the case if the promoter functioned by activating the oxygen.

quoted as examples : mixtures of oxides of iron, nickel, and cobalt with oxides of chromium and thorium; oxides of vanadium and chromium; oxides of manganese and chromium, of copper and zirconium, of lead and tungsten, and of cerium and chromium. A comparison of the results given by these mixtures would be of great value, in particular by the last-named; this consists of two excellent hydrating agents, which under suitable conditions act also as oxygen carriers.

The Incandescent Mantle.

In general, an oxygen-carrier such as manganese dioxide, vanadium pentoxide, or cerium dioxide is used in conjunction with a base such as thoria, alumina, etc., in the making of a gas mantle. A mantle consisting of 0·9 per cent. of ceria together with 99·1 per cent. of thoria is the only one used extensively by reason of its high light emission, strength, and life.

Now, the oxidation of a hydrocarbon in the presence of a catalyst may be considered as taking place in two stages, namely, (1) the addition of oxygen to form an intermediate compound, and (2) decomposition of the latter to give carbon dioxide and water (compare Bone and collaborators, T., 1903 et seq., for papers on the oxidation of hydrocarbons). Thus the maximum catalytic effect would in all probability be obtained by using a powerful oxygen carrier in conjunction with a strong dehydrating agent. Such a mixture as ceria–thoria fulfils these conditions, so that, in part, at all events, the superiority of this mixture may be attributed to the fact that the ceria acts as a promoter to the thoria, its particular function being to form the intermediate compound for dehydration by the thoria (compare Pease and Taylor, loc. cit., who have also suggested that the ceria acts as a promoter). Further, the fact that the light emission falls when the content of ceria is increased above 1 per cent. may be explained on the assumption that the thoria acts, not only as a catalyst, but also as a carrier for the promoter, and, as shown previously (see Experimental part), under these conditions a small increase in the amount of the ceria present is sufficient to cover a large surface of the thoria.

The combustion of hydrogen may be explained on similar lines to those indicated above, but the mechanism of the oxidation of carbon monoxide appears to fall in a different category. Rideal and Taylor (Analyst, 1919, 44, 89) have shown that the preferential combustion of small quantities of carbon monoxide in hydrogen does not take place through the operation of the water-gas reaction, $CO + H_2O \rightleftharpoons H_2 + CO_2$, at low temperatures, iron or copper, with chromium oxide and ceria or thoria added in small quantity,

being used as catalyst. It appears, however, somewhat difficult to account for the action of a poor oxygen activator such as thoria, and further it can be shown that with the same quantity and type of catalyst as was used in the preferential combustion experiments, the water-gas reaction takes place to an appreciable extent at 300°.

The combustion of carbon monoxide under higher temperature conditions than those used by Rideal and Taylor has been considered to take place through the action of the water present (Dixon, *Phil. Trans.*, 1884, **175**, 617; compare also von Wartenberg and Sieg, *Ber.*, 1920, **53**, [B], 2192) as follows :

$$2CO + 2H_2O = 2CO_2 + 2H_2$$
$$2H_2 + O_2 = 2H_2O$$
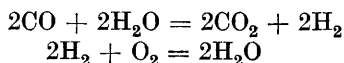
in which case, the functions of the thoria and ceria are similar to those of the catalysts in the water-gas reaction. It is hoped to test the above suggestions experimentally in the near future.

Selective Catalysis.

In working on reactions similar to that of the synthesis of methane, where one or more intermediate compounds are assumed to be formed, it was thought that by adding a suitable substance in small quantity to the catalyst, it should not be impossible, provided the correct physical conditions were obtained, to prevent the reaction proceeding to the methane stage and to obtain interesting products. A few experiments were tried, but the results were entirely negative.

Rosenmund, Zetzsche, and Heise (*Ber.*, 1921, **54**, [B], 425), working on similar lines, found that by the addition of suitable promoters or inhibitants they were able to control the reduction of benzoyl chloride in the presence of palladium in such a manner that the chief product might be benzaldehyde, benzyl alcohol, benzyl benzoate, dibenzyl ether, or toluene. The regulating substances were chosen to contain an element of variable valency, but appear also to have contained one of the ordinary catalyst poisons; for example, quinoline heated with sulphur was most active.

Conclusion.

It has been shown in this paper that

(1) The action of promoters in the synthesis of methane from carbon monoxide and hydrogen, and carbon dioxide and hydrogen in the presence of nickel, depends on the dehydration of an unstable intermediate compound.

(2) Promoters may act selectively. The action of the promoters discussed may be classified temporarily as follows :

(i) The promoter decomposes intermediate compounds formed by the catalyst.

(ii) The promoter causes the reacting substances to combine, the resulting intermediate compound being decomposed by the catalyst.

(iii) The promoter adsorbs or combines with one of the reacting substances, producing a greater concentration of the latter at the surface of the catalyst.

The study of promoters is being continued partly on the lines indicated in this paper and partly with reference to those reactions involving direct hydrogenation of unsaturated compounds. The influence of groups such as OH, NH_2, etc., is being determined not only on the velocity of hydrogenation but also on the type of promoter required.