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Catalytic chemistry and technology of C_1 compounds

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ABSTRACT. New reactions of one-carbon compounds in the presence of heterogeneous and homogeneous catalysts as well as new approaches to the selection of catalysts and the carrying out of traditional catalytic processes involving C_1 compounds are examined. The bibliography includes 214 references.

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I. Introduction

Compounds with one carbon atom have found extensive applications in modern industrial chemistry. The catalytic conversion of methane by water vapour is the principal method for the manufacture of hydrogen and the synthesis gas. Hydrocyanic acid and chloromethanes are obtained from methane. Acetylene is produced by the high-temperature pyrolysis of methane. The synthesis gas obtained by the conversion of methane is the raw material for the manufacture of methanol, which can in its turn be converted into olefins, liquid hydrocarbons, formaldehyde, and other products.

Procedures for the utilisation of C_1 compounds in the preparation of certain petrochemical products (monomers, intermediates, and motor fuels) have been developed vigorously in recent years.

Studies in this field are prosecuted on a broad front: new types of reactions of C_1 compounds are being investigated, new catalysts for processes already known are being developed, and new technological processes are being devised.

The present review deals with a series of new aspects of the chemistry of C_1 compounds of current interest (reactions in the presence of metal complex catalysts, including carbon dioxide fixation processes under mild conditions, direct catalytic synthesis of ethylene from methane, and the conversion of methane into liquid hydrocarbons) and of the technology of certain traditional processes (a new approach to the preparation of catalysts for the conversion of carbon dioxide by water vapour in the synthesis of methanol, the conversion of methane in thermochemical solar energy converters, the use of the principle governing the non-stationary technology in the synthesis of methanol and the oxidation of methanol to formaldehyde under adiabatic conditions). All these aspects are being vigorously developed at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences.

II. Direct catalytic syntheses of hydrocarbons from methane

Reactions involving the direct conversion of methane into valuable chemical products occupy an important place in the problem of catalytic syntheses on the basis of one-carbon compounds. The direct synthesis of ethylene—the key compound in fundamental organic synthesis—from methane is of greatest interest. The development of an effective method of preparation of ethylene from methane would permit a change-over of many petrochemical manufacturing processes to a non-petroleum raw material without altering the structure of these processes.

The conversion of methane into liquid hydrocarbons is also an important and currently interesting problem whose solution will make it possible, apart from all its other aspects, to facilitate the transport of hydrocarbon raw materials from gas deposits to sites where it is utilised.

1. Oxidative dehydrodimerisation of methane

The possibility of converting methane into ethylene even at very high temperatures is limited by the thermodynamic equilibrium.[1] High conversions can be attained only when the reaction is carried out with the participation of oxidants.

The necessity for the use of oxidants greatly hinders the selection of catalysts for this reaction, because, while effectively activating methane, they should at the same time activate oxygen only slightly in order to prevent the extensive oxidation of methane and its conversion products. This factor precludes the use in the given reaction of effective catalysts for the activation of hydrocarbons such as, for example, platinum metals.

The above difficulty can be obviated by carrying out the process in two stages: in the first stage, pure methane is dimerised using the oxygen in the catalyst (oxygen-free dimerisation), while in the second the catalyst is reoxidised by an oxygen-containing gas. In this version, a fairly high selectivity is attained but it is technologically complex and requires the use of catalysts with a high oxygen capacity.

Both a two-stage periodic and a one-stage continuous method for the oxidative dehydrodimerisation of methane are being developed at the present time. The periodic version of the process (with reoxidation of the catalyst) is being developed predominantly by

American investigators, while the continuous method is being studied vigorously in the Federal Republic of Germany, Japan, and the Soviet Union as well as the USA.

Fairly numerous publications devoted to the investigation of the mechanism of the catalytic oxidative dehydrodimerisation have been published during the last two years: the determination of the pathways leading to the formation of the reaction products, the nature of the active centres of the catalyst, and the role of homogeneous stages in the overall process.

(a) Catalysts

The first studies on the dehydrodimerisation of methane to ethylene using solid catalysts were published as late as the 1980's.

The Exxon Company took out a patent for the oxidative condensation of methane with the preferential formation of ethylene.[2] Solid oxides with deposited noble metals were used as the reactant-catalysts. The reaction was carried out with pure methane at 700 °C, the conversion of the methane reaching 44.8% with formation of 8% of ethylene, 3.2% of ethane, and 14.4% of benzene (the residue was coke). The catalyst became rapidly saturated with coke and required prolonged regeneration with oxygen-containing gas.

The interaction of methane with a large number of metal oxides deposited on silica gel has been investigated at 800 °C and a pressure of 15 mmHg.[3,4] At low degrees of conversion, the main reaction products were ethane and ethylene. Thorium dioxide proved to be the most effective catalyst.

Systematic studies on the oxidative dehydrodimerisation of methane via a two-stage mechanism on a large number of metal oxides deposited on Al_2O_3 [5] made it possible to divide these oxides into three groups: inactive, weakly active, and active (Fig.1). The highest yield of the oxidative dehydrodimerisation products (5% for an overall selectivity of 45% with respect to C_2 hydrocarbons) was obtained in the presence of manganese oxide. Here and henceforth the yield of the oxidative dehydrodimerisation products is defined as the fraction of carbon atoms in CH_4 which have been converted into C_2 hydrocarbons (C_2H_4 and C_2H_6) on contact with the catalyst and the selectivity is the fraction of carbon atoms which have been converted into C_2 hydrocarbons relative to the total number of carbon atoms of the methane which has reacted.

A still higher yield is attained in two-stage processes patented by investigators at the Atlantic Richfield Company.[6-22] Deposited oxides of manganese, Group IIIA, IVA, and VA elements, and the lanthanides with added alkali and alkaline earth metals and phosphate ions served as the catalysts in the above studies. The carriers were aluminium, silicon, magnesium, and titanium oxides. Best results were obtained on the $NaMnO_4/MgO-SiO_2$ [18] and Mn_3O_4/SiO_2 [14] systems. The yield of C_2 hydrocarbons at 800 °C was 13.4 and 15.2% respectively in the presence of these systems. The catalysts operate in very short cycles (1–2 min), after which their regeneration is required.

Later analogous catalytic systems were tested under single-stage continuous conditions using a reaction mixture containing oxygen together with methane.[23,24] The maximum yield of hydrocarbons on the Mn_2SiO_4 system at 800 °C was 12.2%.[24]

A higher yield of C_2 hydrocarbons was achieved using nitrous oxide as the oxidant.[25] In the presence of a catalyst containing 12.5% $NaMnO_4$ on MgO at 800 °C and for a reaction mixture containing 50% each of CH_4 and N_2O, yields of 11.7% of ethylene and 5.4% of ethane were attained.

The continuous oxidative conversion of ethane in a mixture with oxygen into C_2 hydrocarbons was first achieved on lead, bismuth, tin, antimony and manganese oxides deposited on alumina and other carriers.[26-28] Best results were obtained on deposited lead oxide catalysts. While the selectivity of the conversion of methane into C_2 hydrocarbons was 50–60%, the yield of the latter was 5%.

Much higher yields were obtained subsequently by the same group of investigators on basic catalysts. In the presence of the 6% NaOH/CaO system at 740 °C and CH_4 and O_2 pressures of 0.35 and 0.14 atm respectively, the yield of C_n ($n \geqslant 2$) hydrocarbons reached 17%.[29,30]

A series of catalysts based on magnesium oxide with added transition metal oxides have also been tested under continuous conditions.[31] The experiments were performed at atmospheric

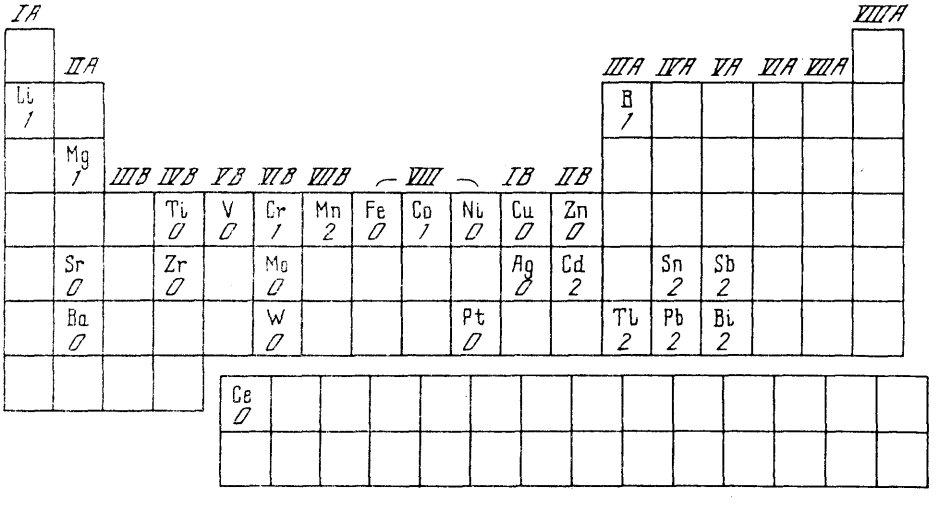


Figure 1. The activity of the oxides of elements in the formation of C_2 hydrocarbons from methane:[5] (*0*) inactive: (*1*) weakly active; (*2*) active.

pressure in a mixture containing 90% CH_4 and 10% O_2. The selectivity of the formation of C_2 hydrocarbons increased with increasing temperature and with decrease in contact time. Best results were obtained on unpromoted magnesium oxide: at 900 °C, the selectivity was 70% for a methane conversion of 9%. Deposited catalysts containing the oxides of Group IIIB elements were also tested under flow conditions.[32] The highest yield of C_2 hydrocarbons (2.3%) was reached in the presence of thallium oxide deposited on an aluminosilicate.

Catalysts not containing variable-valence elements have also been proposed for the oxidative dehydrodimerisation of methane.[33-35] On the 7% Li/MgO catalyst at 720 °C and CH_4 and O_2 pressures of 58 and 26 mmHg respectively, the yield of C_2 hydrocarbons was 19.4% for the ratio $C_2H_4:C_2H_6 = 1:5$. With increase in the pressures of the reactants, the yield falls. An appreciable decrease in the catalyst activity has also been observed during its use for several hours. The low stability of the system has also been noted in another study.[36]

The possibility of the oxidative dimerisation of methane has likewise been demonstrated on lanthanum oxides.[37] Under comparable conditions (725 °C, 40% CH_4, and 1% O_2), approximately the same results were obtained on this catalyst as on the lithium–magnesium system (the yield of C_2 hydrocarbons was approximately 2.5%). The best results were achieved at 725 °C and CH_4 and O_2 pressures in the reaction mixture of 57 and 17 mmHg (the remainder was helium). The yield of C_2 hydrocarbons amounted to 4.7%.

In a study of a series of MgO-based catalysts to which various elements (alkali metals and Group IIIA, IIIB, IVA, and IVB transition elements) had been added,[38] it was established that the yield of C_2-hydrocarbons increases with decrease in the oxidising activity of the catalyst. The latter was estimated from the temperature corresponding to 50% conversion of oxygen. The lowest yield of C_2 hydrocarbons was obtained on catalysts promoted by transition metals and the highest was on the Na/MgO system. At 800 °C and for a methane concentration in the mixture of 2.7%, the yield of C_2 hydrocarbons was 22.4%. An increase in the methane concentration in the mixture produced a sharp fall in the yield of C_2 hydrocarbons.

The influence of the nature of the support on the activity of the lead oxide catalysts in the formation of C_2 products has been investigated.[39] Basic supports proved to be best. The maximum yield of the dimerisation product was reached in the presence of the PbO/MgO system (6.6% of C_2 hydrocarbons at 750 °C and CH_4 and O_2 concentrations of 14 and 1% respectively).

Zeolitic catalysts have also been tested in the reaction involving the oxidative condensation of methane to C_2 hydrocarbons.[40] The Mn/HNa(HSZ)† catalyst, in the presence of which the selectivity in the formation of C_2 reached 50–65% for a methane conversion of 7–19%, was most effective.

Comparative tests under flow conditions on a large number of metal oxides in the oxidative methane dehydrodimerisation reaction have been carried out at 700 °C in the presence of a mixture containing 0.4% O_2 and 18.2% CH_4, the remaining being helium.[41,42] According to the results obtained,[41] which are presented in Fig.2, and in conformity with the results of previous studies, lead and bismuth oxides are some of the most active oxides in the given reaction. Furthermore, a new active catalyst of the oxidative dehydrodimerisation of methane has been discovered, namely samarium oxide. The selectivity of the formation of C_2 hydrocarbons in the presence of this catalyst reached 93%. Unfortunately the authors do not indicate the degree of conversion of methane to which this selectivity corresponds.

Subsequently an attempt was made to improve the catalytic properties of samarium oxide by adding alkali metal compounds.[43] A yield of C_2 hydrocarbons of 21% was attained on samarium oxide modified with lithium at 750 °C and methane and oxygen pressures of 50 and 20 mmHg respectively.

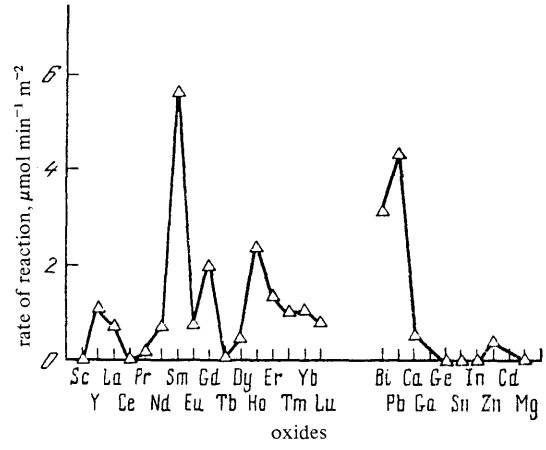


Figure 2. Comparative activities of various metal oxides in the oxidative dimerisation of methane.[42]

On lanthanum aluminate, the yield of C_2 hydrocarbons at 710 °C in a reaction mixture containing 50% of methane and as much air amounted to 12.5%.[44,45] An increase in temperature decreased the yield.

Attempts have been made in a number of studies to improve the properties of the catalysts of the oxidative dehydrodimerisation of methane by promoting them with halides and chalcogenides.[46-51]

Thus it has been suggested that compounds of the chalcogens (S, Se, and Te) be introduced into the catalyst beforehand and that the solid component be periodically made good as the chalcogen is consumed.[46,47] Halogens, especially chlorine, are introduced into the catalyst and a stage involving the treatment of the catalyst with a gaseous promoting agent (methyl chloride) is included in the cycle. Treatment of the catalyst with methyl chloride makes it possible to increase the selectivity with respect to C_n hydrocarbons ($n \geqslant 2$) by 15–20% for the periodic version of the process with reoxidation of the catalyst.

The addition of alkali metal halides to nickel, manganese, samarium, titanium, and zinc oxides[48-51] leads to an overall increase in the yield of C_2 hydrocarbons, mainly as a consequence of the appreciable increase in the yield of ethylene. Thus the yield of C_2 hydrocarbons on nickel(I) oxide promoted with Li_2CO_3 at 750 °C and at methane and oxygen concentrations of 5 and 2.5% respectively reaches 12.7% for a yield of ethylene of 6.9%. When lithium carbonate is replaced by the chloride, the above values are respectively 18.6 and 14.3%.[49] Catalysts promoted with halides are unstable and their activity falls sharply as the halides are decomposed.

†HSZ = high silica zeolite (Translator).

Thus a series of catalytic systems capable of operating under continuous conditions using a reaction mixture incorporating methane and oxygen have now been discovered. The most active catalysts are lead, bismuth, samarium, and manganese oxides. The addition of alkali metals increases the yield of the oxidative dehydrodimerisation products, but diminishes the stability of the catalyst. Promotion with halides also improves the yield of the C_2 hydrocarbons, but these catalysts are rapidly deactivated as a consequence of the loss of the halogen.

The majority of the catalysts ensure a high yield of oxidative dehydrodimerisation products only at a low methane concentration in the reaction mixture and the concentration of ethylene in the converted gas is therefore low even when its yield is high, which hinders its isolation and makes it more expensive.

Table 1 presents the yield of C_2 hydrocarbons in the oxidative methane dimerisation reaction obtained by different workers under continuous conditions.

Table 1. Oxidative dehydrodimerisation of methane in the continuous regime.

Contents in initial mixture		Yield of C_2, %	Refs.
CH_4	O_2		
5	2.5	22.3	[51]
7.6	3.8	19.0	[35]
2.7	1.35	22.4	[38]
20	0.5	6.7	[38]
35	14	17	[29]
50	10	12.2	[24]
30	20	24	Data from the
80	20	20	Institute of Catalysis

(b) The reaction mechanism

The first mechanism of the formation of ethylene from methane and oxide catalysts when the reaction is carried out in accordance with a two-stage scheme using the oxygen of the catalyst was proposed by Keller and Bhasin.[5] The authors suggest that the reaction proceeds via the formation of adsorbed CH_3 groups, which dimerise in the adsorbed state, and that the ethane obtained under these conditions undergoes subsequent catalytic oxidative dehydrogenation to ethylene:

$$2CH_4 + 2M^{2n+}O_n^{2-} \rightarrow 2OH_{ads} + 2CH_{3\,ads} + 2M^{(2n-2)+}O_{n-1}^{2-}, \quad (1)$$

$$2CH_{3\,ads} \rightarrow CH_3-CH_{3\,ads}, \quad (2)$$

$$2OH_{ads} \rightarrow H_2O + O_{ads}, \quad (3)$$

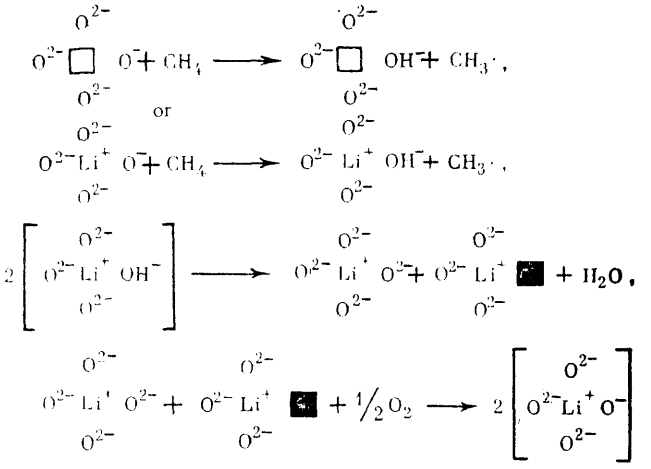
$$2M^{(2n-2)+}O_{n-1}^{2-} + O_2 \rightarrow 2M^{2n+}O_n^{2-}, \quad (4)$$

$$CH_3-CH_{3\,ads} + M^{2n+}O_n^{2-} \rightarrow CH_2=CH_2 + M^{(2n-2)+}O_{n-1}^{2-} + H_2O. \quad (5)$$

Estimation of the free energy of stage (1) yielded the conclusion that, for the majority of active oxides, this stage is thermodynamically allowed.[5] The involvement of adsorbed methyl groups in the oxidative methane dehydrodimerisation reaction has also been suggested in another study.[52] The source of the extensive oxidation products, which are also formed in this process, may be the methyl groups in the carbonium ion form arising when methane interacts with the acid surface centres.[52]

There exists also another view, according to which methyl radicals pass to the gas phase where the dimerisation products are actually formed.[33-35,53-60] In studies of the interaction of methane with the oxide catalysts of its oxidative dimerisation, methyl radicals were detected in the gas phase.[53] The same result was obtained by the lead mirror method in a study of the interaction of methane with deposited manganese oxide catalysts.[56] In their investigation of the generation of $CH_3^{\cdot}$ radicals on the Li/MgO catalysts, Driscoll et al.[53] concluded that the methyl radicals are formed with participation of the O^- ions on the catalyst surface. Reactions leading to the generation of active centres in the formation of methyl radicals according to these workers[55] are presented in Scheme 1:

Scheme 1



where ■ and □ are the anionic and cationic vacancies respectively.

According to the concept developed by Lunsford and co-workers,[35] the appearance of a radical centre in a binary oxide system is associated with the replacement of the divalent magnesium ion by the univalent lithium ion, which has a suitable radius. The introduction of larger ions (for example, Na^+) should not promote the appearance of such centres, which has in fact been confirmed in experiments where sodium carbonate had been added to MgO.[35] On the other hand, the addition of sodium ions to calcium oxide makes it possible, according to the authors' views, to increase the yield of dehydrodimerisation products.

However, it was shown later that, when magnesium oxide is promoted by sodium ions, it is possible to obtain a more effective catalyst of the dimerisation of methane than the lithium–magnesium system.[38] These results throw doubt on the concept of the methane activation mechanism described above.

It has been suggested[61,62] that the peroxide ions O_2^{2-} can function as the active centres of catalysts based on alkaline earth metal oxides modified by alkali metal ions.

In a study of the mechanism of the dehydrodimerisation of methane on lanthanum oxide,[37] it was not possible to observed O^- ions on the catalyst surface. A methane activation mechanism with participation of O_2^- ions was proposed for this oxide. According to the authors,[37] the extensive oxidation products are formed preferentially via two pathways: with participation of the oxygen of

the catalyst surface:

$$CH_3^{\cdot} + O^{2-} \rightarrow CO,\ CO_2$$

and via methylperoxy-radicals:

$$CH_3^{\cdot} + O_2 \rightarrow CH_3O_2^{\cdot} \rightarrow CO,\ CO_2.$$

Another concept of the activation of methane in its oxidative dimerisation reaction has also been put forward.[63-65] It has been established[63] that the overall rate of conversion of methane and the rate of formation of the dehydrodimerisation products increase with increase in the concentration of the basic centres on the catalyst surface. Furthermore, an increase in the formation of C_2 products is promoted by the presence of electron acceptors in the catalyst.[64] In view of these facts and bearing in mind the overall characteristics of the selective reactions of hydrocarbons involving the C–H bond,[65] by analogy with the scheme proposed previously for the activation of propene with formation of the allyl radical,[66] the following scheme may be proposed for the activation of methane in which the involvement of the basic centres of the catalyst and of electron acceptors is postulated:

$$CH_4 \xrightarrow[-H^+]{Nu^-} CH_3^- \xrightarrow[-e^-]{A} CH_3^{\cdot},$$

where Nu^- is the basic centre of the catalyst and A is an electron acceptor. The methyl radical formed should be relatively weakly bound to the catalyst surface. It may be desorbed to the gas phase and dimerise or it may be converted into the methylperoxy-radical $CH_3O_2^{\cdot}$ after interaction with an oxygen molecule.

The mechanism of the gas-phase reactions in the oxidative dimerisation of methane, which has been analysed in detail,[58-62] includes the following main pathways in the reactions of the methyl radical formed as a result of the heterogeneous activation of methane:

$$CH_3^{\cdot} + CH_3^{\cdot} \rightarrow C_2H_6,$$
$$CH_3^{\cdot} + O_2 \rightleftarrows CH_3O_2^{\cdot},$$
$$CH_3O_2^{\cdot} \rightarrow CO,\ CO_2.$$

Analysis of this scheme taking into account the known rate constants for the individual stages yielded an expression for the limiting selectivity in the formation of C_2 hydrocarbons, which agrees well with experimental data.[66]

Thus fairly selective catalysts of the oxidative dimerisation of methane have now been found and the principal features of the process mechanism have been established. However, a high selectivity is attained as a rule at low reactant concentrations or at low conversions, so that the yield of the target products, in the first place ethylene, is low after a single pass. The stability of the catalyst remains an unsolved problem. The question of the nature of the centres for the activation of methane, without the elucidation of which a purposeful selection and improvement of catalytic systems are impossible, also remains controversial.

Nevertheless, on the basis of the results already obtained, one may hope that an effective industrial process for the synthesis of ethylene from methane will be created in the next few years.

2. Conversion of methane into liquid hydrocarbons on zeolitic catalysts

Zeolitic catalysts are widely used in various hydrocarbon reactions. The appearance of new generation zeolites (pentasils) also made it possible to achieve the syntheses of hydrocarbons from compounds containing one carbon atom in the molecule. In particular, the processes leading to the conversion of methanol into hydrocarbons, the preparation of hydrocarbons from the synthesis gas, and the oxidative synthesis of higher hydrocarbons from methane have been achieved. The first two processes have been studied in detail and the results have been surveyed in a number of reviews.[67-70] The synthesis of higher hydrocarbons from methane on zeolites is a comparatively new and little investigated field.

As a consequence of the chemical inertness and thermodynamic stability of methane, the use of high temperatures is suggested in the known single-stage methods for its conversion into other organic compounds. The reactions of methane at 600 °C in the presence of decationated platinum-containing zeolites of the type of pentasil have been investigated at 600 °C.[71] The only hydrocarbon reaction product was benzene, whose yield reached 6%, while the rest consisted of the products of the extensive oxidation of methane. The absence of higher hydrocarbons is apparently associated with thermodynamic limitations.

The "cracking" of methane on nickel-containing pentasil-type zeolites above 400 °C is of interest.[72] The catalyst specimens subjected to a reducing treatment proved to be inactive. Zeolites of the faujasite type also did not exhibit an appreciable activity in this process. Unfortunately, the authors do not quote the composition of the methane reaction products.

The synthesis of higher hydrocarbons from methane in a single technological stage is thermodynamically possible under milder conditions when oxidants are used. Such a process can be achieved via a stage involving the formation of intermediates of type CH_3X, which are obtained in the oxidation of methane:

$$CH_4 + X{-}R \rightarrow CH_3X + HR$$
$$(X - R = \text{oxidant}),$$

and a stage in which CH_3X is converted into hydrocarbons:

$$nCH_3X \rightarrow nHX + C_nH_m.$$

The catalyst of such a process must be bifunctional, i.e. it must contain a component active in the oxidation stage and a zeolite which propagates the conversion of CH_3X into hydrocarbons.

The reactions of methane on zeolitic catalysts in the presence of oxidants (Cl_2, Br_2, O_2, NO, N_2O, NO_2, and SO_3) have been investigated at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences.[73-75] Catalysts of the chlorination or bromination of methane ($ZnCl_2$ and $CuCl_2$) and catalysts of the oxidation of methane (iron, copper, molybdenum, and cobalt oxides) were added, via impregnation, ion exchange, or mechanical blending to the high-silica zeolite in order to accelerate the oxidation stage. In the presence of molecular oxygen, chlorine, or bromine, the extensive oxidation or halogenation products were formed preferentially. In the presence of nitrous oxide as well as halogens at low concentrations, the formation of higher hydrocarbons was observed. On pentasil-type zeolites without acid transition elements, the selectivity of the formation of aromatic hydrocarbons exceeded 90%

under optimum conditions when N_2O was used as the oxidant and the yield relative to the methane passed through the system reached 40%.

The possibility of carrying out the oxidative synthesis of aromatic hydrocarbons from methane on pentasils using N_2O as the oxidant has also been confirmed in another study.[76]

Thus, in the presence of nitrous oxide, it is possible to attain an appreciable yield of liquid hydrocarbons from methane. Further studies should be directed to the replacement of N_2O by a cheaper and more readily available oxidant.

III. New approaches to the synthesis of catalysts and the carrying out of traditional catalytic processes with participation of C_1 compounds

As already mentioned, large-scale catalytic processes based on C_1 compounds, such as the conversion of methane and carbon monoxide, the conversion of methanol into formaldehyde, etc., have now been achieved in practice in the chemical industry. Despite this, the search for effective catalysts of these processes and of new applications of the reactions underlying them is being vigorously continued together with the development of new technological principles governing their occurrence.

In particular, at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences, methods of synthesis of low-temperature catalysts for these processes via the anionic modification of oxides are being developed, studies are being made of the possibility of using the conversion of methane in the thermochemical solar energy converter, and the technology of the synthesis of methanol under artificially created non-stationary conditions and a new technology of the oxidation of methanol to formaldehyde in reactors with adiabatic beds of an oxide catalyst are being developed.

1. Catalysts of low-temperature processes involving the synthesis of methanol and the conversion of carbon monoxide

The application of refined methods for the purification of the synthesis gas by eliminating sulphur-containing compounds promoted a wide-scale introduction of processes involving the synthesis of methanol and the vapour-phase conversion of CO (the ammonia synthesis stage) at low temperatures. The need to purify the gas is associated with the fact that the low-temperature copper-containing catalysts, which are highly effective in these processes, are deactivated in the presence of even small amounts of sulphur compounds as impurities. Both processes take place mainly on copper–zinc–aluminium, copper–zinc–chromium, or copper–zinc–chromium–aluminium catalysts. The importance of these processes for the chemical industry promoted extensive investigation of the mechanism of the reaction of copper-containing catalysts, their phase composition, and the active state of copper.

(a) The active state of copper

In the very first studies on the catalytic properties of copper-containing catalysts of the synthesis of methanol[77–79] and the conversion of CO,[80,81] it was established that copper oxide is rapidly deactivated at temperatures from 200 °C upwards. The introduction of zinc oxide appreciably improves the properties of the catalyst,[78,79,82] while the addition of a third oxide increases its efficiency still more. Aluminium,[83–85] chromium,[82,86,87] cerium,[88] and manganese[89,90] oxides as well as the oxides of other elements are used as the third component of this kind. Aluminium and chromium oxides are the most effective. Catalysts containing these additives have found industrial applications.

It has been suggested[77–79,82] that the rapid loss of activity by copper oxide is caused by its reduction to the metallic state. The introduction of promoting oxides increases the stability of copper oxide. The above hypothesis lacked experimental confirmation for a long time. On the other hand, the view that the activity of the catalyst in the reactions considered is determined by the metallic copper phase, formed on the surfaces of stable aluminium and chromium oxides or zinc–aluminium and zinc–chromium spinels on activation of the catalyst or under the influence of the reaction medium, gained currency.[91–98] In many cases, the metallic copper phase appears in highly active catalysts after the synthesis of methanol or the conversion of CO. According to numerous data,[92,93,97–100] the activity of the catalysts diminishes with increase in the size of the copper crystals. Catalysts containing 50–70 Å copper crystals are the most active in the conversion of CO.[97] However, numerous attempts[101–104] to find a quantitative relation between the area of the metallic copper, determined by the "chemisorption" method, and the activity of the catalysts in both reactions considered proved unsuccessful. The absence of such a dependence makes the idea that the mechanism of the action of copper-containing catalysts is associated with the formation of the metallic copper phase under the reaction conditions less convincing. In principle, one can postulate that the catalytic reaction between the reactants can occur both on the metallic copper and on surface copper ions in oxide compounds stable under the reaction conditions. The overall activity is in this case determined by the surface area of the active components (phases) and the atomic (ionic) activity of copper in these components. In order to solve the problem of the nature of the active phase, it would be necessary to compare the catalytic properties of metallic copper in a specimen where the possibility of the presence of the ionic form of copper has been ruled out with the catalytic properties of various copper-containing compounds stable under the reaction conditions to such an extent that this completely excludes the formation of metallic copper. However, it proved difficult to characterise the catalytic capacity of purely metallic copper, because the massive specimens have a low surface area and the application of deposited catalysts makes it impossible to guarantee the absence of copper in the ionic form.

Thus it has not yet been possible to characterise quantitatively the catalytic properties of metallic copper in reactions involving the synthesis of methanol in the water vapour conversion of CO. On the other hand, the catalytic properties of compounds in which copper is known to be in the ionic form have been investigated for both reactions.

(b) Catalytic properties of copper-containing oxide compounds

The catalytic properties of copper chromites, ferrites, aluminates, and chromite ferrites, in which part of the copper has been substituted by zinc, magnesium iron(II), and other metal ions, have been investigated in CO conversion reactions.[105–107] Partial substitution

of copper ions ensures the stability of the above compounds in the reaction medium up to high temperatures which prevents the formation of metallic copper under the reaction conditions at 200–270 °C. These compounds have the spinel structure, but contain copper ions in different crystallographic positions, surrounded by oxygen ions in tetrahedral and octahedral configurations. In addition, studies have been made of the properties of solid solutions of copper ions in magnesium oxide which are stable under the reaction conditions.[107] It was found that the specific activities of the spinel are comparable to those of the best industrial catalysts, while the solid solution of copper ions in magnesium oxide is much more active than the latter at 270–300 °C. The activation energy depends on the positions of the copper ions: if they are in tetrahedral positions, the activation energy is 9–10 kcal mol^{-1}, while for the octahedral positions it amounts to 19–20 kcal mol^{-1}. In the presence of the copper–zinc–aluminium–chromium industrial catalyst, the activation energy is 8–13 kcal mol^{-1}.[91]

Depending on the component ratios and the conditions of the synthesis in the copper–zinc–aluminium system, the following copper-containing compounds are formed after heat treatment at 350–400 °C (the temperature at which the industrial catalyst is prepared): copper oxide, solid solutions of zinc and aluminium ions in copper oxide,[108–110] a solid solution of copper ions[109–113] or copper and aluminium[109,110,112,114] in zinc oxide, the copper–zinc–aluminium spinel,[99,109,110,115,116] and a solid solution of copper ions in the spinel.[115] As already mentioned, copper oxide and solid solutions based on it are unstable under the conversion reaction conditions and are rapidly deactivated. The copper–zinc–aluminium spinel and the solid solution of copper and aluminium ions are stable in the reaction medium at least up to 500 °C and their activity is not inferior to that of the most active industrial catalysts.

Among the compounds formed in the copper–zinc–aluminium system, only the solid solution of copper and aluminium ions in zinc oxide is not inferior as regards its activity in the synthesis of methanol and the stability under the conditions of this reaction to the most effective of the known industrial catalysts. The copper–zinc–aluminium spinel is stable under the conditions of the synthesis of methanol, but is much less active than in the conversion reaction.[110,117] These results suggest that the rate of synthesis of methanol depends very greatly on the state of the copper ions and that the state of the copper ions which ensures the necessary activation of the reactants obtains only in the solid solution based on zinc oxide. This explains the marked dependence of the activity of the copper–zinc–aluminium catalyst in the synthesis of methanol on the conditions governing its formation, noted by Bondar' et al.[83] and Shishkov et al.[84] The catalytic properties of the system in the CO conversion reaction also depend on the state of the copper ions, but not so markedly.

The first indication of the high activity of copper ions dissolved in zinc oxide was obtained in a study[112] where it was shown that about 10 at.% of copper is dissolved in zinc oxide in the active copper–zinc catalyst. On the other hand, it is known[118] that the method involving substitution in zinc oxide can lead to the dissolution of not more than 1–2 at.% of copper(II). This is due to the low tendency of copper(II) ions to be involved in tetrahedral coordination with oxygen. It has been suggested that the increased solubility is attained as a result of the dissolution of copper(I) ions. Indeed, an increase in the dissolution of copper in a reducing medium has been observed[112,119] and it has been concluded that the aluminium oxide in the copper–zinc–aluminium catalyst plays the role of a support increasing the surface area of the zinc oxide-based solid solution. However, it has been shown[113,115,117,120] that aluminium fulfils more complex functions in this catalyst.

Copper zinc hydroxoaluminate with a high M(II) : M(III) ratio, having a structure of the hydrotalcite (pyroaurite) type,[115,121,122] and copper-aluminium-zinc hydrocarbonate having a structure of the hydrozincite[84,112,113] or aurichalcite[123] type, are precursors of the active zinc oxide-based solid solution in the preparation of the catalyst by the method involving the precipitation of hydroxo-compounds or the mixing of the components. A study by EPR or electronic spectroscopy of the state of copper in the hydroxo-aluminate with a structure of the hydrotalcite (pyroaurite) type and in the copper-zinc and copper-zinc-aluminium hydroxocarbonates with a structure of the hydrozincite type showed[124] that the copper(II) ions are distributed preferentially at distorted octahedral sites. The concentration of copper(II) ions in the hydroxo-compounds exceeds the maximum possible concentration in zinc oxide.[113] As a result of heating at 350 °C,[125] the above hydroxo-compounds decompose with formation of a solid solution of copper and aluminium ions in zinc oxide and, when the content of copper and aluminium is in excess of a certain level, copper oxide and an aluminium spinel are also formed. The content of copper(II) in zinc oxide is (with retention of the homophase structure) approximately 10 at.% in the copper–zinc system and up to 20 at.% in the copper–zinc–aluminium system. If the copper content in zinc oxide in the copper–zinc–aluminium system reaches 35 at.%, then a certain amount of copper oxide is formed simultaneously.

Heat treatment at higher temperatures is accompanied by the evolution of water vapour and CO_2 and leads to a decrease in the copper content in zinc oxide to 1–2 at.%. According to the data of Hadzhieva et al.,[124] 1–2 at.% of copper(II) substitutes the zinc ions in tetrahedral positions in the zinc oxide, while the remainder is distributed in the form of clusters consisting of several ions. The copper ions in the clusters are apparently in a strongly distorted octahedral environment comprising oxygen ions. In the solid solution of copper and aluminium ions in the low-temperature zinc oxide, virtually all the copper(II) ions exist as associated species. The possibility of such distribution of copper ions is apparently determined by the appearance of defects in the zinc oxide structure as a result of the complete removal of OH^- and CO_3^{2-} groups from the oxide. The impurity anions are removed at a fully defined temperature and the low-temperature zinc oxide is therefore anionically modified.

The formation of anionically modified oxides at low temperatures is characteristic of many metals. For example, anionically modified nickel, magnesium, and copper oxides as well as aluminium and chromium spinels have been obtained.[125]

The degree of oxidation of copper ions on the surfaces of copper-containing compounds, stable under the conditions of the reactions considered, has been investigated by various workers.[111,114,126–132] The results obtained suggest that, under the influence of the reaction medium, the copper ions are reduced to copper(I). According to some data,[133,134] the conversion reaction proceeds via intermediate complexes of the formate type formed from the copper(I) ions. There exist contradictory views concerning the mechanism of the synthesis of methanol. Various mechanisms have been examined in reviews.[135,136]

It follows from the data obtained in the studies examined above that the catalytic activity of the ionic forms of copper is sufficiently high to attribute to these forms the high activity of the industrial copper-containing catalysts of the synthesis of methanol and of the water vapour conversion of CO. Among these forms, a high

activity in both processes is shown by associated copper ions forming part of the composition of the low-temperature anionically modified zinc oxide.

(c) Catalytic properties of the skeletal catalysts

As a result of the leaching of copper-zinc and copper-zinc-aluminium alloys, metal oxide systems are formed[137,138] which can be regarded as metallic copper on the surface of which copper and zinc oxides are present.

According to some data,[139,140] leaching results in the formation of porous copper which is responsible for the activity of the catalyst in the synthesis of methanol. Studies by the XPES and XRES‡ methods[132] have shown that, after leaching, structures resembling those formed on the surface of the copper-zinc–aluminium oxide catalyst predominate on the surface of the skeletal [Raney] copper-zinc-aluminium catalyst, namely associated copper ions incorporating also zinc and oxide ions. Under the reaction conditions, copper ions in the +1 oxidation state catalyse the interaction of the adsorbed CO and H_2O. Consequently the activity of skeletal catalysts in the CO conversion reaction is determined by the copper ions in the oxide compounds.

(d) Resumé

The data examined show that the high activity of all the catalysts investigated, apparently including the skeletal catalyst, can be accounted for by the formation of compounds stable under the reaction conditions and containing copper in the ionic form. In the copper–zinc–aluminium and copper–zinc–chromium catalysts, such compounds in the CO conversion reaction may be the copper-zinc-aluminium and copper-zinc-chromium spinels and a solid solution of copper and aluminium (or chromium) ions in zinc oxide, while in the synthesis of methanol a solid solution of copper and aluminium (or chromium) ions in zinc oxide is a formation of this type. In the case of skeletal catalysts, these compounds are apparently formed as films.

A high concentration of copper in zinc oxide is attained by virtue of the formation at low temperatures (below 500- °C) of zinc oxide with a defective structure—anionically modified by CO_3^{2-} and OH^- groups. This structure ensures the stabilisation of copper ions in the form of associated species in which the copper ions are most probably surrounded by oxygen ions in a square planar configuration. The number of defects (and hence the concentration of copper) and, what is most important, the thermal stability of the anionically modified states in air and under the reaction conditions increase after the incorporation of chromium(III) or aluminium(III) ions in the structure.

One should note that the change in the miscibility of copper and zinc oxides as a result of the anionic modification of the oxide matrix, observed in two investigations,[120,125] has been confirmed in a number of other oxides, including oxides with a complex composition. Presumably this phenomenon may be used to regulate the properties of the oxide catalysts not only in the synthesis of methanol and the water vapour conversion of CO but also in other oxidation-reduction reactions.

2. The synthesis of methanol under artifically created non-stationary conditions

A new highly effective method for the synthesis of methanol, based on catalytic processes under artificially created non-stationary conditions, is examined in the present Section.[141–143] The advantages of such processes are manifested when reversible exothermic reactions are carried out. In this case the optimum regime from the standpoint of the yield of the useful product can be obtained under non-stationary conditions in only one catalyst bed and not in several beds as happens in current large-scale industrial plant. This significantly simplifies the apparatus and makes the process less expensive.

(a) The principle of the method

Suppose that the stationary bed of a copper-containing catalyst was heated beforehand to approximately 260 °C, whereupon synthesis occurs at an appreciable rate. The introduction into the catalyst bed of the reaction mixture with an overall concentration of carbon oxides $c_{CO} + c_{CO_2} \simeq 6$–8 vol. % and a hydrogen concentration $c_{H_2} \simeq 80$ vol. % begins at time $t = 0$. The mixture is at a low temperature (~50 °C), at which the rate of synthesis of methanol is negligible. Under these conditions, the sections of the catalyst bed adjoining the point of entry of the reaction mixture begins to cool down and the reaction mixture is gradually heated to the temperature corresponding to the onset of reaction. The central part of the bed then retains a high temperature for a long time for two reasons: owing to the high ratio C_c/C_r of the heat capacities of the catalyst (C_c) and the reaction mixture (C_r) as a consequence of the evolution of the heat of reaction. According to Kiselev and Matros,[144] the thermal front of the exothermic chemical reaction is formed under these conditions and migrates along the bed at a rate which is lower by a factor approximately equal to C_c/C_r than the rate of penetration of the reaction mixture. At a time approximately equal to $(C_c/2C_r)t_c$, where t_c is the time of contact between the reaction mixture and the catalyst bed, the direction of the supply of the reaction mixture is reversed and the thermal front also begins to migrate in the opposite direction. After several such switch-overs, a cyclic reaction regime is established in the catalyst bed.

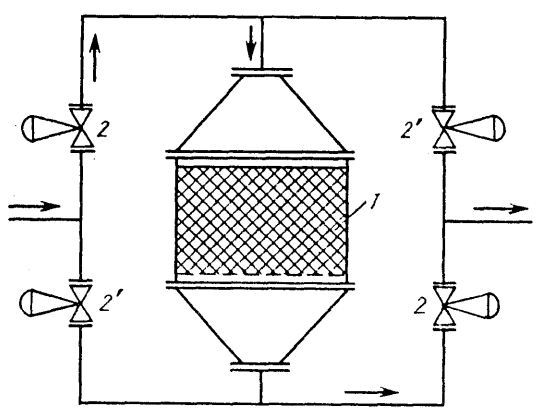


Figure 3. Schematic technological diagram of a reactor with a stationary catalyst bed working in the regime involving the periodic alteration of the direction of supply of the reaction mixture: (*1*) catalyst bed; (*2*) and (*2'*) valves.

The technological scheme for the non-stationary synthesis of methanol described above is fairly simple (it is illustrated in Fig.3). The valves *2* and *2'* shown in the figure open (*2*) and close (*2'*) periodically and simultaneously during the first half-period and

‡X-Ray photoelectron spectroscopy and possibly X-ray fluorescence spectroscopy (Ed. of Translation).

conversely close (*2*) and open (*2'*) during the second half-period, which ensures the establishment of a non-stationary technological regime.

We shall consider briefly the principal disadvantages of the method proposed[145] for the synthesis of methanol under the conditions of the periodic alteration of the direction of supply of the reaction mixture into the stationary catalyst bed.

1. Apart from its principal function of accelerating the chemical reaction, the catalyst plays the role of a regenerative heat exchanger. This makes it possible to make do almost completely without heat exchange equipment, which greatly reduces the requirement for metal in the catalytic unit. For example, the apparatus comprising an expensive and cumbersome external heat exchanger is eliminated in the proposed procedure.

2. Without the introduction of additional energy in the corresponding heat exchange equipment, it is possible to process industrial gases with a low content of carbon oxides, down to $c_{CO} + c_{CO_2} \simeq 0.4$ vol. %. This is of fundamental importance, for example, in the processing of straight-run gases.

3. Conditions which are theoretically nearly optimal from the standpoint of the yield of the useful product are created in the catalyst bed. This makes it possible to employ simple and cheap catalytic apparatus, which is not inferior as regards its characteristics to more expensive and cumbersome industrial apparatus working under traditional stationary conditions. The reason for this is as follows. The synthesis of methanol is a reversible exothermic process and, in the ranges of the temperatures and pressures indicated above, it proceeds close to equilibrium conditions. In the theoretically optimum regime, a decrease in the reaction temperature with increase in the degree of conversion of carbon oxides into methanol is required. When the process takes place in adiabatic catalyst beds under stationary conditions, the opposite picture naturally obtains. Therefore in practice part of the cold gas is conducted through a bypass between the catalyst beds or intermediate heat exchangers are set up in which the reaction mixture is cooled. In the non-stationary regime, there is a section at the exit of the reaction mixture from the catalyst bed where the temperature is reduced and the amount of methanol formed increases. Thus, in a single catalyst bed it is possible to achieve yields of methanol which in the stationary regime are attained when several adiabatic beds are used. Consequently, as a result of a closer approach to the theoretically optimum conditions than in the stationary regime, the design of the reactor and the entire process are greatly simplified.

4. In a catalyst bed working in a non-stationary regime, it is possible to reduce the average temperature by approximately 100 °C. Other conditions being equal (identical initial composition and linear flow rate of the reaction mixture, grain size, and amount of the catalyst), this lowers the hydraulic resistance of the bed by approximately 30%. Furthermore, the overall hydraulic resistance of the system is reduced as a result of the significant simplification of the design of the catalytic apparatus and decrease in the overall length of the tubing.

5. As a result of the simplification of the design of the catalytic unit, which incorporates one catalyst bed, the heat losses to the surrounding medium are reduced severalfold, which is particularly important for the utilisation of straight-run gases for the processing of which it is difficult to create an autothermal regime under traditional stationary conditions.

6. In the existing stationary methods of synthesis, it is necessary to achieve the stabilisation of the initial composition, temperature, and charge of the initial reaction mixture. This requires the creation of a cumbersome and complex automatic control system, especially if account is taken of the time variation of the activity of the catalyst. The non-stationary method permits the processing of the reaction gases with both constant and variable parameters and does not require the development of a special automatic control system.

(b) Mathematical modelling

As already mentioned above, there is no unanimous view concerning the mechanism of the synthesis of methanol on copper-containing catalysts. Thus Pomerantsev et al.[146] and Rozenfel'd and Rusov[147] believe that the process proceeds in accordance with the scheme $CO_2 \rightleftarrows CO \rightleftarrows CH_3OH$. However, in other studies[148,149] it has been suggested that the scheme $CO \rightleftarrows CO_2 \rightleftarrows CH_3OH$ is more probable. The following expressions have been obtained[150] for the rates of synthesis of methanol from CO_2 (w_1) and of conversion of CO (w_2):

$$w_1 = \frac{k_1 c_{H_2}}{1 + b_{H_2O} c_{H_2O}} \left(1 - \frac{c_{CH_3OH} c_{H_2O}}{K_1 c_{H_2}^3 c_{CO_2}}\right),$$

$$w_2 = \frac{k_2 c_{H_2}}{1 + b_{H_2O} c_{H_2O}} \left(1 - \frac{c_{CO} c_{H_2O}}{K_2 c_{H_2} c_{CO_2}}\right),$$

where k_1 and k_2 are the rate constants for the formation of methanol and the conversion of CO respectively, K_1 and K_2 are the corresponding equilibrium constants for the same reactions, b_{H_2O} is the adsorption coefficient for water, and c_i (i = H_2, H_2O, CH_3OH, CO, and CO_2) are the corresponding concentrations.

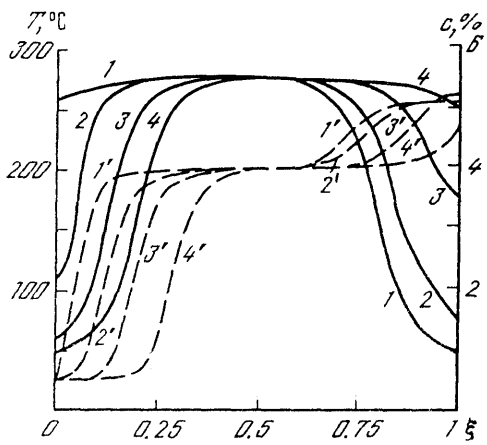


Figure 4. The temperature distribution (continuous lines) and methanol concentration (dashed lines) along the length of the catalyst bed ξ ($0 \leqslant \xi \leqslant 1$) in an established cyclic regime according to mathematical modelling data.[151] The gas moves from left to right. Composition of the initial mixture (vol. %); CO, 3.74; H_2, 81.9; CH_3OH, 0.474; CO_2, 2.033; H_2O, 0.078; N_2, 1.558; CH_4, 10.189. The conventional contact time is 0.5 s, which corresponds to a space velocity of 7200 h^{-1}. Pressure 7.2 MPa; mixture temperature at entry 50 °C; duration of cycle 10 min. The different curves correspond to different times t after the switch-over: (*1*) 0 min (start of half-cycle); (*2*) 1 min; (*3*) 3 min; (*4*) 5 min (end of half-cycle).

Fig. 4 presents examples of the calculation of the temperature and concentration fields in the catalyst bed on the basis of the so called two-phase model taking into account the external heat and mass exchange between the outer surface of the catalyst grain and the stream of the reaction mixture, the longitudinal heat transfer along the catalyst bed, and the internal diffusion inhibition of the reaction within the porous catalyst grain.[151] As can be seen from this figure, a decrease in temperature in the reactor with increase in the degree of conversion of carbon oxide is characteristic of the proposed method. For example, if the initial mixture contains ~5.75 vol. % of carbon oxides and ~0.47 vol. % of methanol, this makes it possible to obtain more than 5 vol. % of methanol at the exit from the bed. We may note that the equilibrium methanol content at 275 °C in the central part of the bed is ~3.9 vol. %, i.e. is appreciably lower.

Calculations have shown that the removal of the heat of the chemical reaction from the central part of the catalyst bed via a heat exchanger permits an increase in the yield of methanol by approximately 15% and an additional gain of heat, which is potentially highly utilisable. In practice both these possibilities are extremely useful. We may note that the yield of methanol in the system considered is much higher than in the traditional four-bed reactor with bypasses for the introduction of the cold gas between the catalyst beds, operating under optimum conditions. An experimental test in the reactor charged with three litres of the catalyst confirmed the possibility of synthesising methanol in a non-stationary cyclic regime and the validity of the principal conclusions reached from the results of mathematical modelling.

3. Oxidation of methanol to formaldehyde in a reactor with adiabatic oxide catalyst beds

The formation of formaldehyde from methanol on oxide catalysts is more economical than on silver-containing catalysts. In connection with the growth of the requirement for formaldehyde, it has become necessary to create plants with a unit capacity in excess of 50 000 to 60 000 tonnes per year. The application of tubular and combined reactors[152] with such capacity is difficult owing to the complexity of their construction and operation. Reactors with adiabatic catalyst beds appear to be most promising.[153]

The principal results of the development of a reactor of this type found by mathematical modelling studies of the kinetics and the temperature and concentration fields in the catalyst bed are briefly summarised in the present Section. The processes within a porous catalyst grain were described in terms of a quasi-homogeneous model. Stationary regimes in the adiabatic bed were determined by analysing the ideal displacement model with respect to matter and heat. The transient regimes in the stationary catalyst bed were calculated with the aid of a model taking into account the mass and heat exchange between the external surface of the grain and the gas stream and also the longitudinal transfer of heat along the skeleton of the catalyst bed.

Since the iron-molybdenum oxide catalyst works at temperatures in the range 220–350 °C[154] and the oxidation of methanol to formaldehyde is accompanied by an appreciable evolution of heat, the process must be carried out in several adiabatic beds arranged in series with removal of heat between them. However, when the process is carried out in this way, the output parameters of the reaction mixture, especially in the first beds, are very sensitive to changes in its input parameters. This hinders the use of catalytic apparatus of this type in carrying out processes involving the partial oxidation of hydrocarbons. Using mathematical modelling methods, it has been possible to put forward a process regime whereby the above difficulties can be overcome.

This required the solution of the following problems: (1) to ensure conditions under which the parametric sensitivity of the output parameters to changes in the input parameters does not exceed that required for technological reasons; (2) to develop an automatic control system which ensures the stabilisation of the technological parameters within specified limits.

The solution of the first problem reduced to the selection of the optimum grain size along the catalyst beds. In the oxidation of methanol to formaldehyde in the presence of the iron–molybdenum catalyst, two consecutive reactions take place: the oxidation of methanol proper and the oxidation of formaldehyde. Kinetic studies have shown[155] that the first reaction is of first order with respect to methanol and is inhibited by water. Formaldehyde hardly influences the rate of oxidation of methanol. The oxidation of formaldehyde is of first order with respect to formaldehyde and is inhibited by methanol and water.

Numerical analysis of the processes occurring on the catalyst grain led to the construction of a model of the observed reaction rates on grains of different size and shape in the temperature range 200 to 350 °C.[154] The characteristics obtained served as the basis for the mathematical modelling of the industrial reactor.

The catalyst grain size was chosen to ensure the permissible parametric sensitivities with retention of a sufficiently high process selectivity. The parametric sensitivity can be reduced by lowering the observed activation energy. When the process passes from the kinetic to the internal diffusion region, the observed activation energy E diminishes by a factor $\exp(\Delta T_{ad}x/RT_0^2)(E/2)$, where ΔT_{ad} is the adiabatic temperature rise in the mixture, x the degree of conversion, and T_0 the input temperature. For the iron-molybdenum catalyst in the specified temperature range, the increase in grain size is virtually the only parameter with the aid of which it is possible to reduce appreciably the activation energy.[156] An increase in grain size improved also the dynamic properties of the adiabatic bed. Furthermore, as a result of the decrease in the observed activation energy with increasing grain size, the possibility of the so called dynamic stoppages is diminished and the transient regimes develop more slowly. Ultimately favourable conditions are created for the automatic control of the process in the bed. However, an increase in grain size, which leads to an increase in the internal diffusion resistance, tends to increase the contribution of the side reaction involving the oxidation of formaldehyde to carbon monoxide and water and requires an increase in the catalyst charge. Thus it is essential to select an optimum catalyst grain size.

For this purpose, calculations have been made of the temperature and concentration fields in the reactor with adiabatic catalyst beds for an initial methanol concentration of 6–6.5 vol. %. The results obtained show that an increase in the grain size R_0 to 3 mm has a significant effect on selectivity in beds III and especially IV but has virtually no influence on the selectivity in beds I and II. The parametric sensitivity greatly diminishes with increase in R_0, reaching the minimum values for $R_0 \geqslant 3$ mm. The analysis led to the selection of the following catalyst grain sizes, R_0 (in mm) in the beds: 3 in beds I and II, 1.5 in bed III, and 1 in bed IV.

It follows from the mathematical modelling data that the adiabatic catalyst beds have the same parametric sensitivity to different input perturbations. Therefore, in order to ensure the stable and reliable operation of the reactor, a special system was developed for the automatic control of the process with removal of

part of the reaction gases via lines bypassing the intermediate heat exchangers.[157]

The results of the mathematical modelling of the reactor with adiabatic catalyst beds were tested and confirmed on the experimental plant of the Novosibirsk Chemical factory with an output of 18–25 kg of 37% formalin per hour. Prolonged use of the experimental plant confirmed that the system for the automatic stabilisation of the temperature regime in the reactor makes it possible to maintain the input parameters to within 1–1.5 °C and the output parameters to within 10–15 °C.

The principal technological and design characteristics of the reactor with adiabatic oxide catalyst beds with an output of 120 000 tonnes of 37% formalin per year are presented below:

Diameter of apparatus, m	4.2
Initial methanol concentration, vol.%	6.5
Blowing rate, $nm^3 h^{-1}$	70000
Linear flow rate, nm s^{-1}	1.4
Overall degree of conversion, %	99.3–99.8
Yield of formaldehyde, %	93.5–94.5
Consumption coefficient with respect to methanol, kg $tonne^{-1}$	423–428
Overall hydraulic resistance, atm	0.4
Conventional contact time	0.38

Thus the possibility, in principle, of oxidising methanol to formaldehyde in a reactor with adiabatic oxide catalyst beds arranged in series has been demonstrated. The application of reactors of this type makes it possible to create plants with a high unit output, such reactors being simple as regards apparatus and easily regulated.

4. The use of the catalytic conversion of methane for the thermochemical transformation of solar energy

The promising nature of yet another somewhat unexpected application of the catalytic reactions of C_1 compounds has been demonstrated most recently. It was established, initially theoretically[158] and then experimentally,[159–161] that the highly endothermic catalytic water vapour or carbonic acid conversion of methane into the synthesis gas can be used for the direct highly effective transformation of solar energy into the energy of chemical fuels. Such transformation is achieved by heating the catalytic reactor with concentrated sunlight up to temperatures of the order of 600–700 °C at which the thermodynamic equilibrium in the mixture of methane with water or CO_2 is displaced towards the high-energy mixture of CO and H_2. The energy stored in the course of the conversion of methane can then be released in another reactor in the form of heat, which is potentially highly utilisable, by carrying out the reverse reaction, also catalytic, involving the conversion of the synthesis gas into methane. With the aid of the above sequence of reactions, it is possible to create fairly effective energy devices with a closed cycle involving the utilisation of C_1 compounds as a chemically active "working heat".

Naturally, in opaque solar catalytic reactors, chemical processes take place in exactly the same way in the presence of the same catalysts as under traditional conditions. However, the efficiency of the solar energy devices definitely depends on the way in which high-density heat fluxes are transferred to the catalyst bed. The design of the catalytic reactors differs greatly in the given case from the usual reactors. A number of such designs with a useful output of several kilowatts have been developed at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences and have been tested under natural conditions.[159–161] In the course of these tests, efficiencies up to 45% in the storage of solar energy and above 20% in the generation of potentially highly utilisable heat (gas temperature up to 700 °C) were recorded during the operation of the closed thermochemical cycle as a whole. Such efficiencies are at present the maximum attained in chemical methods for the transformation of solar energy and the solar catalytic power generating devices developed can be regarded as prototypes of industrial designs.

The prospect for the practical utilisation of chemical methods for the transformation of solar energy depend nowadays on two factors. Firstly, we have the economic factor. All the methods of utilising solar energy known at the present time are more expensive than the traditional methods of generating energy, such as, for example, the combustion of organic fuels, nuclear reactions, etc. In this situation it is to be expected that solar energy will win through gradually as it becomes cheaper, as a result of the scientific and technical progress in this field, while the traditional sources of energy become gradually dearer due to their exhaustion.

The second factor is ecological. Much depends on how dangerous the thermal and chemical pollution of our planet by modern power engineering really is. If it proves intolerable, the development of the ecologically clean solar power engineering may become essential.

IV. Metal complex catalysis in reactions of C_1 compounds

Since its establishment, metal complex catalysis has been and remains a promising field of catalytic chemistry which is associated, firstly, with the possibility, as in this instance, of applying a broad spectrum of highly informative physicochemical research methods and, secondly, with the existence of a solid theoretical basis comprising extensive practical data concerning the reactivity of various coordination and organometallic compounds and the mechanisms of their reactions, which are used in the purposeful search for catalytic systems.[162–169] In order to predict the composition of metal complex catalytic systems, one may use thermodynamic and kinetic analyses of different combinations of stoichiometric reactions of metal complexes, which can be formally incorporated in a closed catalytic cycle.[170] Using this approach, a series of new catalytic systems, suitable for carrying out a wide variety of reactions involving carbon monoxide and formaldehyde, have been discovered at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences.

The problem of the involvement in chemical syntheses of one of the C_1 compounds produced on a large scale, namely carbon dioxide, is of great interest. Here too the application of metal complex catalysts may prove to be extremely promising.

1. Catalytic reactions with participation of carbon monoxide

The liquid-phase conversion of carbon monoxide has been achieved[173] under conditions (temperature, solvent composition, and the nature of the ligands L) such that two stoichiometric reactions with participation of metal complexes can take place simultaneously and at a high rate:

$$L_2MX_2 + CO + H_2O \xrightarrow{2L} L_4M + CO_2 + 2HX, \quad (1)$$

$$L_4M + 2HX \xrightarrow[-2L]{} L_2MX_2 + H_2. \quad (2)$$

The incorporation of these reactions in a closed cycle leads to the

catalytic reaction

$$CO + H_2O \xrightarrow{L_2MX_2} CO_2 + H_2. \quad (3)$$

Special studies led to the discovery of the conditions in the case where M = Pd, L = PPh_3, and X = CF_3COO for reactions (1) [reduction of phosphine complexes of palladium(II)[171]] and (2) [the interaction of $Pd(PPh_3)_4$ with acids[172]] and hence to the determination of the optimal conditions for reaction (3)[173] (Table 3, system *3*).

We may note that the above study[173] was preceded by only two communications[174,175] demonstrating the possibility of achieving the liquid-phase conversion of carbon monoxide (Table 2, systems *1* and *2*).

After the publication of the above investigation,[173] more than twenty metal complex catalytic systems for the liquid-phase conversion of carbon monoxide [the best known of these are presented in Table 2 (systems *4*, *5*, and *6*)], but the catalytic composition proposed by Zudin et al.[173] still remains one of the most active and makes it possible to carry out the reaction under mild conditions (temperature up to 100 °C, atmospheric CO pressure).

Table 2. Catalytic systems for the liquid-phase conversion of carbon monoxide.

No. of system	Composition of complex	Reaction conditions	Activity, mol H_2(mol M)$^{-1}$ h^{-1}	Refs.
1	$Fe(CO)_5$	15% aqueous NH_4OH solution with added $Ba(OH)_2$; 80 °C	0.03	[174]
2	$Rh_6(CO)_6$	aqueous pyridine solution; 450 atm; 210 °C	2.1	[175]
3	$(PPh_3)_2Pd(OAc)_2$	80% aqueous CF_3COOH; 70 °C; CO pressure 0.3 atm	3.0	[173]
4	$K_2PtCl_4 + SnCl_4 \cdot 5H_2O$	20% HCl solution in acetic acid containing 20% of water; 90 °C; CO pressure 0.5 atm	1.0	[176]
5	$Pd(ClO_4)_2 + Ph_2P$–	aqueous solution; 85–100 °C; CO pressure 0.5 atm	0.25	[177]
6	$HRh(PEt_3)_3$	pyridine; 100 °C; CO pressure 20 atm	10.0	[178]

Catalytic synthesis of hydrogen peroxide via the coupled oxidation of carbon monoxide and water has been achieved under conditions ensuring the incorporation in a closed cycle of three stoichiometric reactions of phosphine complexes of palladium:

$$L_2PdX_2 + CO + H_2O \rightleftarrows L_2Pd + CO_2 + 2HX, \quad (4)$$

$$L_2Pd + O_2 \xrightarrow{-2L} L_2PdO_2, \quad (5)$$

$$L_2PdO_2 + 2HX \xrightarrow{L = PPh_3} L_2PdX_2 + H_2O_2. \quad (6)$$

As can be seen, the combination of reaction (4)–(6) in a catalytic cycle makes it possible to achieve the catalytic synthesis of hydrogen peroxide from oxygen and water in accordance with the equation

$$H_2O + O_2 + CO \xrightarrow{L_2PdX_2} H_2O_2 + CO_2. \quad (7)$$

It is noteworthy that in this process the highly endoergic stage involving the oxidation of H_2O by molecular oxygen to H_2O_2 is coupled energetically with the highly exoergic stage involving the oxidation of CO to CO_2. Previously such coupling of endoergic and exoergic stages was achieved in the catalytic synthesis of acetic anhydride from acetic acid, CO, and O_2.[179]

Reaction (7) was initially predicted on the basis of the considerations formulated above and was then achieved in practice.[180] The catalytic solution consisted of the two-phase water–dichloromethane system. The CH_2Cl_2 phase contained $Pd(OAc)_2$ and PPh_3, while the aqueous phase was a 3% solution of titanium(IV) sulphate, which served as a "trap" for the hydrogen peroxide formed. At 20 °C and atmospheric pressure of the gas phase ($CO:O_2$ = 1:1), the rate of formation of hydrogen peroxide was 0.5 mol (g-atom Pd)$^{-1}$ h^{-1}.

The possibility of the coupled oxidation of alkenes and carbon monoxide by molecular oxygen is determined by the same factor as for systems containing hydrogen peroxide, the oxo-complexes of molybdenum and tungsten being effective epoxidising agents. The idea of combining reaction (7) with the reactions

$$L'_nMO_r + H_2O_2 \xrightarrow{-H_2O} L'_mMO_{r-1}(O_2), \quad (8)$$

$$L'_mMO_{r-1}(O_2) + R{-}CH{=}CH_2 \xrightarrow{H_2O} L'_nMO_r + R{-}\underset{OH}{CH}{-}\underset{OH}{CH_2}, \quad (9)$$

arose. Here M = Ti(IV) or Mo(VI) and L' = Ph_3CO. It would thus be possible to achieve the catalytic process

$$CO + R{-}CH{=}CH_2 + O_2 + H_2O \xrightarrow[L'_nMO_r]{L_2PdX_2} CO_2 + R{-}\underset{OH}{CH}{-}\underset{OH}{CH_2}. \quad (10)$$

Experimental test showed that catalytic solutions containing phosphine complexes of palladium and oxo-complexes of molybdenum or tungsten permit the possibility of the coupled oxidation of carbon monoxide and propene to CO_2 and propylene glycol esters respectively. The most complete utilisation of hydrogen peroxide is attained when a mixture of acetic acid and acetic anhydride is used as the solvent. Thus the rate of formation of propylene glycol diacetate (the product of the interaction of epoxypropane or propylene glycol with acetic acid) was 3.6 mol (g-atom Pd)$^{-1}$ h^{-1} for a selectivity in the conversion of propene into this product of 56% in a system comprising (in mol litre^{-1}) $Pd(OAc)_2$ (5×10^{-3}), Na_3MoO_4 (5×10^{-2}), PPh_3 (5×10^{-2}) and $OPPh_3$ (0.1), using the $HOAc:AC_2O$ = 5:1 (by volume) solvent mixture, at 70 °C and a pressure of the $C_3H_6:CO:O_2$ = 1:1:1 gas phase of 1 atm.

In the absence of carbon monoxide, the rate of oxidation of propene is lower by two orders of magnitude than in its presence and the oxidation products are then exclusively carbonyl compounds. The oxidation of the alkene is in this case caused by the oxidation of PPh_3 by palladium(II) acetate, which leads to the formation of $Pd(PPh_3)_4$ and then $(PPh_3)_2PdO_2$. The latter oxidises the alkene in an acid medium to a carbonyl compound.[181]

Reaction (10) has also been achieved in the absence of a solvent, i.e. under the conditions of heterogeneous catalysis. The catalyst consisted of silica gel grains impregnated with PPh_3, $OPPh_3$, $Pd(OAc)_2$, and Na_2MoO_4, the composition of the gas mixture was $C_3H_6:CO:O_2$ = 1:1:1, the temperature was 90 °C, and the space velocity was 15000 h^{-1}. Epoxypropane was formed with a

selectivity up to 20%. The increase in space velocity to 100 000 h^{-1} increased the selectivity to 45%. In the absence of carbon monoxide from the gas phase, epoxypropane was not formed.

Both homogeneous and heterogeneous catalysts very rapidly lost their activity as a result of the occurrence of the PPh_3 oxidation processes.

The synthesis of diethyl ketone from ethylene, carbon monoxide, and water. If the stoichiometric reaction (2) proceeds via the intermediate formation of palladium hydride complexes (experimental proof of this when M = Pd, L = PPh_3, and X = CF_3COO has been published[182,183]), then one may expect that, under conditions ensuring the conversion of carbon monoxide, hydrogen and CO will be inserted in the ethylene double bond. Experimental tests showed[184] that the catalytic reaction involving the hydrocarbonylation of olefins to dialkyl ketones does indeed take place in this case:

$$2C_2H_4 + 2CO + H_2 \xrightarrow{Pd^{2+},PPh_3} C_2H_5{-}\overset{\overset{O}{\|}}{C}{-}C_2H_5 + CO_2. \qquad (11)$$

It is known that diethyl ketone is formed together with other oxygen-containing compounds via reaction (11) in the presence of $PdCl_2$ and pyridine dissolved in 12 M HCl at 195–220 °C and 550–650 atm.[185] In the catalytic system,[184] diethyl ketone is formed at an appreciable rate and with a fairly high selectivity (~80%) already at 30–70 °C and atmospheric pressure.

The addition of hydrogen to the CO + C_2H_4 gas mixture in the system[184] increases the selectivity and especially the rate of formation of diethyl ketone (DEK), which reaches 70 moles of DEK per gramme-atom of palladium per hour at the catalytic solution temperature of 70 °C and atmospheric pressure of the $C_2H_4:CO:H_2$ = 2:1:1 gas mixture. This composition is one of the most active among all the known catalytic systems for the synthesis of DEK from C_2H_4, CO, and H_2.

The catalytic synthesis of the DEK from ethylene, carbon monoxide, and hydrogen can be achieved by the gas-phase method using as the catalyst a solution of the phosphine complexes of palladium and an aromatic sulphonic acid injected into the pores of a mineral carrier, the example, silica gel. The highest selectivity in the formation of DEK (96%) and the highest activity (3 moles of DEK per gramme-atom of Pd per hour) at 80 °C and the $C_2H_4:CO:H_2$ = 1:1:2 composition of the gas phase were achieved using sulphosalicylic acid as the "deposited solvent".

Immobilised metal complexes and catalysts of reactions with participation of CO. The search for new catalytic compositions can be greatly extended using the idea of immobilising metal complexes on the surfaces of carriers. In this case, the synthesis of the catalyst reduces to deliberate construction on the carrier surface of a heterogeneous active centre having the composition and structure which we would have required in solution to effect the specified reaction and which cannot be obtained in solution owing to fundamental difficulties (insolubility, mutual deactivation of the components, etc.).[170,187]

When this approach is used, it is possible to synthesise immobilised active centres containing several different transition metal ions selectively activating definite substrates.

Immobilised phosphine palladium-cobalt complexes as catalysts of the hydroformylation of propene. Cobalt carbonyl complexes are known to be catalysts of the hydroformylation of alkenes. This process takes place under fairly severe conditions—at elevated pressure and temperature. The stage involving the decomposition of acylcobalt carbonyl on treatment with hydrogen, leading to the formation of the target product—an aldehyde, is assumed to be the slowest.[188]

Palladium complexes are known to be effective catalysts of the hydrogenation of both different organic and saturated groups and of metal–carbon bonds.[189] In this connection, the idea arose of using a bimetallic palladium-cobalt phosphine complex to facilitate the hydrogenolysis of the Co–C(O)R bond.

The attempts to realise this idea in the "homogeneous version" were not however successful owing to the high lability of the carbonylphosphine-palladium–cobalt complexes, which are rapidly converted into insoluble compounds. A "heterogenised version" of the synthesis of the heterogeneous palladium-cobalt active centre was therefore effected.

Without dwelling on the details of the "assembly" of such a centre on the silica gel surface (they have already been described[190]), we may note that the activity of the immobilised palladium–cobalt complex in the hydroformylation reaction did indeed greatly exceed the activity of the individual palladium and cobalt complexes. The formation of C_4 aldehydes and alcohols on the $\mathbf{P_3}PdCo_2(CO)_6$ catalyst [where $\mathbf{P_3}$ is the $-O-Si(CH_2CH_2CH_2PPh_2)_3$ ligand group immobilised on SiO_2] was observed already at 40 °C ($H_2:C_3H_6:CO$ = 1:1:1 gas mixture, pressure—3 atm), whereas the $\mathbf{P_3}Pd^0$ and $\mathbf{P_3}Co_2(CO)_6$ catalysts were completely inactive under these conditions. The selectivity in the formation of products with a normal structure reached 88% for the heterometallic complex.[190,191]

The following concept concerning the mechanism of the catalytic action of the heterometallic complex was formulated on the basis of the results obtained by kinetic and physicochemical research methods:[192,193]

the active centre incorporates palladium and cobalt atoms separated by a distance permitting their linkage via the CO bridge bond;

the activation of hydrogen and the alkene takes place at the palladium atom, where the alkyl fragment is also stabilised;

CO is activated following its insertion in the Pd–R bond at the cobalt atom, where the acyl fragment is also stabilised;

the hydrogenolysis of the Co–C(O)R bond takes place with participation of hydrogen activated at the palladium atom.

Thus the action of the bimetallic Pd–Co centre resembles that of a conveyor belt at which each participant performs his operation in the most professional manner: palladium hydrogenates and cobalt carbonylates; their closeness ensures the rapid transfer of the "half-finished product" from one to the other.

2. The hydrocondensation of formaldehyde on metal complexes

The hydrocondensation of formaldehyde,

$$nCH_2O + H_2 \rightarrow C_nH_{2n+2}O_n \qquad (12)$$

has attracted the attention of investigators as a possible method of synthesis of polyols from an extremely readily available raw material—formaldehyde and hydrogen. Reaction (12) is usually carried out in two stages.

(a) Condensation of formaldehyde to a "formose"—a mixture of carbohydrates in which the number of carbon atoms in the molecule is between 5 and 7:

$$nCH_2O \rightarrow C_nH_{2n}O_n. \qquad (13)$$

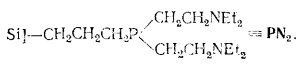
(b) Hydrogenation and hydrogenolysis of the "formose" to polyols, mainly to ethylene glycol, propylene glycol, and glycerol:

$$C_nH_{2n}O_n + H_2 \rightarrow C_2H_6O_2;\ C_3H_8O_2;\ C_3H_8O_3 + H_2O. \qquad (14)$$

The first stage—the condensation of formaldehyde to formose, discovered a long time ago by Butlerov, takes place readily in alkaline aqueous solutions and is catalysed by calcium hydroxide. Much more severe conditions are required to achieve the second stage (H_2 pressure 200 atm, temperature 230–280 °C, catalyst—copper-containing spinels).

The mechanism of the catalysis by calcium(II) ions of the condensation of formaldehyde has been fairly thoroughly investigated. It is believed that the growth of the carbon chain of the carbohydrate takes place when a formaldehyde molecule interacts with the enolic form of the carbohydrate molecule coordinated to a calcium(II) ion.[194] In this connection, the idea arose of introducing into the composition of the active centre for the condensation of formaldehyde a palladium ion, which is capable of catalysing the hydrogenation of the C=C bond of the enol and hence of effecting the synthesis of polyols via reaction (12) in a single stage under mild conditions.

The condensation of formaldehyde takes place in media at pH > 8. The application of the above idea in the "homogeneous" version is therefore difficult, since under these conditions the majority of transition metal ions, including palladium(II) ions, tend to form soluble hydroxides. Difficulties arise also when an attempt is made to apply this idea in the "heterogenised" version. Indeed, the heterogenisation of calcium(II) ions as active centres for the condensation of formaldehyde is problematical, since in alkaline media there is no suitable ligand for this ion with which it might be possible to immobilise it on the carrier surface. It therefore becomes necessary to replace the calcium(II) ion by the ion of another element, for example, chromium(III), which is very close to calcium(II) as regards some of its characteristics (octahedral coordination sphere, ionic radius about 1 Å). Taking into account the ability of chromium ions to form very stable complexes with amine ligands, which are stable in alkaline media, it was decided to use immobilised aminepalladiumchromium complexes to effect reaction (12). The phosphinoamine



was used as the ligand for the synthesis of a heteroatomic palladium–chromium complex. Here it was postulated that the phosphorus atom can serve as a site for the coordination of zerovalent palladium ions while, the ethylamine ligands coordinate chromium(III) ions.

An experimental test showed[194] that the immobilised palladium–chromium complex $PN_2PdCr(OH)_3$ does indeed exhibit an appreciable activity [2.1 mol H_2(g-atom Pd)$^{-1}$ h^{-1}] in reaction (12) under mild conditions (temperature 60 °C, H_2 pressure 1 atm, aqueous formaldehyde solution, HCHO concentration 0.1 M) in contrast to the immobilised monometallic palladium complex $P.Pd^0$ ($P = CH_2CH_2PPh_2$ ligand group immobilised on SiO_2) and the chromium complex $N_2Cr(OH)_3$ [$N_2 = CH(CH_2NEt_2)_2$ ligand group immobilised on SiO_2]. The yield of ethylene glycol amounted to 75% relative to the formaldehyde which had reacted.

The results of the study by physico-chemical methods of the state of palladium and chromium ions in the immobilised complexes and also the analysis of the observed kinetics permitted the conclusion that the synergistic effect is caused by the geometrical proximity in the heterometallic active centre of the fragments responsible for the condensation of formaldehyde and the stabilisation of the enolic form [amine complexes of chromium(III)], on the one hand, and for the activation of hydrogen and the hydrogenation of the C=C bond (phosphine complexes of palladium), on the other.

The preferential formation of ethylene glycol can apparently be explained by the higher rate of hydrogenation of the enolic form of glycolaldehyde compared with the rate of the interaction with the next formaldehyde molecule, leading to the synthesis of glyceraldehyde. The absence of catalytic activity for the hydrocondensation of formaldehyde of catalysts consisting of a mixture of immobilised phosphine complexes of zerovalent palladium and diamine complexes of chromium(III) can be explained by the fact that in this case the "palladium" and "chromium" fragments are not close to one another.

3. The reduction of CO_2 under mild conditions

The photosynthetic "fixation" of carbon dioxide by its reduction to carbohydrates, which occurs in all plants and photosynthesising micro-organisms, annually produces up to 10^{11} tonnes of complex organic substances.[196] An important feature of natural photosynthesis, which constitutes its advantage over the majority of industrial catalytic processes, is its occurrence under extremely mild conditions—close to room temperature and at normal pressures in aqueous solutions at a pH close to 7. The high selectivity of photosynthesis is also striking.

The photosynthetic fixation of CO is usually described by the overall reaction

$$CO_2 + 4H^+ + 4A^- \rightarrow {}^1/_6(C_6H_{12}O_6) + 4A, \qquad (15)$$

where A^- are strong one-electron reductants formed under the influence of light in the photocatalytic charge separation and capable of entering into reversible oxidation-reduction reactions.[196,197]

Naturally, at the present time there is as yet no acute need to reproduce reactions of type (15) on an industrial scale. Nevertheless, the interest in artificial systems capable of reducing CO_2 under mild conditions has increased significantly during the last decade. This is due primarily to the intense development of photocatalytic solar energy converters and the consequent natural endeavour to reproduce the principal chemical reactions underlying natural photosynthesis.[158,198] The solution, in principle, of the problem of the modelling of the photosynthesis in plants, where the reduction of CO_2 is coupled with the oxidation of water to O_2, is especially interesting. The reductants A^- in the photocatalytic systems being developed are as a rule photogenerated strong electron donors: either the reduced forms of several organic or metal complex compounds or the conductivity electrons of a series of semiconductors. Even more work has been carried out on systems in which the reductants A^- are generated by cathodes placed in the reaction volume.

It is noteworthy that studies on the reduction of CO_2 under mild conditions are still in the initial stage and are as a rule restricted to the consideration of the possibility of obtaining under such conditions only the simplest compounds—carbon monoxide, the formate ion, methanol, methane, and, rarely, oxalate and glycolate ions, etc.

The principal difficulties in achieving the reduction of CO_2 under mild conditions (in aqueous solutions of carbonate and/or bicarbonate ions or carbon dioxide at a low pressure of the latter)

can be observed even in a cursory analysis of the characteristic features of the process thermodynamics (Table 3). With the exception of the case of the eight-electron reduction of CO_2 to methane, the equilibrium electrochemical potentials of the reduction of CO_2 are significantly more negative than the equilibrium potential of the two-electron reduction of H^+ ions to molecular hydrogen. Thus the reduction of H^+ to H_2 is thermodynamically preferable to any CO_2 reduction process (with the exception of its reduction to methane). In view of the high energy content of the free products of the one-electron reduction of CO_2 as well as other reduced forms of CO_2 with an odd number of electrons,[202,203] the preparation of stable products necessitates the use of special catalysts ensuring the occurrence of multi-electron processes. As a consequence of the specificity of the characteristics of the CO_2 reduction processes mentioned above, these catalysts must be sufficiently selective to prevent the occurrence of the competing process involving the formation of molecular hydrogen.

Table 3. Standard electrode potentials $E°$ of certain H^+ and CO_2 reduction reactions in aqueous solutions at pH 0 (according to data in Refs. 199–202).

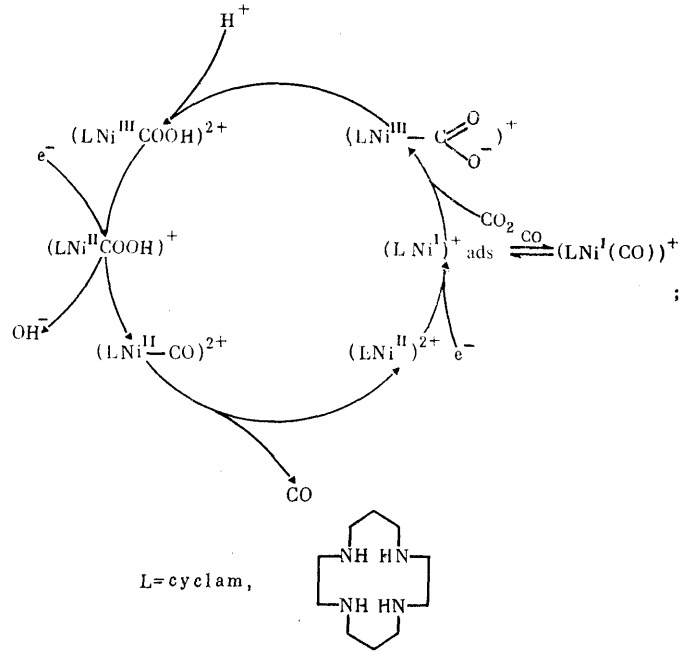
Electrode reaction	$E°$, V (w.r.t.n.h.e-de)
$2H^+ + 2e \rightarrow H_2$	0.00
$CO_2 + e \rightarrow CO_2^-$	−1.31
$CO_2 + 2H^+ + 2e \rightarrow CO + H_2O$	−0.12
$CO_2 + 2H^+ + 2e \rightarrow HCOOH$	−0.19
$2CO_2 + 2H^+ + 2e \rightarrow H_2C_2O_4$	−0.49
$CO_2 + 4H^+ + 4e \rightarrow HCHO + H_2O$	−0.11
$CO_2 + 6H^+ + 6e \rightarrow CH_3OH + H_2O$	−0.04
$CO_2 + 8H^+ + 8e \rightarrow CH_4 + 2H_2O$	0.17

The insufficient selectivity of metallic electrodes as catalysts has in fact precluded significant advances in the development of methods for the selective electrochemical reduction of CO_2 at these electrodes. As was to be expected, at noble metal and also iron and nickel cathodes, where the evolution of hydrogen takes place with a low overpotential, the current yield in the reduction of CO_2 does not usually exceed 10%. The selectivity in relation to the reduction of CO_2 is significantly higher when one uses electrodes made of non-noble metals such as Cd, Sn, Pb, In, and Zn, at which H_2 is evolved with a high overpotential.[204,205] Apparently molybdenum cathodes exhibit the greatest, almost 100%, selectivity in relation to the reduction of CO_2 (in particular to methanol), but this result is attained only at low current densities (up to 1 mA cm^{-2})[199] or when the process is carried out in aprotic solvents.[204,206]

The failures suffered when metallic cathodes were used necessitated the search for other catalysts of both homogeneous and electrode reduction of CO_2. At the present time definite progress has been achieved in this field, which has developed in the very recent years. A fairly wide range of compounds capable of acting as catalysts in the reduction of CO_2 in both electrochemical and photocatalytic systems have been discovered. As was to be expected, the coordinatively unsaturated complexes of certain variable valence metals, which readily incorporate a CO_2 molecule in their coordination sphere, are especially promising.[207,208] Homogeneous or heterogenised cobalt, nickel, and copper complexes with planar nitrogen-containing ligands such as porphins, phthalocyanines, and tetra-azamacrocycles exhibit the highest catalytic activity. For example, the water-insoluble phthalocyanine complex of cobalt(II) deposited on a graphite cathode, which has been investigated at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences, manifested a significant activity and selectivity in the electrocatalytic reduction of CO_2 to CO.

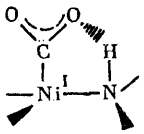
It has been suggested that, in the presence of catalysts of the above type, the reduction of CO_2 takes place in several stages and includes (1) the initial addition of a CO_2 molecule to the central atom of the metal complex subjected to preliminary reduction at the cathode and (2) the reduction of CO_2 and the subsequent release of the reaction products from the coordination sphere of the complex with regeneration of the initial form of the latter. Thus the following schematic catalytic cycle for the electrochemical reduction of CO_2 to CO (Scheme 2) has been proposed[209,210] in the case of a typical catalyst of this kind—the complex $Ni(cyclam)^{2+}$, where cyclam = 1,4,8,11-tetra-azacyclotetradecane.

Scheme 2



It has been established fairly reliably that the substrate for the formation of compounds with reduced forms of carbon does actually consist of CO_2 molecules and not of carbonate or bicarbonate ions from the solution. It has also been suggested that the reduction of CO_2 in the presence of the above catalyst is promoted by the two-centre coordination of the CO_2 molecule via an electrophilic centre (carbon atom) to the nickel(I) ion and via a basic centre (oxygen

atom) to the ligand hydrogen atom bound to nitrogen:



Nevertheless the selectivity in the reduction of CO_2 on the catalyst indicated cannot yet be regarded as entirely satisfactory: a considerable proportion of the reductant is consumed on the evolution of H_2 and not on the reduction of CO_2. Furthermore, CO and the simplest organic C_1 compounds predominate in the products of such reduction, as at metallic electrodes.

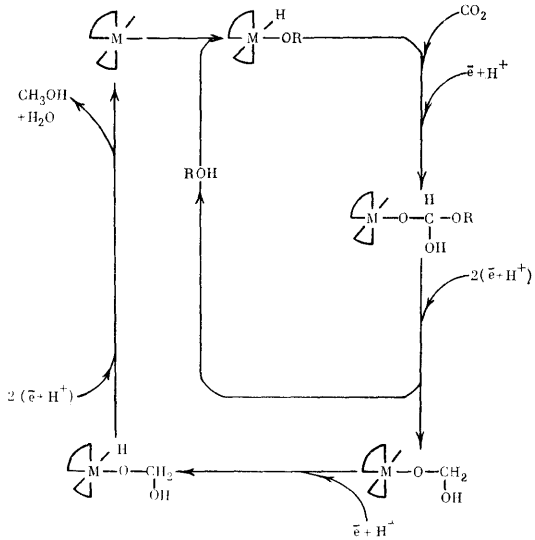
The impression has been created that the modest nature of the advances in devising artificial highly selective systems for the extensive reduction of CO_2 is associated with the fact that the direct reduction of the coordinated CO_2 molecule cannot be sufficiently effective by virtue of the specific thermodynamic features of the process noted above. Indeed, nature has followed another pathway, reducing carbon atoms not directly in the CO_2 molecule itself but in the products of the preliminary carboxylation of certain organic compounds, which can be regarded as cocatalysts of the CO_2 reduction process.

Thus in the classical "Calvin cycle"—a cyclic sequence of reactions leading to the fixation of CO_2 in many plants—the reduction of CO_2 is preceded by its binding to the phosphorylated sugar ribulose-1,5-diphosphate, which decomposes in the presence of the enzyme ribulose diphosphate carboxylase into two molecules of 3-phosphoglyceric acid; only this intermediate gives rise, when acted upon by a powerful reductant, to sugars as the final products with a high selectivity and liberates the initial substrate for carboxylation.

Thus one can assume that, in the development of artificial systems for the extensive reduction of CO_2, it is also useful to employ the reaction sequence "carboxylation of the organic substrate-cocatalyst—reduction of the intermediate carboxylic acid". The first experimental data indicating the reality of this approach have also appeared. Thus a study has been made[211-214] of the electrochemical reduction of CO_2 to methanol in the presence of homogeneous catalysts—the iron complexes of Tiron (1,2-dihydrobenzene-3,5-disulphonate) and oxalate and cyanide anions and chromium oxalate and chloride complexes. The electrochemical reduction took place at electrodes passivated with respect to the evolution of hydrogen by an insoluble but electrically conducting layer of Prussian Blue $KFe^{(III)}[Fe^{(II)}(CN)_6]$. It was observed that the process proceeds only in the presence of primary alcohols and under conditions such that the coordination sphere of the metal complex used as the homogeneous catalyst contains at least one labile ligand capable of being substituted by an alcohol molecule. For example, the aquated iron(III) pentacyanide with a labile water molecule in the first coordinated sphere is catalytically active, while iron(III) hexacyanide or nitroprusside does not show any catalytic activity. The primary alcohol molecule plays the role of a cocatalyst and the process itself is believed to proceed in accordance with Scheme 3. In this scheme, as in the photosynthetic fixation of CO_2, a carboxylated organic compound, coordinated to the homogeneous catalyst in the case considered, is reduced.

Presumably further development of this field will make it possible to create in the future fairly selective and therefore practically important systems for the extensive oxidation of CO_2 under mild conditions.

Scheme 3



* * *

Thus considerable progress has been achieved recently both in the search for new ways of converting one-carbon compounds and in the improvement of the traditional catalytic processes based on such compounds. It may be hoped that new processes using compounds with one carbon atom will be developed in the next few years and that those already introduced into industry will be significantly improved.

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