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Heterogeneous catalytic reactions of carbon dioxide

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Abstract. The most important classes of heterogeneous catalytic reactions involving CO_2 are examined: the incorporation of CO_2 in the C–C, C–H, and C–N bonds with formation of carbonyl- and carboxyl-containing compounds and oxidation of other compounds by CO_2. Reactions of the second class are more promising from the standpoint of the utilisation of carbon dioxide as a chemical raw material and from the standpoint of the solution of the ecological problems involving its utilisation from the gaseous waste discharged into the atmosphere.

The reactions involving the oxidation of C_1–C_7 hydrocarbons and C_1–C_2 alcohols by carbon dioxide, which have been investigated by the authors of this review, are examined in detail. Catalysts based on manganese oxides are most effective in these reactions. The bibliography includes 231 references.

I. Introduction

Considerable interest in the heterogeneous catalytic reactions of CO_2 has been aroused by two factors: (1) the need to combat the greenhouse effect and (2) the exhaustion of the available resources of carbon-based raw materials. We shall examine both these factors.

1. The ecological importance of carbon dioxide

In May 1992, 143 countries signed in Rio de Janeiro an agreement concerning the control of global warming and the reduction of the carbon dioxide waste discharged into the atmosphere. The largest emitter of carbon dioxide is the USA, where 26.7% of the entire carbon dioxide waste or about 1.6 billion tonnes annually is discharged into the atmosphere.[1]

A series of communications concerning the possible consequences of global warming have been published recently. In particular, the influence of the CO_2 waste on changes in the climatic zones on the territory of the former USSR has been considered.[2,3] At first sight, the conclusions reached do not appear very alarming. In most regions, with the exception of highly mountainous ones and possibly the very centre of European Russia, an increase in temperature by several degrees is more likely to have favourable rather than negative consequences: the amount of atmospheric precipitation and ultimately the agricultural productivity will increase; the possible flooding of coastal regions does not appear quite so alarming either.

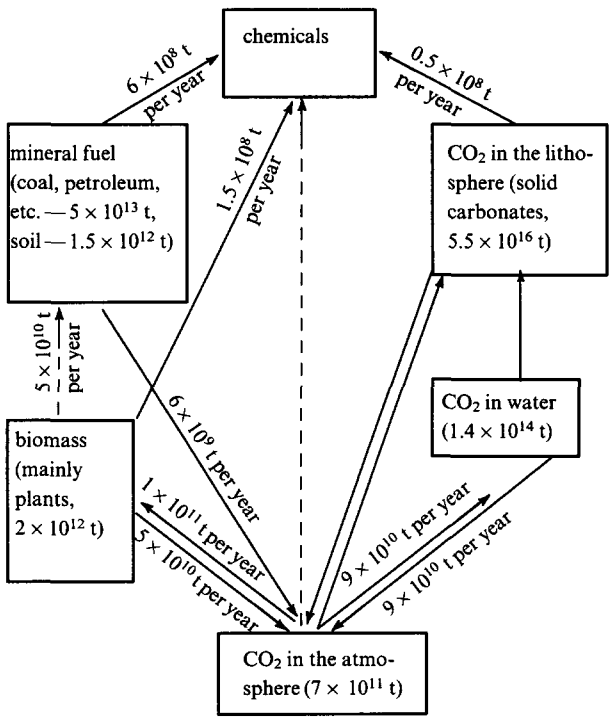
It has to be said that there exists also a different point of view on the consequences of the greenhouse effect. For example, it has been noted[4] that there have been periods during the Earth's history when the average content of CO_2 exceeded the current level by a factor of 5. The periods of the intense emission of CO_2 coincided with an intensification of volcanic activity and led to the rapid growth of numerous life forms. In discussions of this problem, Russian scientists have occupied a 'softer' position than foreign investigators. However, Russia cannot regard itself as an isolated society and if a decision has been reached at an international level (the Rio de Janeiro Conference) concerning the need to reduce the discharge of the greenhouse gases, then Russia — the third emitter of carbon dioxide after the USA and western Europe — must also inevitably participate in this process. We may likewise note that the CO_2 evolved will be partly absorbed by the hydrosphere, the lithosphere, and the biosphere (see the scheme overleaf). However, calculations have shown that such absorption will not compensate for the evolution. About 57% of the evolved CO_2 will remain in the atmosphere. A scheme illustrating the redistribution of carbon dioxide in natural objects is presented below (all the figures are quoted relative to carbon).

Carbon dioxide is not the only substance responsible for the greenhouse effect: the contribution of CO_2 is about 50%, 24% of the effect is due to the freons (chlorofluorocarbons) and N_2O, and 15% is due to methane. At the present time, vigorous research is being prosecuted throughout the world on the replacement of freons by other cooling agents, since freons decompose the ozone layer in the stratosphere. Since the methane molecule absorbs more solar radiation than the CO_2 molecule, the role of methane in the greenhouse effect may actually supercede that of CO_2 in the course of further development of industry and agriculture.

Considering the various methods for reducing the greenhouse effect, the well known Belgian scientist Delmon[5] noted that its

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diminution by 3% requires either (1) the reduction of the felling of forests by 25%, or (2) the abolition of all rice plantations, or (3) the destruction of all ruminants, or (4) the reduction of the world consumption of energy by 7%. Out of the four procedures examined, only the first and the fourth are realistic, although both are very hard to achieve. It is of interest that if one follows the third procedure, then calculations show that the aim of reducing the emission of greenhouse gases by 3% will not be attained. The reduction of the felling of forests and the development of atomic power are extremely important in this connection. One must also not fail to note that from the environmental point of view atomic power is greatly preferable to thermal power.

The waste gases from industry, electric power stations, and transport are powerful contaminants of the atmosphere. In terms of the scale of their harmful effect on the atmosphere, the automobile exhaust gases occupy the first place.[6] The most undesirable components of the exhaust gases are hydrocarbons, CO, and NO and nowadays the efforts of many scientific teams are directed to the fight against these gases. The problem of reducing the amount of CO_2 in exhaust gases is hardly considered.

Naturally, a partial solution of a large number of ecological problems, including the problem of the greenhouse effect, might be to abandon automobile transport as a means of individual mobility and to go over to collective types of transport. However, the world community is not yet ready for such a solution. One cannot rule out the possibility that this question will arise in the XXIst century if the existing trend towards the growth of population and energy consumption and also the impairment of the environmental situation continues.

2. Carbon dioxide as a raw material

The second reason for the increased interest in the chemical processing of carbon dioxide is its utilisation as a raw material. Regardless of the problem of the greenhouse effect, carbon dioxide should be regarded as an important source of chemical raw material in the future. The resources of petroleum and coal are being rapidly exhausted. At the present time, they are estimated as $(5-10)\times10^{12}$ t in terms of carbon. After petroleum and coal, the resources of natural gas are coming to an end. On the other hand, the total amount of CO_2 in the atmosphere and in the ocean is $\sim 1.5 \times 10^{14}$ t (in terms of carbon), i.e. is greater by 1.5 orders of magnitude, while its amount in the lithosphere is greater still — by two orders of magnitude (see the Scheme).

Despite the enormous amounts available, the widescale application of CO_2 as a raw material is hindered by its low concentration in the atmosphere, which is only 0.03% in the present day 'pre-greenhouse' atmosphere (338.6 ppm in 1980). In the lithosphere, CO_2 exists in a concentrated state in the form of natural carbonates, but the decomposition of carbonates requires the expenditure of large amounts of energy. The most promising source of CO_2 as a raw material are probably the waste gases as well as natural gases. The CO_2 content in the natural gas from certain deposits reaches 30%.

In order to stimulate studies on the chemical utilisation of CO_2, it has been proposed in the USA to introduce a special tax on the consumption of fuel amounting to 13 dollars (at 1992 prices) per barrel of the petroleum equivalent (or 57 dollars per tonne of conventional fuel). If the aim is to achieve a 10% reduction of the discharge of CO_2 by 2010, then for a discharge amounting to 8.17 billion tonnes the tax will have to be increased to 44 – 155 dollars per barrel, which will impose a heavy burden on tax payers.[7]

At the end of September 1991, after two year discussions, the European Community adopted a differentiated tax on energy consumption, which will continuously increase from 1993 until 2000. The aim is to stabilise the discharge of CO_2 at the 1990 level.[8]

A major programme concerning the utilisation of CO_2 has been adopted in Japan.[9] Most attention is devoted to chemical methods for the processing of CO_2. The possibility of its being pumped into subterranean strata in order to increase the extraction of petroleum and also of its pumping into the ocean is considered. The latter variant can be achieved, in particular, with the aid of CO_2-fixing microorganisms. The majority of the projects presuppose the pumping of CO_2 into deep layers of the ocean (deeper than 1000 m). Under such conditions, the hydrates $CO_2.nH_2O$ ($n = 5 - 6$), which prevent the dissolution of carbon dioxide in water, are formed at the CO_2 – oceanic water interface.[10]

Thus the need both to combat the greenhouse effect and to employ new forms of raw material in industry requires the chemical processing of large amounts of CO_2. In pure form, carbon dioxide is so far little used. It is employed as a solvent, as an extractant, as a cooling agent, and also for the generaton of a carbon dioxide atmosphere in greenhouses.

II. Utilisation of carbon dioxide

1. Carbon dioxide in the chemical industry

The largest industrial consumers of CO_2 are the producers of carbamide, calcined soda, and salicylic acid. In all these industries, CO_2 is obtained not from the atmosphere but from secondary industrial gases and from solid carbonates (mainly from limestone). The question of the utilisation of the CO_2 evolved on combustion of fuel has so far simply not been part of technological plans.

The world output in the production of carbamide (urea) is 110 million tonnes annually. Carbamide is formed when CO_2 reacts with ammonia under a pressure of 200 atm at 200 °C.

$$2NH_3 + CO_2 \rightleftharpoons NH_4COONH_2 \rightleftharpoons (NH_2)_2CO + H_2O$$

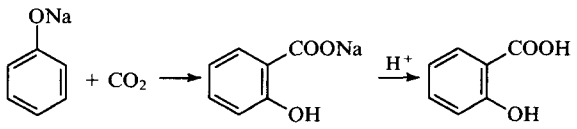
The production of carbamide is a good example of the employment of CO_2 not from an external source but from the resources of the same factory. After the conversion of CO by treatment with steam, hydrogen is used to synthesise ammonia, whilst CO_2 is directed to the manufacture of carbamide.

Another major industry involving the use of CO_2 as the raw material is the preparation of calcined soda by the Solvay method. The world production of cancined soda is about 30 million tonnes annually. Together with CO_2, the reactants are NaCl (in the form of a brine) and ammonia.

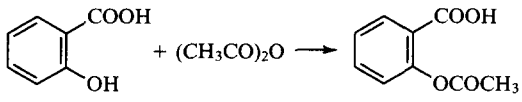
$$NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl$$

Calcined soda is obtained by the heat treatment of $NaHCO_3$, whereupon CO_2 and H_2O are evolved.

The manufacture of salicylic acid is not quite such a large scale process. It is synthesised by carboxylating phenol under pressure (the Kolbe–Schmitt reaction).

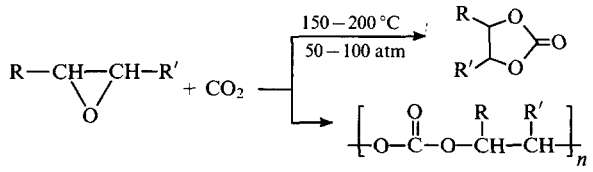


Aspirin (acetylsalicylic acid) is obtained from sallicylic acid.



In 1990, 25 000 tonnes of aspirin were produced in the USA.

A new rapidly developing field in which CO_2 is utilised involves the syntheses of organic carbonates. They are obtained by the interaction of oxiranes with CO_2 in the presence of inorganic and organic halides.

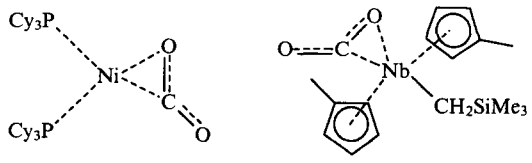


Organic carbonates are used as solvents and extractants, whilst polycarbonates are employed as constructional mateirals.

The examples quoted above virtually exhaust the applications of CO_2 in the chemical industry. On the other hand, scientific research has shown that carbon dioxide can enter into numerous reactions and can serve as the starting material for the synthesis of a series of useful chemical products. Disregarding the evident possibility of using CO_2 for the neutralisation of bases, we shall consider reactions involving the incorporation of CO_2 in transition metal complexes.

2. Carbon dioxide in transition metal complexes

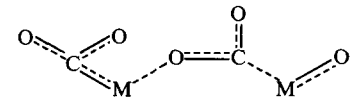
Comnparatively few studies are known in which the binding of CO_2 as a ligand in transition metal complexes has been observed (see the relevant review[11]). Thus the stable nickel complex **1**[12] and the stable niobium complex **2**[13,14] have been described.



1 **2**

Cy = cyclo-C_6H_{11}.

Nonasssociative CO_2 complexes have also been found on the surfaces of transition metal.[15,16] For example, the study of the adsorption and desorption of CO_2 and $CO^{18}O$ on K/Ag(111) by Auger spectroscopy, electron energy loss spectroscopy (EELS), and other methods[15] made it possible to detect both associated and undissociated CO_2 complexes.



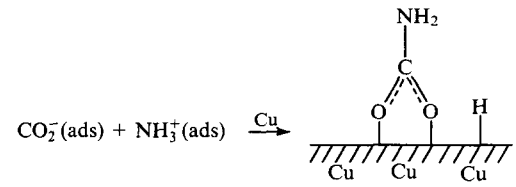
The energy of the bond between CO_2 and the metal in such complexes is low; for example, it is 34.3 kJ mol^{-1} in the complex $W(CO)_5CO_2$.[17] The study of the adsorption of CO_2 on crystalline potassium showed[18] that this entails the formation of oxalate ions $C_2O_4^{2-}$, which permeate under the potassium layer. They decompose into CO_3^{2-} and CO. Complexes similar to those indicated above have been found on potassium-promoted rhodium.[19]

It has been demonstrated by X-ray photoelectron spectroscopy (XPES) and EELS that CO_2 is not chemisorbed on the Cu(100) and Zn(0001) faces of metallic single crystals.[20] The coefficient of the adhesion of CO_2 to these faces is exceptionally low (their lifetime is $\sim 10^{-10}$ s at 20 °C). However, as a result of electron transfer, chemisorbed complexes are formed in the presence of ammonia.

$$CO_2(gas) + e \rightleftharpoons CO_2^-(ads),$$

$$NH_3(gas) \rightleftharpoons NH_3^+(ads) + e,$$

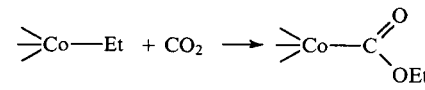
These interact with one another and give rise to adsorbed carbamate.



3

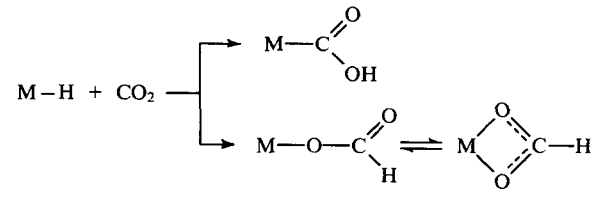
The bidentate carbamate **3** is inclined relative to the surface, so that the two O atoms are nonequivalent. It is of interest that the interaction of CO_2 with H_2O under these conditions does not lead to their joint adsorption.

There have been appreciably more studies on the incorporation of CO_2 in transition metal complexes (Co, Ni, Rh, Pd, Pt, Ir, Cu, etc.) in the M–C, M–H, M–O, and M–N bonds (where M = transition metal).[21,22] When CO_2 is inserted in the M–C bond, carboxylate complexes are formed. For example, the ethyl ester of the metalcarboxylic acid was obtained in the reaction of CO_2 with ethylcobalt.[23,24]

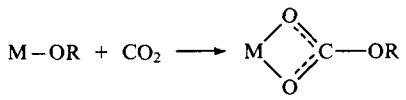


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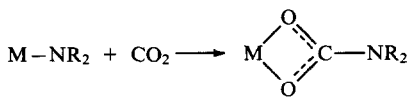
When the carboxylate complex **4** was treated with methyl iodide, ethyl acetate was obtained in a high yield. The carboxylate complexes of Cu, Zn, Ti, Zr, Mn, Fe, Co, Ni, and Rh have been synthesised similarly.[13] The insertion of CO_2 into the M–H bond leads to the formation of formate complexes and in certain cases of metalcarboxylic acids (see, for example, Kolomnikov et al.[24]).



The insertion of CO_2 into the M–O bond results in the formation of complexes with carbonic acid monoesters.



Finally, the insertion of CO_2 in the M–N bond leads to the corresponding carbamate complexes.[14,21]

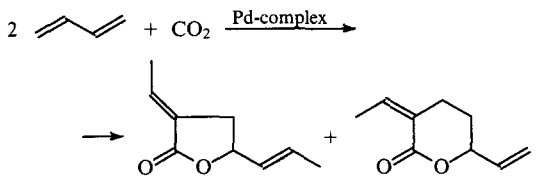


The interaction of CO_2 with organic compounds at the C–H bond constitutes the basis of the catalytic syntheses of carboxy-compounds: acids, esters, lactones, etc. For example, propionic acid and its ethyl ester have been obtained by carboxylating ethene at a high pressure and a temperature of 165 °C on a rhodium complex promoted by hydrogen halides.[25]

$$H_2C{=}CH_2 + CO_2 \xrightarrow[150-700\ atm]{\text{Rh-complex}} CH_3CH_2COOH + CH_3CH_2COOC_2H_5$$

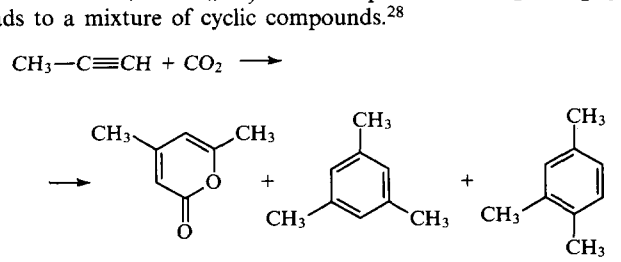
The simultaneous coordination of CO_2 and C_2H_4 to the complex $PtCl(SnCl_3)(PPh_3)_2$ deposited on SiO_2 led to the formation of methyl 3-hydroxypropionate.[26]

The carboxylation of saturated hydrocarbons constitutes an attractive reaction, which, however, is not favoured energetically. The preparation of carboxylic acids in the cracking of $C_{12}-C_{40}$ hydrocarbons in the presence of CO_2 has been described.[9] The interaction of ethyne and diene hydrocarbons with CO_2 affords cyclic compounds.[27]



Cyclic carbonates are formed readily in the interaction of CO_2 with epoxides in the presence of Zn, Ni, Sn, Mg, Al, etc. compounds.

The interaction of CO_2 with methylethyne under a 60 atm pressure on Rh_4 and Fe_xRh_y clusters deposited on SiO_2 or Al_2O_3 leads to a mixture of cyclic compounds.[28]



A surface carbonate is an intermediate.

A number of examples of the use of CO_2 as a cocatalyst for the modification of homogeneous and heterogeneous catalysts are known. For example, CO_2 has been used effectively to regulate the catalytic activity and selectivity of zeolitic catalysts.[29] Carbon dioxide can alter appreciably the activity and selectivity of many catalysts for the oxidative condensation of methane.[30] In the presence of CO_2, oxygen alters the oxidative properties of Fe and Ru complexes.[31]

The examples presented above show that recently CO_2 has been used increasingly for the modification of homogeneous and heterogeneous catalysts. All the catalytic reactions with participation of these complexes which have been investigated belong to the class of reactions in which CO_2 is inserted into C–H, C–O, and C–N bonds. We shall not consider them in detail since they have been described in the reviews mentioned above.

Thus carbon dioxide can enter into numerous reactions and can serve as the starting material for the syntheses of a number of useful chemicals, i.e. the concept of the 'inertness' of CO_2, which existed for a long time, proved to be a myth. Nevertheless, the reactions listed above do not solve the problem of not only the reduction of the emissions of CO_2 but also of its large-scale employment as a raw material. In all these cases, the involvement of CO_2 in a reaction requires large amounts of another fairly expensive and environmentally unfriendly compound (ammonia, phenol, etc.).

The oxidation–reduction reactions in which CO_2 is used as the oxidant are more promising for large scale application. In this case, cheap reductants, mainly hydrocarbons found in natural raw materials (gas, petroleum) or which can be readily obtained from them (coal), could be involved in the reaction with CO_2.

III. Interaction of carbon dioxide with hydrogen

Hydrogen might become the best reductant for carbon dioxide. The most important reactions of CO_2 with hydrogen are the Sabatier reaction [reaction (1)], the Bosch reaction [reaction (2)], the reverse conversion of water gas [reaction (3)], and the syntheses of methanol [reaction (4)], dimethyl ether [reaction (5)], and formic acid [reaction (6)].

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O, \quad \Delta H_{298} = -164.1\ kJ\ mol^{-1}, \tag{1}$$

$$CO_2 + 2H_2 \rightleftharpoons C + 2H_2O, \quad \Delta H_{298} = -14.6\ kJ\ mol^{-1}, \tag{2}$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O, \quad \Delta H_{298} = 42.3\ kJ\ mol^{-1}, \tag{3}$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O, \quad \Delta H_{298} = -49.4\ kJ\ mol^{-1}, \tag{4}$$

$$2CO_2 + 6H_2 \rightleftharpoons CH_3OCH_3 + 3H_2O, \quad \Delta H_{298} = -112.2\ kJ\ mol^{-1}, \tag{5}$$

$$CO_2 + H_2 \rightleftharpoons HCOOH, \quad \Delta H_{298} = 16.7\ kJ\ mol^{-1}. \tag{6}$$

Reactions (1), (2), (4), and (5) are exothermic whilst reactions (3) and (6) are endothermic.[32] In all the reactions listed above, except reaction (6), between one and three water molecules correspond to one molecule of the target product (CH_4, C, CO, CH_3OH, CH_3OCH_3), i.e. a considerable proportion of the expensive hydrogen is consumed on the formation of the cheap and useless water.

1. Synthesis of hydrocarbons

Although the Sabatier reaction (1) leads to the formation of the cheap methane, it is nevertheless frequently used to remove CO_2 from technological gases ('methanation of CO_2').[33] This reaction proceeds at temperatures above 200 °C in the presence of various catalysts, the best of which are ruthenium or nickel on carriers. Depending on the design of the reactor, the process can take place in various regimes: from isothermal to autothermal with a large or small temperature drop across the catalyst bed.[34] Above 590 °C, the equilibrium in reaction (1) shifts to the left: the steam conversion of methane is observed.

A catalytic activity series has been obtained[35] for noble metals deposited on Al_2O_3 and used as catalysts in the reaction under consideration: Ru > Rh > Pt = Ir = Pd. Ruthenium also proved to be the most active of the metallic catalysts deposited on SiO_2: Ru > Co > Ni > Fe.[36] Ruthenium catalysts deposited on membranes are good methanation catalysts.[37] The study of nickel and cobalt catalysts deposited on carbon, Al_2O_3, and SiO_2 showed that the cobalt catalysts on carbon are the most active in

the methanation of CO_2.[38] The lanthanum–nickel alloys are also highly active.[39]

Oxide catalysts are less effective in this process. The spinels $La_{1-x}M_xCoO_3$ (M = Sr or Th) become active in the hydrogenation of CO_2 only after the formation of metallic cobalt.[40] Rhodium accelerates the hydrogenation of CO_2 in CH_4 on the Fe–Mn–O catalyst, while lanthanum slows down the process. In the presence of rhodium, CO_2 is apparently activated by the oxide component, while H_2 is activated by the metallic rhodium.[41]

A similar separation of functions is characteristic also of metals deposited on oxides. When the carrier in the Rh/CeO_2 [42,43] and Pd/CeO_2 [44] catalysts is reduced to Ce_2O_3, the latter acquires the ability to accept CO_2 as a result of the formation of vacancies in the oxide lattice. On the other hand, hydrogen dissociates on rhodium and further methanation takes place. Catalysts obtained by the 'reverse' method — the deposition of the oxides of Al, Zr, Nb, Ta, and W on rhodium foil — have been investigated.[45,46] It was found that AlO_x and FeO_x inhibit the hydrogenation of CO_2, whilst the remaining oxides accelerate it. The authors explain this acceleration by the formation of an anionic vacancy at the metal–oxide interface. The degree of reduction of the oxide in the hydrogenation of CO_2 is greater than in the hydrogenation of CO owing to the higher concentration of H on rhodium. The authors[46] observed a correlation between the acidity of the deposited oxide and the catalytic activity. This was explained by the fact that, in the adsorption of CO or CO_2 molecules on the metal–oxide interface, they are oriented with their oxygen atoms towards the acid Lewis centre. In the case of the Pt/CaO and Pt/MgO catalysts, the alkaline earth metal oxide accepts CO_2, affording CO_3^{2-}, while H_2 dissociates on Pt.[47]

When the hydrogenation of CO_2 is compared with that of CO on metallic catalysts, two interesting features are noted: (1) the rate of hydrogenation of CO_2 to methane appreciably exceeds the rate of methanation of CO; (2) whereas higher hydrocarbons are formed together with methane in the hydrogenation of CO, methane is formed with an almost 100% selectivity in the hydrogenation of CO_2.[48–55]

Only methane is obtained on an iron foil, CO_2 being hydrogenated seven times faster than CO.[52] The activation energy for the methanation of CO_2 on Ru/Al_2O_3 was appreciably lower than that for the methanation of CO.[53] The submonolayer deposition of TiO_2 on rhodium increases the rate of hydrogenation of CO_2 by a factor of 15 and that of CO only by a factor of 3.[48] The selectivity in the conversion of CO_2 into methane on a cobalt foil was 99%, while that in the conversion of CO into methane was only 80%.[54]

All these facts show that CO_2 is reduced to methane via the intermediate formation of CO.

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

$$CO + 3\,H_2 \rightleftharpoons CH_4 + H_2O$$

The complete dissociation of CO and subsequent hydrogenation of C(ads) and O(ads) are necessary for the synthesis of methane and other hydrocarbons.[56]

According to Gupta et al.,[55] the lower temperatures of the methanation of CO_2 compared with CO on Ru/TiO_2 can be explained by the higher reactivity of the metal carbonyls formed initially, the latter being rapidly converted into reactive carbon atoms.

The rate of reduction of CO_2 on the reduced Fe/Al_2O_3 and Re/Al_2O_3 catalysts under thermoprogrammed conditions increases sharply after the addition of 1%–3% of H_2. For example, the interaction of CO_2 with 8% Fe/Al_2O_3 begins at 520 °C when 1%–3% of H_2 is added to the reaction mixture and not at 740 °C, as happens in the absence of H_2. Under these conditions, the rate of reaction increases by a factor of 20–25.

According to the data of Highfield at al.,[58] after the addition of H_2 a new path arises in the interaction of CO_2 and Fe, resembling a chain reaction and requiring a lower activation energy.

$$Fe + 0.5H_2 \rightarrow Fe(H) \quad (8)$$

$$Fe(H) + CO_2 \rightleftharpoons FeHCOO \quad (9)$$

$$FeHCOO + Fe \rightarrow FeO + Fe(H) + CO \quad (10)$$

$$CO_2 + Fe \rightarrow FeO + CO$$

Reaction (8) corresponds to the 'initiation', whilst reactions (9) and (10) correspond to the 'propagation' of the chain reaction. One hydrogen molecule can ensure the conversion of many CO_2 molecules. It is suggested that a surface formate is an intermediate. To test this hypothesis, formic acid was deposited on the surface of iron and rhenium, after which an increase in the rate of methanation was observed.

On the rhenium catalyst in the presence of hydrogen, the Boudouard reaction is also accelerated.

$$CO_2 + C \rightarrow 2CO$$

When 1%–3% of H_2 was added to the stream of CO_2, the rate of conversion of the latter increased by a factor of 20, while the coke oxidation temperature fell by 200 °C.

It is also possible to formulate a chain mechanism of the Boudouard reaction. For this purpose, stage (10) in Schemes (8)–(10) must be replaced by the stage

$$FeHCOO + FeC \rightarrow Fe + Fe(H) + 2CO. \quad (11)$$

In this case, the 'initiation' is evidently again ensured by reaction (8), whilst 'chain propagation' is effected by reactions (9) and (11). At higher H_2 concentrations, reaction (3) takes place on Fe and Re.

The complexes Ru(H)CO, RuOCO, RuCO, and RuHCOO have been detected in an IR spectroscopic study of the $CO_2 + H_2$ reaction on Ru/TiO_2 [49] and Ru/Al_2O_3.[50] However, in most cases these complexes are present on the surfaces of the Al_2O_3, SiO_2, and TiO_2 carriers. In the most detailed studies, the rate of formation of CH_4 was compared with the rate of change in the intensities of the IR bands due to the intermediate adsorption complexes. For example a correlation between the concentration of adsorbed CO and $HCOO^-$ and the rate of methanation has been observed on Ru/TiO_2.[51,52] Hence it was concluded that the reaction has a dissociative mechanism (in the scheme below the symbol 'm' denotes the metal and the symbol 'c' denotes the carrier):

$$CO_2(gas) \rightleftharpoons CO_2(m),$$

$$H_2(gas) \rightleftharpoons 2H(m),$$

$$CO_2(m) + 2H(m) \rightleftharpoons HCOOH(c),$$

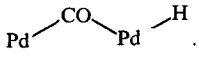
$$HCOOH(c) \rightleftharpoons H(m) + HCOO(c),$$

$$HCOOH(c) \rightleftharpoons CO(m) + H_2O,$$

$$CO(m) + 6H(m) \rightarrow CH_4 + H_2O.$$

On the Rh/Al_2O_3 catalyst, formates are intermediates in reaction (3) and the CO formed in this reaction undergoes methanation.[53] According to the data of Lahtinen et al.[54] and Gupta et al.,[55] the adsorption of H_2 on Rh/Al_2O_3 promotes the adsorption of CO_2, since this involves the formation of the formate, which may decompose into H_2O and CO on Rh or migrate on Al_2O_3, where it is more stable. On Rh/SiO_2, the formate is formed only in the presence of potassium.[56]

An increase in the degree of adsorption of CO_2 in the presence of H_2 has also been observed on deposited palladium,[57] where the complex



is formed. The formation of the formate, which occurs only in the presence of a carrier, is ensured by the spill-over of H atoms.

The formation of formate complexes has been observed by the IR spectroscopic method under the conditions of the interaction of H_2 and CO_2 on deposited ruthenium,[58,59] rhodium,[60-64] and palladium,[65] and nickel.[66]

The study of the interaction of H_2 with CO_2 on Ni(111) [67] and Cu(100) [68] single crystals and also on deposited nickel catalysts,[69,70] with the aid of various spectroscopic methods, showed that formate complexes are formed on their surfaces, their further reactions leading to the evolution of CO and H_2:

$$CO_2(ads) + H(ads) \rightleftharpoons HCOO(ads), \quad (12)$$

$$HCOO(ads) + H(ads) \rightleftharpoons H_2O + CO. \quad (13)$$

Reactions (12) and (13) apparently proceed simultaneously with the methane formation reaction, which require the complete dissociation of CO_2 and H_2 on adsorption.

The formation of higher hydrocarbons in the hydrogenation of CO_2 has been noted in comparatively few studies. For example, an increase in the heat treatment temperature of the Rh/Nb_2O_5 catalyst for the hydrogenation of carbon dioxide promotes an increase in the selectivity in the formation of C_2H_6 compared with CH_4.[71]

The carbides Mo_2C, Fe_3C, and VC proved to be active in the hydrogenation of CO_2;[72] the carbides TiC and SiC are inactive. C_1-C_3 hydrocarbons as well as CO and alcohols are formed in this process. Promotion with copper increases the selectivity in the formation of hydrocarbons.

When a mixture of iron and carbon powders is ground in a ball mill, a mixture of iron carbides is formed. The selectivity in the hydrogenation of CO_2 on this catalyst changes: instead of CO [reaction (3)], C_2-C_4 hydrocarbons and CH_4 are formed. With increase in the duration of grinding, the rate of reaction also increases and the alkanes : alkenes ratio diminishes from 0.37 to 0.16.[73]

On iron catalysts, higher hydrocarbons are formed apparently only in the presence of iron carbide.[74] On Fe-silicalite, higher hydrocarbons were not detected on hydrogenation of CO_2. This has been explained by the difficulty of reducing Fe, which hinders the formation of carbides.[75]

On polycrystalline cobalt, C_1-C_4 hydrocarbons were isolated on hydrogenation of CO, whilst methane and ethane were isolated on hydrogenation of CO_2.[54] The selectivity in the formation of CH_4 on the spinels $La_{1-x}M_xCoO_3$ (M = Sr or Th) increases with increasing degree of reduction, whilst the selectivity in the formation of C_2H_6 falls.[40]

2. The Bosch reaction

This reaction has been used in life support systems for the removal of CO_2 in the form of solid carbon.[34] It is employed also for the preparation of filamental carbon fibres.[76] Reaction (2) can be represented as the sum of reaction (1) and the catalytic cracking of methane:

$$CH_4 = C + 2H_2 \quad (14)$$

The dissociation of CH_4 on nickel proceeds rapidly even at 345 °C.

Reactions (1) and (14) can be carried out in a single reactor, where provision is made for the recirculation and isolation of water from the cycle. Depending on the nature of the catalyst (Ni, Co, Fe), pressure, and the number of times the recirculation has been carried out, the process is performed at temperatures ranging from 500 to 700 °C. There is also a possibility of another variant, where CH_4 is decomposed to $C + 2H_2$ at 500 °C on Ni/SiO_2 in the first reactor, whilst in the second reactor CO_2 is methanated on the same catalyst at 300 °C, after which methane is returned to the first reactor. Filamental carbon is formed, in which Ni remains at the tip of the filament so that the activity is maintained at an unchanged level.[77]

CO_2 has also been reduced to carbon on iron, gallium, and zinc oxides and also on $LaFeO_3$.[78] The yield of carbon on WO_3 at 700 °C was 27%. Graphite was formed in the form of small isolated spots.

3. The reverse conversion of water gas

Reaction (3) proceeds on the same catalyst as the forward conversion of water gas but at a higher temperature (the equilibrium constant exceeds unity only above 530 °C).

The hydrogenation of CO_2 on oxide catalysts (in contrast to metallic catalysts) does not proceed as far as methane but only as far as CO. On oxides, the rate of hydrogenation of CO_2 is lower than the rate of hydrogenation of CO. Among the catalysts, mention should be made of the familiar iron–chromium oxide catalyst for the conversion of water gas. The selective reduction of CO_2 to CO has also been observed on Fe/MgO and Cu/ZnO [79] as well as Fe/C.[80] In addition, new active and selective catalysts for the reduction of CO_2 to CO, such as MoS_2 [81] and WS_2,[82] have been discovered.

Surface formates are produced as intermediates in reaction (3). However, there are data showing that the reaction proceeds via different surface compounds in the forward and reverse directions.[83]

In the hydrogenation of CO_2 on the chromium–manganese oxide catalyst, the only product is CO.[57] The formation of methane is observed only after the deposition of HCOOH on the surface. The mechanism of the reduction of CO_2 includes the interaction of H_2 with the carbonate structures formed initially:

$$H_2 + CO_3^{2-} \rightleftharpoons H_2O + CO + O^{2-}, \quad (15)$$

$$H_2 + O^{2-} \rightleftharpoons H_2O + [\ ], \quad (16)$$

where [ ] denotes a vacancy.

4. The synthesis of methanol and other oxygen-containing compounds

It is technologically inconvenient to synthesise methanol directly via reaction (4), since one third of hydrogen is consumed in the formation of water. The $CO + 3H_2$ mixture is therefore usually employed for the synthesis of methanol:

$$CO + 3H_2 = CH_3OH \quad (17)$$

For a long time, the zinc-chromium oxide catalyst, on which the process occurred with a high productivity at 320–400 °C and a pressure of 300 atm, was mainly used. In the 1960s–1970s new more active copper–zinc oxide catalysts, which made it possible to reduce the temperature to 250 °C and the pressure to 100 atm, were introduced into practical employment.

It was believed[84] that methanol is synthesised via the intermediate hydrogenation of CO. However, the use of the labelled $^{14}CO_2$ and ^{14}CO molecules showed[85] that in reality the species hydrogenated is not CO but the CO_2 formed from the latter. Careful elimination of CO from CO_2 and H_2O sharply reduced the rate of synthesis of methanol and only the formation of CO_2 via the water gas conversion reaction leads to the establishment of a stationary regime in the process. The rate of synthesis of methanol from CO_2 is many times higher than from CO.[86] This enabled the authors[87,88] to reach an unambiguous conclusion about the reaction paths of carbon oxides on oxide catalysts. According to their view, methanol is synthesised in two macroscopic stages. In the first stage, CO is converted by treatment with steam and this is followed by reaction (4).

It has been suggested that up to 5% of CO_2 be added to the synthesis gas in the industrial manufacture of methanol.[10]

The study of the kinetics and mechanism of the $CO_2 + H_2$ reaction on copper–zinc oxide catalysts permitted the conclusion that it proceeds via adsorption substitution stages.[89] Stable surface compounds participate in the reactions

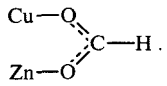
$$X \cdot H_2O + CO_2 \rightleftharpoons X \cdot CO_2 \cdot H_2O \rightleftharpoons X \cdot CO_2 + H_2O,$$

$$X \cdot CO_2 \cdot H_2O + CO \longrightarrow X \cdot CO_2 \cdot H_2 + CO_2,$$

$$X \cdot CO_2 + H_2 \longrightarrow X \cdot CO_2 \cdot H_2 \xrightarrow{2H_2} CH_3OH + X \cdot H_2O,$$

where X is a copper-containing surface centre, which is not part of the copper phase, for example a doublet of copper ions in the zinc oxide lattice.[88] The $X.H_2O.CO_2$ species may comprise the hydroxocarbonate and OH^- ions bound to a single X centre; this complex is hydrogenated to CH_3OH already at 120 °C. However, it is insufficiently stable above 200 °C and most probably does not participate in the synthesis of CH_3OH. The high-temperature chemisorption of CO_2 precedes the formation of CH_3OH and the only path leading to its formation is the adsorption substitution of H_2O.

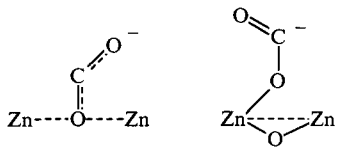
According to the results of Jackson[90] and Walker et al.,[91] the adsorption of CO_2 is dissociative under the conditions of the synthesis of methanol. IR spectroscopy in situ[92–97] made it possible to detect the surface formates, bicarbonates. and carbonates on the surfaces of the $Cu-ZnO-Al_2O_3$ and $Cu-ZnO-SiO_2$ catalysts. $HCOO^-$ complexes have been detected on ZnO and Al_2O_3. There are also data indicating the formation of the bidentate formate



at the interface.

According to Amenomiya and Tagawa,[95] the activity of the catalyst in the synthesis of methanol from CO_2 and H_2 is proportional to the $HCOO^-$ concentration on copper. On the other hand, the $HCOO^-$ concentration on aluminium remains unchanged under the conditions of the catalytic reaction.

After the adsorption of CO_2 on ZnO/SiO_2 and $Cu-ZnO/SiO_2$, two complexes were detected,[94] one of which is bound to the polar surface (**A**) and the other to the nonpolar surface (**B**).



A **B**

Complex **B** is more readily hydrogenated to the formate. Further hydrogenation results in the formation of $CH_3O.Zn$ and CH_3OH. The function of the polar surface consists in the dissociation of H_2 and the supply of H atoms for the hydrogenation of complex **B**. The addition of CO to the $CO_2 + H_2$ mixture inhibits the formation of the formate as a result of the re-reduction of the surface.

Carbonates, bicarbonates, and the CH_3O and CH_2O groups have been detected by NMR on the surfaces of the catalysts under the conditions of the synthesis of methanol from CO_2 and H_2.[98]

Apart from $Cu-ZnO/Al_2O_3$, Cu/ZrO_2 and $Cu-ZnO/ZrO_2$,[99–101] as well as Cu/Ga_2O_3, Cu/Cr_2O_3, and $Cu-ZnO/Ga_2O_3$[95,102] are also active and selective catalysts for the hydrogenation of CO_2 to methanol. It has been shown[102] that Al_2O_3 and ZrO_2 are the true carriers: they increase the surface of the catalyst but do not affect the specific activity of copper. On the other hand, Ga_2O_3 increases the specific activity of copper by 40% and that of Cr_2O_3 by 30%.

Copper is stabilised on the surface of the carrier in the Cu^0 or Cu^+ state.[103,104] It may be that the stable active centre of $Cu^+-[\,]-Zn-O$, where [ ] is an oxygen vacancy, arises at the interface between Cu and ZnO.[100] The role of the reversible absorption of hydrogen by the lattice in the course of the stabilisation of the active centres of the copper catalysts has been noted.[105]

The discussion concerning the mechanism of the reaction and the nature of the intermediates and the active centres in the synthesis of methanol from CO_2 and H_2 is continuing. The vast majority of investigators accept nowadays[87] that methanol is not formed directly from the synthesis gas but via the intermediate formation of CO_2. As regards the active centres of the Cu–ZnO catalyst, it is claimed in some studies that the reaction proceeds only on copper in the Cu^0 state,[106] while in others (see, for example, Sizgek et al.[107]) it is stated that the active centres are both copper and zinc.

It has been shown in a theoretical study[108] that CO_2 is stabilised in a linear form, bound to the surface via an O atom, on Cu^+ and Zn^{2+}, whilst on Cu^0 coordination via the C atom is preferred. In the case of 'O-coordination', methanol may be formed on the Cu^+ and Zn^{2+} centres via the pathway

$$CO_2 + M \xrightarrow{H_2} HCOO-M \xrightarrow{H_2} H_2CO-M \xrightarrow{H_2}$$

$$\longrightarrow CH_3O-M \xrightarrow{H_2} CH_3OH + M,$$

whilst on 'C-coordination' it is produced on Cu^0 and Zn^{2+} centres via the pathway

$$CO_2 + M \xrightarrow{H_2} M-COOH \xrightarrow{H_2} M-CO \xrightarrow{H_2}$$

$$\longrightarrow M-CHO \xrightarrow{H_2} M-CHOH \xrightarrow{H_2}$$

$$\longrightarrow M-CH_2OH \xrightarrow{H_2} CH_3OH + M.$$

It is as yet difficult to say which path predominates. The first intermediate complex in the first path is the formate, which has been detected spectroscopically, whilst in the second it is a metal-carboxylic acid. The existence of active centres participating in the second reaction path appears preferable.

Copper analogues, namely silver[109] and gold,[110] deposited on oxides have also been investigated as catalysts for the synthesis of methanol from CO_2 and H_2. It was found[109] that the $Ag-ZnO-Ga_2O_3/Al_2O_3$ catalyst is more selective than $Cu-ZnO-Ga_2O_3/Al_2O_3$, but the yield of methanol on it is lower.

Carbonates, formates, bridging CO groups, and CH_2O have been detected on the Cu/ZrO_2, Hg/ZrO_2, and Au/ZrO_2 catalysts under the conditions of the synthesis of methanol from CO_2 and H_2.[111] On this basis, the following reaction mechanism has been proposed:

$$CO_2 + H_2 \longrightarrow HCOO^- + H^+ \underset{OH}{\overset{-OH}{\rightleftharpoons}} CO(ads) \xrightarrow{H_2}$$

$$\longrightarrow CH_2O \xrightarrow{H_2} CH_3OH$$

The formate is apparently formed on ZrO_2, whilst H_2 comes from the metal via the spill-over mechanism.

Palladium catalysts deposited on La_2O_3, CeO_2, and TiO_2 have also been used to synthesise methanol from CO_2 and H_2.[112,113] On Pd/CeO_2 at 230 °C and 30 atm, the selectivity in the formation of CH_3OH exceeded 90% for a 3% conversion. The authors[113] noted the role of the spill-over of H atoms from Pd to CeO_2 and observed the reduction of Ce^{4+} to Ce^{3+}.

The study of palladium catalysts on various carriers showed that they are more active in the synthesis of methanol than Cu/ZnO. Pd/Ga_2O_3 is especially active: at 250 °C and a pressure of 5 MPa and for the $H_2:CO_2 = 3:1$ ratio, the turnover number of the reaction on this catalyst is ten times greater than on Cu/ZnO.[114]

The liquid-phase synthesis of methanol from CO_2 and H_2 may be used to solve the technological problem of removal of the excess heat. This process has been achieved on a $Cu-Zn/Al_2O_3$ catalyst; the yield of CH_3OH was 93%.[115]

More reduced forms of the catalyst are apparently needed for the synthesis of higher alcohols from CO_2 and H_2. Ethanol, propanol, and butanol are formed on a bimetallic $Ir-Mo/SiO_2$ catalyst.[116] On a catalyst such as 5% $Rh-Ni-Mn-O/SiO_2$ at 220 °C, a pressure of 50 atm, and for the $H_2:CO_2=3:1$ ratio, the selectivities in the transformation of CO_2 into CH_3OH and C_2H_5OH reached 5.4% and 41.1% respectively for a degree of conversion of 1.6%.[117] Nickel- and ruthenium-containing zeolites with added copper are active in the synthesis of higher alcohols. The selective formation of C_2H_5OH from CO_2 and H_2 on the copper–chromium oxide catalyst is observed when an alkali or a lanthanide is added to it. This can be explained by the need for the presence of OH groups on the catalyst surface in order to activate CO_2.[118]

According to the data of Wang et al.,[119] mainly CO and hydrocarbons are formed on the $K-Cu-Co-Cr-O$ catalyst. The selectivity in the conversion into the C_1-C_6 alcohols is only 1.8%, the fraction of ethanol among the alcohols being 44.0%. The Cu–Ni alloy proved to be an active and selective catalyst for the hydrogenation of CO_2 to a mixture of alcohols. The Ni–Mn and Ni–Co alloys are less selective.[120] The conversion of methanol into a higher homologue has been observed[121] in a mixture with CO_2 and H_2 in contact with a suspension of $Cu_3Zr_2H_{11}$ in solution in an alcohol–benzene mixture. At 210 °C and 25 atm, small amounts of propanol, butanol, and the corresponding ethers were detected in the products.

Hydrocarbons may be synthesised from a mixture of CO_2 and H_2 on Cu–Zn catalysts, methanol being formed as an intermediate. This process is a modification of the familiar 'Mobil process'.

On the Cu–Zn–Cr oxide catalyst mixed with the HY zeolite at 400 °C, carbon dioxide is converted into C_2-C_6 hydrocarbons.[122,123] The conversion of CO_2 with formation of a mixture of methanol and hydrocarbons greatly exceeds the equilibrium yield of methanol under these conditions as a consequence of the shift of the equilibrium in reaction (4) to the right.

Liquid hydrocarbons (up to C_8) have been obtained on a catalyst of the Fischer–Tropsch type containing 95% Fe and 5% Cu at 400 °C and a pressure of 50 atm.[124,125]

It has been suggested[126] that a two-stage flow reactor be employed for the synthesis of petrol from a mixture of CO_2 and H_2. In the first stage (in the first part of the reactor), methanol is synthesised (250 °C, 50 atm) on the $Cu-Zn-Cr-Al-O$ catalyst modified with Ag and Pd. In the second stage, a mixture of C_1-C_6 hydrocarbons is formed on the H–Fe silicate, the structure of which is similar to that of the HZSM-5 zeolite. The overall selectivity in the conversion of CO_2 into petrol reaches 46% and the yield is 71 g litre^{-1} h^{-1}. The authors believe[126] that the CO_2-containing effluent gases from electric power stations may be used in this process.

5. Synthesis of dimethyl ether

It has been noted[127,128] that the best way of overcoming the thermodynamic limitations associated with the synthesis of methanol is the direct synthesis of CH_3OCH_3 from CO_2 and H_2. Dimethyl ether may be formed from the synthesis gas on a mixture of the catalyst for the synthesis of methanol and an acid dehydration catalyst.[129] The conversion of $CO_2 + H_2$ into CH_3OH and $(CH_3)_2O$ was achieved[130] on a mixture of the $Cu-ZnO-Al_2O_3$ catalyst with solid acid catalysts (zeolites, WO_3/SiO_2 silicalite). The use of a type Y zeolite afforded the best result: at 240 °C, the yield was 17% for a selectivity of 55.1% with respect to $(CH_3)_2O$ and of 13% with respect to CH_3OH. On the $Cu-Zn-Cr_2O_3-Al_2O_3$ catalyst mixed with a zeolite, the yield of oxygenated products reached 18.8%.

Another reaction which makes it possible to overcome the thermodynamic limitations involves the conversion of a mixture of CO_2 and H_2 into methyl formate by the carboxylation of the intermediate methanol:

$$2CO_2 + 4\,H_2 \rightleftharpoons HCOOCH_3 + 2H_2O.$$

This reaction has been achieved on a mixture of the methanol catalyst with the K–Fe/L zeolitic catalyst.[131]

6. Synthesis of formic acid

Under standard conditions reaction (6) is thermodynamically unfavourable. For this reason, only negligible yields of HCOOH are observed. In order to increase the yield under mild conditions, alkaline and alkylating agents are used, for example ruthenium and iridium complexes. Methyl formate has been obtained with their aid from the $CO_2 + H_2 + CH_3OH + H_2O$ mixture.[22]

CO_2 has been reduced[132,133] in aqueous solution by Na, Zn, and Al amalgams. Very small amounts of HCOOH were obtained. Triethylammonium formate was formed in the hydrogenation of CO_2 on the complex $[Rh(NBD)(PMe_2Ph)_3]BF_4$, where NBD = norbornadiene, in solution in tetrahydrofuran.[134]

On the whole, the data presented in this section demonstrate that, despite the high cost of hydrogen and the large amount of energy consumed in a series of CO_2 hydrogenation processes, many of them, especially those involving the syntheses of methanol and dimethyl ether, can already be regarded as a basis for large scale industries, serving as an alternative to the CO-based processes. Highly active low-temperature catalysts are necessary for this purpose. As regards scientific theory, the greatest advance achieved in the very recent years has been the detection with the aid of physical methods of intermediate compounds on the catalyst surfaces. Spectroscopic methods have still been inadequately employed in situ.

IV. Interaction of carbon dioxide with methane

The reduction of carbon dioxide by hydrocarbons, i.e. the employment of CO_2 an oxidant, is the most promising procedure for the establishment of large scale processes involving the utilisation of carbon dioxide.

1. Metallic catalysts

The direct interaction of methane with CO_2 on metallic catalysts has been investigated by many workers, starting with Fischer and Tropsch.[135] Kurganova et al.[136] studied the catalytic reactions of an equimolar mixture of methane and carbon dioxide on platinum deposited on various carriers. Platinum deposited on the BAU activated charcoal proved to be the most active. Reaction (18), involving the preparation of the synthesis gas, and to an even greater extent reaction (19), involving the formation of carbon, and reaction (20), in which methane is converted by steam, take place on this catalyst starting at a temperature as low as 350 °C:

$$CH_4 + CO_2 = 2CO + 2H_2, \quad \Delta H = 209.3 \text{ kJ mol}^{-1}, \tag{18}$$

$$CH_4 + 2CO_2 = C + 2CO + 2H_2, \quad \Delta H = 641.1 \text{ kJ mol}^{-1}, \tag{19}$$

$$CH_4 + H_2O = CO_2 + 3H_2, \quad \Delta H = 76.6 \text{ kJ mol}^{-1}. \tag{20}$$

The following reactions are also possible:

$$CH_4 + 3CO_2 = 4CO + 2H_2O, \quad \Delta H = 330.6 \text{ kJ mol}^{-1}, \tag{21}$$

$$2CH_4 + CO_2 = C_2H_6 + CO + H_2O, \quad \Delta H = 16.7 \text{ kJ mol}^{-1}. \tag{22}$$

All five reactions (18)–(22) are endothermic and take place at high temperatures (600–900 °C). At 800 °C, ΔG for the first four reactions is negative, whilst for reaction (22) it is positive but not very large. The equilibrium yield of C_2H_6 in reaction (22) at 800 °C is 13%, which is fairly large.

In the preparation of synthesis gas by reaction (18), $\Delta G = 0$ at 630 °C. Above this temperature, the equilibrium is displaced towards the formation of synthesis gas, while below it it is

displaced towards $CH_4 + CO_2$. The possibility of regulating the direction of the reversible reaction (18), i.e. the formation of synthesis gas at a high temperature and of methane at low temperatures, has been used to devise cells in which solar energy is employed: the endothermic reaction takes place on heating with sunlight, whilst the exothermic reaction is used to give up the energy.[137] The 1% Ru/Eu_2O_3 catalyst, containing 3 nm ruthenium particles having a hexagonal structure, is most suitable for the solution of the problem.[138]

Reaction (18) can be represented as a combination of the methane steam conversion reaction (20) and the reverse conversion of water gas [reaction (3)]. The study of the kinetics of reaction (18) on a nickel catalyst at 800–900 °C showed[139] that its rate is described by the same equation as the rate of the steam conversion:

$$r = \frac{k_1 P_{CH_4}}{1 + k_2(P_{H_2O}/P_{H_2}) + k_3 P_{CO}},$$

where k_1, k_2, and k_3 are constants and P_{CH_4}, P_{H_2O}, P_{H_2} and P_{CO} are the partial pressures of methane, water, hydrogen, and carbon monoxide respectively. The authors[139] explain this by the fact that CH_4 reacts initially not with CO_2 but with H_2O. Reaction (20) is rate-limiting. The hydrogen obtained in this reaction interacts rapidly with CO_2 via reaction (3) with reformation of H_2O.

The kinetics of all three reactions (18), (20), and (3) have been investigated[140] on eight different metallic catalysts deposited on MgO or Al_2O_3. It was found that the rate of reaction (3) exceeds slightly (in some cases by an order of magnitude) the rates of reactions (18) and (20). On the other hand, the rate of reaction (18) is lower than the rate of the steam conversion of methane with the exception of those cases where the latter is carried out on the Ni/MgO and Ni/Al_2O_3 nickel catalysts, where reactions (18) and (20) proceed at similar rates.

According to Blom et al.,[141] the reduced selectivity in the formation of H_2 compared with CO on Ni/Al_2O_3 at 600–800 °C can be explained by the fact that reaction (3) is much faster than the steam conversion of methane [reaction (20)]. Similar data have been obtained also on deposited cobalt catalysts.[142]

In conformity with Eqn (19), the interaction of CH_4 with CO_2 leads to the formation of carbon, which poisons the nickel catalyst. Carbon is formed both from methane on dissociation of the latter into carbon and hydrogen and from CO via the Boudouard reaction. Carbon is formed in the form of carbon filaments, probably on the Ni(111) face.[143]

Various procedures are used for the industrial preparation of synthesis gas from a mixture of CH_4 and CO_2. The so called 'Calcor' process involving the conversion of a natural or petroleum gas in the presence of CO_2, is available.[144,145] The Haldor Topsoe Company uses the $CH_4 + CO_2 + H_2O$ mixtures to reduce the poisoning of the nickel catalyst and the blocking of the tubes with carbon.[140,146–148] The same company has developed the SPARG (9 atm, 900 °C) process, where sulfur vapour, which passivates nickel and prevents the formation of carbon, is added to the active gas. Rostrup-Nielsen[146] believes that the formation of carbon requires an *ensemble* of several nickel atoms: the *ensemble* for the carbonic acid conversion of methane contains a smaller number of nickel atoms.

Inui et al.[149] suggested that joint $CH_4 + CO_2 + H_2O + O_2$ reforming be employed. This makes it possible to solve the problems of both coke formation and energy consumption. Whereas at 350 °C, the catalytic conversion of methane takes place, i.e.

$$CH_4 + 2O_2 = CO + 2H_2O, \quad \Delta H = 803.5 \text{ kJ mol}^{-1}, \qquad (23)$$

above 500 °C the weakly exothermic reaction involving the formation of the synthesis gas takes place:

$$2CH_4 + O_2 = 2CO + 4H_2, \quad \Delta H = -49.0 \text{ kJ mol}^{-1}. \qquad (24)$$

On the very active 6.6% Ni–3.9% CeO_2–2.2% Pt–0.02% Rh/Al_2O_3 catalyst, the degree of conversion of methane in a mixture with CO_2 and H_2O at a space velocity of 73 000 h^{-1} agrees with the equilibrium value, whereas at 358 000 h^{-1} (contact time 0.01 s) it is lower than the latter. However, if O_2 is added to this mixture, it is possible to achieve a yield of hydrogen of 2877 mol litre^{-1} h^{-1}.

The Ni/SiO_2 catalyst exhibits a much higher activity than the oxides CaO and Fe_2O_3. The temperature of the 50% conversion of CO_2 is 640 °C on Ni/SiO_2 and 900–1000 °C on the oxides.[150,151] The above oxides are coated by carbon faster than is nickel. At 800 °C, the degree of conversion of the $CH_4 + CO_2$ mixture into the synthesis gas was 83.1% on Ni/Al_2O_3, 74.2% on Co/Al_2O_3, and only 3.4% on Fe/Al_2O_3. On Ni/SiO_2, the rate of reaction is approximately 1.5 times lower than on Ni/Al_2O_3.[152,153] When the nickel content is less than 13%, the catalyst is fairly resistant to the deposition of coke. In the presence of a high nickel content, carbon filaments are formed.[154]

The use of MgO or CaO–MgO as carriers for nickel[155,156] and cobalt[156] catalysts greatly increases their activity and especially their stability. On interaction with CO_2, the alkaline carrier gives rise to a carbonate, which coats the surface and prevents coke formation.

A layer having the composition $CH_{0.08}$, i.e. close to pure carbon, is formed on nickel foil under the catalytic conditions. The layer has the composition $CH_{0.06}$ on Ni/SiO_2 and CH_2 on Ni/MgO. For this reason, less coke is formed on Ni/MgO. It has been postulated[157] that MgO acts as an electron-donating carrier and retards the dissociation of CH_x. The conversion of CH_x into C_{ads} leads subsequently to the formation of inactive graphite and the deactivation of nickel. It has been observed[159] that the composition of the CH_x fragment on nickel depends on the nature of the carrier: $x = 2.7$ on MgO, 2.5 on ZnO, 2.4 on Al_2O_3, 1.9 on TiO_2, and 1.0 on SiO_2. However, according to the data of Takeyasu et al.,[159] on the nickel catalysts Ni/MgO, Ni/SiO_2, and Ni/α-Al_2O_3 the ratios C:Ni are the same and equal to the corresponding ratio for metallic nickel.

Iron, cobalt, and nickel powders mixed with an ultradisperse ceramic material in proportions of 1:10 exhibit a high activity. At 740 °C, the yield of the reaction product was 94% at a space velocity of 4500 h^{-1} and 71% at 6100 h^{-1}. The catalysts retain their activity for 70 h.[160]

Nickel catalysts deposited on the nonacid MgY and NaY zeolites also exhibit a catalytic activity at 580 °C.[161] The maximum yield was observed in the presence of a 20% nickel content.

Nickel and cobalt metallic particles are probably formed also in the carbonic acid conversion of methane into the synthesis gas on the $Ca_{0.8}Sr_{0.2}Ti_{0.8}Co_{0.2}O_{3-\delta}$ and $Ca_{0.8}Sr_{0.2}Ti_{0.8}Ni_{0.2}O_{3-\delta}$ catalysts.[162] The nickel-containing catalyst is more active: at 755 °C, the degree of conversion of CO_2 was 64.6% and that of CH_4 was 89.6% on this catalyst. Under these conditions, the yield of CO reached 69.0% and that of H_2 54.8%, while the selectivity in the formation of H_2 was 84.8%. Reaction (18) is accompanied by the simultaneous deposition of coke via reaction (19). The basic properties of the surface may promote the occurrence of the oxidation-reduction process on the latter.

Platinum group metals are active catalysts for the carbonic acid conversion of methane.[138,140,151,163–180] The reaction already proceeds at an appreciable rate at 500 °C. It has been shown by the alternate pulse method that CO is formed when the CO_2 pulse is supplied. C_2H_6 and C_2H_4 are formed in the first pulses, i.e. the oxidative condensation of methane takes place. Carbon is less soluble in noble metals than in nickel, but after a time poisoning takes place — slow at 500 °C and rapid at 600 °C.

An evident disadvantage of noble metals is their high cost, while an advantage is their higher activity than that of nickel, cobalt, and iron and a smaller susceptibility to poisoning. Among the catalysts deposited on Al_2O_3, the most active at 500–700 °C is Rh/Al_2O_3[151,162–166] (Ru/Al_2O_3[171,175,178] and Ir/Al_2O_3[174] according to other data) and is followed by Pt/Al_2O_3 and

Pd/Al_2O_3. This series corresponds to the activity series of the catalysts for the dissociation reaction

$$CO_2 \rightleftharpoons CO + O(ads).$$

The activity series $Ru/MgO > Rh/MgO > Ni/MgO > Pt/MgO > Pd/MgO$ has been obtained for metals deposited on MgO.[153] Rhodium and palladium are poisoned to the least extent, but they are the most expensive.

When the same metal is deposited on different carriers, the latter form the following activity series:[171-173,179] $Al_2O_3 > TiO_2 > SiO_2 > MgO$. According to certain data,[165] acid carriers are more active because they promote the dispersion of the deposited metals. However, the formation of carbonates on basic carriers diminishes the deposition of coke.

The high activities of all the deposited noble metals investigated have been demonstrated.[161,168] It is also significant that in almost all cases the gas mixture had the $CO:H_2 = 1$ composition, i.e. virtually no side reactions were observed. Synthesis gas was formed from the initial $CH_4:CO_2 = 1$ mixture at 780 °C with the following yields: 1% on Al_2O_3, 85% on 1% Ni/Al_2O_3, 73% on 1% Pd/Al_2O_3, 89% on 1% Ru/Al_2O_3, 87% on 1% Rh/Al_2O_3, and 89% on 1% Ir/Al_2O_3. The Ni/Al_2O_3 and Pd/Al_2O_3 catalysts were saturated with coke faster than any others. The Ir/Al_2O_3 catalyst proved to be most resistant to coke formation: it retained its activity for 260 h. The yield of H_2 was found to exceed that of CO on Ru/Al_2O_3. When the $13CH_4 + O_2 + CO_2$ mixture is used, the yield of products on Ni/Al_2O_3 may reach 91% and the reaction becomes thermoneutral. The gas obtained from the $4CH_4 + O_2 + 9CO_2$ mixture contained exactly 50% of CO and H_2 and carbon was not formed on the surface.

The iridium and ruthenium catalysts obtained from the iridate ($Ln_2Ir_2O_7$) and ruthenate ($Ln_2Ru_2O_7$) pyrochlores (Ln = Nd, Sm, Eu, Gd) had a high activity.[169,170] These oxides are activated under the reaction conditions, being converted into the corresponding metals.

Mechanisms have been proposed for the reaction under consideration presupposing the dissociation of CH_4 and CO_2. The correlation between the activity series of the catalysts in the $CH_4 + CO_2$ reactions and in the dissociation reaction $CO_2 \rightleftharpoons CO + O$ suggested[158,180] the following mechanism:

$$CH_4 + S = [CH_{x,S}] + (4 - x)H_S = C_S + 2H_2,$$

$$CO_2 + 2S = CO_S + O_S,$$

$$CO_S = CO + S$$

(The symbol S denotes the catalyst surface).

Other investigators[168,173] also postulate the stepwise dissociation of the CH_4 molecule, but the process mechanism includes the Boudouard reaction.

$$CH_4 + O(ads) = CH_3(ads) + OH(ads),$$

$$CH_3(ads) = CH_x + H(ads),$$

$$CO_2 + H(ads) = CO(ads) + OH(ads),$$

$$CH_x + O(ads) = CO + xH(ads),$$

$$2OH(ads) = H_2O + O(ads),$$

$$CO_2 + C = 2CO,$$

$$C + H_2O = CO + H_2.$$

The study of the $CH_4 + CO_2$ interaction on the $Rh/\gamma\text{-}Al_2O_3$ catalyst with the aid of a TAP reactor[181] showed that the reverse Boudouard reaction proceeds exceptionally rapidly and the mechanism involving it is extremely likely.

Above 500 °C (on Rh), carbon forms a supersaturated solution which inhibits the reaction. The reactions

$$CH_2(ads) + CO_2 = CO + H_2O + C(ads),$$

$$CH(ads) + OH(ads) = CO + H_2$$

are also possible.

The ratio $CO:H_2 > 1$, frequently observed in the products, indicates the occurrence of a number of secondary reactions: the conversion of water gas, the hydrogenation of CO, CO_2, etc.

The study of pure metals by XPS and Auger spectroscopy[182] showed that the reactions

$$CH_4 + Z \rightarrow CH_3-Z \rightarrow CH_2-Z \rightarrow CH-Z \rightarrow C-Z,$$

$$CH_x-Z + O-Z = CO + \tfrac{1}{2}xH_2 + 2Z$$

and the equilibrium reaction

$$H_2O + Z = O-Z + H_2$$

(Z is a catalyst surface centre) occur on the surface.

According to this scheme, the carbonic acid conversion of CO_2 requires that the CH_x particles, formed on interaction between methane and the metal, do not last sufficient time to be fully dehydrogenated and that they should have reacted with O_2. In this case, the reaction

$$CO_2 + Z = O-Z + CO$$

is rate-limiting and the carbonic acid conversion of CH_4 is therefore slower than the steam conversion. It is also possible that the rate of the overall process depends on the CO concentration on the surface. Carbon monoxide participates in the reactions

$$CO + Z = CO-Z$$

and

$$CO-Z \rightarrow C-Z + O-Z.$$

C–Z is probably less reactive than O–Z. The metals on which the heat of adsorption of CO is high undergo a greater reduction in their activity following the replacement of H_2O by CO_2.

However, the study of the carbonic acid conversion of methane on Rh/Al_2O_3 and Ir/Al_2O_3 showed that the dissociation of CO_2 into $CO + O_{ads}$ is not observed under the catalytic conditions (700 °C).[183] On the other hand, methane decomposes quantitatively into $C + 2H_2$. There are no CH_x particles on the surface, since all the surface carbon is hydrogenated quantitatively to methane. The authors therefore propose the following reaction mechanism:

$$CH_4 + Rh_S \rightarrow C_S-Rh_S + 2H_2,$$

$$C_S-Rh_S + CO_2 \rightarrow 2CO + Rh_S.$$

Dissociative mechanisms have also been put forward. Analysis of the IR spectra in situ indicate the formation of formate species (apparently on the carrier),[171,184] linear and bridging carbonyls,[185] and CH_x groups.[173,174]

2. Oxide catalysts

A series of oxide catalysts for the oxidative condensation of methane have been investigated.[186-199] Their behaviour in two reactions was compared: (1) $CH_4 + O_2$ (100:1) and (2) $CH_4 + CO_2 + O_2$ (100:100:1). It was found that, on a catalyst with a moderate basicity, an even higher yield of C_2 hydrocarbons is achieved in the $CH_4 + CO_2 + O_2$ mixture than in the $CH_4 + O_2$ mixture. For example, on 50% PbO–MgO the yield of C_2 species was 3.28% in the first reaction and 4.37% in the second; on CaO–BaO–CeO_2, the yields were 2.2% and 3.5% respectively. These results led to the conclusion[188] that the oxygen atoms split off from CO_2 participate in the oxidative dehydrogenation of hydrocarbons:

$$CO_2 \rightarrow CO + O(ads), \quad (25)$$

$$2CH_4 + O(ads) \rightarrow C_2H_6 + H_2O, \quad (26)$$

$$C_2H_6 + O(ads) \rightarrow C_2H_4 + H_2O. \quad (27)$$

Experiments with labelled $^{13}CO_2$ and CD_4 molecules showed that ^{13}CO and C_2D_6 are formed in the reaction.[189] This means

that the CO is obtained only from CO_2 and not as a result of the further oxidation of the hydrocarbon. In the absence of the hydrocarbon, the CO_2 on the catalyst is absolutely unreactive. A certain initial amount of ethane is necessary to initiate the reaction. The conversion of CO_2 is apparently achieved via the reversible conversion of water gas [reaction (3)] by the hydrogen formed in the gas-phase dehydrogenation of ethane with the intermediate dissociative adsorption of CO_2 [reaction (25)]. Thus, in the oxidative dehydrogenation of CH_4 and C_2H_6, the mechanism of the activation of the hydrocarbon is the same regardless of whether O_2 or CO_2 is used as the oxidant.

On pure MgO, synthesis gas is formed via reaction (18), reactions (19) and (21) take place on PbO, while the oxidative condensation reactions (22) and (27) occur preferentially on PbO.MgO. Catalysts with strong basic centres, for example Li/MgO or Ni/ZnO, are less active in the $CH_4 + CO_2$ reaction than in the $CH_4 + O_2$ reaction and are rapidly deactivated.[189]

The carbonic acid conversion of methane has been achieved on vermiculite 22 $MgO.22SiO_2.5Al_2O_3.Fe_2O_3.40H_2O$ at 900–970 °C, for the ratio $CO_2 : CH_4 = 0.5 - 1.5$, and fairly long contact times (10.5–21 s). The degree of conversion of the $CH_4 + CO_2$ mixture into synthesis gas was 99.2%–99.7%. In the empty reactor at even lower rates of supply of the starting material at the same temperature, 62% of CH_4 and 40% of CO_2 were converted, the walls of the reactor becoming coated with a layer of carbon.[190]

The influence of various oxide additives (Cu, Mn, Fe, etc.) on the activity of the nickel catalyst for the carbonic acid conversion of CH_4 has been investigated.[191] Manganese oxides proved to be most effective. The formation of carbon was reduced in their presence, while the degree of conversion of CO_2 increased with increasing manganese content in the nickel catalyst.

Further studies showed that it is possible to do without nickel altogether in carrying out reaction (18). The characteristic features of the $CH_4 + CO_2$ reaction on manganese oxide catalysts have been investigated in detail.[192–203] Under stationary conditions the 5% Ca–12% $Mn-O/Al_2O_3$ catalyst proved to be the most effective. At 870 °C and a space velocity of 900 h^{-1}, the degree of conversion of CH_4 was 83.1%, that of CO_2 was 62.7%, and the selectivity with respect to H_2 was 76.5%. An equimolecular mixture of CO and H_2 was obtained. Extensive oxidation of methane by the catalyst oxygen occurred initially and the conversion of CO_2 did not take place. As the reaction proceeded and the catalyst was reduced, the activation of CO_2 began. The CO and H_2 concentrations then increased continuously. The complete conversion of CO_2 and CH_4 was achieved on the catalyst operating under stationary conditions at 930 °C (the selectivity was 99.7% in the formation of CO and 84.6% in the formation of H_2). The activity of the catalyst was retained for a long time (> 500 h) and carbon was not formed via reaction (19).

The study of the phase composition of the working Ca–MnO/SiO_2 catalyst showed[193] that the more oxidised Mn_2O_3 and Mn_3O_4 phases are reduced during the reaction and only the reduced MnO phase is retained in the catalyst. After the stabilisation of the composition of the catalyst, the formation of the manganese carbide and metallic magnesium phases was not observed.

After the initial treatment of the catalyst with carbon dioxide and subsequent exposure of the former to methane at 850 °C, ethane and ethene are formed, i.e. the oxidative dimerisation reactions (22) and (28) take place, possibly with participation of the carbonate phase.[196]

$$2CH_4 + CO_2 = C_2H_4 + CO + H_2O, \quad \Delta H = 176 \text{ kJ mol}^{-1}, \; T_{\Delta G=0} = 750 \text{ °C}. \tag{28}$$

The yield of C_2 hydrocarbons is 9%.

A decrease in the temperature of the treatment of the catalyst with carbon dioxide raises the yield of C_2H_6 and C_2H_4 to 13%. When the reduction of Mn_2O_3 and Mn_3O_4 has been completed, the yield of C_2 hydrocarbons falls and only synthesis gas is formed in the stationary state. An increase in the degree of conversion of CH_4 hardly affects the selectivity. This may be associated with the establishment of equilibrium in the water gas conversion reaction (3).

The $La-Na-Mn-O/SiO_2$ catalyst exhibits a high selectivity in the conversion of CH_4 into C_2 hydrocarbons under non-stationary conditions.[197] After its treatment with carbon dioxide and subsequent admisison of methane at 800 °C, C_2 hydrocarbons are formed in almost 100% yield, whereas CO is not produced. Consequently the process takes place via the interaciton of CH_4 with the carbonate fragments of the catalysts and not via a multistage oxidation-reduction mechanism:

$$CO_3^{2-} + 2CH_4 \rightarrow C_2H_6 + CO + H_2O + O^{2-},$$

$$CO_3^{2-} + C_2H_6 \rightarrow C_2H_4 + CO + H_2O + O^{2-},$$

$$CO_3^{2-} \rightleftharpoons CO_2 + O^{2-}.$$

The selectivity of another catalyst investigated in the formation of C_2 hydrocarbons, namely $La-Cu-O/SiO_2$ was lower.[197,199] Under alternation conditions, the reaction of CO_2 with the catalyst produced CO, whilst the subsequent reaction with methane gave rise to C_2 hydrocarbons. The oxidation–reduction mechanism is more probable in this case. Under stationary conditions, synthesis gas, and not ethane and ethene, is formed on both catalysts.

The properties of the $La-Mn-O/Al_2O_3$ catalyst proved to be similar to those of $La-Mn-O/SiO_2$.[198,199] The selectivity in the formation of C_2 hydrocarbons in separate interactions did not exceed 5%. The constancy of the rate of reoxidation of the catalyst by carbon dioxide as a function of time can be explained by the occurrence of the reverse reaction involving the reduction of the catalyst by the carbon monoxide formed on reoxidation by reaction (24).

A similar equilibrium has been observed also in the oxidative condensation of methane on the familiar Li–MgO catalyst:[198,199]

$$Li^+[\,] + Li^+O^{2-} + CO_2 \rightleftharpoons 2Li^+O^- + CO \tag{29}$$

[ ] = lattice defect.

The rate of formation of CO in such a process is 40 times lower than in the reoxidation of the manganese systems. Reaction (29) is accompanied by the reaction involving the formation of the stable lithium carbonate Li_2CO_3, which coats the surface and does not therefore participate in the stationary reaction. The selectivity in the formation of hydrocarbons on the Li–MgO catalyst by the $CH_4 + CO_2$ reaction was only several tenths per cent.

The rates of formation of hydrogen under the conditions of the stationary catalytic reaction on $Ca-MnO/Al_2O_3$ (3×10^{-3} mol g^{-1} h^{-1}) and in the reductive reaction between CH_4 and the catalyst (1.7×10^{-3} mol g^{-1} h^{-1}) are comparable. On the other hand, the rate of the interaction of CO_2 with the reduced catalyst (reoxidation of the catalyst) exceeds the rate of the reduction. Thus, in contrast to the metallic catalysts,[139,167] the rate-limiting stage on the magnesium oxide catalysts is apparently the cracking of methane with formation of surface carbon deposits, which are then rapidly oxidised. The presence of manganese oxide in the catalyst increases the rate of oxidation of carbon on the surface. Carbon dioxide interacts with MnO giving rise to a surface carbonate, which reacts with carbon.[191,196]

Scheme 1

$$CH_4 + MnO \xrightarrow{a} MnO...C + 2H_2,$$

$$CO_2 + MnO \overset{b}{\rightleftharpoons} MnCO_3,$$

$$MnCO_3 + MnO...C \xrightarrow{c} 2MnO + 2CO,$$

$$MnCO_3 + H_2 \xrightarrow{d} MnO + CO + H_2O,$$

$$MnO...C + H_2O \xrightarrow{e} MnO + CO + H_2.$$

According to X-ray diffraction data, the MnO and $MnCO_3$ phases are stationary under the catalytic conditions: appreciable oxidation and reduction is not observed and the catalysis does not take place via the mechanism involving the alternate oxidation and reduction of the catalyst. Nevertheless, one may postulate

that intermediate oxidised forms are produced in stage *c* after the decomposition of the carbonate:[199]

$$3MnCO_3 + H_2O \rightleftharpoons Mn_3O_4 + 2CO_2 + CO. \quad (30)$$

The possibility that the carbonates perform transport functions in relation to oxygen has been noted in a study[204] where the oxidative dimerisation of methane with the use of O_2 on $La_2O_3-BaCO_3$ was investigated. The following equation for the rate of reaction arises from Scheme 1:

$$r = \frac{k_1 P_{CH_4}}{1 + (1/k_2k_3)(P_{CO}^2/P_{CO_2}) + k_2 P_{CO_2}},$$

where P_{CH_4}, P_{CO} and P_{CO_2} are the partial pressures of CH_4, CO, and CO_2 respectively and k_1, k_2, and k_3 are the reaction rate constants (Scheme 1). This equation has been confirmed by experimental data.

The introduction of potassium and chromium into the catalyst alters the nature of the process and reaction (21) becomes dominant. On $K-Cr-Mn-O/SiO_2$, the reaction apparently proceeds via the oxidation-reduction mechanism. The second transition metal oxide (Cr_2O_3) participates in the reoxidation. It apparently forms an interface, which facilitates the oxidation-reduction process. When CO_2 is employed, the oxygenating capacity in the oxidative process on $K-Cr-Mn-O/SiO_2$ is much smaller (by a factor of 8) than in the case where O_2 is used.

The $CH_4 + CO_2$ reaction may serve as the first stage in the synthesis of higher hydrocarbons. A two-stage process has been proposed,[202] according to which in the first reactor at 950–970 °C methane undergoes the carbonic acid conversion on manganese silicate modified with 21.8%–2.4% of K_2O with complete conversion of the starting material. In the second reactor, the synthesis gas is converted into C_2-C_3 alkenes with a selectivity of 20%–26% on a catalyst containing 8.1%–9.4% of Fe and 2.2%–6.9% of K on Al_2O_3 at 415–425 °C.

The reverse reaction (18) may be employed in devices utilising solar energy the forward reaction proceeds under the influence of solar energy, whilst the reverse reaction takes place at a low temperature. Owing to the lower selectivity of the reverse reaction, the process efficiency is 54%.[205]

The results presented in this section show that recently there has been a considerable growth of interest by investigators in the interaction of methane with carbon dioxide. Both reaction components are cheap and one may hope to be able to devise large scale processes on their basis. In particular, this applies to the preparation of synthesis gas. As regards the final carbonic acid condensation of methane, the prospects for its industrial application are so far not quite so evident.

Nickel catalysts are most often employed to obtain synthesis gas, but they are poisoned by carbon. Iridium and ruthenium catalysts are active and are not poisoned by carbon, but they are expensive. Finally, the oxide catalysts based on MnO and the rare earths are not poisoned, but they operate at a high temperature and their productivity is inadequate. The mechanisms of the action of the metallic and oxide catalysts are apparently different. Methane is readily dissociated on the former, but the activation of CO_2 is difficult whilst the opposite situation obtains on the latter.

V. Interaction of carbon dioxide with other paraffins

1. Interaction with ethane

When CO_2 interacts with ethane, both the oxidative dehydrogenation of the latter to ethene [reaction (28)] and the formation of synthesis gas [reaction (31)] and carbon [reaction (32)] may take place.2).

$$C_2H_6 + 2CO_2 \rightarrow 4CO + 3H_2, \quad (31)$$
$$\Delta H_{298} = 247.9 \text{ kJ mol}^{-1},$$

$$C_2H_6 + 2CO_2 \rightarrow CO + 3H_2O + 3C. \quad (32)$$

The study of the oxidative dehydrogenation of ethane with the aid of CO_2 showed that manganese oxides serve as a base for the most active and stable systems for the activation of CO_2 and hydrocarbons.[191–193, 195, 196, 202, 204, 206–210] With increase in the manganese concentration in the $Mn-O/SiO_2$ system from 8% to 17%, the degree of conversion of C_2H_6 at 800 °C, a space velocity of 3600 h^{-1}, and for the ratio $CO_2 : C_2H_6 = 1.5$ increases from 65.1% to 73.1%, the degree of conversion of CO_2 rises from 42% to 46.2%, the selectivity with respect to C_2H_4 increases from 52.5% to 61.0%, while the yield of C_2H_4 increases from 34.3% to 44.5%. On the 17% MnO/Al_2O_3 catalyst, the degrees of conversion of C_2H_6 and CO_2 were approximately the same, but the selectivity in the formation of C_2H_4 was somewhat smaller (46.6%). Under the same conditions, reactions (31) and (32) occurred on the nickel catalyst, which was rapidly poisoned as a consequence of coke formation.

A number of oxides (of antimony, zinc, vanadium, and iron), used in the hydrocarbon dehydrogenation reactions, were tested as additives to manganese oxide. The degree of conversion of CO_2 on the $Mn-Sb-O$ and $Mn-Zn-O$ systems was low. A 58% conversion was observed on $MnO-V_2O_5$, but the selectivity in the formation of C_2H_4 was low. The $Mn-Fe-O/SiO_2$ system proved more active, but a high level of selectivity (67%) is attained on this catalyst only during the initial period of its operation (up to 3 h), after which the selectivity falls.

Comparison of data on the catalytic activity of the $Mn-Fe-O/SiO_2$ system and its phase composition under stationary conditions in situ and also under reduction and reoxidation conditions showed that manganese oxides are reduced to MnO during the reaction, while iron oxides are reduced to α-Fe and the carbide. This is apparently the cause of the decrease in selectivity with respect to C_2H_4, the increase in the degree of conversion in reactions (31) and (32), and the saturation of the surface by carbon. Hence it was concluded that the modifying additive to the base oxide should be sought among variable-valence metal oxides exhibiting a catalytic activity in the dehydrogenation reactions and not reduced to the metal under the reaction conditions. Chromium oxides possess such properties. On the 5% Cr–17% $Mn-O/SiO_2$ catalyst, the selectivity with respect to C_2H_4 reaches 70% at 800 °C. A further increase in selectivity is observed when the catalyst is modified by alkali and alkaline earth metal oxides. After the introduction of 1.5% of K into this catalyst, the reaction selectivity at 830 °C increased from 65.4% to 76.8% for ethane and CO_2 conversions of 82.6% and 52.3% respectively. The yield of C_2H_4 was 55.7% for $C_2H_4 : CO \approx 1$. Under these conditions, the degrees of conversion of C_2H_6 and CO_2 on the $Cr-O/SiO_2$ catalyst, which contains no manganese, are low.

The study of the degrees of conversion of C_2H_6 and CO_2 showed that the selectivity with respect to C_2H_4 initially increases with increase in the $CO_2 : C_2H_6$ ratio and then attains a plateau (for $CO_2 : C_2H_6 > 2.5$). This effect is probably associated with the increasing degree of oxidation of the surface and with decrease in the contribution of the extensive cracking of ethane. Such variation of the selectivity differs significantly from that observed in the oxidative dehydrogenation of C_2H_6 in the presence of oxygen, where the selectivity with respect to the alkene fell with increase in P_{O_2}.

Reaction (18) can be carried out also under conditions with separate oxidation and reduction steps. In this regime, C_2H_6 is converted into C_2H_4 on reduction of the catalyst, whilst the reoxidation of the later results in the reduction of CO_2 to CO.

Bearing in mind the data showing that the dehydrogenation and extensive conversion of ethane occur on different centres, one may put forward the following mechanism for the reactions of methane in a general form:

$$\begin{array}{l} C_2H_6 \xrightarrow{I} RO \longrightarrow C_2H_4, \\ \quad\quad\quad\quad \downarrow \\ C_2H_6 \xrightarrow{II} R \longrightarrow \text{extensive conversion products} \end{array} \qquad (33)$$

The mode of conversion of ethane is determined by the ratio of the oxidised and reduced centres (RO : R), an increase which results in an increase in selectivity with respect to ethene. As the degree of conversion of ethane increases and CO accumulates in the reaction medium, the catalyst surface is reduced by carbon monoxide and process II predominates. The rates of the parallel processes specified in reaction (33) may be described by the equations

$$r_I = k_1 P_{C_2H_6}[RO],$$

$$r_{II} = k_2 P_{C_2H_6}[R].$$

The RO and R centres are linked by the equilibrium reaction $R \leftrightharpoons RO$.

From the stationary condition [R] + [RO] = 1 and the equations for r_I and r_{II}, we obtain the expressions

$$r_I = \frac{k_1 k_3 P_{C_2H_6} P_{CO_2}}{k_3 P_{CO_2} + k_{-3} P_{CO}},$$

$$r_{II} = \frac{k_2 k_{-3} P_{C_2H_6} P_{CO}}{k_3 P_{CO_2} + k_{-3} P_{CO}}.$$

The following equation can be formulated for the process selectivity:

$$S = \frac{r_I - r_{II}}{r_I} = 1 - \frac{k_2 k_{-3} P_{CO}}{k_1 k_3 P_{CO_2}}.$$

It explains the decrease in selectivity with increasing degree of conversion. The concave form of the curve relating the rate of reaction to the degree of conversion in the temperature range 700–830 °C can be accounted for by the inhibition of the reaction by the CO formed.

The equations for r_I and r_{II} differ from the corresponding equation for the oxidation-reduction process involving the oxidation of alkanes by oxygen. In the latter case, the denominator represents the sum $k_{Ox}P_{CO_2} + k_{Red}P_{C_nH_m}$.[207] The inhibition by ethane is not observed in this case.

The rate of reoxidation of the catalyst by carbon dioxide (0.7×10^{-3} mol g^{-1} h^{-1}) is comparable to the rate of its reduction by ethane (0.6×10^{-3} mol g^{-1} h^{-1}). However, the activation energy for the reoxidation reaction (109 kJ mol^{-1}) is significantly lower than the activation energy for the reduction reaction (176 kJ mol^{-1}).

The study of the phase composition of the K–Cr–Mn–O/SiO_2 catalyst *in situ* showed[206] that the Mn_3O_4 phase, observed initially, is gradually reduced and is converted into the new phase MnO. The degree of dispersion of the manganese-containing phase increases as the reaction proceeds.

The following mechanism of the dehydrogenation of ethane in the presence of CO_2 on K–Cr–Mn–O/SiO_2 was proposed on the basis of all the results obtained:[168]

Scheme 2

$$C_2H_6 \xrightarrow{a} C_2H_4 + H_2 \text{ (thermal process)},$$

$$C_2H_6 + Cr^{3+}O^{2-} \xrightarrow{b} C_2H_5 + Cr^{2+}OH^-,$$

$$C_2H_5 + Cr^{3+}O^{2-} \xrightarrow{c} C_2H_4 + Cr^{2+}OH^-,$$

$$C_2H_6 + MnCO_3 \xrightarrow{d} C_2H_4 + MnO + CO + H_2O,$$

$$2Cr^{2+}OH^- \xrightarrow{e} Cr^{2+}O{-}Cr^{2+} + H_2O,$$

$$Cr^{2+}O{-}Cr^{2+} + MnCO_3 \xrightarrow{f} 2Cr^{3+}O^{2-} + MnO + CO,$$

$$MnO + CO_2 \overset{g}{\rightleftharpoons} MnCO_3.$$

In addition, one should include here the cracking reaction, which reduces the selectivity.

$$C_2H_6 + Cr^{2+} \xrightarrow{h} Cr^{2+}...CH_x + \tfrac{1}{2}(6-x)H_2.$$

$$Cr^{2+}...CH_x + Cr^{3+}O^{2-} \xrightarrow{i} 2\,Cr^{2+} + CO + \tfrac{1}{2}xH_2.$$

The Boudouard reaction

$$CO_2 + C \longrightarrow 2CO \qquad (34)$$

also takes place with an activation energy of 201 kJ mol^{-1}, but its contribution under stationary conditions is low.

Scheme 2 makes it possible to explain why the yield of CO greatly exceeds that of hydrogen: at 700 °C, the ratio $CO : H_2$ is between 5 and 8, whilst at 830 °C it is between 1.5 and 2. This means that the contribution of the thermal pyrolysis of methane (reaction *a* in Scheme 2) is relatively small.

The activation of the manganese catalyst by chromium and the distinctly observed synergism are probably due to the fact that, being mobile, the manganese containing phase (MnO) participates during reoxidation in transferring oxygen from CO_2.

$$\begin{array}{l} MnO...[\ ]_L Cr^{2+}O^{2-}Cr^{2+}O_L^{2-} + CO_2 \longrightarrow \\ \longrightarrow MnCO_3...[\ ]_L Cr^{2+}O^{2-}Cr^{2+}O_L^{2-} + CO_2 \longrightarrow \\ \longrightarrow MnO + CO + O_L^{2-}Cr^{3+}O^{2-}Cr^{3+}O^{2-} \end{array} \qquad (35)$$

The oxidation-reduction mechanism of the decomposition of manganese carbonate plays an important role under these conditions. The reduction of Cr^{3+} to Cr^{2+} during the reaction is indicated by the decrease in the magnetic susceptibility of chromium.

The above mechanism is supported by data on the thermal desorption of CO_2.[209] During the thermoprogrammed heating of the Mn–O/SiO_2 catalyst, pretreated with CO_2, the evolution of CO_2 is observed at three temperatures — 335, 425, and 750 °C — owing to the nonuniformity of the adsorption centres. The activation energies for desorption are 93 ± 8, 226 ± 8, and 293 ± 8 kJ mol^{-1} under these conditions. During the thermal desorption of CO_2 from a surface treated with hydrogen before adsorption (500 °C, 4 h), three types of centres are also observed, their capacity with respect to CO_2 being somewhat lower probably as a result of the removal of some of the oxygen centres during the reduction of the catalyst by hydrogen. The activation energies for desorption do not change under these conditions. The activation energies for the thermal desorption of CO_2 are close to those for the thermal desorption of oxygen under the same conditions. This may indicate the similarity of the nature of the centres for the activation of CO_2 and O_2 and identical principles governing the manganese catalysts in the carbonic acid and oxygen conversions.

On the other hand, in the thermal desorption of CO_2 from the Cr–Mn–O/SiO_2 catalyst, only one high-temperature peak is observed (the activation energy for desorption is 233 ± 8 kJ mol^{-1}). Such a change in the thermoprogramming diagram (TPD) on passing from Mn–O to Cr–Mn–O is evidently associated with the reoxidation of Cr^{2+} by the intermediate CO_2-accepting manganese-containing phase. The decrease in the degree of adsorption of CO_2 during the preliminary reduction of the catalyst by hydrogen indicates that the carbon dioxide adsorption centres are regular O^{2-} lattice ions on the basic surface. The strong CO_2-accepting centres in the high-temperature region are probably less reactive in the reoxidation of Cr^{2+}. Consequently the strength of the basic centres determines the stability of the carbonate structure and hence the degree of reoxidation of the oxidation-reduction centres. Centres with a moderate basicity are needed for the acceptance of CO_2 and the reoxidation of Cr^{2+}, which is in fact observed when the system

contains the weakly basic oxide MnO. The presence of an interface between MnO and CrO under these conditions probably facilitates the reoxidation of CrO.

The capacity with respect to oxygen of the catalytic system $Cr-O/SiO_2$, which contains no manganese oxide, is significantly lower after its reoxidation by CO_2 than the similar capacity of the $Cr-Mn-O/SiO_2$ system. From this standpoint, the $Cr-Mn-O$ composition can be regarded as bifunctional: on the one hand, it activates CO_2 on the basic centres and, on the other, it converts the hydrocarbon on the oxidation-reduction centres.

The oxygen capacity and the rate of oxidation of the catalyst can be altered by adding oxygen to the $C_2H_6 + CO_2$ mixture. For a particular $CO_2:O_2$ ratio, it is posisble to attain the optimum degree of oxidation of the surface, which ensures a high selectivity in the conversion of C_2H_6 into C_2H_4.[195] The reoxidation activation energy is significantly higher than the activation energy for the decomposition of the carbonate fragments. This is probably one of the reasons for the lower oxygen capacity of the catalysts reoxidised by carbon dioxide compared with their capacity when they are reoxidised by O_2.

The activation energies for the reoxidation of $Cr-Mn$ catalysts of different composition are the same (this also applies to the $V-Mn-O$ catalyst), although their oxygen capacities are different. This means that, although CO_2 is initially bound to Mn, the second element (Cr, V) determines the rate of reoxidation.

The centres on which oxygen is bound and the oxygen ions formed promote also the transition of CO_2 to the activated state. The mobile oxygen species pass from the manganese carbonate phase via spill-over to the chromium oxidation-reduction centres.

Another example of oxides with a moderate basicity having oxidation-reduction centres is provided by lanthanide oxides. Thus the oxidative dehydrogenation of ethane has been achieved on La_2O_3.[211] Under these conditions, La_2O_3 is converted into the hexagonal carbonate $La_2O_2CO_3$, which is in fact the active phase. Other lanthanide oxides do not form monocarbonates and are much less active than La_2O_3.

2. Interaction with propane

In the heterogeneous-catalytic conversion of propane by reaction with CO_2 on different catalytic systems, three reactions take place to different extents: oxidative dehydrogenation of propane to propene [reaction (36)], its degradative cleavage to C_2H_4 [reaction (37)], and its extensive conversion with formation of CO and H_2 [reaction (38)].

$$C_3H_8 + CO_2 \rightarrow C_3H_6 + CO + H_2O, \quad \Delta H_{298} = 165.3 \text{ kJ mol}^{-1}, \tag{36}$$

$$2C_3H_8 + 2CO_2 = 3C_2H_4 + 2CO + 2H_2O, \tag{37}$$

$$C_3H_8 + 3CO_2 = 6CO + 4H_2. \tag{38}$$

Like the interaction of ethane with CO_2 [reaction (31)], reaction (38) is of interest as a method of preparation of a synthesis gas with an increased CO content. According to the data of Mamedov et al.,[192] the degree of conversion of CO_2 in an equimolar mixture with propane is 80%–85% on a nickel catalyst at 750 °C. However, the process is accompanied by extensive coke deposition.

The $CO_2 + C_3H_8$ reaction has been investigated on the Ni/SiO_2, Rh/SiO_2, and Pd/SiO_2 catalysts at 600 °C. The Ni/SiO_2 catalyst proved to be the most active and selective: the degree of conversion reached 92% and the selectivity in the formation of $CO + H_2$ reached 70%–80%. According to the authors,[212] the rate-limiting stage is the dissociation of propane:

$$C_3H_8 + 2Ni \rightarrow 2NiCH_2 + CH_4.$$

This is followed by the reactions

$$CH_4 + Ni \rightleftharpoons NiCH_2 + H_2,$$

$$NiCH_2 + CO_2 \rightleftharpoons Ni + 2CO + H_2,$$

$$NiCH_2 + 2CO_2 \rightleftharpoons Ni + 3CO + H_2O,$$

$$Ni + CO_2 \rightleftharpoons NiO + CO,$$

$$NiCH_2 + NiO \rightleftharpoons 2Ni + CO + H_2,$$

$$NiO + H_2 \rightleftharpoons Ni + H_2O.$$

The manganese oxide systems proved to be active and stable catalysts for the oxidative-reductive dehydrogenation of propane via reactions (36) and (37) with formation of propene and ethene.[192, 196, 204, 213]

In the presence of $Mn-O/SiO_2$, the conversion of propane into C_2-C_3 alkenes proceeds more selectively than on the nickel catalyst. At 800 °C, the yield of C_2-C_3 alkenes is 47% relative to the propane passed through the system. With increase in temperature, their yield diminishes, but the yield of CO and H_2 increases. Preliminary treatment of the catalyst with carbon dioxide increases the selectivity for the formation of the C_2-C_3 compounds. After preliminary treatment with hydrogen, the overall degree of conversion of propane and CO_2 increases, but the selectivity for the formation of alkenes falls. Evidently the selective degradation of propane to ethene and methane and the oxidative dehydrogenation to propene take place on the oxidised surface, whereas on the reduced surface propane undergoes cracking with formation of carbon fragments, which are oxidised by carbon dioxide to CO. Thus the overall characteristics of the conversion of propane are similar to those of the conversion of ethane.

The best catalyst for the selective conversion of propane by CO_2 is, for ethane, the 1.5% K–5.5% Cr–17% $Mn-O/SiO_2$ system. At 830 °C, a space velocity of 3600 h^{-1}, and for $CO_2:C_3H_8 = 1.5$, a degree of conversion of C_3H_8 of 96.0%, a degree of conversion of CO_2 of 52.0%, a selectivity in the formation of the C_2H_4 and C_3H_6 hydrocarbons of 75% (80% in the case of C_2H_4), a yield of C_2-C_3 alkenes of 72%, and the $CO:(C_2H_4 + C_3H_6)$ ratio = 1.4 were attained on this catalyst. At 890 °C, the ratio $CO:(C_2H_4 + C_3H_6)$ increases to 4. The amount of hydrogen present in the reaction product is smaller by a factor of 5–8 than that of CO. With increase in the degree of conversion, there is a considerable fall in the selectivity in the formation of alkenes. This behaviour can probably be accounted for by the higher degrees of conversion of the hydrocarbon and the formation of a reaction mixture with more effective reducing properties than in the case of ethane.[196]

After the reduction of the catalyst by propane, the rate of formation of C_2-C_3 alkenes diminishes: the rate of formation of C_2H_4 on the oxidised surface is 2–3 times greater than on the reduced surface. It must be emphasised that, in the interaction of propane with a catalyst pretreated with air, the extensive oxidation products (CO and CO_2) are formed preferentially. This can apparently be explained by the fact that, when the catalyst is treated with air, chromium passes to a higher oxidation state (up to Cr^{6+}) than in Cr_2O_3. On the other hand, the intermediate state of chromium (Cr^{3+}) is responsible for the formation of C_2-C_3 alkenes. Manganese oxides are reduced in the stationary state to MnO (according to X-ray diffraction data obtained in situ). This phase participates in the oxygen transport and maintains chromium in the Cr^{3+} oxidation state [see reaction (35)].

The $Cr-O/SiO_2$ catalyst is less active and selective. Evidently without MnO it is impossible to maintain chromium in the oxidised state.

Under stationary conditions with $C_3H_8:CO_2 = 1-1.2$, the amount of coke formed does not exceed 3.6% relative to the weight of the catalyst. Electron microscopy shows that, after the treatment of the catalyst under nonstationary conditions, coke is present on the surface in two forms: as filamental carbon and in the form of flat scales Under stationary conditions, filamental carbon is not formed. This is associated either with the absence of metallic inclusions in the catalyst (Cr^0) or with the rapid interaction of the nuclei of the carbon phase with CO_2 in

accordance with the Boudouard reaction. Coke is removed from the $Mn-Cr-O/SiO_2$ catalyst at a much lower temperature (610 °C) than from $Mn-O/SiO_2$ (870 °C).

A scheme for the oxidative pyrolysis of propane in the presence of CO_2 (Scheme 3) has been proposed.[168] It is similar to the scheme for the $CO_2 + C_2H_6$ interaction on the $K-Cr-Mn-O/SiO_2$ catalyst (Scheme 2). According to Scheme 3, C_2H_4 is formed mainly on the Cr^{3+} centres, while CH_4, CO, and H_2 are formed on the Cr^{2+} centres; MnO ensures the activation of CO_2. The gas-phase reactions of the radicals are not included in the scheme.

Scheme 3

$$C_3H_8 + Cr^{3+}O^{2-} \xrightarrow{a} C_3H_7^{\cdot} + Cr^{2+}OH^-,$$

$$C_3H_7^{\cdot} + Cr^{3+}O^{2-} \xrightarrow{b} C_2H_4 + CH_3O^-...Cr^{2+},$$

$$CH_3O^-...Cr^{3+} \xrightarrow{c} Cr^{3+}O^{2-} + CH_3^{\cdot},$$

$$CH_3O^-...Cr^{2+} \xrightarrow{d} Cr^{2+}[\ ] + \text{extensive oxidation products}$$

$$C_3H_8 + 2[\ ]Cr^{2+} \xrightarrow{e} C_2H_4...Cr^{3+} + C...Cr^{2+} + 2H_2,$$

$$C_2H_4...Cr^{2+} \xrightarrow{f} CH_4 + C...Cr^{2+},$$

$$C_2H_4...Cr^{2+} + [\ ]Cr^{2+} \xrightarrow{g} 2C...Cr^{2+} + 2H_2,$$

$$2Cr^{2+}OH^- \xrightarrow{h} Cr^{2+}[\ ] + Cr^{2+}O^{2-} + H_2O,$$

$$Cr^{2+}[\ ] + Cr^{2+}O^{2-} + MnCO_3 \xrightleftharpoons{i} \rightleftharpoons 2Cr^{3+}O^{2-} + MnO + CO,$$

$$C...Cr^{2+} + Cr^{3+}O^{2-} \xrightarrow{j} 2Cr^{2+}[\ ] + CO,$$

$$MnO + CO_2 \xrightleftharpoons{k} MnCO_3.$$

The first two stages in Scheme 3 may be combined into one, i.e. the Scheme may be formulated also without the participation of free radicals, although their formation in the high-temperature interaction of alkanes with oxides is extremely probable. If it is postulated that, in the case where the process proceeds via a parallel reaction mechanism, the catalyst may be reduced both by the initial hydrocarbon and by CO, the rate of the selective formation of ethene from propane may be expressed by the equation

$$r_{C_2H_4} = \frac{k_1 P_{C_3H_8} k_2 P_{CO_2}}{k_1 P_{C_3H_8} + k_2 P_{CO_2} + k_3 P_{CO}}.$$

However, under real conditions the catalyst is reduced by the hydrocarbons 17 times more slowly than by carbon monoxide (the rate of oxidation of CO is 17 times higher than the rate of the extensive oxidation of propene). We then have $k_3 P_{CO} \gg k_1 P_{C_3H_8}$ and the rate equation is transformed into

$$r_{C_2H_4} = \frac{k_1 P_{C_3H_8} k_2 P_{CO_2}}{k_2 P_{CO_2} + k_3 P_{CO}}.$$

The activation energy for the formation of ethene from propane is 151 kJ mol^{-1}, which is close to the value obtained in the case of ethane (167 kJ mol^{-1}), confirming the similarity of the mechanisms of the primary activation of these hydrocarbons on the $K-Cr-Mn-O/SiO_2$ catalyst. The kinetic equations for the conversion of ethane and propane are also similar and differ from the corresponding equations describing the oxidation of alkanes by oxygen.

The chemistry of the interaction of propane with CO_2 on metals (Ni) and oxides (MnO_x) is different. On the former, synthesis gas is formed selectively, whilst on the latter C_2-C_3 alkenes are formed preferentially. On metals, propane dissociates into C(ads) or CH_x, whereas on oxides hydrogen is split off from propane or oxidative cracking takes place. On metals, CO_2 reacts with carbon via the reverse Boudouard reaction, whilst on oxides it interacts with hydrogen (the reverse water gas conversion).

On zeolitic catalysts, the oxidative dehydrogenation of propane in the presence of CO_2 takes place at lower temperatures and is directed towards aromatisation.

$$2C_3H_8 + 2CO_2 = C_6H_6 + 2H_2O + 3H_2 + 2CO$$

The interaction of propane with CO_2 on the Zn-HZSM-5 catalyst (10% of H atoms replaced by Zn) has been investigated.[214,215] It was observed that CO_2 greatly increases the conversion of C_3H_8, suppressing the formation of coke. The yield of CO exceeds the conversion of CO_2, which indicates the partial formation of CO from propane via coke. At 550 °C, the maximum degree of conversion of C_3H_8 was 68.4%, whilst that of CO_2 was 13.1%. A mixture of C_1 and C_4 hydrocarbons as well as aromatic hydrocarbons is also formed with a selectivity in the formation of the aromatic hydrocarbons of 50.8%. The first reaction stage is the dehydrogenation of propane, which is initially faster in the absence of CO_2, but the deactivation in the presenc e of CO_2 is very slow. This indicates a considerable role for the Boudouard reaction.

Among the zeolites investigated, the highest activity in the oxidative aromatisation of propane in the presence of CO_2 was shown by Zn-ZSM-5. On H-ZSM-5 and Na-ZSM-5, the yield of aromatic hydrocarbons from C_3H_8 in the presence of CO_2 was somewhat higher than in its absence, whilst on Pt-ZSM-5 it was lower. This can be explained by the higher cracking capacity of platinum in relation to propane. In the reaction involving the formation of synthesis gas, the zeolitic catalysts can be arranged in the following activity series: Pt > Zn > Ga > H-ZSM-5.[216]

We have already mentioned studies in which the influence of CO_2 on the reactions of hydrocarbons on zeolites was investigated. it may be that in these studies too the positive effects of CO_2 can be accounted for by its oxidising properties, for example by its interaction with the coke formed.

3. Interaction with n-butane

The conversion of n-butane by reaction with CO_2 also proceeds on manganese-containing oxide catalysts.[204,209] At 630-650 °C and for the ratio $n\text{-}C_4H_{10}:CO_2 = 1-1.2$ on the $Cr-Mn-La-V-O/SiO_2$ catalyst, the degree of conversion of n-butane reached 81%-84%, whilst the selectivity for the formation of C_2-C_4 alkenes reached 76%-78%. Oxidative cracking predominates over oxidative dehydrogenation: more C_2H_4 is formed than C_3H_6 and the amount of the latter is greater than that of C_4H_8. The selectivity with respect to synthesis gas reached 22%-24%, CO and H_2 being obtained in approximately equal amounts, in contrast to the reaction of CO_2 with ethane and propane.

Consequently, the simple catalytic or noncatalytic dehydrogenation

$$C_4H_{10} = C_4H_8 + H_2$$

and the oxidative dehydrogenation

$$C_4H_{10} + CO_2 = C_4H_8 + CO + H_2O$$

take place to only a limited extent. The principal reaction path is oxidative cracking with formation of alkenes and synthesis gas:

$$C_4H_{10} + CO_2 = 2C_2H_4 + CO + H_2O,$$

$$C_4H_{10} + CO_2 = C_3H_6 + 2CO + 2H_2,$$

$$C_4H_{10} + CO_2 = C_2H_4 + CH_4 + 2CO + H_2.$$

Direct cracking

$$C_4H_{10} \rightarrow C_3H_6 + CH_4,$$

apparently also makes a considerable contribution, which is indicated by the high CO_2 content in the final gas. However, it is not clear why this process proceeds to a very limited extent in the absence of CO_2.

It is of interest that the MnO/SiO_2 catalyst, which contains no vanadium and has more basic properties, exhibits a higher selectivity in relation to dehydrogenation. It may be that, as in the case of C_2-C_3 hydrocarbons (see above), oxidative dehydrogenation of n-butane with the aid of CO_2 proceeds via the formation of intermediate carbonates, while oxidative cracking (or simply cracking) takes place with participation of more reduced centres.

4. Interaction with isobutane

The dehydrogenation of isobutane with participation of carbon dioxide can be described by the equation

$$\text{iso-}C_4H_{10} + CO_2 = \text{iso-}C_4H_8 + CO + H_2O, \quad (39)$$
$$\Delta H = 195.4 \text{ kJ mol}^{-1}.$$

In the absence of the catalyst, the degree of conversion of isobutane in a mixture with CO_2 (or N_2) to isobutene at 665 °C is 19%; under these conditions, CO_2 does not react. In the presence of the $K-Cr-Mn-O/SiO_2$ catalyst at 670 °C, the degree of conversion of iso-C_4H_{10} is 35%–36%, whilst that of CO_2 is 5.8%; on the $K-Cr-Mn-O/Al_2O_3$ catalyst, the degree of conversion of iso-C_4H_{10} increases to 50% and that of CO_2 increases to 9%–10%; on $Cr-Mn-O/Al_2O_3$ (in the absence of potassium), the degree of conversion of iso-C_4H_{10} reaches 61%–66% and that of CO_2 reaches 20%–29.5%.[204, 209, 217] The selectivity with respect to the main product (iso-C_4H_8) on the last catalyst is 78%–81%. CO and H_2 are also formed in equal amounts. This distinguishes this process from those involving ethane and propane, where $CO : H_2 = 7$.

Preliminary treatment of the catalyst with hydrogen does not lead in this case, in contrast to the reactions of ethane and propane, to a decrease in the yield of the alkene, whilst preliminary treatment with CO_2 reduces both the yield and the selectivity. The selectivity in the cleavage of isobutane into propene and methane increases under these conditions. As the reaction proceeds, the selectivity and activity of the catalyst increase similarly: this also distinguishes the above process from reactions involving ethane and propane, where the selectivity with respect to the alkene increases as the surface is oxidised.

The reaction of CO_2 with isobutane has also been investigated under the conditions of their separate interaction with the catalyst. When isobutane came into contact with the surface at 670 °C in the absence of CO_2, iso-C_4H_8, CO, H_2, C_3H_6, and CH_4 were obtained. The rate of formation of CO in such interaction of iso-C_4H_{10} with the surface is significantly lower (by a factor of 12–30) than the rate of its formation under stationary conditions. Calculations showed that under stationary conditions only 3%–4% of CO is the result of the regeneration of the coke-saturated catalyst by the reaction

$$C + CO_2 \rightarrow 2\ CO.$$

However, this reaction ensures the activity of the catalyst for a long time.

The study of the oxidation of hydrogen by carbon dioxide on this catalyst showed that the rate of formation of CO under these conditions is comparable to the rate of its formation under stationary conditions. Consequently, the main path leading to the formation of CO under stationary conditions is reaction (3).

The rate of formation of CO in the interaction of CO_2 with the reduced catalyst is also appreciably lower (by a factor of 10 in the case of the $Cr-Mn-O/SiO_2$ catalyst) than the rate of formation of CO under stationary conditions at 670 °C [reaction (39)]. It is observed preferentially at temperatures above 700 °C.

Consequently, at 600–700 °C the interaction of isobutane with CO_2 represents mainly the sum of two consecutive reactions:

$$\text{iso-}C_4H_{10} \rightarrow \text{iso-}C_4H_8 + H_2, \quad (40)$$
$$H_2 + CO_2 \rightarrow CO + H_2O.$$

The overall mechanism of the reactions of iso-C_4H_{10} on the Mn–Cr catalyst can be represented by Scheme 4.

Scheme 4

$$\text{iso-}C_4H_{10} + Cr^{3+}O^{2-} \xrightarrow{a} \text{iso-}C_4H_9 + Cr^{2+}OH^-,$$
$$\text{iso-}C_4H_9 + Cr^{3+}O^{2-} \xrightarrow{b} \text{iso-}C_4H_8 + Cr^{2+}OH^-,$$
$$2Cr^{2+}OH^- \xrightarrow{c} Cr^{2+}[\ ] + Cr^{2+}O^{2-} + H_2O,$$
$$MnO + CO_2 \overset{d}{\rightleftharpoons} MnCO_3,$$
$$H_2 + MnCO_3 \xrightarrow{e} H_2O + CO + MnO,$$
$$H_2 + Cr^{3+}O^{2-} \xrightarrow{f} H_2O + Cr^{2+}[\ ],$$
$$Cr^{2+}[\ ] + CO_2 \xrightarrow{g} Cr^{3+}O^{2-} + CO.$$

Dehydrogenation (in addition to the thermal dehydrogenation) takes place with participation of the reduced centres, probably chromium ions. The presence of hydrogen in the gas phase shows that oxidative dehydrogenation does not predominate over direct dehydrogenation. H_2 interacts with CO_2 apparently via the $MnCO_3$ carbonate fragments (reactions *d* and *e* in Scheme 4).

The kinetic equation for the process differs from the equation describing the interaction of ethane and propane with CO_2 and has the form of the Mars–Van Krevelen equation:

$$r_{\text{iso-}C_4H_8} = \frac{k_1 P_{\text{iso-}C_4H_{10}} k_2 P_{CO_2}}{k_1 P_{\text{iso-}C_4H_{10}} + k_2 P_{CO_2}}.$$

This shows that the role of the reduction of the catalyst by the carbon monoxide formed during the reaction is small. The change in the reaction kinetics on passing from C_2H_6 and C_3H_8 to iso-C_4H_{10} is probably caused by the lower energy of the C–H bonds in isobutane, which ensures their cleavage with participation of less oxidised or carbonate centres. In this case, hydrogen should be present in the reaction mixture.

At a high temperature (750–900 °C), the reaction does not proceed via carbonates but via the dissociative adsorption of CO_2 and subsequent oxidative dehydrogenation.

$$\text{iso-}C_4H_{10} + [O] \rightarrow \text{iso-}C_4H_8 + H_2O,$$

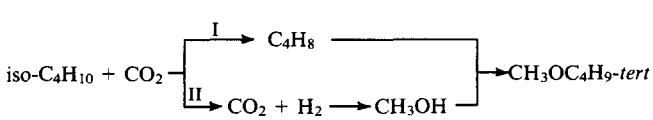
$$CO + H_2O \rightleftharpoons CO_2 + H_2.$$

In both cases, the last reaction is the equilibrium conversion of water gas, leading to an equilibrium mixture of H_2, CO, H_2O, and CO_2.

The hydrogen formed in the dehydrogenation of isobutane is not fully oxidised [only half of its participates in the subsequent reduction of CO_2 in accordance with the equilibrium reaction (3)]. This results in the formation of a mixture containing iso-C_4H_8, CO, and H_2 as the main products. The selectivity for the formation of the side products (C_3H_8 and CH_4) is about 10%.

The addition of n-butane to the reaction mixture does not alter the characteristics of the dehydrogenation of isobutane by carbon dioxide.[217]

The simultaneous formation of isobutene and synthesis gas in the reaction of isobutane with CO_2 makes it possible to propose a new process for the preparation of *tert*-butyl methyl ether — the high-octane component of nonethylated petrol.



Reaction I is endothermic (155 kJ mol^{-1}), whilst reaction II is exothermic (92 kJ mol^{-1}). The combination of these reactions makes it posisble to diminish by a factor of 2 the energy consumption in reaction I.

5. Interaction with n-heptane

Studies have shown[194,218] that, on interaction with CO_2 on manganese oxide catalysts, heavy alkanes undergo mainly oxidative cracking. Under stationary conditions, it proceeds without the accumulation of coke fragments and a high degree of conversion of the hydrocarbon is attained. By altering the nature of the hydrocarbon employed and the catalyst, it is possible to direct the process towards the formation of light alkenes, alkanes, and also isomeric paraffinic hydrocarbons.

On $K-Mn-O/Al_2O_3$, $La-Mn-O/Al_2O_3$, and La–Mn/NaY, the reaction takes place at 540–670 °C. Oxidative cracking with formation of H_2, CO, CH_4, C_2H_4, C_3H_6, and C_4H_8 is observed. The La–Mn/NaY catalyst is more active in cracking than $La-Mn-O/Al_2O_3$ and $K-Mn-O/Al_2O_3$. The degree of conversion of n-heptane on this catalyst at 670 °C reaches 100% for a low degree of conversion of CO_2 (4.2%). On $La-Mn-O/Al_2O_3$, the overall degree of conversion of n-heptane is lower (86.4% at 670 °C), but that of CO_2 is higher (30.2%). In addition, a low yield of H_2 ($CO:H_2 = 10$) was observed on La–Mn/NaY, whilst on $La-Mn-O/Al_2O_3$ and $K-Mn-O/Al_2O_3$ carbon monoxide and H_2 were formed in equal amounts. It follows from the foregoing that $La-Mn-O/Al_2O_3$ and $K-Mn-O/Al_2O_3$ are more active in the activation of CO_2.

The reduction of CO_2 with the formation of CO probably proceeds via several paths: as a result of the oxidation of H_2 (a cracking product) by carbon dioxide and via the gasification of the surface carbon fragments.

Experiments have been carried out on the reoxidation of the $La-Mn-O/Al_2O_3$ catalyst by treating it with CO_2 after the stationary oxidative cracking process. The rate of reoxidation at 620–670 °C is constant in time, i.e. the saturation of the surface is not observed. The interaction of H_2 with CO_2 has also been investigated. The rate of formation of CO in this reaction was somewhat lower than in the conversion of heptane by reaction with CO_2.

The rate of formation of CO under stationary conditions at 670 °C is 14 times higher than in the reoxidation of the catalyst. This shows tht the oxidation of the catalyst

$$MnO + CO \rightleftharpoons MnCO_3,$$

$$3MnCO_3 \rightleftharpoons Mn_3O_4 + CO + CO_2$$

is not the main path leading to the formation of CO under stationary conditions. Reaction (3) does not proceed via the direct alternate oxidation-reduction

$$H_2 + [O] \rightarrow [\ ] + H_2O,$$

$$[\ ] + CO_2 \rightarrow CO + [O],$$

but via the 'associative' interaction of H_2 with the surface carbonates:

$$H_2 + MnCO_3 \rightarrow CO + H_2O + MnO.$$

In the stationary state, an intermediate carbonate structure participates in the process.

Another source of CO is reaction (40), i.e. the interaction of CO_2 with carbon deposits. This ensures the selective oxidative (carbonic acid) cracking and a stable activity of the $La-Mn-O/Al_2O_3$ and $K-Mn-O/Al_2O_3$ catalysts without the accumulation of coke fragments on the surfaces.

The low rate of formation of CO on the La–Mn/NaY catalyst is apparently associated with the formation of stable carbonates. Presumably decationated zeolites modified with manganese should serve as a base for an effective catalyst for the cracking process in the presence of CO_2.

Thus the oxidative cracking of n-heptane with the aid of CO_2 may be described by the following equations:

$$C_7H_{16} \rightarrow C_4H_8 + C_3H_6 + H_2,$$

$$C_7H_{16} \rightarrow 3C_2H_4 + C^* + 2H_2,$$

$$H_2 + CO_2 \rightleftharpoons CO + H_2O,$$

$$C^* + CO_2 \rightleftharpoons 2CO.$$

Summarising the results of the study of the oxidative interaction of C_4-C_7 alkanes with CO_2, we may note that experiments have demonstrated the possibility of the simultaneous formation of alkenes and synthesis gas. In contrast to the familiar cracking and dehydrogenation processes, this path makes it possible to employ CO_2 as the starting material.

Nickel-containing compounds are known to be deposited from petroleum during catalytic cracking on zeolitic catalysts and to poison the latter as a consequence of the increased coke formation. CO_2 has been used to passivate this process.[219] The $C_7H_{16} + CO_2$ reaction has been investigated on the $Ni-La-8\%\ MnO/Al_2O_3$ catalysts containing between 0.5 mass% and 2.5 mass% of lanthanum and nickel. With increase in the nickel content, the degrees of conversion of C_7H_{16} and CO_2 at 670 °C increase. It is especially important that the presence of CO_2 in the mixture ensures the maintenance of the stable activity of the catalyst, whereas in the traditional catalytic cracking an increase in the CO_2 content entails an increase in coke formation and a decrease in the catalyst activity. If CO_2 is replaced in the reaction mixture by N_2, the overall activity falls and the yield of C_4 hydrocarbons diminishes, but that of C_2 hydrocarbons increases, i.e. the undesired extensive cracking takes place. In the absence of manganese, nickel is reduced to the metallic state even in the presence of CO_2, which also leads to deactivation. Evidently manganese promotes the binding and activation of CO_2 in accordance with the scheme

$$MnO + CO_2 \rightleftharpoons MnCO_3,$$

$$MnCO_3 + Ni \rightarrow MnO + NiO + CO.$$

In conclusion of this section about the reactions of hydrocarbons in the presence of CO_2, we may note certain general features. The mechanisms of the activating effect of CO_2 on the reactions of C_1-C_3 and C_4-C_7 hydrocarbons are different. In the case of the lower alkanes, CO_2 enters into an oxidation–reduction interaction with the catalyst, after which the surface O^{2-} ions oxidise the hydrocarbon. The reaction takes place at a high temperature (750–850 °C). The decrease in temperature to 550–650 °C in the oxidative aromatisation of propane on zeolitic catalysts can be accounted for by the greater role of the reverse Boudouard reaction [reaction (40)] in this process.

In the conversion of C_4 hydrocarbons (at 650–700 °C), the first stage is their direct dehydrogenation, after which hydrogen is oxidised by reaction with CO_3^{2-}. (We examined the accelerating effect of hydrogen on the reactions with participation of CO_2 in Section III).

The principal path in the interaction of higher hydrocarbons with CO_2 (at 650–750 °C) is oxidative cracking, the reverse Boudouard reaction [reaction (40)], i.e. the interaction of C* with CO_2, playing a major role in the reaction mechanism. The activation of carbon dioxide and not of the hydrocarbons is rate-limiting. The hydrogen evolved accelerates the Boudouard reaction.

Manganese-containing catalysts can be used to convert both groups of hydrocarbons. This can be explained, firstly, by the fact that manganese oxides gives rise to moderately stable carbonates, which are capable of decomposing under reaction conditions. Secondly, manganese affords oxides capable of being readily oxidised and reduced under the reaction conditions.

When alkaline (Na, K) oxides are added, the stability of these carbonates increases, while the addition of acid oxides (Mo, V) diminishes the stability. Alkaline oxides shift the process towards oxidative dehydrogenation, whilst acid ones shift it towards oxidative cracking. The surface carbonates participate in the oxidation-reduction reactions with the hydrocarbon or hydrogen.

VI. Oxidation reactions of carbon dioxide with other compounds

Transition metal and lanthanide oxides also catalyse the oxidative reaction of CO_2 with other organic compounds.

1. Interaction of carbon dioxide with the carbon fragments in cracking catalysts

The regeneration of the coke-saturated cracking catalyst is known to involve combustion processes entailing the development of high temperatures, which reduce the process efficiency. The use of CO_2 instead of O_2 for the regeneration makes it possible, in principle, to increase the process efficiency.[220-222]

In the interaction of the coke-saturated zeolite-containing KNTsU-B catalyst with CO_2 at 680 °C and a space velocity of the supply of CO_2 of 900 h^{-1}, the degree of conversion of CO_2 does not exceed 1%. The rate of regeneration of the catalyst modified by manganese acetate (5% Mn) after saturation with coke exceeds by a factor of 15 the rate of regeneration of the unmodified catalyst under similar conditions. Apart from CO, methane is also formed, the rate of its formation being greater by a factor of 1.3 than the rate of formation of CO. Hydrogen is detected only in trace amounts.

When the coke-saturated catalyst is modified with chromium, an increase in the rate of formation of CO is also observed. In this case, $CO:CH_4 = 4-5$. On regeneration of the coke-saturated catalyst modified by lanthanum carbonate with CO_2, the formation of CO has already begun at 400 °C.

The modifying additives can be introduced into the catalyst during its preparation, before its employment in cracking and its regeneration. When 5% of lanthanum is introduced into the zeolite-containing catalyst Tseokar-2, the regeneration with the aid of CO_2 begins at 400 °C. Under programmed heating conditions, the thermogram showed two maxima corresponding to the formation of CO ($E = 138$ and 226 kJ mol^{-1}) and a maximum corresponding to the evolution of CH_4 ($E = 201$ kJ mol^{-1}). H_2 is also evolved during the heating process.

The stoichiometric equations for the formation of CO, H_2, and CH_4 can be expressed in the form

$$CH_x + CO_2 \rightarrow 2\,CO + \tfrac{1}{2}xH_2,$$

$$2CH_x \rightarrow CH_4 + C + (x - 2)H_2.$$

For $x = 2$, the overall equation assumes the following form:

$$2CH_2 + CO_2 \rightarrow CH_4 + 2CO,$$

whence it follows that methanation and the Boudouard reaction take place in the oxidation of CH_x fragments by CO_2.

Thus the effective acceptance of CO_2 by manganese or lanthanum oxides ensures a high rate of oxidation of the surface CH_x fragments.

The processing of heavy petroleums is greatly hindered by the presence of heavy metals (Ni and V) in them, mainly in the form of porphyrins, which are deposited on the surfaces of the catalyst. These metals greatly increase the poisoning and coke formation. In this case too, the addition of manganese proved useful. In the presence of manganese, nickel appreciably accelerates the regeneration of the catalyst by CO_2.[219] On the other hand, the oxidation of vanadium by carbon dioxide is retarded in the presence of MnO_x or La_2O. The positive effect of CO_2 reduces in this case to the stabilisation of the surface as a result of its being blocked by the lanthanum and manganese carbonate fragments, which prevents the deactivation of the catalyst by vanadium.[223]

It is well known that the gasification of coal by CO_2 or H_2O is accelerated by alkaline additives. Tunnels are formed in the layer of carbon beneath the alkalies (K, Na, Li, Ba, and Ca oxides) deposited on it. Evidently here too the carbon formed interacts with the carbonate ions.[224]

2. Interaction with other hydrocarbons

In the absence of a catalyst, ethene does not interact with CO_2 at temperatures below 750 °C. A low degree of conversion of C_2H_4 (up to 12%) is observed at 750-820 °C with formation of CH_4, C_4H_6, C_3H_6, and traces of C_2H_4. Mainly synthesis gas is obtained on the nickel catalyst under these conditions.

$$C_2H_4 + 2CO_2 = 4CO + 2H_2 \qquad (41)$$

Up to 2%-3% of butadiene is also evolved. The degree of conversion of ethene at 750 °C is 65%.

On Ru/Al_2O_3 and $Ru-Co/Al_2O_3$, carbon dioxide interacts with hex-1-ene at a low temperature (100 °C) and a pressure of 10-35 atm.[225] Alkenes, ethers, aldehydes, and ketones have been detected in the products; the degree of conversion has not been reported.

The use of the $Mn-O/SiO_2$ oxide catalyst (see Refs 200, 204, 226, and 227) in the reaction of ethene with CO_2 led to the formation of butadiene and propene. On the 17% $Mn-O/SiO_2$ catalyst at 820 °C, a degree of conversion of C_2H_4 of 22.3% was attained, that of CO_2 was 11.6%, and the selectivity was 25.0% with respect to C_4H_6 and 18.0% with respect to C_3H_6. We may note that the reaction involving oxidative dimerisation with the aid of CO_2, i.e.

$$2C_2H_4 + CO_2 \rightarrow C_4H_6 + CO + H_2O, \quad \Delta H = 243 \text{ kJ mol}^{-1} \qquad (42)$$

is highly endothermic and thermodynamically unfavourable ($\Delta G > 0$). However, CO, H_2, CH_4, C_3H_6, and C_4H_8 are also formed under the catalytic conditions, so that it is difficult to carry out an exact thermodynamic calculation for these conditions. Treatment of the $Mn-O/SiO_2$ catalyst with carbon dioxide reduces the selectivity with respect to C_4H_6 and C_3H_6, whilst treatment with hydrogen increases it. A different behaviour has been observed with alkanes. The process proceeds on the reduced catalyst.

On Cr_2O_3/SiO_2, the degree of conversion of C_2H_4 at 820 °C was 27.3%, that of CO_2 was 14.8%, and the selectivity was 39.0% with respect to C_4H_6 and 24.2% with respect to C_3H_6.[226] Surface carbonate fragments participate in the process. At low temperatures (400-600 °C), the oxidation of the CH_x fragments by CO_2 takes place in accordance with the scheme

$$CH_x + CO_3^{2-} \rightarrow CH_xO + CO + O^{2-},$$

$$CH_xO \rightarrow CO + \tfrac{1}{2}xH_2.$$

At high temperatures (600-750 °C), carbon monoxide is formed mainly from carbon:

$$CO_3^{2-} + C \rightarrow 2CO + O^{2-}.$$

We may note that the characteristics of the interaction of CO_2 with ethene are not the same as those of its interaction with alkanes. Thus, in the $C_2H_4 + CO_2$ reaction, the addition of the acid oxide WO_3, instead of a basic one, to Mn/SiO_2 increased the degree of conversion of C_2H_4 and the selectivity in the formation of C_3H_6 and C_4H_6.

On the 2% W-17% $Mn-O/SiO_3$ catalyst at 820 °C, a space velocity of 2700 h^{-1}, and for $C_2H_4:CO_2 = 1$, the degree of conversion of C_2H_4 was 30.1%, that of CO_2 was 12.4%, and the selectivity was 33.4% with respect to C_4H_6 and 20% with respect to C_3H_6.

On the 2% W-5.5% $Cr-O/SiO_2$ catalyst, the best parameters for the conversion of C_2H_4 and for the selectivity in the

formation of butadiene were attained; the catalyst was not saturated with coke under the reaction conditions. At 820 °C, the degree of conversion of C_2H_4 was 30.5%, that of CO_2 was 13.7%, and the selectivity was 50.2% with respect to C_4H_6 and 30.6% with respect to C_3H_6; CO, CH_4, C_3H_6, and C_4H_8 were also formed. The degree of conversion of CO_2 was 2–3 times smaller than that of ethene. This is apparently associated with the fact that CO_2 is consumed in the interaction with the coke deposits and the contribution of this reaction is small compared with the target reaction.

During the operation of the 2% W – 5.5% Cr – O/SiO_2 oxide catalyst, the WO_3 and Cr_2O_3 phases are detected in its composition. After the attainment of the stationary state, the WO_3 phase ceases to be detected, while a large proportion of Cr_2O_3 is reduced, which is indicated by the decrease in the intensity of the corresponding band in the spectrum by a factor of 15–20.

The study of the kinetics of the $C_2H_4 + CO_2$ reaction on the Cr – W – O/SiO_2 catalyst showed that the rate of formation of C_4H_6 and C_3H_6 increases with increase in the degree of conversion to 25%, after which it begins to fall. The activating effect of the reaction products, especially CO, is apparently due to the reduction of the surface, which promotes the activation of ethene. Extensive oxidation of the target product is not observed. When no account is taken of the homogeneous pyrolysis of ethene, the rate of accumulation of butadiene is expressed by the following equation according to Mirzabekova and Mamedov:[226]

$$r_{C_4H_6} = \frac{kP^2_{C_2H_4}k_{-r}P_{CO}}{k_rP_{CO_2} + k_{-r}P_{CO}},$$

where k is the reaction rate constant and k_r and k_{-r} are the rate constants for the reoxidation and reduction of the catalysts.

The rate of the overall catalytic conversion of ethene in the mixture with CO_2 into butadiene at 820 °C is greater by a factor of 5–6 than the rate of the thermal pyrolysis.

The rate equation for the accumulation of butadiene differs significantly from the rate equations for the carbonic acid converiso of alkanes (see above). This difference is caused by the nature of the tungsten – chromium catalyst. In contrast to the catalysts for the conversion of alkanes, it exhibits a high Lewis acidity, as a result of which its accepting capacity in relation to CO_2 is reduced and the CO formed during the reaction does not affect quite so much the state of the surface.

The study of the interaction of propene with CO_2 on the Mo – Mn – O/SiO_2 catalyst made it possible to observe the occurrence at 640 °C of partial oxidation with formation of formaldehyde (8% selectivity) and acrolein (32% selectivity) for degrees of conversion of C_3H_6 and CO_2 of 25.0% and 12.0% respectively.[227] Degradative decomposition with formation of products of the radical reactions (C_2H_4 and CH_4) predominates at higher temperatures.

On the K – Cr – Mn – O/SiO_2 catalyst, the process proceeds in the direction of the formation of the synthesis gas in accordance with Eqn (41). This is probably associated with the fact that the intermediates are oxidised to CO on the oxidised catalyst surface.

The possibility of the conversion of ethene into butadiene suggests a new scheme for its preparation from natural gas:

$$CH_4 \rightarrow C_2H_4 \rightarrow C_4H_6.$$

The interaction of toluene with CO_2 on a $Pd/\gamma\text{-}Al_2O_3$ catalyst promoted by Ce, Y, Sm, and La oxides has been investigated.[228]

$$C_6H_5CH_3 + CO_2 \rightarrow C_6H_6 + 2CO + 2H_2,$$
$$\Delta H = 209.7 \text{ kJ mol}^{-1}.$$

At 400 °C, the ratio C_6H_6 : CO was 0.41 on $Pd(Ce)/\gamma\text{-}Al_2O_3$ and 0.83 on $Pd/\gamma\text{-}Al_2O_3$. Lanthanide oxides retard the activation of the catalyst. When CO_2 is admitted, the catalyst is oxidised.

$$Pd + CO_2 \rightarrow PdO + CO.$$

When toluene is brought into contact with this catalyst, stoichiometric amounts of C_6H_6, CO_2, CH_4, CO, and H_2 with a small content of xylene are formed. The subsequent introduction of CO_2 leads to the appearance of slightly higher amounts of CO, evidently due to the coke formed from toluene. The overall process mechanism is

$$C_6H_5CH_3 \xrightarrow{Pd} [C_6H_5CH:] + H_2 \xrightarrow[CO_2]{PdO} C_6H_6 + CO + Pd(0).$$

The CeO_2 phase in contact with palladium gives rise to the Pd^{2+}/Pd^0 and Ce^{4+}/Ce^{3+} couples, facilitating thereby the oxidation of palladium.

3. Interaction with alcohols

The attempt to combine the dehydrogenation of methanol to formaldehyde with the reduction of carbon dioxide to CO is of considerable interest.

$$CH_3OH + CO_2 \rightarrow CH_2O + CO + H_2O, \quad \Delta H = 204.2 \text{ kJ mol}^{-1}. \tag{43}$$

This makes it possible to employ CO together with the unreacted methanol in the reaction involving carbonylation to methyl formate and the process can be carried out in accordance with a scheme balanced with respect to carbon.

The oxide compositions Mn – O, Mo – Mn – O, Fe – Mn – O, Cr – Mn – O, Cu – Mn – O, and Mo – Cr – Mn – O deposited on SiO_2 have been investigated in the reactions considered.[229] The catalysts without manganese were relatively inactive. The 10% Mn – 5.5% Cr – 5% Mo – O/SiO_2 catalyst showed the highest activity and selectivity at 560–750 °C (space velocity 900–7200 h^{-1}, $CH_3OH:C_2 = 1$). Under stationary conditions, reaction (43) was accompanied also by others:

$$CH_3OH + 2CO_2 \rightarrow 3CO + 2H_2O, \tag{44}$$

$$CH_3OH \rightarrow CH_2O + H_2, \tag{45}$$

$$H_2 + CO_2 \rightarrow CO + H_2O,$$
$$CH_3OH \rightarrow CO + 3H_2. \tag{46}$$

At 650 °C, the degree of conversion of CH_3OH was 30.2%, that of CO_2 was 14.6%, the selectivity with respect to CH_2O was 91%, and the yield of formaldehyde was 27.5%.

Under nonstationary conditions, the reduction of the catalyst by methanol or H_2 lowers the selectivity in the formation of CH_2O. The reoxidation of the catalyst by oxygen increases the selectivity. The reoxidation of the reduced Mn – O/SiO_2 catalyst by carbon dioxide takes place above 700 °C and is accompanied by the formation of CO. Consequently the low activity of the catalyst under stationary conditions is associated with the low rate of its reoxidation. It increases markedly in the case of the binary Cr – Mn, Mo – Mn, and Cu – Mn catalysts At the beginning of operation of the fresh catalyst, a high selectivity with respect to formaldehyde is observed, but, as the reaction proceeds, it falls, probably owing to the reduction of the catalysts by the reaction mixture.

Formaldehyde does not have an inhibiting effect on the conversion of methanol. Under the reaction conditions, it is converted into CO and CO_2 with a low degree of conversion. The rate of reaction is proportional to the CH_3OH pressure and, up to a certain surface coverage, the CO pressure. Subsequently it attains a constant value. The rate of formation of formaldehyde may be expressed by the kinetic equation

$$r_{CH_2O} = r'_{CH_2O} - r''_{CH_2O}$$

$$= \frac{k'P_{CH_3OH}P_{CO_2}}{k_rP_{CO_2} + k_rP_{CO}} - \frac{k''P_{CH_3O}P_{CO_2}}{k_rP_{CO_2} + k_{-r}P_{CO}},$$

where r'_{CH_2O} and r''_{CH_2O} are the rates of formation and decomposition of CH_2O.

The principal stages in the reaction on the Mn–Cr–Mo–O catalyst are presented in Scheme 5 below.[229]

Scheme 5

$$CH_3OH + Cr^{3+}O^{2-} \xrightarrow{a} CH_2O + Cr^{2+} + H_2O,$$

$$MnO + CO_2 \overset{b}{\rightleftharpoons} MnCO_3,$$

$$MnCO_3 + Cr^{2+} \overset{c}{\rightleftharpoons} Cr^{3+}O + MnO + CO,$$

$$CH_2O + Cr^{3+}O \xrightarrow{d} CHOCr^{2+}H,$$

$$CHOCr^{2+}H + Cr^{3+} \xrightarrow{e} CO + 2Cr^{2+}H,$$

$$2Cr^{2+}H \xrightarrow{f} 2Cr^{2+} + H_2.$$

The $Cr^{3+}O$ centres correspond to the Cr_2O_3 phase. The Mo_8O_{23} phase has also proved useful. Both phases have been detected by X-ray diffraction. Thus methanol is dehydrogenated with participation of the oxidised chromium and molybdenum phases, whilst the reduced manganese oxide phase participates in the activation of CO_2.

We may note that the Cr–Mo–Mn–O/SiO_2 catalyst has more acid properties than Cr–Mn–O/SiO_2. The presence of acid centres has been confirmed in a study of the desorption of ammonia. The acid centres apparently activate methanol, whilst the basic centres (MnO) activate CO_2. The reduction of the catalyst increases the rate of the extensive cleavage of CH_2O.

The data on the conversion of methanol in the absence of CO_2 show that a significant amount of formaldehyde is formed via the direct dehydrogenation [reaction (45)], but is obtained mainly via reaction (43). In the absence of the catalyst, the rate of conversion of methanol is insignificant.

The oxidation of methanol to formaldehyde by CO_2 or the $CO_2 + O_2$ mixture may prove convenient compared with the direct dehydrogenation or oxidation with O_2, since it makes it possible to carry out the process via a thermally neutral mechanism.

The interaction of ethanol with CO_2 on manganese oxide catalysts has been investigated. Mainly the same products as in the Lebedev reaction are obtained: thus butadiene is obtained from the alcohol.[230]

$$2\ C_2H_5OH = C_4H_6 + 2\ H_2O + H_2 \qquad (47)$$

For reasons which have not so far been explained, reaction (47) stops after the attainment of a certain limiting yield, which is appreciably lower than the yield allowed by thermodynamics. The use of CO_2 makes it possible to increase the yield of C_4H_6. The reaction was carried out at 500–600 °C and a space velocity of 1000–3600 h^{-1} in the presence of the Cu–Mn–O/Al_2O_3 catalyst. C_4H_6 and C_4H_8 predominate in the ethanol conversion products. C_2H_4, CH_4, and H_2 have also been obtained. When a $C_2H_5OH + N_2$ mixture is used at 550 °C, the selectivity in the formation of C_4H_6 is 43% for a degree of conversion of C_2H_5OH of 52%. The replacement of nitrogen by CO_2 increases the degree of conversion of C_2H_5OH to 63% and the selectivity with respect to C_4H_6 to 60%, the degree of conversion of CO_2 amounting to 16% under these conditions. The ratio $CO : H_2$ in the contact gas is close to unity, while the concentration of butadiene exceeds by a factor of 2–3 the concentrations of CO and H_2.

The overall stoichiometric equation can be expressed in the form

$$4\,C_2H_5OH + CO_2 \rightarrow 2\,C_4H_6 + CO + H_2 + 5\,H_2O. \qquad (48)$$

Bearing in mind that the generally accepted mechanism[230] of the Lebedev reaction [reaction (41)] presupposes the combination of the dehydrogenation, hydrogenation, condensation, and hydration stages, CO_2 probably prevents the extensive hydrogenation of the aldol condensation products by reacting with the hydrogen formed as an intermediate, increasing thereby the selectivity in the formation of C_4H_6.

The effectiveness of CO_2 as an oxidant in the presence of manganese oxide catalysts both in the conversion of methane[194] and in the condensation of ethanol to C_4H_6 may be important for the alternative synthesis of C_4H_6 from natural gas and CO_2 in accordance with the scheme

$$C_4H_6 + CO_2 \longrightarrow CO + H_2 \longrightarrow C_2H_5OH \longrightarrow C_4H_6 + CO + H_2$$

It follows from the foregoing that carbon dioxide may be used as an oxidant not only for alkanes but also for other organic substances, including alkenes and alcohols. Some of these reactions are of potential practical importance, but the number of investigations of this kind is so far small.

VII. Conclusion

The data presented show, contrary to widespread ideas, that carbon dioxide is capable of entering into a wide variety of reactions with other compounds. The most important classes of reactions involving CO_2 are as follows: (1) the incorporation of CO_2 in the C–C, C–H, and C–N bonds with formation of carboxy- and carbonyl compounds; (2) the oxidation of other compounds by CO_2. The reactions of the first class occur at low temperatures and are catalysed by homogeneous transition metal complexes, while those of the second class are as a rule carried out at a high temperature and are accelerated by metals or transition metal oxides.

Despite the numerous studies carried out, high yields of useful products and appreciable reaction rates have so far been achieved in only a few of them. This is associated with various thermodynamic and kinetic difficulties. One of the main causes of this for reactions of the first class is that the energy of the bond between CO_2 and the transition metal atom in the complex is low (20–60 kJ mol^{-1}) and there is insufficient time for the CO_2 molecule in the coordination sphere to react with another molecule: its lifetime is insufficient. The CO_2 molecule has a filled electron shell and its reactivity is therefore low. Hence it is necessary to increase its reactivity by using another, more effective catalyst or by introducing another ligand. Incidentally, this problem is outside the scope of the present review.

As regards reactions of the second class, in most cases thermodynamic limitations prohibit their occurrence at a low temperature, whilst at a high temperature not every catalyst is able to operate: problems of mechanical strength, resistance to sintering, etc. arise. The most important task is therefore to seek new reactions which do not occur at quite such high temperatures but are promising as regards their economic and environmental aspects and also to seek new catalysts. This requires in its turn the elucidation of the rules governing the selection of the catalysts and the kinetics and mechanisms of the reactions, in particular the paths in the surface reactions, with the aid of physical methods in situ. The application of the latter is difficult at high temepratures, although isolated examples exist, as shown above.

Numerous catalytic and noncatalytic reactions of the first class are known, in which carboxylic acids, esters, carbamates, etc. are formed. However, at present one can only speak of two processes achieved on a large scale — the syntheses of urea and salicylic acid. This does not of course mean that such processes will not develop extensivley in the future.

However, nowadays reactions of the second class — the employment of carbon dioxide as an oxidant — are more promising both from the standpoint of the use of CO_2 as the starting material and from the standpoint of the solution of the environmental problem of the utilisation of CO_2 from gaseous waste. The largest scale process in which CO_2 is used as an

oxidant is the synthesis of methanol. It has been discovered recently that the compound reacting with hydrogen is not CO, as thought previously, but the CO_2 obtained from CO. It would be attractive to synthesise CH_3OH directly by the $CO_2 + H_2$ reaction, although from the thermodynamic standpoint it is preferable to obtain dimethyl ether rather than methanol.[112,113] The synthesis of higher alcohols from CO_2 and H_2 also has apparently a number of advantages compared with the synthesis from CO and H_2.[85,231]

For so long as cheap methods for the preparation of hydrogen have not been found, the reactions of CO_2 with a cheap starting material — hydrocarbons and other organic compounds — are preferable. Such reactions can lead to large scale syntheses of C_2H_4, C_3H_6, C_4H_6, and CH_2O and also would make it possible to devise an alternative method of preparation of the $CO + H_2$ synthesis gas.

The catalytic reactions involving the reduction of C_1-C_7 hydrocarbons and C_1-C_2 alcohols in their interaction with CO_2 were examined above. A disadvantage of the highly active metallic catalysts (Ni, Co, and Fe) is their rapid poisoning by coke. Among the catalysts investigated, the manganese oxide systems proved to be the most effective. There are still many obscure questions concerning both the mechanism of the action of manganese and the kinetics of the above processes.

An essential condition for the correct selection of the catalyst is the selection of systems capable of accepting and activating CO_2. The acid nature of CO_2 necessitate the employment of a catalytic system with basic properties. However, alkali and alkaline earth metals, which form stable carbonates, are ineffective. Moderately strong bases forming carbonates with reduction of CO_2 are needed. Such requriements are met by manganese oxide and apparently certain lanthanide oxides. Their acid and oxidation-reduction properties may be altered by adding other oxides.

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