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Mechanism of the Catalytic Hydrogenation of Oxides of Carbon to Methane

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The present review examines the mechanisms of the formation of methane from carbon monoxide and dioxide and hydrogen in the presence of contact catalysts based on metals of the iron group (chiefly nickel). The experimental results obtained by various methods are examined, the reactive forms of the adsorbed molecules and the signs of their charges are considered, and particular attention is paid to the determination of the reactive complexes under the conditions preceding the start of the catalytic reaction, and the results of kinetic studies. It is shown that there is a significant difference in the mechanisms of the hydrogenation of carbon monoxide and dioxide to methane. This difference is attributed to the poisoning effect of carbon monoxide on the processes involved in the hydrogenation of CO_2. Attention is drawn to a number of results which are of considerable importance for the solution of the problems of the catalytic purification of hydrogen from oxides of carbon. The bibliography contains 129 references.

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I. INTRODUCTION

Syntheses based on carbon monoxide and hydrogen (and to a much smaller extent on carbon dioxide and hydrogen), from their discovery[1-3] up to the present, have attracted considerable attention from many research workers. This is due to the variety of possibilities for the practical utilisation of reactions involving the catalytic hydrogenation of oxides of carbon. A large number of versions of the synthesis of hydrocarbons, the synthesis of methanol, and the direct synthesis of higher alcohols[4,5] are among the reactions of carbon monoxide with hydrogen which have been carried out on the industrial scale.

The possibilities of synthesis from oxides of carbon and hydrogen apparently have not been fully realised. Moreover, with other components in the reaction mixture it is possible to carry out the most rational production of complex end products. Examples of such processes are the preparation of higher alcohols by the oxo-process[5] and the synthesis of amines from carbon monoxide, hydrogen, and ammonia[6,7].

The mechanisms of all these reactions and of other reactions which have not yet been realised but which are thermodynamically possible may be the same in the initial stages, so that the study of these stages is of considerable interest. Usually, however, the compositions of the reaction products are complex, and this makes it very difficult to obtain a true picture of the process. If, however, we exclude from consideration some stages of the reaction, it is possible to simplify the problem and to concentrate attention on the study of the first stages of the synthesis. This can be done by studying the formation of methane, since in this way it is possible to investigate in purest form the primary stages of the reaction of oxides of carbon with hydrogen. This possibility has been underestimated, apparently because there are no reviews devoted specially to the mechanism of the synthesis of methane, whereas studies of the mechanism of formation of the higher hydrocarbons are published periodically[8-16].

As the simplest aliphatic hydrocarbon, methane exhibits the basic features of its homologous series, so that the study of the mechanism of its formation is of primary importance in the investigation of the synthesis of alkanes.

In this study, it is naturally necessary to choose reaction conditions under which the formation of methane is the only process or at least the predominant process. A decisive feature is the selection of a highly selective and active catalyst, in the presence of which the most definite results are obtained; it is also desirable that the results be of practical use.

Nickel is one of the most active catalysts for the synthesis of methane from carbon monoxide and hydrogen[17]. The other metals of the iron group have lower activities. Nickel, cobalt, and iron can be arranged in the same sequence with reference to the conversion of carbon dioxide into methane[1,2,18-22]. The present review deals chiefly with results obtained with nickel catalysts, which in our view are of greatest interest.

II. MECHANISM OF THE FORMATION OF METHANE FROM CARBON MONOXIDE AND HYDROGEN

The hydrogenation of carbon monoxide to methane can be regarded as the simplest example of the synthesis of hydrocarbons. This makes it possible on the one hand to introduce existing theories of the synthesis of hydrocarbons to explain the mechanism of formation of methane, and on the other hand, as shown above, it makes it possible to some extent to use the results obtained to understand the mechanism of formation of higher hydrocarbons.

The earliest theory of hydrocarbon synthesis was the carbide theory[23-27], which was subsequently found to be inadequate to explain these processes in the presence of catalysts based on metals of the iron group[9]. In fact, carbide formation cannot be an intermediate stage in the synthesis of methane from carbon monoxide and hydrogen, since the temperature of hydrogenation of the surface nickel carbide is higher than the temperature of appreciable methane formation[28] and the rate of the synthesis is much greater than the rate of carbide formation[29-33].

Other widely held ideas, in addition to the carbide theory, have included various schemes according to which oxygen-containing substances—methanol[34] or formaldehyde[5]—are intermediate products. Attempts to detect formaldehyde or methanol in the synthesis of methane on a nickel catalyst were unsuccessful, however[35]. Moreover, it was shown[36] that on a cobalt catalyst the yield of hydrocarbons when methanol is used as starting material is less than that obtained when a mixture of carbon monoxide and hydrogen is used. The formation of hydrocarbons from methanol is evidently a secondary process involving carbon monoxide and hydrogen obtained by the decomposition of methanol.

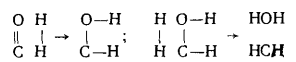
A suggestion related to these hypotheses was put forward by Fischer and coworkers[17], according to whom the reaction with carbon monoxide leads to the intermediate formation of the metal carbonyl, which is then reduced with the formation of methane. A similar explanation for the synthesis of hydrocarbons was put forward by Pichler[5,16].

In contrast to early hypotheses based on Sabatier's theory of phase intermediate compounds[37], the idea of primary compound formation represents a definite change towards modern theories of catalytic action, which make use of the concept of intermediate *surface* compounds[38,39]. In connection with these theories, the search for reactive surface complexes and radicals is acquiring primary importance.

Orlov's suggestion[40] that methylene radicals are formed in the primary stages of the hydrogenation of carbon monoxide

$$CO + 2H_2 \rightarrow CH_2 + H_2O$$

was later verified experimentally by Eidus and Zelinskii[41], who proved the existence of CH_2 radicals in the methylation of benzene to toluene. It was established that the CH_2 species are formed from carbon monoxide and hydrogen[29]. On the basis of the results obtained, Eidus[36] concluded that on cobalt and nickel contact catalysts the primary stages of the process involve the successive hydrogenation of carbon monoxide first to an unstable oxygen-containing group, and then to the methylene radical:



A similar mechanism was proposed by Hamai[42].

The idea that an adsorbed complex of HCOH is formed provided the basis of the mechanism of hydrocarbon synthesis proposed by Anderson[5,43]. This mechanism differs from Eidus' scheme[9] in the subsequent stages of hydrocarbon chain formation. In a study of syntheses based on carbon monoxide and hydrogen in the presence of iron catalysts, Bashkirov and coworkers[44-46] also concluded that these processes should involve the production of an unstable intermediate adsorption complex which contains carbon, hydrogen, and oxygen atoms and is the precursor of both hydrocarbons and alcohols.

The conclusion that an intermediate compound of this kind exists was also reached[47] on the basis of a study of the Fischer–Tropsch synthesis in the presence of a nickel catalyst. Similar ideas were put forward by Eidus[48] and by Gibson and Clarke[49] on the basis of a study of the synthesis of hydrocarbons from carbon monoxide, hydrogen, and ethylene.

Thus irrespective of the composition of the products, the formation of a primary complex is assumed in all schemes of catalytic synthesis from carbon monoxide and hydrogen. The existence of this compound has not yet been confirmed experimentally, however, although this problem is a central problem in the study of the mechanisms of various reactions of carbon monoxide with hydrogen.

The possibility of existence of *adsorption complexes* in itself does not prove that they play a leading part in the reactions. In order to reach this conclusion it is necessary to rely on the results of direct kinetic studies, which make it possible to determine the limiting stage of the reaction.

The available data[50,51] indicate that the adsorption of the components of the reaction cannot be taken as the limiting stage. Similarly, the desorption of the reaction products does not determine rates of hydrogenation on nickel contact catalysts[50]. Study of the infrared spectra of water[52] showed that it is not adsorbed on a nickel contact catalyst, and it has also been shown[53] that methane and water are not adsorbed on a nickel–chromium catalyst.

On the other hand, the results of kinetic studies of the process indicate that the rate of formation of methane is determined by the reaction of carbon monoxide and hydrogen adsorbed on the surface of the contact catalyst.

It has been found by the static method[54] that at 271° and H_2/CO ratios from 2 to 20 in the presence of a nickel wire catalyst the rate of formation of methane is approximately proportional to the pressure of hydrogen and is retarded by carbon monoxide. A similar conclusion was reached by Luyten and Jungers[55], who studied the formation of methane in a static system at 300° and H_2/CO ratios from 1 to 6 in the presence of nickel deposited on kieselguhr. The reaction rate was given by the equation

$$W = k \cdot p_{H_2}^{0.9} \cdot p_{CO}^{-0.2}.$$

The heat of activation was 27 kcal mole^{-1}. This value differs considerably from the value 35 ± 1 kcal mole^{-1} found by Nicolai and coworkers[56], although the studies were carried out under identical conditions, on similar contact catalysts. The discrepancy is apparently due to the non-steady state of the catalyst surface.

The flow method has been used[50] to make a detailed study of the kinetics of the synthesis of methane at atmospheric pressure on an industrial nickel–kieselguhr contact catalyst in the range 300–350° at H_2/CO ratios from 1.2 to 4. The limiting stage of the process is the reaction between a molecule of carbon monoxide adsorbed on the contact surface and three molecules of hydrogen, according to the equation

$$W = \frac{p_{CO} \cdot p_{H_2}^3}{(A + Bp_{CO})}$$

where A and B are constants.

The retarding influence of carbon monoxide at high concentrations, observed in the works cited, is apparently due to the fact that the CO covers the contact surface to a considerable extent, leading to a corresponding decrease in the degree of covering of the surface by hydrogen. Moreover, in this instance there is a possibility of a change in the phase composition of the contact catalyst as a result of the formation of nickel carbides. Changes in the phase composition can be avoided if the studies are carried out at low concentrations of carbon monoxide in a large excess of hydrogen. The kinetic relationship obtained in this way by a flow-circulation method with a nickel–chromium catalyst at 135–175° and a concentration of carbon monoxide in hydrogen equal to 0.3 vol. % has the form[57,58]

$$W = k \cdot p_{CO}^0 \cdot p_{H_2}^0$$

which indicates directly that the process takes place by a Langmuir–Hinshelwood mechanism. The zero order of

the reaction with respect to both components can be attributed to the non-uniformity of the nickel surface with respect to the adsorption of carbon monoxide and hydrogen under the given conditions. Non-uniformity of the surface with respect to the adsorption of hydrogen at room temperature was established[59-61] by the differential isotopic method, and the non-uniformity of the surface of iron catalysts in the synthesis of hydrocarbons has also been observed[62]. Studies by a method enabling the change in the weight of the catalyst during the contact process[57] to be observed established that under the conditions of the experiment at 160° the degree of covering of the nickel surface by carbon monoxide amounts to about 1/3, and 2/3 of the surface is covered with hydrogen. This apparently explains the fact that the heat of activation (16.2 kcal mole^{-1}) is less than that in the works cited above[55,56], in which the degree of covering of the surface by carbon monoxide might have been much greater, because of the high concentration of CO in the gaseous phase. From these results it follows that in all examples of the synthesis of methane and higher hydrocarbons from carbon monoxide and hydrogen, on nickel catalysts at least, the reaction components interact in the adsorbed layer. This indicates that the adsorption complexes produced may play a leading role in syntheses from carbon monoxide and hydrogen. The detection of these complexes is therefore of considerable interest in the investigation of the mechanism of the catalytic formation of hydrocarbons.

The formation of adsorption complexes can be established if their steady-state concentration is sufficiently high. To determine the temperature range corresponding to the existence of adsorption complexes, it is necessary not only to establish that the limiting stage is the reaction in the adsorption layer, but also to establish whether the rate of the catalytic reaction is controlled by the rate of formation or the rate of transformation of the complexes. These stages can be studied experimentally by measuring the temperature dependence of the contact potential difference (c.p.d.) in the reaction mixture. The formation of adsorption complexes generally leads to a marked change in the contact potential difference relative to the values for each of the reagents.

For example, in the reaction of carbon monoxide and hydrogen on zinc oxide a decrease in the value of the c.p.d., which remained constant at the temperatures of catalysis, was observed[63]. In this instance the rate of the hydrogenation of carbon monoxide is limited by the rate of transformation of the adsorption complexes formed[64]. A different picture is observed in the hydrogenation of carbon monoxide in the presence of a nickel–chromium contact catalyst[65]. The temperature dependence of the c.p.d. is given by a characteristic curve with a minimum corresponding to the highest concentration of the adsorption complexes. With increase in temperature the value of the c.p.d. under the conditions of catalysis becomes close to its value for the adsorption of carbon monoxide. This indicates that the catalyst surface carries adsorbed carbon monoxide, and the rate of the contact process is determined by the rate of its conversion into chemisorption complexes. Thus in the reduction of carbon monoxide to methane on nickel, the rate of formation of the reaction complexes is the rate-determining stage of the reaction. It may be assumed that this is also true of the synthesis of methane from carbon monoxide and hydrogen in the presence of catalysts based on iron and cobalt.

It is clear from the foregoing that studies carried out under the conditions directly preceding catalysis are of greatest value in the investigation of the mechanism of the process. The study of the adsorption of the reaction components under these conditions, both separately and in mixtures, is acquiring primary importance, and may give important information on the formation and composition of the adsorption complexes.

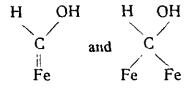
In spite of an extensive literature devoted to the adsorption of hydrogen and carbon monoxide on metallic contact catalysts, however, comparatively few studies have been made of the adsorption of these reagents and their mixtures under conditions close to those of catalysis or at the temperatures of catalysis.

Among studies of this kind carried out for cobalt Fischer–Tropsch contact catalysts, mention may be made of studies[66-71] of the adsorption of carbon monoxide and hydrogen, and their mixtures, in the range 25–97°. It was shown that at 97° over a period of 12 h, the formation of hydrocarbons, water, or carbon dioxide from CO and H_2 is not observed, whereas at 110°, methane was detected in the gas[67]. Special experiments established that cobalt carbonyls are not formed at 53, 76, or 97°,[70] that is the adsorption relationships were studied on an almost unaltered contact surface. In the study of the adsorption of mixtures of CO and H_2 it was established that the adsorption of each gas from the mixture is greater than the adsorption of the individual gas at the same partial pressures. With increase in the total pressure, the adsorption of carbon monoxide is greater from the mixture with CO : H_2 = 1 : 2 than from the mixture with CO : H_2 = 1 : 1. The adsorption of hydrogen is characterised by the opposite relationship[66,69]. With increase in temperature the quantity of adsorbed hydrogen increases, the dependence of the quantity of adsorbed carbon monoxide on the quantity of adsorbed hydrogen tending towards a linear relationship, and this, in the opinion of the authors cited[66], may indicate the formation, on the catalyst surface, of chemisorbed complexes which are possibly intermediate products in the Fischer–Tropsch synthesis. The same conclusion was reached by the other authors cited[69], who showed that the ratio of carbon monoxide and hydrogen adsorbed on the contact surface reaches 1 : 1 at 97°. This may indicate the formation of a complex with the composition HCOH. In other work[67], however, the value of this ratio for the same temperature was 2 : 1, and it was concluded that the complex ≡C–H is formed. The mutual intensification of adsorption, observed with consecutive adsorption of the components[68,70,71], also indicates strong chemical interaction between carbon monoxide and hydrogen in the adsorption layer.

These results of adsorption measurements on cobalt contact catalysts, however, cannot establish sufficiently clearly the compositions of the stoichiometric chemisorption complexes[72]. This is due, in particular, to the lack of information on the chemisorbed forms of the molecules of carbon monoxide and hydrogen and their reactivities; this makes it impossible to reach definite conclusions regarding the participation of various forms of chemisorbed molecules in the formation of the surface complexes.

To some extent these difficulties were overcome in a study[72] of the adsorption and desorption of carbon monoxide and hydrogen on a deposited iron catalyst at 50°. As with the cobalt contact catalysts, the adsorption measurements could not prove the formation of chemisorption complexes, since it was shown that, in addition to the formation of reactive forms of the molecules, irreversible adsorption of part of the gas took place, and this fraction did not take part in the formation of complexes. To eliminate the contribution from the irreversible adsorption, the authors cited used a method involving desorption with decrease in

pressure. It was established that, irrespective of the CO : H_2 ratio in the original mixture, a gas mixture with the almost constant ratio 1 : 1 is desorbed from the contact surface after 38 h. This indicates the existence of a weakly-bound chemisorbed complex, which decomposes on desorption. After determination of the composition of the chemisorption complex, we are faced with the problem of its structure and the type of bonds present. Linear and bridged bonds are formed when carbon monoxide is adsorbed on iron [73,74]. In this connection, two structures are possible for the complex HCOH:



A choice between these structures can be made on the basis of work by Blyholder and Neff [75], who used infrared spectroscopy to study the reaction of carbon monoxide and hydrogen on the surface of a deposited iron catalyst. The authors cited established that at 180°, complexes of the type



are formed, where R may be either a hydrogen atom or a hydrocarbon radical with unsaturated bonds. Although this structure differs slightly from that proposed by Eidus, it may be concluded that it is formed by the reaction of hydrogen with carbon monoxide adsorbed in linear form. An interesting feature is that at temperatures at or close to room temperature the authors cited, in agreement with Eischens [76], did not observe reaction between carbon monoxide and hydrogen. This work [75] is almost the only proof of the existence of surface complexes obtained by infrared spectroscopy; this is apparently due to the fairly high concentration of the complexes at 180°.

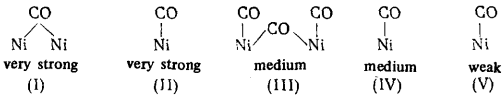
A number of studies [28,57,63,65] have been made of the reactive forms of adsorbed molecules, their interactions, and the part played by the primary complexes in the synthesis of methane from carbon monoxide and hydrogen in the presence of a nickel–chromium catalyst.

The study of the adsorption of carbon monoxide and hydrogen, separately and in a mixture, was carried out at 75°, since at low temperatures carbon monoxide may form volatile nickel carbonyls, which decompose above 60°, [77] and formation of methane begins at temperatures slightly greater than 80°. [78] Thus the conditions established corresponded to those directly preceding the start of the catalytic reaction. Under these conditions the adsorption of the gases takes place only on the nickel surface, and neither hydrogen nor carbon monoxide are adsorbed on the chromium oxide used as carrier.

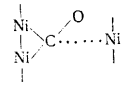
In a number of papers it has been suggested that in hydrogenation on nickel contact catalysts, hydrogen may penetrate into the interior of the catalyst, with a significant influence on the catalytic activity [79–84]. The adsorption of hydrogen and carbon monoxide was therefore studied [28,63,65] both on a clean nickel catalyst surface (treated specimens) and on specimens containing dissolved hydrogen (untreated specimens).

It was established that on the treated catalyst specimen, hydrogen is adsorbed at 75° by a dissociative mechanism, and the surface acquires a positive charge [65]. When dissolved hydrogen is present in the nickel, however, the adsorption is accompanied by the transfer of electrons from the catalyst, and the adsorbed hydrogen acquires a negative charge [65]. This result shows that dissolved hydrogen has a significant influence on the adsorption properties of nickel.

Carbon monoxide is adsorbed on nickel in molecular form. Study of the infrared spectra of the adsorbed molecules [85–87] showed the existence of at least five forms of bonding between carbon monoxide and the nickel surface, with different structures and bond strengths:



The production of a given form depends on the crystal structure of the nickel [87]. With crystalline specimens, the production of bridged (I) and linear (II) forms is observed primarily, but at higher degress of covering, linear groups are produced on nickel atoms which already have chemisorbed carbon monoxide by a bridging type of bond (III). On disordered crystallites, carbon monoxide is much less strongly chemisorbed, and only in linear structures (IV) and (V). Recently, another form of bridging bond has been found [88]:



The formation of this bond is facilitated by comparatively low pressures of carbon monoxide, when the neighbouring Ni atoms are not bonded to CO molecules by other types of bond.

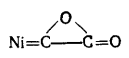
Some authors doubt the existence of bridging bonds. Thus calculation by the MO method [89] showed that all available data on the infrared spectra of chemisorbed CO can be explained by assuming only a linear form of bonding for carbon monoxide adsorbed on various surface centres. The strengths of the bonding and the frequencies of the CO stretching vibration also differ. This view is held by other authors [90], who however do not exclude completely the possibility that a small proportion of the carbon monoxide molecules are adsorbed in bridged form. These views, however, are not fully justified.

The production of the various forms of adsorbed carbon monoxide apparently depends on the conditions of the experiment. For the adsorption of carbon monoxide on a treated specimen of nickel–chromium catalyst at 75°, it was established that at low pressures the chemisorption is accompanied by the production of a bridged form of bond [type (I)], and that with increase in pressure the nature of the bonding changes, and a surface layer of the single-centre type is formed [28], in agreement with the results of other studies [85,89,91]. The layer of chemisorbed gas is positively charged, and when the bridged structure changes to the linear structure there is no change in the electronic properties of the catalyst surface [65].

Each type of adsorption should evidently be characterised by bonds of different strength between the adsorbate and the contact surface, so that the form of bonding should determine, in particular, the thermal stability of the adsorbed carbon monoxide and its stability towards hydrogenation. For the bridged structure, decomposition of carbon monoxide is not observed up to 300°, and its hydrogenation begins only above 140°. Carbon monoxide joined to nickel by a linear bond is hydrogenated at a temperature slightly greater than 80°. Thus the linear form of bonding for the adsorbed carbon monoxide is weaker than the bridging form, and hence more reactive. This form is apparently of types (IV) or (V).

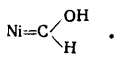
The presence of adsorbed and dissolved hydrogen in the contact catalyst influences the properties of the nickel towards the adsorption of carbon monoxide. The dissolved hydrogen alters the electronic properties of the metal. Thus changes have been observed[92] in the infrared spectra of carbon monoxide adsorbed on nickel, corresponding to the change from linear structures to bridging structures, depending on the thoroughness with which hydrogen was removed from the metal after reduction. In agreement with these observations, according to published data[28], in the adsorption of carbon monoxide on an untreated nickel–chromium catalyst, sorbed hydrogen is displaced from the contact catalyst into the gaseous phase, and a linear form of bond is produced between the adsorbed carbon monoxide and the contact surface. As with the adsorption of CO on a clean nickel surface, the layer of carbon monoxide is positively charged[65].

The influence of dissolved hydrogen on the adsorption properties of the contact catalyst is due to the two-layer adsorption of carbon monoxide[28]

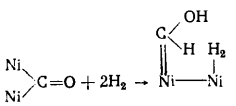


As a result of the formation of the chemisorption bond between the carbon monoxide molecule and the contact surface, the bonds in the CO molecule are weakened to such an extent that two CO molecules interact with the rupture of one carbon–oxygen bond and the formation of a carbon–carbon bond.

The determination of the forms of the adsorbed molecules makes it possible to examine the mechanism of the adsorption of carbon monoxide and hydrogen from their mixtures. Carbon monoxide is adsorbed in linear form. At the same time the adsorption of hydrogen increases. The absorption of hydrogen in the presence of carbon monoxide takes place slowly, evidently due to chemical reaction with the formation of complexes of a type corresponding to the enol form of formaldehyde:

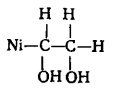


The formation of complexes of this kind also takes place if hydrogen is adsorbed on a contact catalyst on which carbon monoxide has previously been adsorbed by the two-centre mechanism. The bridged type of bond is converted into the linear type with the formation of a complex, and the molecular hydrogen is adsorbed on the liberated centres of the nickel



The mean rate of formation of the complex at 75° corresponds to the transformation of 5.6×10^{-7} cm³ CO cm^{-2} Ni h^{-1}; the concentration of adsorption complexes formed amounts to ~ 10^{15} per 1 cm² nickel surface.

The reaction between hydrogen and carbon monoxide adsorbed in two layers leads to the formation of complexes of the type



at a mean rate corresponding to the transformation of 12.8×10^{-7} cm³ CO cm^{-2} Ni h^{-1} and the concentration of the complexes amounts to ~ 3.8×10^{16} per 1 cm² nickel. The possibility of formation of carbon–carbon bonds during the adsorption of carbon monoxide and hydrogen from their mixtures was proposed[75] on the basis of a study of the infrared spectra.

The concentrations of the complexes formed are sufficient for their detection by infrared spectroscopy. This in turn would have been significant evidence for the existence of surface compounds of this type. The failure of Blyholder and Neff[52] to detect adsorption complexes on a nickel contact catalyst at 180° and above by this method can apparently be attributed to the excessively high temperature of the experiment, at which the complexes formed are readily transformed into the final products. The suggestion, made by the authors cited[52], that the reacting substances are much less firmly bound to the nickel than to the iron catalyst, on which it was possible to detect surface compounds at 180°, [75] can be disputed: at this temperature, the reaction on iron does not take place very intensively, whereas in the presence of the more active nickel the reaction rate is quite high, and this leads to a sharp decrease in the concentration of chemisorption complexes.

Unlike Koelbel and coworkers[72], Vlasenko and coworkers[28] detected stoichiometric chemisorption complexes, indicating that all the adsorbed carbon monoxide has the same reactivity.

Thus surface compounds of at least two types—a type corresponding to the enol form of formadehyde and a type containing two carbon atoms—may be formed on the surface of the nickel contact catalyst, depending on the conditions of adsorption. The existence of complexes with two carbon atoms indicates that under certain conditions of the synthesis of hydrocarbons, at least on nickel contact catalysts, carbon–carbon bonds may be produced even in the stage of carbon monoxide adsorption. The possibility of existence of primary complexes not only with one carbon atom but also with a larger number of carbon atoms was pointed out by Eidus[10]. The possible role of complexes of this type in the synthesis of hydrocarbons requires further detailed study, but they are not formed in the hydrogenation of carbon monoxide in a large excess of hydrogen, since only methane and water are detected in the reaction products.

The information obtained in the study of the adsorption of mixtures of carbon monoxide and hydrogen on a nickel–chromium catalyst under the conditions preceding the start of catalysis[28] shows that hydrogen is adsorbed on nickel chiefly in the form of molecules. The almost complete absence of atomic hydrogen in the synthesis of hydrocarbons was demonstrated by Craxford and Rideal[25]; the absence of dissociative adsorption of hydrogen was also noted for nickel with ethylene present in the gas[93]. Thus hydrogen is adsorbed in the form of molecules both under the conditions of formation of methane and also apparently in the synthesis of hydrocarbons on nickel, cobalt, and possibly iron catalysts. The fact that dissociation of the hydrogen molecules does not take place during adsorption on these metals is due to the influence of the adsorbed carbon monoxide. The electronic state of the catalyst surface, and hence its adsorption properties, change in such a way that there is a decrease in the energy of the bonding between the hydrogen molecules and the surface, so that decomposition of the molecules to form atoms does not take place. The adsorption of hydrogen on the nickel–chromium catalyst is accompanied by the formation of a negatively charged layer of chemisorbed gas [H_2^-] on the surface[65], due to the presence of dissolved hydrogen in the contact catalyst. These regular features of the adsorption of hydrogen are apparently preserved under the conditions

of the synthesis of higher hydrocarbons, since the catalysts for the synthesis always contain dissolved hydrogen.

In the synthesis of methane, and also apparently in the synthesis of higher hydrocarbons, carbon monoxide is adsorbed in the form of molecules with the production of a linear form of bond between the chemisorbed species and the surface atoms of the nickel; the chemisorbed layer of $[CO^+]$ is positively charged[65].

The oppositely charged adsorbed molecules of hydrogen and carbon monoxide interact in the adsorption layer. The primary products of this interaction may be adsorption complexes of the type corresponding to the enol form of formaldehyde; the existence of these complexes on metallic contact catalysts of the iron group can be taken as established. The formation of these complexes $[HCOH^+]$ takes place at a high rate[28] and is accompanied by a decrease in the work function[65]. The rate of their formation limits the rate of the catalytic conversion of carbon monoxide into methane. This is confirmed not only by the results of the measurement of the contact potential difference[65] but also, in particular, by the results of a kinetic study of the reaction in the presence of a nickel–chromium contact catalyst[57], since the rate of formation of the complexes at 75°[28] almost coincides with the hypothetical rate of the catalytic process at this temperature. In the subsequent stage, the oxygen-containing complexes apparently react in the adsorption layer with hydrogen molecules, to produce methylene radicals and water. In subsequent changes, the methylene radicals may undergo either polymerisation with the formation of hydrocarbon chains or hydrogenation to form methane.

These regular features of the mechanism of the conversion of carbon monoxide into methane on a nickel–chromium catalyst are apparently general in character and are observed in the synthesis of hydrocarbons on nickel, cobalt, and possibly iron catalysts.

Thus the following is the most probable scheme for the mechanism of the reduction of carbon monoxide to methane on these catalysts[28,65]:

1. $[\ ] + e + H_2 \rightarrow [H_2]^-$
2. $[\ ] + CO \rightarrow [CO]^+ + e$
3. $[CO]^+ + [H_2]^- \rightarrow [HCOH]^+ + e$ (slow stage)
4. $[HCOH]^+ + [H_2]^- \rightarrow [CH_2] + H_2O + [\ ]$
5. $[CH_2] + [H_2]^- \rightarrow CH_4 + e + [\ ]$†

For the synthesis of higher hydrocarbons, the fifth stage of this scheme should reflect not the reaction of methylene radicals with hydrogen, but their polymerisation.

III. MECHANISM OF THE FORMATION OF METHANE FROM CARBON DIOXIDE AND HYDROGEN

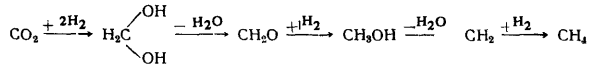
The mechanism of the hydrogenation of carbon dioxide, unlike that of the reduction of carbon monoxide, has been very little studied, although the study of the behaviour of carbon dioxide in its reaction with hydrogen is necessary for carrying out the catalytic purification of technological gases—a problem whose importance has been increasing recently. Moreover, the study of the mechanism of the synthesis of methane from carbon dioxide, in view of the high selectivity of the process, is of undoubted theoretical interest and makes it possible to develop more penetrating ideas regarding the nature of the hydrogenation of carbon monoxide.

Two proposed schemes for the mechanism of the synthesis of methane from carbon dioxide and hydrogen have been discussed in the literature. One of these was proposed by Bahr[94], who considers, on the basis of experimental data, that in the presence of Fe–Cu, Cu–Cr_2O_3, and Co–Cu–ZnO contact catalysts the reduction of carbon dioxide to methane is accompanied by the intermediate formation of carbon monoxide. This view is supported by research workers who have studied the hydrogenation of carbon dioxide on ruthenium contact catalysts[95] and in the presence of catalysts based on metals of the iron group and on various binary systems[96–100].

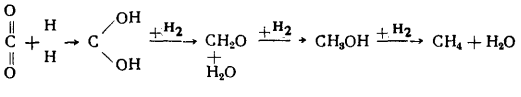
A number of facts, however, cast doubt on the correctness of Bahr's ideas. If the hydrogenation of carbon dioxide were accompanied by the intermediate formation of carbon monoxide, it might be possible under certain conditions to obtain higher hydrocarbons from CO_2, yet the hydrogenation of carbon dioxide on metallic contact catalysts of the iron group, unlike the reactions of carbon monoxide, are characterised by a high selectivity. Thus it has been shown[98,101–105] that in the presence of nickel and cobalt catalysts carbon dioxide is converted only into methane, and the formation of a small quantity of higher hydrocarbons was detected only in some instances, when mixed iron–cobalt[97] and copper–cobalt[98] contact catalysts were used. This must be due to a difference in the mechanisms of the hydrogenation of these oxides. Carbon dioxide is apparently hydrogenated to methane without the intermediate formation of carbon monoxide. Evidence in support of this is also provided by the behaviour of carbon monoxide and dioxide when these are present together in the gas. In a study of the hydrogenation of the oxides of carbon on nickel contact catalysts, Fischer and Pichler[102] showed that carbon dioxide is not hydrogenated in the presence of carbon monoxide and does not influence the transformation of the latter. These results were subsequently confirmed[56,106].

The independent mechanism of the conversion of carbon dioxide into methane is confirmed by studies of the process in the presence of a nickel–chromium catalyst. As already noted, in the presence of this catalyst carbon monoxide begins to undergo hydrogenation only above 80°.[78] Thus if the formation of methane from carbon dioxide were accompanied by the intermediate formation of carbon monoxide, it would not be observed below the temperature of the start of the hydrogenation of CO. It has been established[107], however, that carbon dioxide is hydrogenated at an appreciable rate even at 70° and below.

The idea that carbon dioxide reacts by an independent mechanism (without the intermediate formation of carbon monoxide) was reflected in a hypothesis put forward by Medsforth[108], who proposed the following scheme for the formation of methane from carbon dioxide:



Later, Medsforth's scheme was developed in detail by Pichler[109], who suggested that the hydrogenation of carbon dioxide takes place with atomic hydrogen present on the surface of the contact catalyst. According to Pichler, the reaction of carbon dioxide is described as follows:



† The symbol [ ] denotes a vacant active centre on the catalyst surface. The symbols in square brackets represent adsorbed species.

Bahr's theory[94], and the theories of Medsforth[108] and Pichler[109], start from the assumption that carbon dioxide is adsorbed on the surface of the contact catalyst in the initial stage of the process. This opinion is also held by other workers[56,103,110,111], who studied the kinetics of the hydrogenation of carbon dioxide to methane by static and flow methods. Thus it has been shown[56] that at various partial pressures of the reagents and with change in the total pressure from 0.1 atom to 1 atm in the temperature range 180–300° in the presence of a catalyst consisting of nickel on kieselguhr, the dependence of the reaction rate on the total pressure P is described by an equation of the Langmuir type

$$W = \frac{aBP}{1+BP},$$

where B and a are constants. In the opinion of the authors cited, hydrogen and carbon monoxide are comparatively weakly adsorbed on the surface of the contact catalyst. The heat of activation was 13.1 kcal mole^{-1}.

Binder and White[103], who studied the kinetics of the reaction in a flow system at atmospheric pressure in the temperature range 260–400° on a nickel–kieselguhr catalyst at stoichiometric H_2/CO_2 ratio and also in an excess of carbon dioxide, concluded that the rate-limiting stage of the process is the reaction between one adsorbed molecule of CO_2 and two (or four) dissociated hydrogen molecules. Although the kinetic equations effectively describe the experimental facts, this mechanism, in the opinion of the authors cited themselves, may be fictitious.

In a study of the kinetics of the hydrogenation of carbon dioxide above atmospheric pressure (up to 30 atm) in the presence of a nickel contact catalyst on kieselguhr[110], it was also suggested that four adsorbed hydrogen molecules react with one CO_2 molecule on the contact surface. The experimental results indicate that the activation energy has values in the range 13.1–13.9 kcal mole^{-1}. The authors cited[110] consider that the adsorption of CO_2 is weaker than the adsorption of hydrogen by a factor of 10–20.

In contrast to these studies, in which mixtures with a high concentration of carbon dioxide were used, other studies[111] were carried out at a very low concentration of CO_2 in the original gas (0.1%). The studies were carried out in a flow system at atmospheric pressure in the comparatively narrow temperature range 160–180°. A nickel–chromium contact catalyst obtained by reducing nickel chromate was used. The reaction rate is described by the empirical equation

$$W = k \cdot C_{CO_2}^{0.5},$$

indicating that carbon dioxide is adsorbed on the contact surface. The heat of activation was found to be 20.5 kcal mole^{-1}, which is much greater than the heat of activation given in the works cited earlier[56,110]. The discrepancy is due to the fact that one of the studies[111] was carried out on a contact catalyst which contained nickel oxides in addition to reduced nickel[112].

The theory of hydrogenation of carbon dioxide in an adsorption layer, developed on the basis of these studies, is disputed, however, and is not confirmed by work carried out by other experimental methods.

Although a number of workers[113–120] have shown that carbon dioxide is firmly bound to a clean nickel surface, the behaviour of CO_2 in the presence of hydrogen was not studied until recently. The only work in this direction was an attempt[121] to interpret the kinetic results of Binder and White[103] on the basis of a study of the separate adsorption of carbon dioxide and hydrogen at the temperatures of the synthesis. The mutual influence of the components during the adsorption of a mixture of gases, however, as shown for the example of carbon monoxide and hydrogen, may be considerable and may play a significant role in the reaction mechanism.

Despite the fact that in the absence of hydrogen the bond formed by carbon dioxide with the nickel surface is fairly strong, the CO_2 molecule is weakly bound to the surface under the conditions of the contact process. This follows from the results of kinetic studies[56,103] which indicated that carbon dioxide is bound to the contact surface. Thon and Taylor[122], however, in an interpretation of the mechanism of the hydrogenation of carbon dioxide, considered it unnecessary to assume that the CO_2 is adsorbed on the contact surface. On the basis of the idea that the active centre is a hydrogen atom chemisorbed on the catalyst, they suggested that this atom reacts with a molecule of carbon dioxide from the gaseous phase. Thus the same experimental results[56] have led research workers to different conclusions regarding the hydrogenation of carbon dioxide. It is obvious that kinetic data alone cannot confirm a particular reaction mechanism directly. For this, other independent methods are required.

A flow-circulation gradient-free method has been used[53] to study the kinetics of the synthesis of methane in the presence of a nickel–chromium contact catalyst by a procedure which makes it possible to follow directly the change in the weight of the catalyst during the reaction[123]. The kinetic results[53,58] are described by equations of first order with respect to carbon dioxide and of zero order with respect to hydrogen:

$$W = k \cdot p_{CO_2}^{1} \cdot p_{H_2}^{0}.$$

A change in the weight of the contact catalyst was not observed during hydrogenation, even at low temperatures (as far as 125°). It may therefore be assumed that under the conditions of the contact process there is no significant adsorption of carbon dioxide and the products of its transformation. This is confirmed by results[121] which showed that neither methane nor water are adsorbed on the surface of a nickel contact catalyst at the temperature of the synthesis. The results of the kinetic study were confirmed by a study[124] of the change in the contact potential difference during the hydrogenation of CO_2 on a nickel–chromium catalyst. When a mixture of hydrogen and carbon dioxide was introduced on to the untreated contact catalyst, the work function remained unchanged relative to that in an atmosphere of hydrogen. Moreover, sharp changes in the work function with change in temperature were not observed. This indicates that adsorption of carbon dioxide and the formation of complexes influencing the electronic structure of the catalyst does not take place on the surface of a contact catalyst containing dissolved hydrogen. The fact that carbon dioxide is not adsorbed on the surface of a contact catalyst containing adsorbed and dissolved hydrogen is also confirmed by direct data on the adsorption of CO_2 at 20°,[125] when the reaction rate is small[107].

Thus recent experimental results refute the suggestion that the start of the formation of methane from carbon dioxide on nickel catalysts is preceded by the adsorption of both components of the reaction, and indicate that hydrogen adsorbed on the contact surface reacts with molecules of carbon dioxide in the gaseous phase.

Since neither carbon dioxide nor the products of its transformation under the conditions of the synthesis of methane are adsorbed on the catalyst surface, the regular features of the adsorption of hydrogen under these conditions should apparently be the same as those under the

conditions of its separate adsorption on an untreated catalyst specimen. Thus under the conditions of the conversion of carbon dioxide into methane, the adsorbed hydrogen is present in the atomic state, and this surface layer has a negative charge[65].

The results of these studies show that the first stage in the reaction is not the reaction between molecules of carbon dioxide and hydrogen adsorbed on the contact surface. This introduces a significant correction into Pichler's scheme, given above. The experimental results also make it possible to introduce various other changes and refinements into this scheme.

The facts that the weight of the contact catalyst remains unchanged[53,123] and that the work function remains constant under different temperature conditions of the contact process[124] indicate that the transformation of carbon dioxide takes place either in the bulk or on the catalyst surface with a very low concentration of intermediate compounds, that is with a very low lifetime for these compounds in the adsorbed state. If, however, the complexes of the formaldehyde type (CH_2O) given in the scheme were formed on the catalyst surface, the formation of methane from CO_2 on the nickel–chromium contact catalyst could not be observed below 80°,[78] so that at these temperatures the complexes do not react, as was shown in an examination of the mechanism of the hydrogenation of carbon monoxide. Moreover, carbon dioxide is converted into methane at a lower temperature.

Although the formation of complexes of the type corresponding to the enol form of formaldehyde in the gas volume is quite possible, the hydrogenation of these complexes to methanol appears unlikely. In fact, if methanol were formed as an intermediate product in the hydrogenation of carbon dioxide, its conversion into methane should not have taken place at a lower rate than the formation of methane. The synthesis of hydrocarbons from methanol, however, takes place as a result of the reaction of CO and H_2 produced by the decomposition of the alcohol, and not by the direct transformation of methanol[36]. It therefore appears more probable that the enol complexes are converted into methylene radicals CH_2, as in the hydrogenation of carbon monoxide.

From the foregoing, the most probable scheme for the formation of methane from carbon dioxide and hydrogen appears to be one in which the formation of complexes of a type corresponding to the enol form of formaldehyde takes place initially, and in which the subsequent transformations are analogous to the stages in the hydrogenation of carbon monoxide, but with the significant difference that in the reduction of CO_2 these changes take place not on the catalyst surface, but in the volume of the gas. This probably explains the high selectivity of the process with respect to the formation of methane, since in this instance neither condensation of the enol complexes nor polymerisation of methylene groups can apparently take place.

For an understanding of the mechanism of a catalytic process, it is of considerable importance to determine the composition and structure of the intermediate compound, whose rate of formation determines the observed reaction rate. In accordance with the scheme being considered, it is assumed that the limiting stage of the process involving the conversion of carbon dioxide into methane is the stage involving the formation of the dioxymethylene radical, which can be regarded as an isomer of formic acid.

Golodets and Roiter[126] showed that evidence in support of the proposed composition and structure of an active complex is provided by agreement between the thermodynamic characteristics of the activated complex, such as the heat and entropy of activation calculated from kinetic data, and the values of these quantities calculated approximately for the assumed activated complex.

Analysis of the experimental entropy of activation of the hydrogenation of carbon dioxide on a nickel–chromium catalyst[58] showed that the first stage of the reaction apparently does involve the formation of dioxymethylene radicals, and that the rate of this stage determines the overall rate of the process.

On the basis of the foregoing, the mechanism of the hydrogenation of carbon dioxide is most probably represented by the following scheme[58,124]:

1. $2[\ ] + 2e + H_2 \rightarrow 2[H]^-$
2. $2[H]^- + CO_2 \rightarrow [HCOOH] \rightarrow 2[\ ] + C(OH)_2 + 2e$ (slow stage)
3. $C(OH)_2 + H_2 \rightarrow H{-}C{-}OH + H_2O$
4. $H{-}C{-}OH + H_2 \rightarrow CH_2 + H_2O$
5. $CH_2 + H_2 \rightarrow CH_4$‡

According to this scheme, the process is initiated by the activation of only the hydrogen on the catalyst surface, after which the reaction takes place in the gas volume.

The proposed scheme agrees with the experimental results of the study of the process on a nickel–chromium catalyst, within the limits of the sensitivity of the methods of study. It may be of general significance for the synthesis of methane in the presence of catalysts based on nickel. Evidence in support of this is indicated by the fact that the same value is obtained for the heat of activation (13.1–13.9 kcal mole^{-1}) in studies of the kinetics of the process at extremely low (as far as 0.4%) concentrations of carbon dioxide[53] and at concentrations close to the stoichiometric ratio at atmospheric pressure[56] and at pressures up to 30 atm[110]. From this it follows that over a wide range of partial pressures, carbon dioxide does not react with the contact surface and the same mechanism is observed for the synthesis of methane.

IV. HYDROGENATION OF CARBON MONOXIDE AND DIOXIDE PRESENT TOGETHER IN THE GAS PHASE

A knowledge of the mechanism of contact reactions makes it possible not only to explain the observed kinetic features but also to predict the possibility of carrying out these reactions in other more complex examples. In this connection it is appropriate to examine data on the synthesis of methane from carbon monoxide and dioxide on the basis of theories of the mechanisms of the transformation of these oxides.

The transformation of carbon monoxide and dioxide on nickel catalysts has been studied[56,102,106]. It was established that CO_2 is not hydrogenated in the presence of carbon monoxide and does not influence the transformation of CO. Nicolai and coworkers[56], in particular, considered that the oxides of carbon are hydrogenated according to their adsorbability. Since in the presence of hydrogen, carbon monoxide is adsorbed more strongly than CO_2, the authors cited assumed that in the presence of adsorbed CO, adsorption of carbon dioxide is impossible, so that the surface reaction of CO_2 with hydrogen is impossible. This view is incorrect, however, since under the conditions of the hydrogenation of CO_2, carbon dioxide is not adsorbed, even in the absence of carbon monoxide.

‡ See footnote to page No. 733.

The results obtained by Nicolai and coworkers[56] were also discussed by Thon and Taylor[122], who suggested that the active centre is a hydrogen atom adsorbed on the catalyst surface. When carbon monoxide and dioxide are present in the gas under the conditions of the hydrogenation, the CO and CO_2 compete for these active centres. Since the carbon monoxide molecules react more rapidly with the active centres under these conditions, the CO is hydrogenated, and not the carbon dioxide. This suggestion cannot be correct, however, since the mechanism of the transformation of carbon monoxide is different from that of the hydrogenation of carbon dioxide.

A difference in the behaviour of carbon monoxide and dioxide was observed in a study of the hydrogenation of their mixtures on a nickel–chromium catalyst in a large excess of hydrogen at various concentrations of the oxides of carbon in the gas[127]. Under these conditions, as in the process at high concentrations of the oxides of carbon[56,102,106], the rate of hydrogenation of carbon monoxide is independent of the presence of carbon dioxide in the gas. Observation of the change in the weight of the catalyst in addition to kinetic studies showed that the increase in weight corresponds to the values observed for the hydrogenation of carbon monoxide in the absence of CO_2. From this it follows that when the oxides of carbon are present together in the mixture with hydrogen, only the processes involving the transformation of the carbon monoxide take place on the contact surface. Hydrogenation of carbon dioxide does not take place at all over a wide range of CO concentration. These results indicate that carbon monoxide is a powerful poison for the hydrogenation of CO_2 on nickel catalysts.

These ideas regarding the mechanisms of the formation of methane from carbon monoxide and dioxide enable the kinetic features of the hydrogenation of mixtures of these oxides to be explained in terms of the influence of adsorbed carbon monoxide on the position of the equilibrium for the dissociation of molecular hydrogen adsorbed on the catalyst surface:

$$[H_2] \rightleftarrows 2[H] .$$

The presence of carbon dioxide in hydrogen has no influence on the electronic state of the catalyst surface, and hence on its adsorption properties. In this instance the equilibrium is displaced to the right, that is the hydrogen is adsorbed chiefly in atomic form, which is active with respect to the carbon dioxide present in the gaseous phase.

In the presence of hydrogen, carbon dioxide is not adsorbed on nickel. Carbon monoxide is readily chemisorbed on the contact surface and alters its properties: when carbon monoxide is present, the equilibrium for the dissociation of H_2 is displaced to the left, and hydrogen is adsorbed on the nickel surface chiefly in the form of molecules, that is in a form which is active with respect to adsorbed CO molecules but is not capable of reacting with CO_2 molecules from the gaseous phase.

Thus the poisoning of the catalyst, by carbon monoxide, with respect to the hydrogenation of CO_2 is not due to simple blocking of the active centres by carbon monoxide. Similarly, it cannot be regarded as a result of competition between the molecules of carbon monoxide and dioxide for the active regions of the surface. This phenomenon results from differences in the mechanisms of the hydrogenation of the oxides of carbon, and the poisoning influence of adsorbed carbon monoxide is not a direct influence, but results from a change in the electronic state of the catalyst, leading to the production of forms of adsorbed hydrogen which are unable to reduce CO_2.

It is only at a very low concentration of carbon monoxide, when its hydrogenation takes place under external transition conditions, that the concentration of atomic hydrogen on the nickel surface becomes sufficient for the rate of transformation of carbon dioxide to become appreciable, and this is in fact observed[127]. The equilibrium for the dissociation of molecular hydrogen is apparently displaced considerably to the right in those instances when the formation of methane from carbon monoxide takes place in the range of external diffusion and the concentration of CO on the contact surface is close to zero, so that the carbon monoxide cannot alter the properties of the surface significantly.

Thus the possibility of carrying out the reduction of carbon dioxide in the presence of carbon monoxide is determined by the macro-kinetic features of the transformation of the latter.

This conclusion has a number of consequences, which may be of practical importance for the fine catalytic purification of gases from oxides of carbon by transformation into methane.

The purification of gases from oxides of carbon obviously must be carried out in the range of external diffusion with respect to CO. It is only under these conditions that the degree of transformation of carbon dioxide achieved is the same as that in the absence of carbon monoxide and that most complete removal of traces of both substances from the gas can be effected. This agrees with the results of a study[128] of the purification of a nitrogen–hydrogen mixture from oxides of carbon on a nickel–chromium catalyst.

Carbon monoxide is a powerful poison with respect to the hydrogenation of many substances, particularly unsaturated compounds, on nickel. In a number of contact processes, for example the hydrogenation of ethylene, benzene, and phenol, carbon dioxide is not a catalyst poison. In these instances the removal of carbon dioxide from the hydrogen used for the hydrogenation is not necessary, whereas purification from carbon monoxide is required. This selective removal of carbon monoxide can be carried out under the conditions of hydrogenation in the external transition range, when almost no hydrogenation of carbon dioxide takes place. The possibility of carrying out the purification in this way has been demonstrated[129]. It should, however, be noted that these conditions can be used only when very thorough purification of the gas from carbon monoxide is not required.

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Examination of the mechanism of the synthesis of methane from carbon monoxide and hydrogen indicates that the most probable reaction scheme is that proposed by Eidus. The accumulated data obtained by various methods make it possible to establish the reactive forms of the adsorbed molecules and the signs of their charges, and also to demonstrate fairly reliably the existence of chemisorbed complexes of a type corresponding to the enol form of formaldehyde. Strong evidence in support of their existence is provided by information obtained from the infrared spectra of the surface compounds. Success in these studies, however, requires the accumulation of these complexes in sufficient concentration. This may be achieved by carrying out the reaction of the adsorbed molecules of carbon monoxide and hydrogen under the conditions immediately preceding the catalytic action and, in view of the low rate of formation of the complexes, when the process has proceeded for a sufficient length of time.

The mechanism of the synthesis of methane from carbon dioxide and hydrogen differs significantly from the mechanism of the reduction of carbon monoxide.

The mechanism of the poisoning action of carbon monoxide, demonstrated for the example of CO_2, may be of general importance for finding the most rational solution to the problem of carrying out the important industrial processes involved in the hydrogenation of organic substances (benzene, phenol, ethylene, etc.), where it is known that the presence of carbon monoxide in the synthesis gas poisons the catalyst. In these instances, hydrogen is subjected to thorough purification to remove carbon monoxide. If the concentration of carbon monoxide in the original gas is such that under the conditions of the hydrogenation of the organic substances the reduction of CO takes place under external diffusion conditions, however, preliminary purification of the hydrogen from CO apparently is not required.

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