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Modern problems in the synthesis of methanol

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ABSTRACT. The state of research into, and the available information about, the macroscopic and detailed mechanisms of the synthesis of methanol from carbon oxides and hydrogen, the characteristic features of the technology of the industrial process, the catalyst used, and the kinetic models of the reaction on the most important copper-containing catalysts are examined. The results of studies on the mechanism of the reactions occurring, including studies using tracer atoms, are dealt with in greatest detail. The bibliography includes 102 references.

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I. Introduction

The synthesis of methanol from carbon oxides and hydrogen is one of the most important processes in modern chemical industry. The process, based on the overall reaction $CO + 2H_2 = CH_3OH$, not only ensures the formation of methanol—the most important chemical product and intermediate—but also provides an effective way of processing the carbon oxides obtained as side products in a wide variety of industries or specially generated in the processing of natural gas, heavy residues, and other carbon-containing raw materials.

The synthesis of methanol is also of independent interest as the simplest model selective catalytic hydrogenation reaction; the features of this reaction characterise the properties of carbon—one of the most important elements of the Periodic System. Because of both these characteristics, the relevant information forms part of the foundations of chemical science.

The industrial importance of the synthesis of methanol has stimulated unflagging interest by investigators in its physicochemical principles. This interest received an additional stimulus in the 1970s both for economic reasons (overestimation of the role of the alternative sources of raw materials, the prospect of new requirements—the manufacture of protein-vitamin concentrates, etc.) and because of the intrinsic logic of the development of the relevant research.

The point is that at the beginning of the 1970s the physicochemical principles of the synthesis of methanol appeared to be entirely complete, including, in particular, the known mechanisms of the reactions occurring and the characteristic features of the action of catalysts, and at the same time a thoroughly developed technology of the industrial process existed. Only the absence of an adequate kinetic model and certain specific features of the process, which could not be accounted for within the framework of the generally accepted ideas, appeared to be somewhat unsatisfactory. The appearance in the middle 1970s of a series of publications claiming that these generally accepted ideas were incorrect and that even the macroscopic mechanisms of the reactions occurring in the synthesis were incorrect (methanol was obtained as a result of the hydrogenation of CO_2 and not CO) stimulated additional research in order to test these claims, to uphold the existing concepts, etc.

Together with these rather tactical aspects, the strategic problem of the development of new physicochemical principles of the industrial process also arose, since the existing principles were based on the rejected concepts. The current interest of this problem was due to the fact that, from the standpoint of new ideas about the reaction mechanisms, the process technology existing at the time might have proved to be non-optimal.

The combination of such varied motives resulted in the problems of the synthesis of methanol occupying one of the leading places among the topics in research publications on chemistry during the last decade. The aim of this communication is both a survey of the available data and the consideration of the key problems of the new physicochemical principles of the synthesis of methanol.

From the author's point of view, the characteristic features of the development of research in the field under consideration are also of a certain methodological interest because the intertwining of fundamental and applied problems and the role of fundamental knowledge in the solution of applied problems from first principles are strikingly manifested here.

II. Brief description of the synthesis of methanol

The industrial synthesis of methanol from carbon oxides and hydrogen was first achieved in 1923 (Ref. 1, p. 6). In connection with the large-scale requirements for methanol and the wide variety of the available and potential sources of raw materials (natural gas, waste from the manufacture of acetylene and other substances, heavy petroleum residues, coal, etc.), the industrial output of methanol has increased rapidly, approaching at the present time 20 million tonnes annually. At the same time the process technology developed in the first place as a result of the improvement of the catalysts employed and the reactor designs.

During the course of almost half a century, the principal catalyst of the synthesis of methanol was the zinc-chromium catalyst, which makes it possible to conduct the process with a fairly high productivity at temperatures in the range 320–400 °C. However, as a result of the unfavourable equilibrium in the overall reactions involved in the synthesis of methanol from both CO and H_2, i.e.

$$CO + 2H_2 = CH_3OH + 90.73 \text{ kJ mol}^{-1},$$

and from CO_2 and H_2, i.e.

$$CO_2 + 3H_2 = CH_3OH + H_2O + 49.53 \text{ kJ mol}^{-1},$$

the process has to be carried out at high pressures of the order of 30 MPa.[1] Moreover, owing to the relatively high temperature of the synthesis, a number of side products are formed (ethers, aldehydes, ketones, higher alcohols, etc.), which lowers the quality of the methanol obtained.

The unfavourable thermodynamics and the high exothermicity of the synthesis of methanol made it desirable to perform the industrial process in a gas circulation system. The methanol formed and water are usually separated by cooling the gas mixture. After the separation of methanol, the cold gas is returned to the cycle including the procedure where it is returned directly to the reactor by means of by-passes, lowering thereby the temperature in the catalyst bed.[2]

In the 1960s–1970s, the zinc–chromium catalysts were displaced by new generation catalysts based on compositions with copper oxide as the main component. Copper-containing catalysts are characterised by a significantly higher activity, which made it possible to reduce the temperature of the industrial process on average to the level of 250 °C. This made it possible in its turn to carry out the synthesis at much lower pressures—5 to 10 MPa.

The characteristic features of the industrial plant for the manufacture of methanol have been described in a number of monographs (see, for example, Karavaev et al.[1]). In modern plant for the synthesis of methanol, the catalyst is usually distributed in the form of successive adiabatic beds, between which the cold gas is introduced via by-passes. There exist also alternative technical solutions for the reaction unit, which can be constructed, for example, in the form of a system of a large number of tubes (tubular reactor), the catalyst being placed either in the tubes or in the space between them and the gas mixture is cooled using boiling water under pressure.

This design (from the Lurgi company) makes it possible to carry out the process under nearly isothermal conditions and also to use the main bulk of the heat of reaction to obtain relatively more valuable steam at a pressure of 4 MPa. However, in view of the design complications, the output of individual plants of this type so far lags behind the corresponding outputs of methanol synthesis plants based on reactors with adiabatic catalyst beds.

In both versions, the process technology has been thoroughly developed and provides for a high degree of processing of the raw material and utilisation of the heat of reaction. A fundamental disadvantage of the existing technologies is perhaps only the relatively low output per unit catalyst volume, which amounts to ~ 0.3 tonne m^{-3} h^{-1} (at a pressure of 5–8 MPa) in the best schemes, which is significantly lower than the values which could be achieved judging from the activities of the catalysts employed (~ 1 tonne m^{-3} h^{-1}). The possibilities for increasing the efficiency of the process arising in this connection can be realised but only on the basis of a detailed revision of its physicochemical principles, which constitutes a powerful stimulus to research in this field.

III. Catalysts for the synthesis of methanol

The achievement of the industrial synthesis of methanol in the 1920s coincided with the period of the rapid development of research into heterogeneous catalysis. During a historically short period, a number of brilliant names appeared in this field (A A Balandin, S Z Roginskii, V I Ipat'ev, Schwab, Taylor, and many others) as well as interesting theories and concepts. The testing of the catalytic properties of various materials and the search for new materials were prosecuted especially vigorously, which gave rise to a broad front of research into catalysts of the synthesis of methanol. At the beginning of the 1930s, the fundamental data bank concerning the catalytic properties of various substances in the synthesis of methanol was established in the journal and patent literature. In the patents of the 1920s, it was suggested that MgO and Al_2O_3 with added oxides of Pb, Bi, Te, Zn, Cd, Cu, Sn, Sb, Si, B, and Ti as well as K, Na, Mg, V, Cr, Mo, Fe, Ni, Co, Cu, Ag, Zn, Cd, Hg, Pb, As, Sb, Bi, Be, Mn, Al, Ge, Si, Ti, Zr, Th, U, Ca, Ba, W, etc. compounds be used as catalysts of this process[3] (see also Dolgov[4]). In fact, all the elements whose compounds are used nowadays in various combinations or are being investigated as catalysts for the synthesis of methanol are listed here. The specific features of copper-containing systems were also noted. The formation of completely pure methanol in the presence of copper catalysts using Group II and III metal oxides was pointed out.[5]

At the end of the 1920s, two groups of the most valuable catalysts were already defined—the copper-containing and zinc–chromium catalysts. According to Dolgov,[4] the productivity of the copper-containing catalysts under optimum conditions is 1.5–2 litres of methanol per litre of the catalyst per hour at 15 MPa and that of the zinc–chromium catalyst is 1–1.5 litres CH_3OH $litre^{-1}$ h^{-1} at 30 MPa. On comparing these data with modern developments (see, for example, Kotowski et al.[6]), one may conclude that the level of activity of the copper-containing and zinc-chromium catalysts has changed little since the 1920s–1930s. The foundations of the modern methods of preparation of catalysts for the synthesis of methanol—by the coprecipitation and mixing of the oxides—were also laid at the same time.

The first generation industrial catalysts comprised zinc–chromium catalysts, apparently first proposed by the BASF company.[7] Their advantage over the copper-containing catalysts was their relatively low sensitivity to catalytic poisons.

The development of methods for the purification of the synthesis gas played a decisive role in the displacement of the zinc–chromium catalyst by the second-generation copper-containing systems.[1,8–10] The quality of the methanol, the impurity content in which is significantly reduced when the synthesis is carried out on copper-containing catalysts, also played a significant role.[11,12]

Despite the very wide variety of the compositions of the copper-containing catalysts recommended for use, one can nevertheless differentiate two leading compositions: the copper–zinc–aluminium and the copper–zinc–chromium oxide systems. The range of the recommended ratios of the individual components in such catalysts is extremely wide. However, the composition of industrial catalysts is fairly close to a standard; in all cases their content of the main components is 50–70 wt.% CuO, 20–30 wt.% ZnO, and 5–15 wt.% Al_2O_3. The productivity of such catalysts (according to the data in

one of the patents[13] †) after operation for hundreds of hours amounts to 1–1.5 kg litre^{-1} h^{-1} at 250 °C, a pressure of 5 MPa, a space velocity of 40 000 h^{-1}, and for the initial mixture composition with 10 vol.% CO, 10 vol.% CO_2, and 80 vol.% H_2. Such high productivity per unit volume of the catalyst is not obtained in industrial practice, where the productivities within the framework of various technological schemes amount to 0.1–0.3 kg litre^{-1} h^{-1} at a pressure 5 MPa.

Copper-containing catalysts have been described in numerous surveys and reviews.[1,6,8–10,14–18] Catalysts of the ICI and Lurgi companies are most widely used (see, for example, Refs. 13 and 19–21). These are as a rule copper–zinc–aluminium compositions obtained by coprecipitation from solutions of the salts with subsequent heat treatment and reduction, which is usually carried out directly in the synthesis column. A Soviet catalyst of analogous composition is known under the designation SNM-1 Severodonetskii Nizkotemperaturnyi Metanol'nyi (the North Donets Low-temperature Methanol) [catalyst].[22]

Since the 1970s, these catalysts have dominated the market: virtually all new plants for the synthesis of methanol have been constructed using such catalysts.[8,9] The principal advantages of the copper-containing catalysts arise from the possibility of carrying out the synthesis at relatively low temperatures and pressures, which entails, as already mentioned, a sharp increase in the quality of the methanol obtained. Their main disadvantage is a relatively low stability, which is responsible for their low operating life (1–2 years).

The search for additives increasing the activity and stability of copper-containing catalysts is continuing. In particular, the influence of added Mn, Ba, B, V, W, Ag, and the lanthanides ‡ has been investigated.[23–25]

Among the new systems, palladium-containing catalysts on various carriers are most popular in research (see, for example, Refs. 26–30), but they are so far inferior in the level of their activity to the industrial catalysts, exhibiting in addition a relatively low selectivity with respect to methanol.

The most vigorous search has probably been prosecuted in the field of new methods for the preparation and moulding of copper-containing catalysts combined with tests of new components of the copper-containing compositions.

Catalysts of the Raney type, obtained by leaching copper, zinc, and aluminium alloys, have been investigated in a series of studies.[31–36] For the optimum composition of the initial alloy (33–43 at.% Cu, 7–17 at.% Zn, and 50 at.% Al), the activity of such catalysts approaches that of the industrial specimens with a similar selectivity. In order to attain a high activity and selectivity, CO_2 must be present in the synthesis gas.[31]

Another way of creating catalysts on the basis of alloys consists in their oxidation-reduction treatment, which leads to the formation of a complex heterogeneous system incorporating both oxide and metallic phases. Among catalysts of this type, the Cu–Th systems showed the greatest activity in the synthesis of methanol.[37,38] When the intermetallic compounds Th_2Cu, $ThCu_2$, $ThCu_{3.6}$, $ThCu_6$, as well as the $ThCu_5$ and ThCu alloys (95 and 5 wt.% respectively) were used, the catalysts obtained from the intermetallic compounds $ThCu_6$ and $ThCu_{3.6}$ proved to be most active; their activity was superior to that of the industrial catalysts (up to 3 kg CH_3OH litre^{-1} h^{-1} at 240 °C, 6 MPa, space velocity 22 600 h^{-1}, and the ratio H_2 : CO = 2.4). Catalysts based on Th–Cu as well as Cu–Zr, Cu–Hf, Cu–Ti, and Au–Zr alloys are less active[39,40] and this also applies to the Cu–lanthanide (Ho, Pr, Ce, Nd) alloys.[41–43]

In the series of catalysts based on the intermetallic compounds Zr_2Cu, ZrCu, and $ZrCu_4$, the activity of the specimen obtained from the intermetallic compound having the intermediate composition ZrCu proved to be the highest and close to that of the industrial catalysts. The specimen based on CuHf was less active.[44,45]

The conditions in the oxidation–reduction treatment of the intermetallic compounds in the preparation of the catalysts influence significantly their activity.[46,47] The optimum composition of the gas mixture for the synthesis of methanol in the presence of such catalysts is also unknown. Therefore one cannot rule out the possibility of a future increase in the level of their measured activity.

The use of the plasmachemical method for the preparation from solution of a methanol synthesis catalyst whose component ratios correspond approximately to the composition of the SNM-1 catalyst has been reported.[48] The activity of this catalyst approaches that of its prototype—the SNM-1 catalyst.

The possibilities for the improvement of the properties of the copper-containing catalysts by altering the conditions governing the formation of the active phase and the technology of the preparation of the catalyst are being investigated. In particular, methods have been proposed for a sputtering heating-drying procedure in the preparation process,[49] for the preparation of a microspherical catalyst by granulation in a liquid medium,[50] and also a method for the modification of the catalyst by introducing organic additives during the coprecipitation process,[51] which ensures an almost twofold increase in activity. The characteristic features of the formation of the active phase have been analysed in a series of studies.[52,53] In relation to the copper-cement catalysts, these features have been discussed by Golosman et al.[54] Variation of the technology of the preparation of the catalysts has not so far led to a sharp increase in their activity.

IV. The macroscopic mechanism of the synthesis of methanol

As mentioned in the introduction, the question of which particular carbon oxide gives rise to methanol on hydrogenation has become in the last decade the subject of a fairly sharp controversy. By 1975, the generally accepted view was that the interaction of carbon oxide with hydrogen constitutes a set of consecutive reactions: the reduction of carbon dioxide to the monoxide:

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (1)$$

and the reduction of carbon monoxide to methanol:

$$CO + 2H_2 \rightarrow CH_3OH\ , \qquad (2)$$

† See also Hydrocarbon Proc., 1981, **60**(11) 183.

‡ Catalysts with these additives have been described in a number of patents (BRD P. 2 154 074 and 2 163 317; B. P. 1 371 638 and 2 037 176; French P. 2 049 193 and 2 113 467). The patent information about catalysts containing boron additives in the copper–zinc and copper–zinc–aluminium compositions (Japanese P. 54-37 108; US P. 3 971 535; B. P. 2 047 556 and 2 064 352), which makes it possible to increase the productivity to 3.5–3.8 kg CH_3OH litre^{-1} h^{-1} at 260 °C, 7 MPa, and a space velocity of 20 000 h^{-1} for the synthesis gas composition with 23 vol.% CO, 3 vol.% CO_2, and 70 vol.% H_2, is apparently of greatest interest.

or in a more compact form:

$$CO_2 \underset{-H_2O}{\overset{H_2}{\rightleftarrows}} CO \xrightarrow{2H_2} CH_3OH. \quad (3)$$

The mechanism (3) put forward for the first time by Boomer and Morris[55] and Dolgov and Karpinskii,[56] whilst appearing fairly self-evident from general chemical standpoints, was nevertheless based on the experimental observation that CO appears in the reaction mixture in the synthesis of methanol from CO_2 and H_2,[55,56] its concentration passing through a maximum as a function of time.[56] Generally speaking, such behaviour of the system is characteristic of consecutive reactions but in the given instance this observation is not sufficient to justify the mechanism (3) because the reaction which is the reverse of reaction (1), namely the conversion of CO by water, i.e.

$$CO + H_2O \rightarrow CO_2 + H_2. \quad (4)$$

should take place (and in fact does take place) under the conditions of the synthesis of methanol. The mechanism involving the synthesis of methanol from CO_2 and H_2, which is an alternative to the mechanism (3), i.e.

$$CO + H_2O \rightleftarrows CO_2 + H_2 \xrightarrow{+2H_2} CH_3OH + H_2O, \quad (5)$$

also entails an increase in the CO concentration as a function of time, because of the reduction of CO_2, and its subsequent decrease due to the ultimate conversion of both carbon oxides into methanol. In order to infer the reaction mechanism, a more detailed analysis is evidently required.

The applicability of the mechanisms (3) and (5) to the description of the synthesis of methanol has been the subject of a sharp controversy, which has not come to an end during the last decade. At the present time, there is a fairly complete experimental data bank, which makes it possible to summarise the results of this controversy. In the first place, this applies to research in which tracer atoms were employed.

1. The tracer atom method

The tracer atom method yields perhaps the most clearest information about the macroscopic mechanism of a chemical process which, when combined with other kinetic data, makes it possible to establish as a rule a sequence of transformations of various compounds participating in the system of chemical reactions.

At the present time, the synthesis of methanol is one of the reactions most fully investigated by this method: "tracers" for all the atoms (C, H, and O) forming part of the composition of the methanol molecule have been used in the published studies. This series of investigations of the macroscopic mechanism can now be regarded as completed except for some ambiguity in the treatment of data obtained using labelled oxygen, which will be discussed below.

^{14}C-Labelled carbon. We shall consider initially the ways in which carbon atoms are transferred, data for which are least distorted by the isotope exchange with the catalyst surface. Studies using the radioactive carbon isotope ^{14}C [57-60] were the first example of the use of the tracer atom method for the investigation of the mechanism of the synthesis of methanol. The method has been used in both possible versions: the introduction of labelled ^{14}CO and $^{14}CO_2$ into the reacting gas mixture. If the exchange of carbon between CO and CO_2 is not too great, then, by measuring the radioactivity of the methanol obtained, it is possible to establish unambiguously which of these compounds is its carbon-containing precursor.

The reaction was carried out in a circulation apparatus with continuous removal of methanol in a cooled trap, incorporated in the cycle, on the SNM-1 copper-containing oxide catalyst under conditions approaching those in the industrial process (pressure ~5 MPa, temperature 180–250 °C, different compositions of the gas mixture).[57-60] The high rate of circulation of the gas ensured the differential operation of the reactor. The data on the distribution of radioactivity in the carbon-containing components of the reaction mixture in experiments with added ^{14}CO are presented in Table 1 and those with added $^{14}CO_2$ are in Table 2.

Table 1. Distribution of radioactivity in the products of the synthesis of methanol from the $^{14}CO + CO_2 + H_2$ mixture on the SNM-1 catalyst.[57,58,60]

Components of reaction mixture	Amounts, litres		Concentration, vol.%		Specific radioactivity, counts min^{-1} (mg $BaCO_3$)$^{-1}$	
	initial	final	initial	final	initial	final
180 °C; P_{av} = 4.8 MPa						
CO	0.38	0.55	1.2	2.1	406	189
CO_2	6.8	4.2	22.0	18.0	0	9
CH_3OH	0	2.0	—	—	—	5
218 °C; P_{av} = 5.2 MPa						
CO	0.39	0.55	1.1	1.9	406	194
CO_2	6.0	4.3	19.0	17.0	0	11
CH_3OH	0	2.1	—	—	—	7
250 °C; P_{av} = 5.3 MPa						
CO	0.4	3.1	1.1	11.9	406	30
CO_2	7.6	2.7	19.5	10.7	0	16
CH_3OH	0	2.2	—	—	—	11

Note. The specific radioactivity of methanol characterises the integral sample removed continuously during the experiment.

Table 2. Distribution of radioactivity in the products of the synthesis of methanol from the $CO + {}^{14}CO_2 + H_2$ mixture on the SNM-1 catalyst (240 °C, 5 MPa).[58,61]

Components of reaction mixture	Amount, litres		Concentration, vol.%		Specific radioactivity, count min^{-1} (mg $BaCO_3$)$^{-1}$		
	initial	final	initial	final	initial	integral	final
CO	22	16.5	30	30	0	430	490
CO_2	2.9	2.2	4.0	4.0	5900	1480	790
CH_3OH	—	6.0	—	—	—	1500	1380

As can be seen from the amount of carbon oxides and methanol in the system, in all cases the final degrees of conversion of the carbon oxide into methanol were considerable (~0.3), being attained under conditions of a limited isotope exchange between the carbon oxides with the exception of experiments at high temperatures, where the differences between the radioactivities of carbon oxides nevertheless remain sufficiently large to be able to infer the source of carbon in methanol.

The clearest results of experiments with labelled CO in the initial mixture (Table 1) were obtained at low temperatures, because the final specific radioactivities of the carbon oxides in these experiments differed markedly. The specific radioactivity of methanol was then actually lower than that of CO_2. Since the specific radioactivity of methanol corresponds to an integral sample removed continuously in the course of the experiment, i.e. is intermediate between the specific radioactivities of the initial and final portions of methanol, the data in Table 1 show quantitatively that the entire methanol obtained was formed directly from CO_2, by-passing CO. Incidentally, this was favoured by the composition of the initial mixture in which the CO_2 concentration was much higher that that of CO.

On the other hand, the data in Table 2 were obtained under the conditions of an appreciable excess of CO in the initial and final mixtures. Since this experiment was most fundamental, integral samples of the gas mixture, specially removed throughout the experiment simultaneously with the removal of methanol samples, were also analysed for this experiment. As can be seen, the specific radioactivities of methanol and CO_2 in the integral sample are almost identical and greatly exceed the specific radioactivity of CO, i.e. methanol was formed exclusively from CO_2. The total amount of CO ultimately converted into methanol (via the stage involving the conversion of CO by reaction with water) during the experiment exceeds by a factor of two the initial amount of CO_2 in the mixture.

Hence follows the quantitative conclusion that methanol is synthesised on the copper–zinc–aluminium SNM-1 catalyst only directly from CO_2; the reactions of CO proceed only in accordance with the water gas process, i.e. the set of reactions occurring is described by Scheme (5).

Fig. 1 presents data on the dynamics of the changes in the distribution of the specific radioactivity in the synthesis of methanol from the CO + H_2 mixture with added $^{14}CO_2$ on the zinc–chromium catalyst.§ As before, current analyses of the gas mixture were compared here with analyses of integral methanol samples. Although the synthesis of methanol is accompanied in this case by an appreciable exchange of the label between the carbon oxides, the data in the figure leave no doubt that methanol is formed, at least to a large extent, via the hydrogenation of CO_2. The estimated lower limit to the contribution of mechanism (5) is 70%. Incidentally, judging from the data presented, the situation is in this case entirely analogous to that observed for the copper–zinc–aluminium catalyst.

Apparently Scheme (5) is characteristic of oxide catalysts for the synthesis of methanol on which CO_2 behaves as a highly reactive reactant, while CO is actually not hydrogenated but is merely converted into CO_2 by reaction with water. The situation is completely different on metallic catalysts. Thus the following results have been obtained on premelted iron catalysts under the conditions of the synthesis of alcohols for a low degree of conversion of carbon oxides (7%) and an insignificant exchange between them:[58]

Component	CO_2	CO	C_1–C_2 Alcohols
Initial specific radioactivity, counts min^{-1} (mg $BaCO_3$)$^{-1}$	5120	0	—
Final specific radioactivity, counts min^{-1} (mg $BaCO_3$)$^{-1}$	5100	3	12

Evidently the contribution of mechanism (5) , i.e. the contribution of the synthesis of methanol from CO_2 and H_2, is 0.2%. Although the composition of the gas mixture in this experiment was favourable for the reactions of CO (the CO content was ~25 vol.% and that of $^{14}CO_2$ was 2 vol.%), it is clear that Scheme (3) reflects here the main reaction channel.

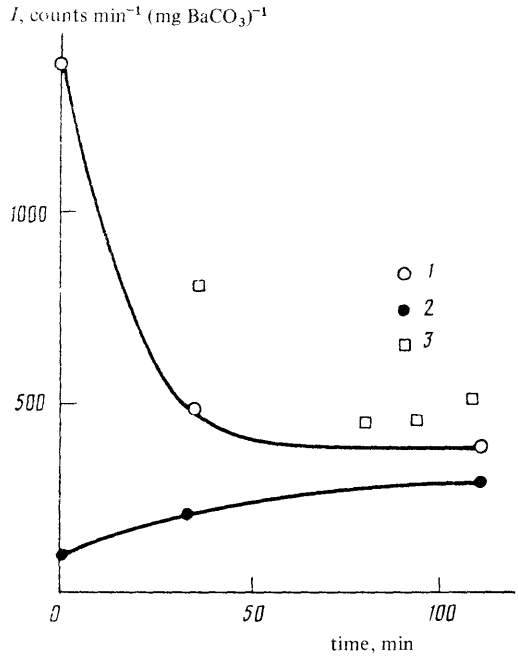


Figure 1. Evolution of the specific radioactivity of the components of the reaction mixture in the synthesis of methanol on the zinc–chromium catalyst; *1*) CO_2; *2*) CO; *3*) CH_3OH.

The results of experiments with labelled ^{14}CO and $^{14}CO_2$ were described in detail, because they yield virtually unambiguous information about the mechanism of the synthesis. This was extremely significant, because the results described and the conclusions conflicted with the generally accepted ideas and initially encountered natural disbelief. However, in 1985 it was reported[62] that these results were reproduced by a group of English researchers and recently the authors themselves[63] published a relevant paper.

In their experiments,[63] methanol was obtained in a flow reactor on a copper–zinc–aluminium catalyst at 250 °C and a pressure of 5 MPa. Five gas mixtures in which the content of CO_2 was varied from 10 vol.% (for a CO content of ~10 vol.%) to a negligible content, amounting to 0.01 vol.% (21.7 vol.% CO), were used.

In order to estimate the fraction of methanol formed via the hydrogenation of CO [the contribution of mechanism (5)], the specific radioactivity of CH_3OH was compared with the average specific radioactivity of carbon oxides at the entry to and exit from the reactor. As can be seen from the data presented above (Tables 1 and 2), this procedure is entirely acceptable for small changes in the specific radioactivities of the components. However, it leads to inaccurate estimates if the changes in the specific radioactivity are large and permits the determination of only the lower limit to the contribution of the mechanism considered, which

§ The data were obtained by Yu B Kagan, E V Slivinskii, G I Lin, S M Loktev, and L G Liberov with participation by the author.

differs fairly considerably from the true contribution (Table 2). In order to obtain more accurate results, the specific radioactivity of methanol must be compared in this case with that of the integral gas samples, as was done above.

Among the five mixtures used in the above study,[63] the compositions of three were in the range of concentrations characterised previously.[57–59] The contribution of mechanism (5) in these experiments was 1.0, in agreement with the above estimates. For the other two mixtures, distinguished by a low CO_2 content, the specific radioactivity of CO_2 changed markedly during the synthesis, which led to the errors noted above. For the mixture containing CO_2 and CO in proportions (in vol.%) of 0.45 : 23, the contribution of mechanism (5) was estimated as 0.7 (lower limit). For the mixture with 0.01 vol.% CO_2 (see above) this contribution was not estimated because of the large error. Nevertheless, it is clear from the data for the specific radioactivities at the exit from the reactor [0.012 mc mol^{-1} for CO, 4.54 mc mol^{-1} for CO_2, and 4.88 mc mol^{-1} for methanol (integral sample)] that mechanism (5) is at least dominant in this case too.

We may note that, for a low CO_2 content in the mixture (0.01 vol.%), methanol was formed only in trace amounts, in agreement with the data of Kagan et al.[58]

Summarising the information about the macroscopic mechanism of the synthesis of methanol obtained using ^{14}C, one may note the fruitfulness of the isotope method in dealing with problems of this kind. Table 3 gives a compilation of results obtained for the synthesis on various catalysts, including industrial specimens. Evidently, the mechanism of the synthesis of methanol is different for different catalysts. When the synthesis is performed on oxide catalysts, in the first place copper-containing catalysts, the source of carbon in methanol is CO_2. On metallic catalysts, whose representative is the premelted iron catalyst, the source of carbon in methanol (in the fraction of C_1-C_2 alcohols) is CO and the fraction of methanol formed from CO_2 does not exceed 0.2%.

Table 3. Compilation of the results of studies on the mechanism of the synthesis of methanol in the presence of various catalysts using ^{14}C.

Catalyst	Labelled molecule	Reaction conditions			Methanol precursor	Refs.
		P_{CO_2}, MPa	P_{CO}, MPa	T°, C		
$CuO-ZnO-Al_2O_3$	CO, CO_2	0.16—1.3	0.07—1.7	180—250	CO_2	[57, 58, 60]
$CuO-ZnO-Al_2O_3$	CO, CO_2	0.0005—0.5	0.35—1.2	250	CO_2	[63]
$ZnO-Cr_2O_3$	CO_2	0.34	2.3	330	CO_2	[58]
Fe (premelted catalyst)	CO_2	0.2	2.3	173	CO	[58]

^{18}O-Labelled oxygen. The results of the study of the mechanism of the synthesis of methanol using water containing ^{18}O have been described by Klier[64] at the 8th International Congress on Catalysis in 1984. The synthesis was carried out in an integral flow reactor at a pressure of 7.5 MPa on a copper–zinc oxide catalyst using an atomic ratio of 30 : 70. Water (1 vol.%), two thirds of the oxygen atoms of which were in the form of ^{18}O, was added to a gas mixture with a ratio $CO:H_2 = 30:70$. The space velocity of the mixture was about 10^4 h^{-1} and the reaction temperature was 225 °C. The data obtained for the fluxes of the substances at the entry to and exit from the integral flow reactor (in mmol h^{-1}) are presented below:

Components	CO	$C^{18}O$	CO_2	$CO^{18}O$	$C^{18}O_2$	H_2O	$H_2{}^{18}O$	CH_3OH	$CH_3{}^{18}OH$
Entry	184.00	0	0	0	0	2.20	4.10	0	0
Exit	110.33	0.67	5.49	0.40	0.01	0.29	0.01	64.91	2.29

From these results, the authors[64] concluded that CO and H_2O participate in the synthesis of methanol. This conclusion cannot be accepted without stipulation, especially bearing in mind the integral nature of the reactor and the appreciable degrees of conversion. We shall therefore carry out a more rigorous analysis of the data. In the first place, we shall determine the isotope fractions of ^{18}O (the fractions of ^{18}O among all the oxygen atoms in the molecules of a given type) in different oxygen-containing components of the reaction mixture at the exit from the reactor. The isotope fractions of ^{18}O can be calculated from the data presented above and have the following values:

For CO: $0.67/(110.33+0.67)=0.6\%$;
For CO_2: $(0.40\cdot2+0.01)/(5.49+0.40+0.01)=3.6\%$;
For H_2O: $(0.01/(0.01+0.29)=3.3\%$;
For CH_3OH: $2.29/(64.91+2.29)=3.4\%$.

Simple comparison of the values obtained shows that only CO cannot be regarded as a source of oxygen in methanol, since the isotope fraction of ^{18}O in CO at the exit from the reactor (this is its maximum value) is significantly lower than in CH_3OH. As regards H_2O and CO_2, the isotope fractions of labelled oxygen in these substances are almost the same and close to the value in methanol, i.e. on the basis of the data under discussion they can both be regarded as possible sources of oxygen atoms in the methanol molecule. CO_2 can be regarded as a more probable source of oxygen under these conditions, because it is the product of the conversion of CO by water and its isotope composition is affected by the integral nature of the reactor to the same extent as the isotope composition of methanol. On the other hand, the isotope fraction of ^{18}O in water measured at the exit is minimal (its value at the entry to the reactor is 65%) and, if the water oxygen had been used in the formation of the methanol molecule, one might have expected a higher level of the label in methanol.

The test undertaken by Liu et al.[62] did not confirm the conclusion[64] that the water oxygen is involved in the formation of the methanol molecule. In experiments with CO_2 and H_2O labelled in the oxygen, the authors[62] reached the conclusion that the reactions involving the hydrogenation of CO and CO_2 to methanol, the conversion of CO by water, the exchange of oxygen between CO_2 and CO, the rapid exchange between CO_2 and H_2O, and also the exchange with the catalyst lattice oxygen take place in the system. According to the method adopted,[62] the catalyst was treated with a standard mixture until the attainment of a constant radioactivity, after which 30 min experiments were performed with mixtures containing labelled compounds, the system being evacuated for 15 min between experiments. The initial rates of transfer of the label were analysed.

For this method, the state of the catalyst surface depends on its "biography", i.e. on the mixture composition in the previous experiment, and changes significantly from experiment to experiment. In this sense, the most important component on the surface is H_2O, whose surface concentrations are appreciable and do not diminish notably after evacuation for 15 min at 220 °C as in the course of the catalytic experiment.[65–67]

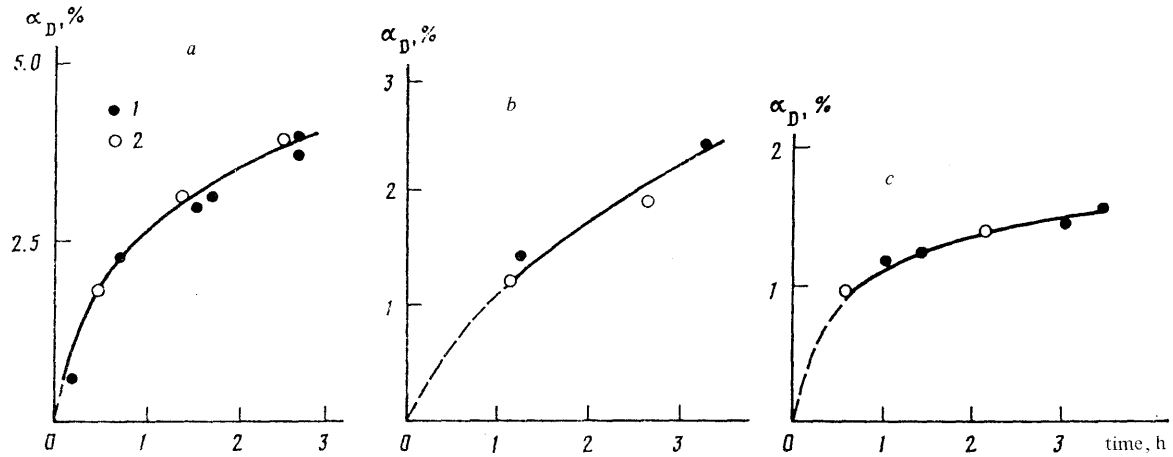


Figure 2. Kinetics of the accumulation of the fraction of the D isotope in hydrogen (*1*) and in methanol (*2*) in the synthesis of methanol from mixtures of different composition (mol%): *a*) CO (17.0), H_2 (72.9), and D_2O (0.49) ($V_0 = 7 \times 10^5$ h^{-1}); *b*) CO (10.5), CO_2 (10.0), H_2 (72.1), and D_2O (0.54) ($V_0 = 1.2 \times 10^6$ h^{-1}); *c*) CO (0.7), CO_2 (18.3), H_2 (75.7), and D_2O (0.54) ($V_0 = 1.2 \times 10^6$ h^{-1}) (the composition of the circulating gas with added D_2O towards the end of a 3 h circulation period).[69]

The strongly bound water on the catalyst surface participates, on the one hand, in the conversion reaction with CO from the gas phase and in adsorption substitution reactions[65,68] and, on the other hand, can undergo oxygen exchange with adsorbed CO_2 (judging from the data of Liu et al.[62]). These effects may introduce appreciable distortions precisely into the initial rates of transfer of the label. The above considerations are confirmed directly by the observed[62] appearance of labelled compounds when unlabelled reactants are used.

One may conclude that the presence of strongly bound water on the surface participating in isotope exchange, adsorption substitution, and CO conversion reactions, leads to a lag of the manifestations of the isotope composition of the reactants in the observed isotope composition of the products, which introduces a significant error in the measurement of the initial rates of formation of the labelled products. The data of Liu et al.[62] therefore require a more detailed analysis and their conclusions require further justification. For these reasons one cannot, in particular, rule out fully the postulated[64] involvement of water in the synthesis of methanol.

Overall, the experiments with labelled oxygen yield least definite results because of the presence of strongly bound water on the surface and the rapid oxygen exchange between CO_2 and H_2O. The absence of the transfer of oxygen from CO to the methanol molecule may be regarded as perhaps the only reliably established fact; the participation of the CO_2 and H_2O oxygen in the construction of the methanol molecule remains controversial.

Labelled hydrogen. The use of deuteriated water for the study of the mechanism of the synthesis of methanol unexpectedly proved extremely productive, despite the occurrence of rapid isotope exchange processes between water, the hydroxy-group of methanol, and the hydroxy-groups on the surface. The experiments with deuteriated water were performed first in the study already mentioned.[64] In these experiments, a copper-zinc oxide catalyst and an integral flow reactor were also used. The long contact times (space velocity $\sim 10^4$ h^{-1}) led to extremely low concentrations of water at the exit from the reactor. The initial mixture contained CO, H_2, and D_2O. The results of the experiments are presented in Table 4, where our calculated isotope fractions of deuterium in hydrogen, water, and methanol at the exit from the reactor are also compared.

Table 4. The transformations of D_2O under the conditions of the synthesis of methanol for long contact times (space velocity $\sim 10^4$ h^{-1}, CO + H_2 + D_2O mixture).

Parameters	Fluxes of mixture components, mmol h^{-1}								Isotope fraction of deuterium, %		
	H_2	HD	CO	CO_2	D_2O	H_2O	CH_3OH	CH_2DOH	H_2	H_2O	CH_3 group
A. Data of Vedage et al (Ref.64): 225 °C, 7.5 MPa, catalyst sample 2.45 g											
At entry	429.5	0	184	0	16.6	0	0	0	0	100	—
At exit	289.3	10.2	95.8	15.4	0.2	0.8	63.0	9.8	1.7	20	4.5
A. Data of Lin et al (Ref.69): 240 °C, 5.4 MPa, catalyst sample 3 g											
At entry	2290	0	840	0	17.75	0	0	0	0	100	—
At exit	1930	18.3	650	13.2	0.23	4.35	166	8.6	0.5	5.0	1.6

As can be seen from Table 4, an appreciable amount of deuterium appears in the CH_3 group of methanol, its isotope fraction exceeding approximately by a factor of three the isotope fraction in hydrogen.

The appreciable transfer of deuterium from the water molecule to the CH_3 group of methanol constitutes grounds for the conclusion that water participates in the synthesis of methanol,[64] which at any rate does not conflict with the data discussed above and obtained

using labelled oxygen, imparting a fairly rigorous character to their interpretation. Furthermore, the participation of water in the synthesis immediately brings to the fore the hydroxy-groups at the active centres on the surface in the possible mechanisms, which leads to preference being given to particular mechanisms of the synthesis. Thus the conclusion that water is involved in the synthesis is fundamental.

On the other hand, the low concentrations of water (and CO_2) in the reaction mixture and the relatively long contact times, which are responsible for the high concentration of methanol at the exit from the reactor (Table 4), increase sharply the possible contribution of secondary reactions to the observed deuterium transfer pathways under the conditions of the study of Vedage et al.,[64] so that the conclusion that water participates in the synthesis becomes insufficiently reliable. We therefore reanalysed the pathways leading to the transfer of deuterium from water under the conditions of the synthesis of methanol.[69,70] The reaction was carried out in flow and flow-circulation high-pressure apparatus on an industrial copper–zinc–aluminium oxide catalyst over a wide range of contact times: the space velocity was varied from values of the order of 10^4 h^{-1} (which corresponds to the conditions in the experiments of Vedage et al.[64]) to 10^6 h^{-1}. In the latter case, the occurrence of secondary reactions, especially further reactions of methanol, noted by Kotyaev et al.,[71] is reduced to a minimum.

Table 4 presents data[69] obtained for long contact times, modelling the conditions in the experiments of Vedage et al.,[64] and shows that the results of Klier and co-workers were reproduced under our conditions: the isotope fraction of deuterium in the CH_3 group of methanol exceeds by a factor of ~ 3 the isotope fraction of deuterium in hydrogen in both experimental series, although it does remain significantly lower than the average isotope fraction of deuterium in water.

Table 5. The synthesis of methanol on the SNM-1 copper–zinc–aluminium oxide catalyst for short contact times (temperature 240 °C).[69]

10^{-6} × space velocity, h^{-1}	Overall pressure, MPa	Partial pressures of components of synthesis gas, MPa				Fluxes at exit, mmol g^{-1} h^{-1}	
		CO	CO_2	H_2	D_2O	CH_3OH	H_2O
0.7	5.0	0.85	0.034	3.6	0.024	38.3	103
1.2	5.4	0.56	0.54	3.9	0.029	24.2	126
1.2	5.4	0.037	0.99	4.1	0.029	20.8	126

Experiments with short contact times were performed[69] in a circulation system, so that the content of deuterium in the circulating hydrogen gradually increased. The rates of this increase remained fairly low (usually 1–2% per hour) to ensure the possibility of a quantitative analysis of the data in terms of the quasi-stationary approximation. The results of experiments for mixtures of different composition (including the CO + H_2 + D_2O mixture analogous to that used by Vedage et al.[64]) are presented in Fig. 2 and the experimental conditions are indicated in Table 5.

The isotope fraction of deuterium in water varied in these experiments from 100% at the beginning of the reactor to 70 or 40% (experiments with the CO + H_2O mixture) at the exit, i.e. amounted on average to 85 and 70% throughout the reactor respectively.

These conditions were significantly more favourable for the transfer of deuterium to the CH_3 group of methanol than in the experiments of Vedage et al.[64] However, as can be seen from Figure 2, the isotope fraction of deuterium in the CH_3 group of methanol proved significantly lower than in water and virtually corresponded quantitatively to the isotope fraction of deuterium in hydrogen. Hence it followed that the transfer of deuterium from water to the CH_3 group of methanol does not occur at all under the conditions of its synthesis.

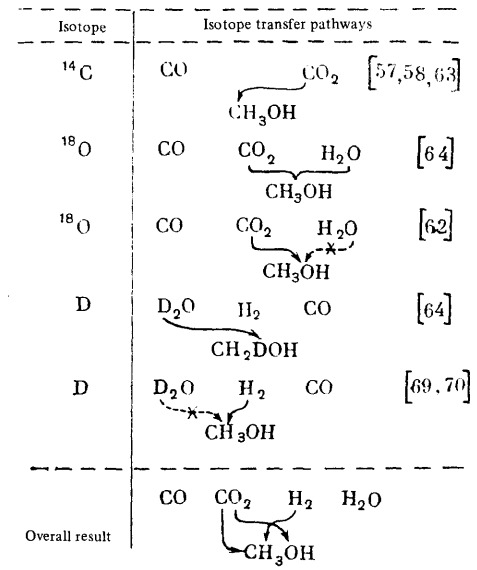
This result makes it possible not only to disprove the specific mechanism providing for the involvement of water in the synthesis of methanol[64] but also to reject all mechanisms of the synthesis of methanol with participation of the surface hydroxy-groups, whose exchange with water takes place at an extremely high rate. Additional information is provided by the appearance of deuterium in the CH_3 group for long contact times. The most probable cause of this is either exchange occurring during the reverse reaction [see Scheme (5)] or the occurrence of secondary reactions of the methanol itself. Among the latter, one should apparently consider primarily the formation of methyl formate with its subsequent hydrolysis:[67,71]

$$2CH_3OH = HCOOCH_3 + 2H_2,$$
$$HCOOCH_3 + H_2O = CH_3OH + HCOOH,$$
$$HCOOH = CO_2 + H_2.$$

This naturally constitutes only a tentative pathway, in contrast to the previous unambiguous conclusions.

The results of studies on the mechanisms of the synthesis of methanol on copper-containing catalysts using labelled atoms are summarised in Scheme 6.

Scheme 6 ¶



(6)

Evidently the methanol molecules include C atoms from CO_2, O atoms from CO_2 (or H_2O), and H atoms from H_2 (but not from H_2O). Thus methanol is obtained as a result of the hydrogenation of CO_2.

¶ The numerals in square brackets denote references (Ed. of Translation).

2. Kinetic analysis

Together with the tracer atom method, information about the reaction mechanism can also be obtained using other versions of kinetic analysis. Such information is usually reliable only as regards the sequence of the experimentally observed reactions of the chemical compounds; mechanisms involving the postulated intermediate substances, whose concentration cannot be measured, are always hypothetical to a lesser or greater extent. As regards the macroscopic mechanisms of the synthesis of methanol, i.e. the sequence of the reactions of carbon oxides, kinetic analysis leads to unambiguous conclusions. Such analysis has been carried out[60,61] (see also Kagan and co-workers[72,73]). Here we shall deal briefly with the most important results.

In the comparison of the alternative Schemes (3) and (5), data on the kinetics of the reactions of mixtures of CO_2 and H_2 without CO under conditions where the reaction time is sufficiently short to prevent the attainment of equilibrium in the water gas reactions (1) and (4) are most informative. The ratio of the selectivities with respect to the methanol formed and CO (relative selectivities) and its dependence on the contact time (for flow systems) yield unambiguous information about the sequence of the reactions of carbon oxides.

Indeed, within the framework of Scheme (3), methanol is obtained as the product of consecutive reactions with the intermediate formation of CO, whose initial concentration is zero. On reduction of the contact time τ to extremely low values, the relative selectivity $\gamma = x_{CH_3OH}/x_{CO}$ should then tend to zero:

$$\gamma_0 = \lim_{\tau\to 0}\gamma = \lim_{\tau\to 0}(x_{CH_3OH}/x_{CO}) = \lim_{\tau\to 0} W_2/W_1 = 0$$

[x_i are the degrees of conversion of CO_2 into the corresponding products and W_1 and W_2 are the rates of reaction (1) and (2) respectively], and diminishes with decrease in contact time in all cases.

Within the framework of Scheme (5), the reactions involving the conversion of the $CO_2 + H_2$ mixture into methanol and CO should occur as parallel processes, so that, for short contact times, the relative selectivity should behave in an arbitrary fashion (depending on the observed kinetics of both reactions) and should not become zero at $\tau \to 0$.

The experimentally observed dependences of the relative selectivity on contact time under the conditions of the synthesis of methanol from the $CO_2 + H_2$ mixture on the industrial SNM-1 copper–zinc–aluminium oxide catalyst at a pressure of 5 MPa and different temperatures are illustrated in Fig. 3.[61] The fragments of the curves shown refer to the rgion of short contact times such that there is insufficient time for the attainment of the water gas reaction equilibrium. Evidently, the relative selectivity curves do not start from the origin of coordinates, as should have been expected according to Scheme (3), which immediately demonstrates the inapplicability of the latter to the description of the reactions of carbon oxides in the given system.

Another method of kinetic analysis, which is close to a thermodynamic study, involves comparison of the observed concentrations of the reaction mixture components with their permissible values within the framework of the mechanisms of the reactions occurring. Thus, according to Scheme (3), CO is obtained in reaction (1) and is consumed in the synthesis of methanol via reaction (2). In the synthesis of methanol from $CO_2 + H_2$ mixtures, the amount of CO formed via reaction (1) cannot exceed the value permitted by the equilibrium in this reaction. Part of the CO formed is consumed in the synthesis of methanol, because its current concentration (like the concentration of water) must always be somewhat lower than the equilibrium value [as regards reaction (1)].

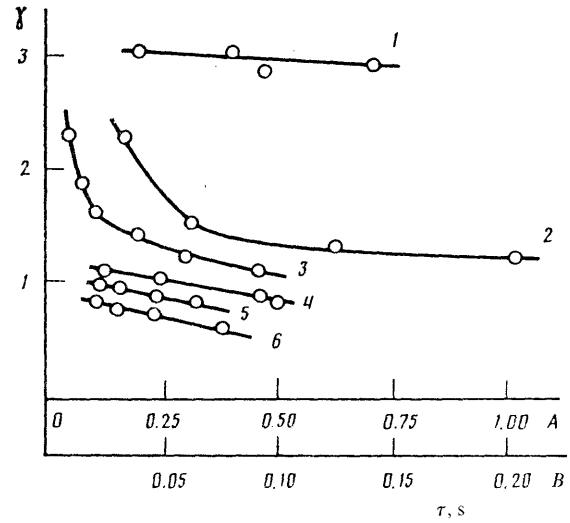


Figure 3. Dependence of the relative selectivity on contact time under the conditions of the synthesis of methanol on the SNM-1 catalyst from the $CO_2 + H_2$ mixture at different temperatures (°C): *1*) 180; *2*) 200; *3*) 220 (*A* scale); *4*) 240; *5*) 250; *6*) 260 (*B* scale).[61]

On the other hand, within the framework of Scheme (5), the concentrations of CO and H_2O should initially increase the equilibrium values (in relation to the water gas reaction) and should then exceed them, since CO_2 is consumed in the synthesis of methanol, while water is formed in this synthesis. Fig. 4 illustrates the kinetics of the accumulation of CO under the conditions of the synthesis of methanol from the $CO_2 + H_2$ mixture on the SNM-1 catalyst at 5 MPa and 220 °C and compares them with the equilibrium values corresponding to the observed concentrations of other participants in reaction (1).[61] Evidently, the kinetics of the accumulation of CO correspond rigorously to Scheme (5) and conflict with Scheme (3). The fundamental importance of these data is due to the fact that the synthesis of methanol is highly selective, since there are no other pathways leading to the formation or consumption of CO or water apart from the synthesis itself. Analogous data for the concentration of water under the conditions of the synthesis of methanol, greatly exceeding the equilibrium values in relation to reaction (1), have been obtained[74] for the zinc–chromium catalyst, although they have in fact not received due recognition.

The results of the calculation of the equilibrium composition in the synthesis of methanol for mixtures with a relatively low CO concentration compared with CO_2, especially for the initial $CO_2 + H_2$ mixtures, are even more striking. According to the calculations,[75–78] the observed concentrations of methanol at the exit from the reactor in the presence of various copper-containing

catalysts greatly exceed the equilibrium values calculated on the basis of Scheme (3), i.e. on the hypothesis that methanol is synthesised from CO and H_2.

The data presented permit the unambiguous conclusion concerning the pathways leading to the reactions of carbon oxides on the oxide catalysts. Methanol is synthesised in two macroscopic stages:

(1) the conversion of CO by water:

$$CO+H_2O \rightleftarrows CO_2+H_2 \quad (7)$$

and (2) the formation of methanol from CO_2 and H_2:

$$CO_2+3H_2 \rightleftarrows CH_3OH+H_2O. \quad (8)$$

V. The process in the catalyst bed

From the results examined in the previous Section, one can assume that, in the presence of the industrial oxide catalysts, methanol is synthesised according to Scheme (5), i.e. it includes reactions (7) and (8). The natural question arises what is the importance of this information for characterising the properties of the overall process. This is particularly significant, since, within the framework of the fairly common approach to the control and optimisation of the process, one can use the kinetic equation found empirically and not related directly to its mechanism. The synthesis of methanol is an extremely clear example of the imperfection of an approach of this kind.

The most evident changes in the properties of the process are associated with the change in the stoichiometric reaction equations: a reactant changed (CO_2 instead of CO) and an additional reaction product (water) appeared. Attention is in fact concentrated on their influence in the search for a kinetic equation. The synthesis from CO_2 + H_2 mixtures and not the synthesis from the ternary mixtures (of CO, CO_2, and H_2), where the interconversions of the carbon oxides mask their influence on the rate of formation of methanol, is thus the object of such search. Indeed, even in the first kinetic study of the synthesis of methanol from CO_2 and H_2 a marked inhibition by water was noted, the observed reaction order with respect to the substance proved close to −1 under conditions important in practice.[60]

The foregoing does not, however, exhaust the possibilities of the situation. In the system of reactions (7) and (8), water behaves as a reactant in reaction (7) and as a product in reaction (8). On the one hand, it is essential for the generation of CO_2 and, on the other, it inhibits the synthesis of methanol proper. The combination of reactions (7) and (8) actually represents a cyclic process, resembling a chain reaction, in which water behaves as a transferring agent for the excess oxygen atom from the complex preceding the formation of a methanol molecule to carbon dioxide. The observed rate of synthesis of methanol is then mainly determined by the concentration of water in the reaction zone and the latter is the result of the balance between reactions (7) and (8). Hence follows the unexpected conclusion that the catalyst of methanol synthesis, proceeding in accordance with scheme (5), must manifest a high activity in the conversion of CO by water as a necessary condition for its effectiveness in the synthesis of methanol itself. Thus a change in the macroscopic mechanism of the synthesis of methanol entails new approaches to the selection of catalysts for this process.

In order to characterise more fully the features of methanol synthesis in terms of its kinetic aspect, we turn to Fig. 4. Evidently, for the ternary mixtures of CO, CO_2, and H_2 usually employed in the synthesis of methanol, the form of the curves in Fig. 4 remains the same (it is determined by the absence of water from the initial mixture) and only the ascending branch of the CO concentration curve begins with non-zero values.

We shall consider the situation in various sections through the flow reactor. In the input section, the CO + CO_2 + H_2 mixture contains no water: reaction (7) proceeds from right to left, i.e. in the direction of the reduction of CO_2 to CO under conditions remote from equilibrium. As the reaction mixture moves along the catalyst bed, the reduction of CO_2 to CO and the synthesis of methanol in the system result in the accumulation of water, the ratios of the concentrations of the components approaching the equilibrium ratios for the water gas reaction (7). As the reaction mixture migrates further, its CO concentration rises "above the equilibrium value" and the reverse transition from CO to CO_2 begins (the conversion of CO by water), the CO concentration passes through a maximum, and then gradually falls as methanol accumulates, still exceeding the equilibrium values, like the concentration of water.

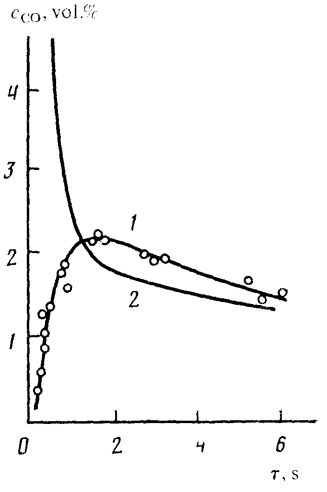


Figure 4. Dependence of the concentration of carbon monoxide on contact time under the conditions of the synthesis of methanol from the CO_2 + H_2 mixture in the presence of the SNM-1 catalyst (220 °C, 5 MPa): *1*) current concentration; *2*) equilibrium concentrations corresponding to the observed concentrations of the other components.[60,61]

Thus in different sections of the catalyst bed, reaction (7) proceeds both under conditions remote from and close to equilibrium and, furthermore, on either side of the equilibrium. We may recall that the kinetics of reaction (7) combined with reaction (8) determine the current concentration of water in the system and correspondingly the rate of synthesis of methanol. Hence it follows that, in order to construct the kinetic model of the methanol synthesis process, it is necessary to achieve in the first place a detailed kinetic characterisation of the conversion of CO by water under conditions remote from, close to, and on either side of the equilibrium. These exceptionally severe requirements virtually rule out the possibility of obtaining a reliable kinetic model by the usual empirical search. Its

development requires the knowledge of the detailed mechanism of the CO conversion reaction, which does in fact make it possible to construct a theoretical kinetic model.

An unusual situation arises in which the necessity for the solution of a purely applied problem poses a task whose performance is feasible only within the framework of serious fundamental studies. One can also conclude that the transition from Scheme (3) to Scheme (5) entails the necessity for new approaches also to the selection of catalysts for the synthesis of methanol and to the determination of its characteristics.

VI. The detailed mechanism of the synthesis of methanol

In order to analyse the detailed mechanism of methanol synthesis, it would be necessary to use in the first place the results of spectroscopic studies, which make it possible to operate with specific intermediate compounds on the catalyst surface. However, despite the relatively wide-scale development of such studies (see, for example, the studies in Refs. 15, 16, 79–82), their kinetic component usually proves to have been insufficiently thoroughly worked out to be able to construct a reliable sequence of reactions of the observed surface compounds or at least to assess unambiguously their role in the mechanism of the catalytic synthesis of methanol. The synthesis mechanisms put forward are therefore not only hypothetical but actually conflict with one another and the results of synthetic studies, in particular those carried out by the tracer atom method. Only the presence of virtually all the possible carbon-containing surface compounds (carbonyls and methoxy-, formyl, formate, and carbonate groups) on the catalyst surface as well as correlations between the intensities of the corresponding adsorption bands and the catalytic properties of the specimen have been reliably established.

The study[81] in which spectroscopic measurements *in situ* were accompanied by kinetic measurements is an exception in the above series of investigations. It has been shown that, in the synthesis of methanol from the $CO_2 + H_2$ mixture on the copper–zinc–aluminium oxide catalyst, the rate of synthesis varies in parallel with the intensity of the 1640 cm^{-1} absorption band, which has been assigned to the copper formate complex.

The interpretation of the data of the above study[81] is complicated by the fact that the observed formate structure may prove, with equal probability, to be an intermediate in the synthesis of methanol and the product of the reactions of methanol, for example, those mentioned in the discussion of experiments with deuteriated water. The latter becomes more probable bearing in mind that the formate structure is formed readily with participation of the molecules of both CO_2 and CO from the gas phase. If this structure is a precursor of methanol, then it must be regarded as a common intermediate in the synthesis of methanol and in the conversion of CO by water (as is assumed by Amenomiya and Tagawa[81]). However, in this case there should have been a transfer of the carbon label from CO to methanol which has not been observed experimentally. Correspondingly, the assignment of the formate structure to an intermediate in the synthesis of methanol would conflict with the direct experiment.[58,63,83]

Unexpected progress in the development of ideas about the detailed mechanism of the synthesis of methanol arose as a result of studies on the reactions of stable surface compounds under non-stationary conditions, an incomplete survey of which has been published.[65] In these studies, the reactions of chemisorbed water, CO, and also methanol were investigated[84] at atmospheric pressure and the temperatures of the industrial process. Both the object of study and the conditions far from those of the real synthesis permitted the expectation of only academic results. Ultimately, however, it was found that, even at insignificant concentrations of water in the gas phase, the surface of industrial catalysts is covered by strongly bound water, the characteristic desorption times of which at the temperatures of the catalysis amount to tens of hours and more. This water can be removed from a limited number of surface centres as a result of conversion by the gas phase carbon monoxide and also the adsorption substitution reaction[68] with formation of another strongly chemisorbed species.

The most important of the substitution reactions is

$$X\cdot H_2O + CO_2 \rightleftarrows X\cdot CO_2\cdot H_2O \rightleftarrows X\cdot CO_2 + H_2O, \qquad (9)$$

where X is a copper-containing surface centre, not belonging to the copper phase, for example, a doublet of copper ions in the zinc oxide lattice. The nature of the copper centres (impurity defects or an impurity "phase" at the boundaries) is determined by their ability to undergo oxidation-reduction reactions at a catalysis temperature of 250 °C in the interaction with H_2O and CO_2 (oxidants) and with CO and H_2 (reductants), whereas copper itself in the form of an individual phase is not oxidised by water. Since these centres are the only reactive sites on the catalyst surface (at any rate in the presence of water in the gas phase), they are virtually the only possible candidates for the role of active centres in the synthesis of methanol. This thesis is supported by the fact that the removal of water from other surface sites takes place via its diffusion to the centres considered with subsequent liberation to the gas phase as a result of the conversion reaction with CO.[65,85]

It has also been shown that H_2O and CO_2 are bound to the active centres much more strongly than CO and H_2, since, in the presence of water and carbon dioxide in the gas phase, the surface compounds involving their participation predominate absolutely.

The conclusions described have been confirmed by thermal desorption studies, which also made it possible to detect the formation of a second, less strongly bound form of CO_2 in the presence of H_2O.[66,67,71]

Thus the situation on the surface under the conditions of the synthesis of methanol has been unexpectedly significantly simplified: in fact, apart from H_2O, one need consider the presence of only two carbon-containing components, which are represented by chemisorbed CO_2 with different bond strengths. It has been shown[86] that the hydrogenation of both forms of CO_2 leads to the formation of methanol.

The role of these forms in the stationary process remains obscure in the sense of the contribution of their reactions to the observed process kinetics. Nevertheless the characteristics of the synthesis of methanol must be significantly different in the presence of different forms of CO_2 in the process [see reaction (9)]. In particular, one may note that the reduction of the intermediate form containing H_2O can occur under the conditions of the synthesis not only with participation of hydrogen but also with participation of CO via the reaction

$$X\cdot CO_2\cdot H_2O + CO \rightarrow X\cdot CO_2\cdot H_2 + CO_2 \qquad (10)$$

with formation of the complex $X.CO_2.H_2$, the existence of which has been pointed out, for example, by Dyatlov.[87] Reaction (10) does not conflict directly with the results of studies using carbon and oxygen

tracer atoms discussed above. Indeed, despite the direct involvement of CO in reaction (10), the C and O atoms from CO_2 alone can be incorporated in the $X.CO_2.H_2$ complex formed and hence in the methanol molecule. However, in this complex at least one of the hydrogen atoms must be bound directly to the carbon atom and subsequently, on formation of methanol, should be found in the CH_3 group. Then reaction (10), if it is a stage in methanol synthesis, should lead to the incorporation of hydrogen from water in the CH_3 group of methanol. We have seen that in experiments using D_2O such incorporation does not occur in the stationary process. Hence it follows that the transformations of the complex $X.CO_2.H_2O$ via reaction (10) do not contribute significantly to the stationary process in the synthesis of methanol.

It follows from the above reasoning that methanol is synthesised via the hydrogenation of chemisorbed (strongly bound) CO_2 by the gas-phase hydrogen:

$$X\cdot CO_2 + H_2 \rightarrow X\cdot CO_2\cdot H_2 \xrightarrow{2H_2} CH_3OH + X\cdot H_2O. \qquad (11)$$

The combination of reactions (9) and (11) actually provides a mechanism through which methanol is synthesised from CO_2 and H_2. Reaction (9) was discussed above. Its characteristic times correspond to the characteristic times of the catalysis. Reaction (11) evidently takes place in several stages. Judging from the fact that, despite their wide variety, all the kinetic descriptions of methanol synthesis (see below) agree that the observed reaction order with respect to hydrogen is close to unity, the first stage of reaction (11) is the slowest.

Two products are formed as a result of reaction (11)—H_2O and CH_3OH, which may remain on the centre or can be released into the gas phase. If the methanol molecule remains on the surface, then its interaction with the centre results in the extensive reduction of the latter[84,85] and the transformation of the methanol itself. Such a sequence of stages is in fact no longer catalysis.

If both species remain on the centre, then the reverse reaction is the most probable outcome.

If both molecules formed are released into the gas phase, then simple inspection shows that the reverse process cannot occur.

Indeed, by carrying out all the stages of the process in the reverse direction, we arrive at the $X.CO_2$ state, from which CO_2 is not desorbed, at any rate during a period comparable to the reaction time, and can only undergo the substitution reaction (9) in the reverse direction. This means automatically that the reverse reaction begins with the interaction of CH_3OH not with a free centre but with a centre containing chemisorbed water ($X.H_2O$). By virtue of the principle of microscopic reversibility, the same state should complete the forward reaction, which is actually consistent with the formulation of reaction (11). In fact, we consider degenerate schemes owing to the irreversible chemisorption of individual components.

The combination of reactions (9) and (11) provides a detailed mechanism of methanol synthesis (Scheme 12). The slow stage (3) is shown in the scheme as irreversible, although it can naturally proceed also in the reverse direction. On the basis of this scheme, it is possible to obtain a theoretical kinetic model of methanol synthesis from CO_2 and H_2, which will be done in the next Section.

Scheme 12

$$\begin{array}{l} X\cdot H_2O + CO_2 \overset{1}{\rightleftharpoons} X\cdot CO_2\cdot H_2O \overset{2}{\rightleftharpoons} X\cdot CO_2 + H_2O \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad {\scriptstyle 3}\downarrow H_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad X\cdot CO_2\cdot H_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad {\scriptstyle 4}\uparrow\downarrow 2H_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad X\cdot H_2O + CH_3OH \end{array} \qquad (12)$$

VII. Kinetics of the synthesis of methanol

The kinetic models of methanol synthesis are extremely varied, especially those obtained up to 1975,[1] where the very formulation of the research was based on incorrect ideas about the macroscopic process mechanism. In their final conclusions about the studies in this field, Popov et al.[88] stated that there are no models describing satisfactorily the experimental kinetic data over a wide range of conditions. Nevertheless, the corresponding models—we shall call them the first generation models—continue to appear also in studies of recent years. As an example, one may quote recent publications.[89,90] The kinetic model proposed in the first of these is based in essence on Natta's approach[91] developed later by Pasquon.[92] It is based on the kinetic equation

$$W = \frac{f_{CO}f_{H_2}^2 - f_{CH_3OH}/K_e}{(c_1 + c_2 f_{CO} + c_3 f_{CO_2} + c_4 f_{H_2})^2}, \qquad (13)$$

where f_i are the fugacities of the corresponding compounds, K_e is the equilibrium constant of the methanol synthesis reaction, and c_i are constants. In this model, no account is taken, in particular, of the strong influence by H_2O on the rate of synthesis of methanol and also of the complex influence of CO_2, established in a series of investigations.

The simpler equation[90]

$$W = k\left(P_{CO}P_{H_2}^2 - \frac{P_{CH_3OH}}{K_e}(P_{CO}P_{H_2}^{0.5})\right)^{-1.3}, \qquad (14)$$

where P_i are the partial pressures, is open to analogous comments. The formal nature of these models is evident in the light of data on the macroscopic mechanism of the synthesis of methanol.

The second generation models proved to a large extent the consequence of new ideas about the mechanism of the synthesis and hence of the tests and subsequently allowance for the influence of H_2O and CO_2 on the observed rate of reaction. The first study on these lines was apparently performed in investigations[60,94,95] where the strong inhibition of the synthesis of methanol by water was demonstrated. Over a wide range of temperatures, space velocities, and pressures, the kinetics of the synthesis of methanol from mixtures with a high CO_2 content on the industrial SNM-1 catalyst were described by the equation

$$W = kP_{H_2}/(1 + bP_{H_2O}). \qquad (15)$$

According to this equation, CO does not influence the rate of synthesis of methanol at all, the rate being virtually determined by the partial pressure of H_2O. The striking differences between this model and the kinetic first generation models are evident, which clearly demonstrate that the contribution by constrained solutions to the construction of kinetic models of stationary processes is still considerable. We may note that Eqn. (15) is an approximation to the theoretical kinetic model[96] at high CO_2 concentrations in the system.

A theoretical kinetic model of methanol synthesis can be obtained from the detailed mechanism presented in the preceding Section. The structure of this model is now determined by the form of the mechanism and only the establishment of the reaction order with respect to hydrogen requires an additional hypothesis about the slow stage of the process. Assuming that this stage is the addition of the first hydrogen molecule, we obtain the following expression after appropriate rearrangements:

$$W = k_3K_1P_{CO_2}P_{H_2}/[K_1P_{CO_2} + K_{-2}P_{H_2O} + K_1K_{-2}P_{CO_2}P_{H_2O} + (k_3/k_2)\,P_{H_2}(K_1P_{CO_2} + k_2/k_{-1} + 1)], \quad (16)$$

where k_i and K_i are the rate and equilibrium constants of the corresponding stages in the mechanism. Within the framework of this assumption, the last term of the denominator can be omitted, since it includes a small quantity (k_3/k_2) as a comultiplier. One then obtains a relatively simple kinetic equation (applicable only for a very low CO_2 concentration):

$$W = \frac{k_3K_1P_{CO_2}P_{H_2}}{K_1P_{CO_2} + K_{-2}P_{H_2O} + K_1K_{-2}P_{CO_2}P_{H_2O}}. \quad (17)$$

Eqn. (17) differs from the usual models by the non-linearity in the denominator, which is characteristic of reactions with participation of strongly chemisorbed species. At high CO_2 concentrations, Eqn. (17) simplifies and assumes the form of Eqn. (15).

Among other second generation kinetic models, the model proposed by Temkin, Shubov, and co-workers[97,98] merits attention in the first place. The kinetic equation describing the experimental data for methanol synthesis and for the reverse reaction of methanol with water on the SNM-1 catalyst at atmospheric pressure has the following simplified form:

$$W = \frac{k_+P_{H_2}P_{CO_2}(1 - P_{CH_3OH}P_{H_2O}/K_eP_{H_2}^3P_{CO_2})}{(1 + k_1P_{CO_2} + k_2P_{CH_3OH}/P_{H_2})(1 + k_3P_{H_2O}/P_{H_2} + k_4P_{CO})}. \quad (18)$$

Eqn. (18) is very close to the equations of the theoretical kinetic model, differing by the presence of additional terms reflecting the inhibition of the reaction by methanol and CO; furthermore, according to Eqn. (18), the inhibition by water weakens with increase in the partial pressure of hydrogen. However, these features are not supported by experiment, at any rate at an elevated pressure. In particular, the partial pressure of hydrogen has no influence on the intensity of the inhibition of the synthesis of methanol in the presence of the SNM-1 catalyst by water at 5 MPa according to the experimental data quoted by Malinovskaya et al.[78]

Table 6. The influence of added methanol on the rate of its formation in the presence of the SNM-1 catalyst at 5 MPa in a flow reactor (P_{CO_2} = 10 atm, P_{H_2} = 35 atm).

Temperature, °C	P_{CH_3OH}, atm (at entry)	Rate of formation of CH_3OH, mol g^{-1} s^{-1}	Remarks
220	0	8.0	Before supply of CH_3OH
220	1.7	8.6	With added CH_3OH
220	0	8.0	After supply of CH_3OH
240	0	9.2	Before supply of CH_3OH
240	1.4	10.0	With added CH_3OH
240	0	9.6	After supply of CH_3OH

The absence of an inhibiting effect by methanol is shown by the data in Table 6 obtained by G I Lin and co-workers in the author's laboratory. As can be seen, in the series of consecutive experiments (with and without the supply of methanol to the reactor) on the SNM-1 industrial catalyst in the presence of methanol in the initial mixture, the rate of its synthesis at least does not increase, which agrees with earlier data.[60] Thus the experimental test makes it necessary to give preference to Eqn. (17) for the theoretical kinetic model.

A description close to Eqn. (17) has been proposed on the basis of an investigation of the mechanisms of methanol synthesis in the study[81] discussed above. According to Amenomiya and Tagawa,[81] the rate of synthesis of methanol is determined by the equation

$$W = kK_{CO_2}P_{CO_2}P_{H_2}/(1 + K_{CO_2}P_{CO_2}), \quad (19)$$

where k and K_{CO_2} are constants.

Evidently, at extremely low H_2O concentrations, Eqn. (19) approaches Eqn. (16) of (17). Since the experimental data[81] were obtained precisely under such conditions (extremely low degrees of conversion), the absence from Eqn. (19) of allowance for the inhibiting effect of water, which has been reliably established experimentally,[60,97,98] becomes understandable.

Overall, one may conclude that, although the theoretical kinetic model [Eqns. (16) or (17)] descerves to be given preference, all the second generation models [Eqns. (15)–(19)] reflect relatively similar relations and differ sharply from the first generation models represented here by Eqns. (13) and (14).

In conclusion we shall deal briefly with certain equations which have appeared in recent years and which can be regarded as intermediate between the first and second generation models.

The influence of CO_2 on the rate of synthesis of methanol has been interpreted[99] as a consequence of the oxidation-reduction reactions of the active centres (oxidised by carbon dioxide and reduced by carbon monoxide). In conformity with these ideas, a "correction" term containing p_{CO_2} was introduced into the traditional kinetic model.

However, the dependence of the rate of synthesis on the CO_2 concentration observed in the above study[99] was partly due to the inhibition by the water formed on reduction of CO_2. The inhibition of the synthesis by carbon dioxide has not been confirmed (see, for example, Refs. 81, 95, and 97). Nor has the concept of the oxidation reactions of the centres under the influence of CO_2 been confirmed. Experiments using the D and ^{18}O isotopes have shown that water and not CO_2 is the main oxidant for the reduced catalyst.[100]

On the basis of chemisorption data, heat changes, and other characteristic features of the process, a mechanism has been proposed[101] for methanol synthesis and the kinetic model which follows from it. Since, however, the author[101] postulates a weak adsorption of water and water is in fact the species most strongly bound to the active centres (see above), further consideration of this model is evidently pointless.

Finally, in a recent study[102] an empirical description has been proposed for the kinetics of the synthesis of methanol involving the combination of both synthetic pathways: from CO and from CO_2. The absence of an appreciable contribution by the synthesis from CO on copper-containing catalysts was discussed above.

The rapid evolution of kinetic models for methanol synthesis described may serve to some extent as an illustration of the influence of ideas about the mechanism (not even the detailed mechanism but the macroscopic mechanism) of the process and its kinetic description. Although empirical kinetic descriptions are based on independent experiments and seemingly should not depend on the corresponding ideas, nevertheless such influence undoubtedly follows if only from a simple comparison of the first and second generation kinetic models.

In conclusion of this Section, we shall illustrate the applicability of the theoretical model (15) to the description of methanol synthesis on the SNM-1 industrial catalyst.[96] Fig. 5 presents the kinetic curves for the synthesis of methanol from the $CO_2 + H_2$ mixture at pressures of 7.6 and 10.1 MPa and a temperature of 240 °C. The curves relating the degree of conversion to contact time plotted in the figure were calculated for the model based on Eqn. (17) (taking into account the process reversibility) and for the analogous model for the reduction of CO_2 to CO, the parameters of the equation being determined from experimental data obtained at 5 MPa. Evidently, the experimental points fit on the calculated curves, i.e. the equation correctly reproduces the dependence of the rate of synthesis both on the contact time and on the pressure in the system.

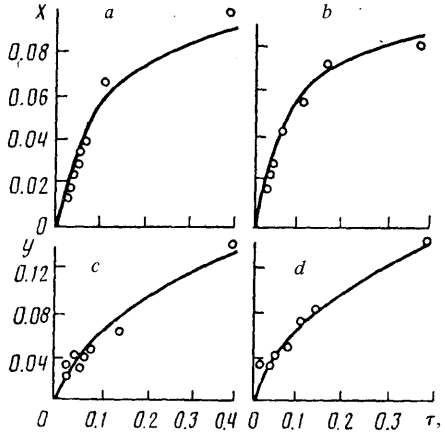


Figure 5. Kinetics of the reduction of CO_2 to CO (*a* and *b*) and of the synthesis of methanol (*c* and *d*) from the CO_2 (23 vol. %) + H_2 (68 vol. %) mixture at 240 °C and pressures of 7.6 MPa (*a* and *c*) and 10.1 MPa (*b* and *d*): curves—calculation; circles—experiment (*x* and *y* represent the degrees of conversion).[96]

The existence of a theoretical kinetic model permits the analysis of the existing technological schemes for the manufacture of methanol and makes it possible to reveal their deficiencies and to discover the possibilities for a sharp increase in productivity per unit volume of the catalyst compared with the existing technological schemes. Although these data are outside the framework of this review, they undoubtedly illustrate the intertwining of fundamental and applied problems in chemical practice.

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The above discussion shows that the synthesis of methanol is at present one of the most thoroughly investigated catalytic processes. The studies on the macroscopic mechanisms of the synthesis on basic copper-containing catalysts can be regarded as completed. Important information has also been obtained about the detailed mechanisms of the reactions occurring. Although here our knowledge is still incomplete—the structure of the intermediate surface compounds is unknown (probably this is one of the carbonate structures)—on the basis of the existing data it is possible to construct a well-founded mechanism of methanol synthesis, which enables us to discover the structure of the theoretical kinetic model of the process. Having at one's disposal a theoretical kinetic model, it is possible to solve various applied problems, including the problem of the development of a new highly efficient technology for the industrial process. This is apparently the most important aspect of the studies in the present stage.

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