Reviews

Construction of the reaction networks for heterogeneous catalytic reactions: Fischer—Tropsch synthesis and related reactions

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The key approaches to the generation of reaction networks for the synthesis of products from CO and H_2 are considered. The selection rules for the elementary steps on the surface of heterogeneous catalysts are formulated. Data on the surface compounds and steps related to reactions of CO and H_2 are analyzed and a set of transforms (models of elementary steps) for generation of the reaction network are selected. Eight variants of generation of reaction networks for the formation of C_1 products with different sets of transforms (12 to 31) were tested in computer experiments, and eight reaction networks comprising 34 substances and 132 to 1647 elementary steps were obtained. The pathways to CO_2, CH_4, and CH_3OH and pairs of compounds CH_4, CO_2 and CH_4, HCOOH obtained from the reaction network (220 elementary steps) are compared with the published schemes.

Key words: Fischer—Tropsch synthesis, reaction mechanism, reaction network, elementary steps, computer generation of mechanisms.

Introduction

In the last two decades, the interest in syntheses based on CO and H_2, mainly hydrocarbon syntheses, has constantly increased.[1—9] Studies of the kinetics and mechanism of the syntheses from CO and H_2 have been surveyed in a number of reviews.[10—16] However, the problem of generation of a unified reaction network describing the formation of diverse products in the Fischer—Tropsch synthesis for any catalysts and conditions, formulated 20 years ago[10] has not yet been solved.

In construction of kinetic models for intricate reactions, full reaction networks can be used either wholly[17—21] or partially (as "blocks" "cut out" of the com-

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mon mechanism network).[3,22] Examples of using reaction networks comprising 296, 1000, and even 3000 elementary steps are documented.[17—19] Dealing with extensive reaction networks is facilitated by the development of empirical[23—25] and *ab initio*[26—38] methods of calculation of the heats and activation energies of steps on the surface of metal catalysts. The calculation methods provide estimates of the contributions of steps and blocks of steps to the process kinetics, and thus they transform the reaction network into a real basis for compiling a kinetic model.

A series of recent publications have been devoted to the development of a rational strategy for the mechanistic studies and construction of kinetic models of complex multistep and multipath reactions, first of all, metal-complex-catalyzed processes involving organometallic intermediates.[39—41] This strategy is based on preliminary advancement of hypothetical mechanisms, which are generated using computer programs. The ChemNet program has been developed on the basis of the input data on the generalized elementary steps involved in organometallic catalysis (so-called "transforms").[41,42] It is used to obtain the reaction networks from which one can extract pathways to any individual product (or several products formed in conjugation). The MECHEM program [43—48] allows generation of sets of simple mechanisms that do not contradict the imposed constaints. The experience in working with these programs accumulated while putting forward hypotheses on the mechanisms of organometallic catalysis[49—51] and some heterogeneous processes[52—54] is rather useful for the generation of the reaction network for the formation of C_1 products of the Fischer—Tropsch synthesis. Previously, a similar problem has been solved using the Ugi algorithm,[20] but the elementary steps thus obtained were debatable.

During computer generation of very large reaction networks, the selection and preliminary substantiation of steps, intermediates, and generalized transforms acquires special significance.

This work is devoted to the analysis of the problem of elementary character of steps in heterogeneous catalysis and in the Fischer—Tropsch synthesis, selection of intermediates for syntheses based on CO and H_2, selection of generalized transforms in the form convenient for the ChemNet program, generation of the reaction network, and analysis of mechanistic hypotheses on C_1 product formation (CH_4, CH_3OH, HCOOH, and CO_2).

1. The problem of elementary character of reactions on the surface of heterogeneous catalysts

During many years, the theory of heterogeneous catalysis has employed the analogy between compounds formed on the surface and organometallic coordination compounds in solutions.[11,13—15] However, the difficulty of identification of surface compounds, specific surface structure, and the role of collective properties of a solid make the description of elementary steps in heterogeneous catalysis less definite than that for homogeneous organometallic catalysis. Examples of elementary steps taken from studies devoted to the Fischer—Tropsch synthesis and other hydrocarbon transformations demonstrate how much the approaches to identification of elementary steps in heterogeneous and homogeneous catalysis differ (here we retain the designations of the active sites M, l, S accepted in the studies cited):

$$\mathrm{MCO + M \rightleftharpoons M{-}C + M{-}O,} \qquad (1)[10]$$

$$\mathrm{M{-}C + H_2 \rightleftharpoons M{-}CH + H,} \qquad (2)[10]$$

$$\mathrm{l{=}C{=}O + l \rightarrow l{=}C + l{=}O,} \qquad (3)[21]$$

$$\mathrm{l{=}CH{-}OH + H_2 \rightarrow l{=}CH_2 + H_2O,} \qquad (4)[21]$$

$$\mathrm{CO + 2\,S \rightleftharpoons CS + OS,} \qquad (5)[3]$$

$$\mathrm{CO + 2\,M \rightarrow M_2CO,} \qquad (6)[20]$$

$$\mathrm{M_2CO + 3\,M \rightarrow M_3C^{\bullet} + M_2O,} \qquad (7)[20]$$

$$\mathrm{CH_3CH_2\ (ads.) \rightarrow CH_3\ (ads.) + CH_2\ (ads.).} \qquad (8)[55]$$

The same reaction of CO bond cleavage can be described as bimolecular step (3) involving two sites, trimolecular step (5) involving two sites, or tetramolecular step (7) involving five sites.

Let us consider the selection rules for elementary steps in homogeneous reactions. Analysis of a database on elementary reactions of coordination and organometallic compounds and steps used in organometallic catalysis (~3000 steps)[56,57] showed that a reaction can be considered elementary (concerted) if several theoretically substantiated and heuristic rules are fulfilled.[56]

(a) the molecularity of steps in the forward and backward directions does not exceed 2;

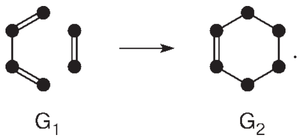
(b) the occupied frontier orbitals of the reactants and products are symmetry correlated (Woodward—Hoffmann);

(c) the difference between the numbers of cleaved and formed bonds does not exceed 1;

(d) the topology of bond redistribution is simple (linear or cyclic);

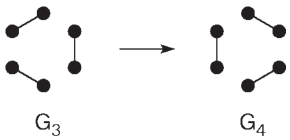
(e) the number of nuclei that change the coordinates during an elementary act is few (the Reiss—Teller least motion principle[58]).

By the topology of bond redistribution, one means the structure of a graph produced by superposition of the graphs representing the bonds that are cleaved and those that are formed. Any chemical reaction can be represented graphically by removing the groups and atoms not involved in the bond transformation. Thus the Diels—Alder reaction can be represented as graphical equation (9), which describes bond redistribution



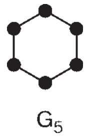
(9)

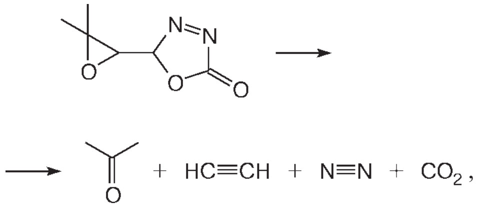
Then we can remove the bonds remaining intact; this gives Eq. (10), reflecting the *type of reaction*.[56]



(10)

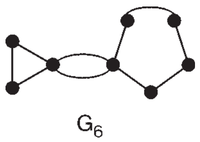
The superposition of graphs G_3 and G_4 gives graph G_5, which is called topology identifier[56] or reaction type topology.[59] The topology identifier represents in a simplified form the topology of the transition state (in this case, cyclic). If simultaneous cleavage and/or formation of multiple bonds is assumed, multiple branches arise in graphs G_3, G_4, and G_5 and form additional rings in topology identifiers. In the analysis performed,[56,57] it was found that among steps that can be soundly regarded as elementary, one can hardly find steps with mixed (linear and cyclic) or more complex (polycyclic) identifiers. Reactions with complex topology previously termed[60—62] reactions with "coarctate" transition states are not elementary, in our opinion. These reactions, for example





(11)

involve changes in the coordinates of many nuclei; therefore, synchronization of vibrations of nine bonds in different directions, which is needed for the fragmentation of four molecules, seems unlikely. In addition, the quality of the quantum-chemical calculations of the potential energy surfaces used to substantiate the elementary nature of the "coarctate" reactions[60—62] raises doubts.[63] According to the microscopic reversibility principle, in the case of reversible steps close to equilibrium, the molecularity of the reverse step should not be high either. However, in considering "coarctate" reactions as elementary steps, this fact has often been neglected.



When using the above-mentioned selection rules for elementary steps of heterogeneous processes, one should take into account specific features of chemical reactions on the surface. These rules are considered in the following sections.

1.1. Limited mobility of intermediates

The notions "adsorbed species" and "intermediate" are also used as synonyms. In this work, the term "adsorbed species" is understood as a molecule or a molecular fragment on the surface of a catalyst (H, CO, CH_3, $CH_2{=}CH$, *etc.*). The term "intermediate" will be used to describe a surface compound comprising the adsorbed species and the surface atoms bound to it (active sites). This brings to light a direct analogy between heterogeneous and homogeneous metal complex catalysis: the adsorbed species stands for a ligand and the intermediate stands for a metal complex with the ligand. As a rule, intermediates do not migrate over the surface, while adsorbed species, conversely, do migrate from one site to another until they meet a reactive species. The transfer of an adsorbed species from one site to another occurs as a result of surface diffusion or desorption followed by re-adsorption or adsorption-assisted desorption[64]

$$B + X_iA \rightarrow A + BX_i. \qquad (12)$$

The steps in which adsorbed species migrate from one active site to another play a key role in the kinetics of hydrogenation[65] and other reactions[66]

$$Z_1H + Z_2 \rightarrow Z_1 + Z_2H. \qquad (13)$$

Thus, an elementary step on the surface involves the intermediates formed upon migration of adsorbed species rather than the species formed originally. For example, according to a hypothesis, in the heterogeneous Fischer—Tropsch process, more reactive alkyl group migrates over the surface until it meets an adsorbed methylene group — CH_2— and binds to it. It was also found[67] that chemisorption is accompanied by restructuring of the surface layer due to the migration of surface atoms from one layer to another. This is especially pronounced in the case of strongly bound adsorbed species (C, ≡CH, $\equiv CCH_3$). Surface restructuring is usually fast on the bond vibration time scale ($\sim 10^{-12}$ s); therefore, under steady-state conditions, the surface can be regarded as formed. However, there are examples[67] in which the time of surface rearrangement is close to the characteristic time of the catalytic reaction. In these cases, these steps and the diffusion of surface metal atoms should be regarded as steps of the catalytic process.[68] In the simulation of the Fischer—

Tropsch synthesis in this paper, we do not consider these steps.

1.2. Nature of the active sites and the ways of substrate binding

To elucidate the mechanism of catalysis and to derive the equation for the rate of each step, it is rather important to understand the nature and the structure of the active site. In most cases, the surface reactions are described using the mass action law in the form of Langmuir—Temkin equation.[69] The use of the mass action law is complicated by the following circumstances.

1. The surface consists of structurally and energetically different fragments (biographical nonuformity).
2. The interactions of adsorbed species with one another influence the surface properties (induced nonuformity), which, in turn, changes their reactivity.
3. Upon adsorption, molecules can occupy several sites on the catalyst surface (multi-center adsorption).
4. Dissociation of molecules upon adsorption results in simultaneous existence of one-center and multi-center adsorbed species.
5. In some cases, excited species are formed in the course of adsorption and surface reactions.[70,71]

The problem of application of the mass action law for the surface (the law of acting surfaces[72]) in the case of multi-center localized adsorption has not been strictly solved even for homogeneous surfaces. The problem is that only for low coverages ($\theta_i \to 0$), is the portion of the surface occupied by a multi-center (m-site) adsorbed species θ_{im} proportional to the portion of free (one-site) centers raised to power m ($\theta_{im} \propto \theta_{01}{}^m$). For medium coverage, this dependence does not hold. As early as 1938, analysis of the two-center adsorption of the CO molecule carried out in terms of a statistic approach[72] showed that, with allowance for two- and one-site centers, the adsorption isotherm differs substantially from the isotherm of "simple" Langmuirian adsorption. Later, the use of the law of acting surfaces was analyzed in detail and analytical expressions for different cases, including multi-center adsorption of molecules of different sort, were derived.[69] Computer experiments simulating the adsorption, in particular, by the Monte Carlo method are still actively carried out.[72—84] The range of arguments supporting the multi-center binding of most species (even such as H and CH_3) extends and the number of models used to describe multi-center localized adsorption increases.[69,80] However, in the practice of kinetic investigations and in the works dealing with the Fischer—Tropsch synthesis, simple Langmuirian models are mostly used.[3,20,22] Examples of using more complex models are scarce.[81—83] In particular, they refer to interpretation of the differences between the activities of the faces of cobalt single crystals in CO dissociation.[83]

1.3. Molecularity of elementary steps

The molecularity of surface reactions is the basis for the use of the mass action law. As a rule, it is more difficult to attain a geometric configuration of the reacting species favorable for the transition state on the surface than in the bulk. Therefore, if one assumes that the molecularity of steps in the bulk should not be greater than two, this rule should also apply to surface reactions.

Evidently, steps (5)—(7) do not satisfy the molecularity requirement. In addition, when including a step of type (7) in kinetic models, researchers ignore the fact that this requires the presence of *three adjacent* M atoms, *i.e.*, the M_3 ensemble. The concentration of these ensembles for medium and high coverages is not proportional to $[M]^3$ (see Section 1.2). The step[85]

$$*H + **CO + 2* \leftrightarrow **COH + 3*, \qquad (14)$$

(the asterisks mark the active sites) also appears to be poorly justified from the standpoint of molecularity, because in the form it has been used in kinetic simulation, this step is tetramolecular in both directions.

1.4. Other selection rules for elementary steps on the surface

In our opinion, together with the rule restricting the molecularity of step and the Woodward—Hoffman rule, the constraints related to the numbers of cleaved and formed bonds and the topology of bond redistribution are also applicable to the selection of steps on the surface. For example, the topology of step (3) is bicyclic; therefore, this step is unlikely to take place as a concerted process. The problem of the possibility of concerted and synchronous formation/cleavage of multiple bonds deserves special analysis.

$$l{=}C{=}O + l \to l{=}C + l{=}O$$

Topology identifier

The use of the rules of orbital symmetry conservation during a concerted (elementary) reaction on the surface is rather difficult because this requires analysis of the orbital symmetry for an intricate intermediate comprising surface metal atoms. Evidently, due to the low symmetry of the surface species, the application of these rules to the surface would not be very strict. As a first approximation, one can only note that reaction (4) with hydrogenolysis of the C—O σ-bond without direct participation of active site l in bond redistribution is, most likely, forbidden for symmetry reasons.

1.5. Constraints on the form of transforms for the formal generation of elementary steps

Analysis of the experimental and theoretical studies devoted to the nature of elementary steps on the surface and the above-described selection rules and the requirements of formal algorithms allows one to formulate the constraints that will be used in this work for the computer generation of steps:

(1) we consider mainly reactions between chemisorbed species;

(2) consideration does not include steps involving free radicals; the steps of transfer of adsorbed species from one site to another (in order to reduce the number of variants resulting from the use of combinatorial algorithms); multi-center bonds; and reactions whose transition states do not involve the active site (metal atom), for example

$$\mathrm{MCH_2OH + H_2 \rightarrow MCH_3 + H_2O}; \qquad (15)$$

(3) each metal atom of the surface (active site M) is considered as formally monovalent, *i.e.*, it is assumed to form only one bond with the adsorbed species;

(4) the transition state of an elementary step involves no more than two metal atoms (this constraint is related to the large number of steps generated by the computer program);

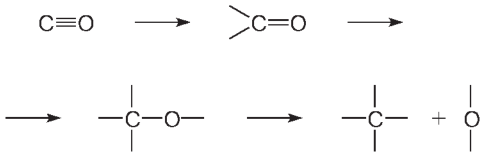
(5) when two active sites participate in a step, the M—M doublet and bond rupture in this doublet are formally considered, for example,

$$\begin{matrix}\mathrm{H{-}H}\\ \mathrm{M{-}M}\end{matrix} \longrightarrow \begin{matrix}\mathrm{H} & \mathrm{H}\\ | & |\\ \mathrm{M} & \mathrm{M}\end{matrix}. \qquad (16)$$

This record is needed for normal operation of combinatorial algorithms and, in addition, it emphasizes that the step involves two neighboring metal atoms (sites).

2. Substantiation of the nature of intermediates, probable elementary steps, and transforms

The transforms considered below were chosen in such a way as to describe the required processes of bond cleavage and formation. The synthesis of hydrocarbons and oxygen-containing compounds from CO and H_2 implies cleavage of the bond in the CO molecule and formation of C—C, C—H, and O—H bonds.



$$\mathrm{C{\equiv}O} \longrightarrow \rangle\mathrm{C{=}O} \longrightarrow -\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{O}- \longrightarrow -\overset{|}{\underset{|}{\mathrm{C}}}- + \overset{|}{\underset{|}{\mathrm{O}}} \qquad (17)$$

The formation of hydrocarbons and oxygen-containing compounds is also accompanied by dissociation of the C—H and O—H bonds. It is clear that these processes should take place on the metal (and metal oxide) surface and involve intermediates containing M—H, M—C, and M—O bonds. Now we consider various types of intermediates.

2.1. Nature of the intermediates in the reactions of CO with H_2 on the surface of metal catalysts

To choose the notation for the designation of intermediates that would be convenient for the computer generation of the reaction network, we shall consider the possible types of adsorbed molecules and species and the composition and structure of intermediates that can be involved in the Fischer—Tropsch synthesis. The number and structure are given for each adsorbed species (either in the text or in Figs. 1—4). The way of presentation of adsorbed species does not reflect the preferred type of coordination but it is the form convenient for the ChemNet computer program.

Hydrogen (M—H, I_1). Chemisorption of H_2 on the surface of a transition metal yields various intermediates.[86] Dissociative adsorption is characterized by low activation energies.

Metal	Crystal plane	E_a /kcal mol^{-1}	Ref.
Ru	(0001)	0	24
Fe	(110)	0	24, 87
Pt	(332)	0	88
Pt	(111)	0.5—1.5	88
Cu	(111)	5—10	89
Cu	(100)	11.5	90
Cu	(110)	14.3	91

On some transition metal surfaces, the H_2 molecule is first trapped to give an adsorbed molecular complex of H_2. Dissociation of the H_2 molecule takes place either directly or *via* the formation of a molecular complex. Depending on the temperature and the local surface concentrations of adsorbed species, hydrogen atoms are able to reconstruct the metal surface in different ways.[92,93] On a reconstructed surface, hydrogen can be coordinated by one, two, three (for example, Ni(100)-(2×1) [92] and

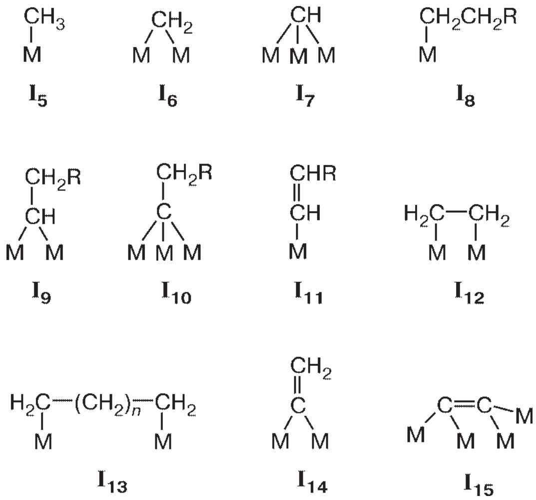


Fig. 1. Intermediates with hydrocarbon fragments.

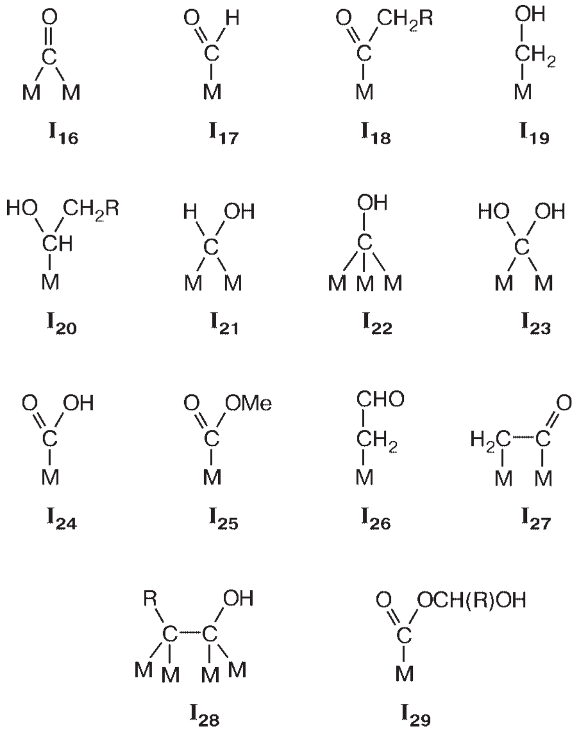


Fig. 2. Intermediates with oxygen-containing fragments with the M—C bonds.

Ni(111)[92]), or four (for example, Ni(100)-(1×2)[92]) metal centers of the lattice.

Some of the hydrogen atoms are dissolved in the bulk of the solid phase.[94—100] In the thermal desorption spectra (TDS), the peaks of the physically adsorbed hydrogen normally differ from those of chemisorbed forms.[86] The H atoms that diffuse from the subsurface layers can be much more reactive than the hydrogn adsorbed on the surface. Ethylene hydrogenation on Ni(111) is accomplished by hydrogen atoms that diffuse from the lattice, while the terminal species of type $\mathbf{I_1}$ are nonreactive, which is confirmed by the data of high resolution electron energy loss spectroscopy (HREELS).[94] It was shown that hydrogenation of CH_3—M ($\mathbf{I_5}$) also involves the subsurface hydrogen.[101,102]

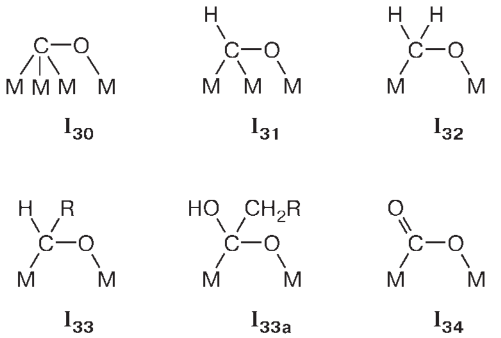


Fig. 3. C- and O-bonded bridged intermediates.

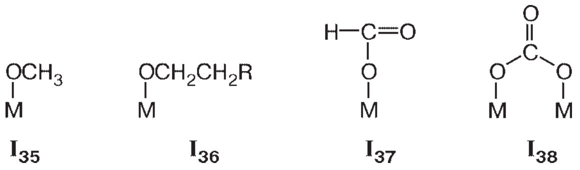


Fig. 4. Oxygen-containing intermediates with the M—O bond.

The activation energy of hydrogen diffusion in the crystal lattice is usually low. For example, this value for Pd(100) is ~1 kcal mol^{-1}.[86] An attempt was made to explain the higher activity of the subsurface hydrogen by assuming a two-step mechanism in which the first step is transfer of the H atom from the bulk of the solid to the surface and the second step is reaction between this atom and the terminal CH_3 group.[103] The intermediate form of hydrogen resembles the bridging hydrogen coordinated by three metal atoms. The "standard" interaction between a tricoordinated bridging methyl group and a tricoordinated hydrogen atom, which was suggested previously, proved to be less favorable than the reaction with the subsurface hydrogen.[103] For Pd, it was shown that the subsurface hydrogen also plays an important role in CO hydrogenation to the CHO group.[104] In this study, all types of hydrogen-containing intermediates are modeled by intermediate $\mathbf{I_1}$ to avoid an increase in the number of reactions of the same type in the reaction network.

Carbon (M_4C, I_2). The carbon atoms adsorbed on the surface (C (ads.)) are key intermediates in the carbide mechanism of the Fischer—Tropsch synthesis.[105—107] The chemisorbed carbon atoms actively reacting with hydrogen were detected by surface Auger spectroscopy (Fe, Ni, Ru[108—111]), IR spectroscopy combined with the transient response kinetic analysis (Ru[112]), HREELS (Ru(1010)[113]), and NMR spectroscopy (Ru[114]). No atoms of this type were detected on the Co surface,[15] although this metal is believed to favor the dissociation of CO.

The carbon atoms in the lattice surface layer are often called surface carbide. Normally, the phases of amorphous and crystalline carbon on the surface are not considered as an adsorbed form of carbon, although under certain conditions, amorphous carbon can be hydrogenated to give hydrocarbons. It was shown[115—117] that the bulk carbon in solid iron and nickel catalysts can participate in the formation of hydrocarbons but the rate of the transformation is very slow, and the contribution of the depth C atoms to the total amount of products is relatively low. Therefore, intermediate $\mathbf{I_2}$ can be regarded as the reactive form of carbon.

Oxygen (M—O—M, I_3) and hydroxy (M—OH, I_4). The existence of surface oxides formed during CO hydrogenation was established for Fe[118] and Co.[119] Presumably,[120] they also occur in Ni. Oxides play a special role in the synthesis of hydrocarbons on a cobalt catalyst.[121] The possible sources of hydroxy groups on the surface are species $\mathbf{I_3}$ or H_2O molecules. Surface hydroxy groups are not formed apparently upon water dissociation. This reaction is endothermic (>20 kcal mol^{-1}).[31] The formation of hydroxy groups is assumed, in particular, in the reaction of water with adsorbed carbon on supported Ru and Co catalysts.[122] According to IR spectroscopy,[120,123] surface hydroxy can be detected in the oxidation of hydrogen on virtually all Group VIII metals of the Periodic System. The hydroxy groups were identified on the following surfaces: Ag(110),[124,125] Cu(110),[126] Cu(111),[127] Pt(111),[128—131] Pt(100),[132] Pd black,[133] Ni(110),[134,135] Rh(100),[136] Fe(110),[137] and Ru(0001).[138] Numerous structures with bridging μ_2-, μ_3-OH groups and μ_2-, μ_3-, μ_4-O groups were detected in transition metal complexes with hydroxo and oxo ligands.[139] The presence of this type of structures on the surface also cannot be ruled out. Indeed, density functional theory[140] (DFT) calculations show that coordination by three metal atoms is the most stable state of the O and OH species on most (111) surfaces of Group VIII and IB metals.

Water-gas shift reaction is a component of the Fischer—Tropsch mechanism; intermediates $\mathbf{I_3}$ and $\mathbf{I_4}$ appear in many mechanisms proposed for this reaction.[141,142] However, in the water-gas shift reaction, these intermediates might be attached to the support rather than to the metal.[143]

Adsorbed water molecules are also formed under conditions of the Fischer—Tropsch synthesis. When generating the reaction networks, we shall assume (to reduce the combinatorial search) that water molecules participate in all reactions from the gas phase.

Methyl ($\mathbf{I_5}$) and alkyls ($\mathbf{I_8}$) are considered as immediate precursors of methane ($\mathbf{I_5}$) and higher hydrocarbons[144—146] ($\mathbf{I_8}$) and are regarded to be the most well-known surface compounds.[13,14] Alkyls were found on the surfaces of Ag(111), Au(111), Au(100), Cu(111), Cu(110), Cu(100), Cu(poly), Fe(100), Mo(110), Ni(100), Ni(111), Pd(111), Pd(100), Pt(111), Pt/SiO_2, Rh(111), Ru(0001), polycrystalline tungsten,[14] and cobalt films.[147] Alkyls of almost all transition metals are known in coordination chemistry.[148,149]

Methylene ($\mathbf{I_6}$) is yet another important intermediate involved in the carbide mechanism; it is the main "building block" for the chains of higher hydrocarbons. The possibility of formation of Fischer—Tropsch products involving methylene produced by decomposition of diazomethane, dihalogen-substituted alkanes, or ketene on the catalyst surface was proved using labeled carbon atoms.[8,14,150,151] The formation of methylene during CO hydrogenation was established for Fe (Raman and IR spectroscopy)[15] and Ni surfaces (secondary ion mass spectrometry).[152] Methylene can be prepared by decomposition of $^{13}CH_3NO_2$ or $^{13}CH_2N_2$ on various surfaces.[8] Methylene has been generated on the surfaces of rhodium, ruthenium, and cobalt Fischer—Tropsch catalysts. In the case of Co/SiO_2 and Ru/SiO_2 catalysts, the formation of isotopically mixed alkenes and alkanes was observed. On Rh/SiO_2 and Rh/Ce/SiO_2, either only CO or only labeled methylene served as the source of carbon. The amount of mixed compounds was very low. Oxygenates were found to contain little labeled carbon.

Data on the formation of methylene on Pt(111), Fe(110), Pd(100), Pd(100), Ni(100), Cu(100), Cu(110), and Mo(110) have been reported.[14]

Alkylidene ($\mathbf{I_9}$). Alkylidene species have been less studied than methylene. They are mainly known in transition metal complexes with small numbers of d-electrons.[153] Alkylidene groups are known in iron complexes.[154] Surface ethylidene has also been obtained by decomposition of diiodoethane on the Pt surface.[13] Data on the existence of $=CHCH_3$ on Pt(111) and Cu(100) have been reported.[14] The possibility of existence of these intermediates in the mechanism of the Fischer—Tropsch synthesis was noted only in one study.[155]

Methylidyne ($\mathbf{I_7}$). Participation of methylidyne ($\mathbf{I_7}$) in the formation of C—C bonds has been reported.[156,157] This species was detected on the Fe,[15,117,158] Ni,[159] Ru(0001), Ru(1120),[160,161] Pd(100),[162] Pd(111),[163] Pt(111),[164] and Ni(111) [165] surfaces.

Alkylidyne ($\mathbf{I_{10}}$). An alkylidyne ligand was detected in iron and cobalt complexes.[166,167] It is well known that ethylidyne is formed from ethylene and acetylene (in particular, in the presence of CO) on the Pt(111),[168—173] Pt(100),[174] Rh(111),[175] Rh(100),[176] Ru(0001),[177—179] Pd(111),[163,180] and Ir(111) [181] surfaces and on some supported catalysts (Ni,[182] Pd,[183,184] Pt,[184,185] Ru,[184] and Rh [184]). Ethylidyne has also been observed on V(110)/C, Mo(110)/C, Ni(111), and Pt(110) surfaces and on an oxygen-reconstructed Pt(100) surface. The vibrational spectra and the results of experiments with isotope labeling demonstrated that the ethylidyne can be formed during CO hydrogenation in the presence of Rh/Al_2O_3.[186] On the basis of a study of the model reaction with the ruthenium cluster, the only mechanism of the Fischer—Tropsch synthesis with participation of higher alkylidyne species was proposed.[187]

Polymethylenes $\mathbf{M{-}(CH_2)_2{-}M}$ ($\mathbf{I_{12}}$) and $\mathbf{M{-}(CH_2)_{\mathit{n}}{-}M}$ ($\mathbf{I_{13}}$). The presence of di-σ-bonded ethylene ($\mathbf{I_{12}}$) was established by FT IR spectroscopy on Pt/Al_2O_3,[188] by photoemission spectroscopy on Rh(100),[189] and by adsorption calorimetry on Pt(110) and Pd(100).[190] Data on the vibration frequencies of bridging ethylene for Pt(111),[191,192] Ru(001),[193] Mo(110),[194] Fe(110), Fe(111), Ni(110), Ni(111), Ni(100), Ru(001), Pd(100),[188] and Fe(100) [195] were published. Ethylene is adsorbed on a hydrogen-coated surface mainly in the form of π-complexes.[189,195] Metallacyclopropane intermediates have been found on the surface of Ni/SiO_2.[196] An organometallic ring with four carbon atoms from cyclobutane has been found on the surface of Ru(0001).[197] According to the carbide mechanism of the Fischer—Tropsch synthesis,[106] compounds of the polymethylene series are formed upon condensation of methylene groups on the catalyst surface. The hypothesis of polycondensation has now been entirely rejected; however, intermediates $\mathbf{I_{12}}$ and $\mathbf{I_{13}}$ might be formed *via* other pathways.

Organometallic rings are analogs of $\mathbf{I_{12}}$ and $\mathbf{I_{13}}$ in organometallic chemistry. Dimetallacyclobutane has been detected in Os and Fe tetracarbonyl clusters.[182] Bridged σ-organometallic ethylene compounds are also known.

Vinyl ($\mathbf{I_{11}}$). The existence of surface vinyl ($\mathbf{I_{11}}$) on various metals was established rather reliably;[178] it can be prepared by direct decomposition of vinyl halides (Pt).[81] However, participation of this species in the Fischer—Tropsch synthesis has not been confirmed so far. Nevertheless, it is considered to be a key intermediate in a mechanism of the Fischer—Tropsch synthesis[33] that was proposed relying on the fact that inclusions of labeled vinyl were found in the synthesis products obtained on Ru and Rh catalysts. Surface vinyl has been proposed as an intermediate for ethylene decomposition on Ni(100), Pt(100), Pd(100), and Ag(111), acetylene hydrogenation on Ni[5(111)-(110)] and Ru(0001), and decomposition of vinyl halides on Ag(111), Cu(100), and Pt(111).[14] The formation of vinyl on the Pd(111) [198] and Pt(111) [172] surfaces upon decomposition of vinyl iodide or photodecomposition of 1,1,2-trichloroethane on Pt(111) has also been reported.[199] The vinyl intermediate has been found to participate in the ethylene conversion into ethylidyne on Rh(111) [200] and Pt(111).[201] Vinyl can exist on the surface in two configurations, namely, σ-vinyl (see Fig. 1) and η^2-vinyl.

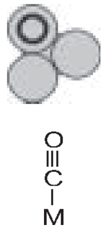
Vinylidene ($\mathbf{I_{14}}$). Quite a few vinylidene complexes of transition metals, in particular, Ru and Os complexes, are known in coordination chemistry.[202,203] Vinylidene ($\mathbf{I_{14}}$) results from decomposition of olefins and other hydrocarbons on the Ru(0001) surface partially covered by oxygen,[204] on the Pt(100)-(1×1),[205] Rh(100),[176] Ni(100), and Ru(0001) surfaces, and also on the partially CO-covered [206,207] Pd(111) surface.[208] Vinylidene can form from acetylene on Pt(211) [209] and Pd(111) [198,210] surfaces. Apparently, vinylidene is formed in the acetylene decomposition to carbon and hydrogen on the W(211) surface[211] and in the acetylene trimerization on Pd(111).[212] Vinylidene group can result from the reaction between the surface carbon and methylene on Fe(110).[213] Adsorbed vinyl can also be a source of vinylidene, which was observed on Pt(111).[201]

In the mechanisms of the Fischer—Tropsch synthesis, this type of intermediate was proposed only once as a precursor of the metallacyclopropylidene derivative that gives rise to linear and branched hydrocarbons.[201]

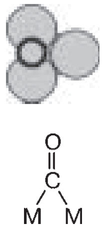
Dicarbon ($\mathbf{I_{15}}$). According to calculations,[214] the C_2 dimer with a double bond coordinated to four metal atoms ($\mathbf{I_{15}}$) is an energetically more favorable form of surface carbon than separate C atoms. This dimer can serve as a precursor of ethylene and other C_2 products. The C_2 molecules are formed on the Ag(110) surface,[215,216] and C_2 fragments with various type of bonding exist in ternary carbides of transition metals $M_xM^*_yC_z$, where M = Ln, Sc, Y, Th;[217] M* = Fe, Co, Cr. Formally, these groups are the products of ethylene deprotonation, *i.e.*, C_2^{4-} anions existing as μ_2- and μ_3-bridging groups with a C—C bond length (l_{C-C}) equal to 1.30—1.47 Å (Ln_2FeC_4, Sc_3CoC_4, Ln_3FeC_4). Some carbides of this class ($ScCrC_2$) contain C_2 groups with l_{C-C} = 1.6 Å; hence, they can be regarded as completely deprotonated ethane bound to six metal atoms. Organometallic complexes containing bridging C_2 groups connected to two[218] or four[219] metal atoms are also known.

Now we consider the group of oxygen-containing adsorbed species containing an M—C bond (or bonds) (see Fig. 2).

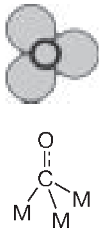
Carbon monoxide ($\mathbf{I_{16}}$). Diverse forms of adsorbed CO molecule bound to one, two, three, or more metal atoms have been detected on the surface (see Ref. 220 and references therein).



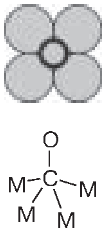
Terminal group
(on any surface)



Bridging group
(on any surface)

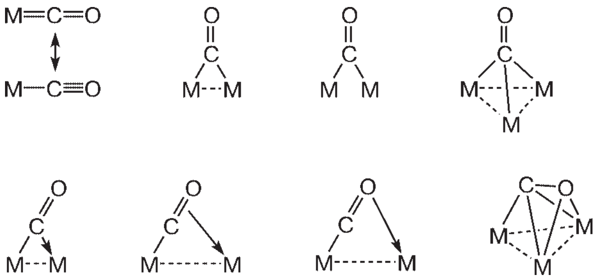


Bridging group
(on the (111) surface)



Bridging group
(on the (100) surface)

Adsorption of CO has been studied on virtually all metal surfaces both experimentally and theoretically. At low coverages, the configuration with the CO axis perpendicular to the surface is the most stable.[221] As the surface is covered, some CO molecules can become somewhat bent due to repulsion forces. Even more diverse of CO bonding are considered in organometallic chemistry:[222]



It cannot be ruled out that these types of bonding also arise on catalyst surfaces. In computer generation, we used only the bridging form **I$_{16}$**.

Formyl (**I$_{17}$**) is considered to be an intermediate of chain initiation in classical insertion mechanisms.[223,224] The formyl ligand has been found in many transition metal complexes[11] (in particular, a number of Fe complexes are known [4,225,226]) in both the η^1 and η^2 forms (**I$_{17}$** and **I$_{31}$**, respectively, see Fig. 3). Formyls with η^1 and η^2 types of bonding were detected in CO hydrogenation on Ru(0001) by the HREELS method.[227,228] The intermediate identified in CO hydrogenation on Ru—Co/SiO$_2$, Ru/SiO$_2$, and Co/SiO$_2$ as the methane and methanol precursor might be the adsorbed formyl species.[229] The generation of formyl was observed in methanol decomposition on the Pd(110) surface,[230] in the formation of methanol from synthesis gas on a supported rhodium catalyst,[231] and also in the reaction of CO and H$_2$ with the Pd/A$_2$O$_3$ surface.[104] The problem of intermolecular synthesis of the formyl group (**I$_1$** + **I$_{16}$**) has not been developed theoretically.

Acyl (**I$_{18}$**) is considered in the mechanisms of the Fischer—Tropsch synthesis to result from CO insertion into the metal—alkyl bond and regarded as a possible precursor of aldehydes and carboxylic acids.[10] Compound **I$_{18}$** is a typical intermediate of olefin hydroformylation on Co and Rh metal complex catalysts, detected by the isotope response method combined with *in situ* IR spectroscopy.[232—234] Acyl intermediates have been observed by spectroscopy on the Rh(111),[235,236] Ru(0001),[237,238] Pt,[239] and Pd(111) [240] surfaces. It was suggested on the basis of studies by *in situ* IR spectroscopy, mass spectrometry, and X-ray photoelectron spectroscopy that acyl is formed in CO hydrogenation with the Ru/SiO$_2$, Co/SiO$_2$, and Ru—Co/SiO$_2$ [229] catalysts.

Hydroxymethyl (**I$_{19}$**). Hydroxymethyl is often considered in Fischer—Tropsch mechanisms; it is rather well known in organometallic chemistry, for example, in the chemistry of iron[241,242] and ruthenium[242] compounds. This species has not been identified and characterized on the surface of metallic catalysts or supports.

1-Hydroxyalkyl (**I$_{20}$**). The formation of the hydroxyalkyl intermediate has been suggested in CO insertion mechanisms.[224,243] This type of ligand is known for the Mn complex;[244] it readily undergoes β-elimination to give an aldehyde. This group has not been identified on the surface of metal catalysts or supports.

Hydroxymethylene (**I$_{21}$**). The mechanisms of the Fischer—Tropsch synthesis proposed in a number of studies [245,246] were underlain by the hypothesis of condensation of hydroxymethylene (**I$_{21}$**). This ligand was obtained from CO and H$_2$ and identified in a rhenium complex.[247] The CH$_2$O species have been repeatedly detected on the surface of catalysts of the Fischer—Tropsch synthesis,[248,249] but most researchers regard this intermediate as adsorbed formaldehyde, which is readily formed at low temperatures on the surfaces of metals and oxide supports (see below).

Hydroxymethylidyne (**I$_{22}$**) **and dihydroxymethylene** (**I$_{23}$**). The hypotheses[223,250] of the formation of compounds **I$_{22}$** and **I$_{23}$** on the surface have not yet received experimental support; however, attempts at theoretical substantiation have been made.[31]

Hydroxycarbonyl (**I$_{24}$**). Hydroxycarbonyl ligands have been identified for a number of Group VIII metal complexes by IR and NMR spectroscopy and X-ray diffraction analysis,[251,252] and also on the Ni surface.[253] In developing the Fischer—Tropsch mechanisms, the COOH was considered as a probable precursor of carboxylic acids.[153] Based on theoretical calculations, it was concluded that adsorbed hydroxycarbonyl is an intermediate in the decomposition of methanol to CO$_2$.[31]

Methoxycarbonyl (**I$_{25}$**) is well known in catalysis by metal complexes,[254,255] but its participation in the Fischer—Tropsch synthesis has been proposed only hypothetically.[256] We were unable to find any publications on spectroscopic detection of alkoxycarbonyl species on the surface.

Formylmethyl (**I$_{26}$**). Derivatives of higher aldehydes have been proposed as intermediates in the Fischer—Tropsch synthesis on the basis of a model reaction involving a Fe cluster and mechanistic studies of the Fischer—Tropsch synthesis on the Co/SiO$_2$ catalyst by isotope labeling.[257] We found no spectroscopic data on this type of adsorbed species.

Ketene (**I$_{27}$**) **and adsorbed enol** (**I$_{28}$**). π-Complexes of ketenes have been studied in organometallic chemistry.[258—260] In investigations of surface reactions in heterogeneous catalysis, ketene, like diazomethane, is treated as a methylene precursor. Dissociation of ketene on the surface depends on temperature and on the contact time. The probability of dissociation increases with an increase in temperature. Adsorbed ketene molecules were observed on the following surfaces: Fe(110),[213] Ag(111),[261] Pt(111),[262,263] and Ru(0001).[237,264] In the last-mentioned study, three adsorption patterns were observed, namely, η^2-C=C, η^2-C=O, and η^3-C=C=O. Ketene decomposes and is hydrogenated by decomposition products at relatively low temperatures. At 200—400 K on Ru(0001), ketene decomposes to give CO, H_2, ethylidyne, and other C_nH_x fragments (n = 1, 2). Ketene is adsorbed on Pt(111) at 100 K to give di-σ-(C,C)-adsorbed ketene. At temperatures above 300 K, ketene decomposes with evolution of CO and methane to the gas phase. When Ru(0001) is modified by copper, ketene migrates to copper atoms to give a π-complex.[265] Participation of ketene (**I$_{27}$**) and enol (**I$_{28}$**) has been considered in the number of mechanisms of the Fischer—Tropsch synthesis.[5,245]

Hydroxyacyl (I$_{29}$). The hypothesis of the formation of the hydroxyacyl intermediate in the Fischer—Tropsch synthesis proposed previously[4] was confirmed in the reaction of CO insertion in the Mn hydroxyalkyl complex.[266]

η^2-(C,O)-Adsorbed species. Figure 3 shows η^2-coordinated form of CO (**I$_{30}$**) and the formyl group (**I$_{31}$**) and other adsorbed species attached to the surface *via* C and O atoms. The intermediate **I$_{30}$** should be regarded as hypothetical because this species has not been detected in the studies of CO adsorption. Some reasons for the existence of this species were advanced relying on the data obtained by chemical methyl iodide traps.[267] The alkylation of μ_4-η^2-CO with methyl iodide was considered in five systems: Ni/SiO_2, Ni/Al_2O_3, Co, Co/Al_2O_3, and Pd/SiO_2. Acetone was found to form only on the Pd catalyst and methyl *tert*-butyl ether is formed on other catalysts.

We consider μ_4-η^2-CO because this is a convenient species for working with software for generation of hypothetical mechanisms. In addition, for bond cleavage in an adsorbed CO molecule, CO normal to the surface must become inclined. Inclination of the CO axis toward the surface does not always result in the formation of an intermediate in which oxygen would be bound to the metal atom but this possibility cannot be ruled out. Formyl was found to exist in the η^2-configuration **I$_{31}$** (see above).

Formaldehyde (I$_{32}$) and other aldehydes (I$_{33}$). The formation of formaldehyde from CO and H_2 in the Fischer—Tropsch synthesis is thermodynamically forbidden. Nevertheless, the existence of μ-η^2-bonded formaldehyde (**I$_{32}$**) on a metal surface is quite probable. The intermediate **I$_{32}$** is involved in the known insertion mechanism.[223] In another publication[224] dealing with the Fischer—Tropsch mechanisms that include CO insertion, preference is given to η^2-bonded formaldehyde (π-complex type). Iron complexes with η^2-formaldehyde ligand[268] and zirconium complexes with μ-η^2-ligand[269] have been identified. Adsorbed formaldehyde, which is an intermediate in methanol decomposition giving CO and H_2, has also been found on the Ni surface by X-ray photoelectron spectroscopy.[15] Coordination of the carbonyl groups of other aldehydes on two centers (**I$_{33}$**) has been described.[223] Unusual intermediate **I$_{33a}$** has been proposed (see Fig. 3).[223] Formaldehyde can be produced from adsorbed methoxy radical upon β-elimination. As for most of other carbonyl compounds, η^1-binding of the CH_2O molecule through the O atom is the predominant pattern on Group IB metals, and η^2-binding is preferred on Group VIII metals.[270]

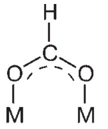
Carbon dioxide (I$_{34}$). A type of binding of the CO_2 molecule similar to formaldehyde has been found on the surface of rhodium[271] using LEED. The formation of chemisorbed CO_2 as **I$_{34}$** or a similar π-form has also been found for the Fe(111) surface[272,273] and also for the Rh(111) (on steps) and Rh(100) (on terraces) surfaces.[274] Other forms of CO_2 adsorption have also been considered theoretically;[273] but they are all represented by **I$_{34}$** in the computer generation. This intermediate is expected to participate in the mechanisms of CO_2 hydrogenation and CO disproportionation.

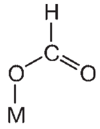
Below we consider intermediates with M—O bonds (see Fig. 4).

Methoxy and alkoxy (I$_{35}$ and I$_{36}$). The formation of methoxy (**I$_{35}$**) is typical of methanol synthesis and decomposition on copper—zinc catalysts. In the case of Pd/Al_2O_3,[275] Pt/Al_2O_3,[276] and Rh/SiO_2,[277] methoxy stabilized on the support atoms were detected. These groups are able to migrate over the active metal surface and to be either dehydrogenated yielding formaldehyde or recombine with other adsorbed species. The methoxy species has also been detected by kinetic trapping for Ni/Al_2O_3, which is a typical methanation catalyst.[278] The adsorbed methoxy species was obtained and characterized on the surfaces of Pt(110),[279] Pt(111),[280] Cu(110),[281] Mo(110),[282] Co/Mo(110),[283] Rh(111) and Rh(111)-(2×2)O,[284,285] Rh(100),[286] Ni(111),[287,288] Ni(110),[289,290] Pd(111),[240,291] Pd(100),[292] Fe(100),[293,294] and Ru(0001).[295] In the majority of studies, low-temperature adsorption of methanol serves as a source of methoxy.

Quite a few alkoxide compounds (**I$_{36}$**) of various metals are known, in particular, those catalyzing the Fischer—Tropsch synthesis.[296] The formation of adsorbed CH_3CH_2O species in syntheses from CO and H_2 has been detected on the Rh surface.[297] In the literature on the Fischer—Tropsch mechanisms, this intermediate has been considered as a hypothetical precursor of alcohols.[10,223] Ethanol forms alkoxy on Fe(100).[294]

Formate (I$_{37}$) is a frequent surface compound, which has been studied extensively in relation to the methanol synthesis and water-gas shift reaction. Formate has been characterized by a variety of methods; the adsorbed species exist as two configurations, **A** and **B**.[298]


A


B

The former is more stable but we used the latter because multicenter bonds in intermediates have not been considered in this variant of reaction network generation (see Section 1.5).

The questions of which phase is active and what is the role of the support are debated in the literature on methanol synthesis. Some supports influence appreciably the course of the reaction. For example, in a study of methanol synthesis from CO and H_2 catalyzed by ZrO_2/SiO_2 and $Cu/ZrO_2/SiO_2$, ZrO_2 was found[299] to play an important role in the formate formation. In the hydrogenation of CO_2 on Cu/ZrO_2 and $Cu/ZrO_2/SiO_2$, the formate is also formed with participation of zirconium dioxide.[300] In the case of Cu/ZnO and $Cu/ZnO/Al_2O_3$, formate arises, apparently, both on the surface of copper, which appears to be an active phase and on the support surface.[301,302] In a study of the reaction of CO_2 and H_2 with CuO supported on various materials (SiO_2, Al_2O_3, TiO_2, ZrO_2, and MgO), formate was detected in all cases but in some cases, the HCOO group was attached to the support.[303]

The surface formate formed on Cu(111), Cu(110), and Cu(100) single crystal planes has been studied both theoretically and experimentally (see Ref. 304 and references therein). Formate is also produced in the reaction of HCOOH with Ni(111),[305] Ni(110),[306] Ru(0001),[307,308] Pt(111),[309] K/Pd(100),[310] and Rh(111) [311] surfaces. Methanol reacts with oxygen on the Pt(111) surface being oxidized to formate.[312] Formate is among the products of the Fischer—Tropsch reaction between CO and H_2 catalyzed by K/Ru(0001).[313] This species was also identified on the Ag(110) surface.[314]

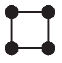
Formate was detected in a study of the Fischer—Tropsch synthesis on the surface of ruthenium catalysts.[112] In this case, potassium formate found on the potassium promoter could be converted into methane or methanol. According to the data of IR spectroscopy, formate also arises on rhodium catalysts.[315] A hypothetical mechanism of the synthesis of organic acids involves the formate formation.[256]

Carbonate (I_{38}). The possibility of formation of carbonate species (I_{38}) on the surface of CO hydrogenation catalysts has been studied. These species were identified in a study of methanol synthesis catalyzed by copper—zinc systems (*in situ* IR spectroscopy[316]) and Ni-catalyzed CO hydrogenation.[317] These intermediates are not usually included in the mechanisms of the Fischer—Tropsch formation of hydrocarbons; nevertheless, their role may prove significant in the mechanisms that do not imply dissociative activation of CO. Carbonate was found to arise in the reactions of CO_2 with the Ag(110) surface containing pre-adsorbed oxygen,[318,319] CO_2 with KOH/Ag(111),[320] a H_2+CO+O_2 mixture with Gd(0001),[321] CO_2 with Cs/Fe(110) and K/Fe(110),[322] methanol with $Pt/CeO_2—Al_2O_3$ and $Pt/CeO_2—SiO_2$,[323] a H_2+CO mixture with polycrystalline Rh [324] and K/Ru(0001),[313] CO_2 with K/Pt(111) containing pre-adsorbed oxygen,[325] CO_2 with Na/Pd(111),[326] and CO_2 with K/Pd(100).[327]

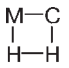
Methylenedioxy (M—O—CH_2—O—M, I_{39}). According to NMR spectroscopy,[328] intermediate I_{39} arises in the reaction of paraformaldehyde with the ZnO/Al_2O_3 surface. This compound was also identified by the HREELS technique[329] on the Ag(110) surface during oxidation of formaldehyde and by temperature-programmed desorption and isotope labeling.[330] Analysis of vibrational spectra showed[331] that the methylenedioxy is also formed in the oxidation of acetone on Ag(111). According to electron microscopy, this group is also produced on the Cu(110) surface upon oxidation of methanol.[332,333] Adsorbed methylenedioxy on the Cu(111) surface has been studied by density functional theory.[334]

2.2. Elementary steps and transforms in the Fischer—Tropsch mechanisms

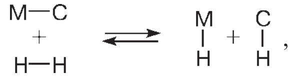
To select the transforms, we shall first consider the main types of elementary steps and topology identifiers determining them (see Section 1). Analysis shows that most elementary steps in metal-complex catalysis and heterogeneous catalysis by metals involve simultaneous (concerted) cleavage and formation of two pairs of two-electron bonds (including π-bonds). These steps are described by four-membered cyclic topology identifier G_7. Other types of topology identifiers are also possible but more rarely encountered. In this study, we consider them in less detail.


G_7

If a combination of four elements (C, H, O, and metal M) involved in elementary steps of the Fischer—Tropsch synthesis are arranged at the vertices of graph G_7, a *labeled topology identifier* is formed. This name is derived from the notion of the *labeled graph*, which implies a graph with labeled vertices. Subsequently, in this paper, we shall use the term *topology identifier* and omit the word "labeled." Each topology identifier can be matched by *generalized transforms*. For example, topology identifier **3** (Fig. 5) is matched by the following generalized transform:



3



$$\begin{array}{c}M{-}C\\+\\H{-}H\end{array} \rightleftarrows \begin{array}{c}M\\|\\H\end{array} + \begin{array}{c}C\\|\\H\end{array}, \tag{18}$$

which can be made more detailed by specifying the substituents at the C atom. It can also be used in the general form shown here.

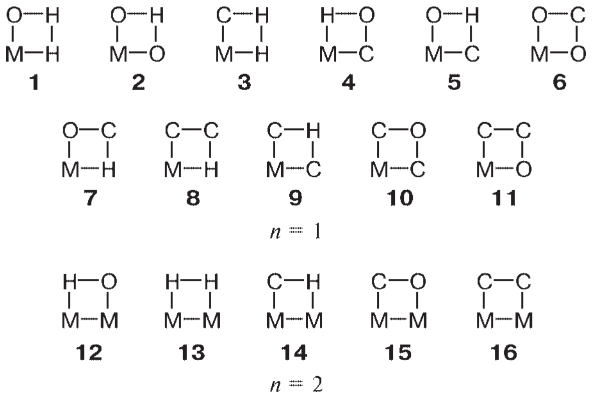


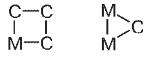
Fig. 5. Labeled topology identifiers for the steps of the Fischer—Tropsch synthesis.

To select the set of transforms plausible for constructing the reaction network for the syntheses from CO and H_2, it is expedient to list all the possible topology identifiers and thus to specify all types of elementary transforms in the most general form and then to select the transforms that have been theoretically or experimentally substantiated.

The four elements (M, C, H, and O) can be located at the vertices of graph G_7; therefore, the task is to arrange these elements at the four vertices of the cyclic graph taking into account the relevant constraints

$$M_nC_mH_xO_y \text{ for } n + m + x + y = 4;$$
$$n = 1, 2; m = 0, 1, 2; x = 0, 1, 2; y = 0, 1, 2.$$

In terms of the Polya theorem, coloring the vertices of a square into four colors can give 27 topology identifiers (12 with n = 2 and 15 with n = 1). Of the twelve graphs with n = 2, six graphs in which the M atoms are arranged diagonally should be removed because they refer to the exchange reactions of adsorbed species. In addition, three identifiers with the O—O edge are also to be rejected because no formation of peroxides takes place in the syntheses from CO and H_2. In the group of identifiers with n = 1, two graphs with a diagonal arrangement of the H atoms represent symmetrical exchange by hydrogen. These are degenerate elementary steps in which the reactants and the products are identical. The remaining 16 topology identifiers are shown in Fig. 5.



17 **18**

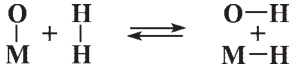
If the group of identifiers **1—16** (see Fig. 5) is supplemented by one more identifier (**17**) with n = 1 and m = 3 and by identifier **18** with a three-membered ring corresponding to the reaction

$$\overset{M}{\underset{M}{|}} + :C{=}O \longrightarrow \overset{M}{\underset{M}{>}}C{=}O, \qquad (19)$$

we obtain a set of identifiers sufficient for the description of the steps of formation of any products of the Fischer—Tropsch synthesis within the framework of the accepted constraints. We shall analyze possible elementary steps involving intermediates $\mathbf{I_1}$—$\mathbf{I_{38}}$ and transforms that follow therefrom according to the topology identifiers. Only cyclic four-membered transition states reflecting the simultaneous cleavage and formation of two pairs of two-electron bonds (including π-bonds) will be taken into account. The transition state with a three-membered ring is considered only in elementary step (19), *i.e.*, nondissociative adsorption of CO. In terms of the valence-bond method, used in this study, the addition of the CO molecule to the M—M bond (reaction (19)) can be regarded as the addition of the singlet carbene $:CH_2$ or isonitrile.

A generalized transform can be presented for each identifier. Let us consider transforms **T1—T17**.

T1:



$$\overset{O}{\underset{M}{|}} + \overset{H}{\underset{H}{|}} \rightleftharpoons \overset{O-H}{\underset{M-H}{+}}$$

The step of hydrogenolysis of the M—OZ bond can be responsible for heterolytic decomposition (activation) of the H_2 molecule catalyzed by oxides.[335]

$$H_2 + M{-}OZ \rightleftharpoons M{-}H + H{-}OZ \qquad (20)$$

In catalysis by metal complexes, the necessity of participation of basic centers (in particular, M—O bonds) in the heterolytic activation of H_2 was repeatedly proven, in particular, in relation to Pd^{II} compounds, namely, XPdOH, XPdOR, and XPdOAc.[335,336] In forward and backward reactions (20), Z is represented by M ($\mathbf{I_3}$), H ($\mathbf{I_4}$), R ($\mathbf{I_{35}}$, $\mathbf{I_{36}}$), HCO ($\mathbf{I_{37}}$), and CO_2M ($\mathbf{I_{38}}$). It was found[337] that H_2 is evolved in the back reaction on treatment of transition metal hydride complexes with H_2O and ROH.

T2:

$$\overset{O}{\underset{M}{|}} + \overset{H}{\underset{O}{|}} \rightleftharpoons \overset{O-H}{\underset{M-O}{+}}$$

The step of alcoholate hydrolysis,[336,338]

$$M{-}OR + H{-}OH \rightarrow M{-}OH + RO{-}H, \qquad (21)$$

well-known in coordination chemistry can also involve another hydroxy-containing species $\mathbf{I_4}$; this gives $\mathbf{I_3}$.

$$M{-}OR + H{-}OM \rightarrow M{-}OM + RO{-}H \qquad (22)$$

If in reactions (21) and (22), R = R´CO, these reactions become a source of carboxylic acids. The substituent R can be represented by a C atom connected to three ($\mathbf{I_{30}}$), two ($\mathbf{I_{31}}$), or one ($\mathbf{I_{32}}$, $\mathbf{I_{33}}$) metal atoms. In this case, these reactions yield intermediates containing a COH group.

T3:

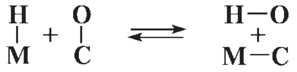
$$\begin{matrix}\mathrm{C}\\ |\\ \mathrm{M}\end{matrix} + \begin{matrix}\mathrm{H}\\ |\\ \mathrm{H}\end{matrix} \rightleftharpoons \begin{matrix}\mathrm{C{-}H}\\ +\\ \mathrm{M{-}H}\end{matrix}$$

The step of hydrogenolysis of the M—C (M—R) bond accompanied by elimination of hydrocarbons by the Eley—Rideal mechanism has been considered by various researchers who studied the Fischer—Tropsch mechanisms:[106,339,340]

$$\mathrm{M{-}R + H_2 \rightleftharpoons M{-}H + RH.} \tag{23}$$

Reactions of this type are also well-known in organometallic chemistry. Data concerning the existence of η^2-complexes with molecular hydrogen[341] and the presence of weakly adsorbed H_2 on the surface of promoted iron catalysts[5] makes it possible to state that reaction (23) involves, most likely, preliminary coordination of H_2 on the metal center. Quantum-chemical analysis[342] of the reaction of $(\eta^5\text{-}C_5H_5)_2ZrCH_3^+$ with H_2 showed that precoordinated hydrogen participates in the transition state. The reaction reverse to hydrogenolysis can take place on the catalyst surface. The reaction of alkanes with the surface species containing ZrH and TaH gives rise to surface metal alkyls[343] *via* the same transition state as the forward reaction.[342] It is evident that reaction (23) is a block of elementary steps; however, when constructing the reaction network, this block can be used as a single transform by imposing a constraint according to which M—R is not a fragment of the M—C=O type because hydrogenolysis of the M—C(O)— bond is unknown.

T4:



$$\begin{matrix}\mathrm{H}\\ |\\ \mathrm{M}\end{matrix} + \begin{matrix}\mathrm{O}\\ |\\ \mathrm{C}\end{matrix} \rightleftharpoons \begin{matrix}\mathrm{H{-}O}\\ +\\ \mathrm{M{-}C}\end{matrix}$$

The generalized transform **T4** describes the addition of metal hydride to carbonyl (forward direction)

$$\mathrm{M{-}H + XYC{=}O \rightleftharpoons M{-}(XY)C{-}OH} \tag{24}$$

and nucleophilic addition of H_2O or ROH to the metal-bonded acyl (reverse direction)

$$\mathrm{M{-}C(O)R + H_2O \rightarrow M{-}H + HO{-}C(O)R.} \tag{25}$$

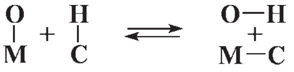
The possibility of formaldehyde insertion according to reaction (24) giving MCH_2OH ($\mathbf{I}_{19}$) assumed in a Fischer—Tropsch mechanism[224] (with participation of π-coordinated formaldehyde) has been proved for rhodium hydride complexes.[344] The back β-H-elimination was observed in the thermal decomposition of Re complex (formation of acetaldehyde[345]). Reaction (26) proceeding in both directions is known for Co and Rh hydride complexes with CO_2.[346,347]

$$\mathrm{M{-}H + O{=}C{=}O \rightleftharpoons M{-}C(O)OH} \tag{26}$$

In the case of transition metal complexes, the addition of M—H to the formyl intermediates ($\mathbf{I}_{17}$) to give hydroxymethylene intermediate $\mathbf{I}_{21}$ is also possible.[247,348,349]

Reaction (25) is a step (perhaps, a block of elementary steps) in alkene and alkyne hydrocarboxylation and hydrocarbalkoxylation and in the carbonylation of haloaromatic compounds involving metal complex catalysts.[350] The occurrence of reactions (24)—(26) has not been confirmed in the studies on heterogeneous catalysis by metals; however, they are often found in the metal complex catalysis. Thus, it is expedient to use the corresponding transforms for the generation of the reaction network for the Fischer—Tropsch synthesis.

T5:



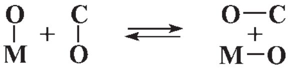
$$\begin{matrix}\mathrm{O}\\ |\\ \mathrm{M}\end{matrix} + \begin{matrix}\mathrm{H}\\ |\\ \mathrm{C}\end{matrix} \rightleftharpoons \begin{matrix}\mathrm{O{-}H}\\ +\\ \mathrm{M{-}C}\end{matrix}$$

Protodemetallation of organometallic compounds (hydrolysis, alcoholysis, and acidolysis) are well known in the chemistry of organometallic compounds[222,351]

$$\mathrm{M{-}R + XO{-}H \rightarrow M{-}OX + RH,} \tag{27}$$

where X = H, R, RCO, and M. The occurrence of this reaction in heterogeneous catalysis has not yet been confirmed, although it raises no doubts. The forward reaction is possible only for hydrocarbons with high acidity of the C—H bond.

T6:



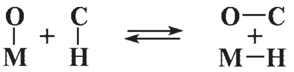
$$\begin{matrix}\mathrm{O}\\ |\\ \mathrm{M}\end{matrix} + \begin{matrix}\mathrm{C}\\ |\\ \mathrm{O}\end{matrix} \rightleftharpoons \begin{matrix}\mathrm{O{-}C}\\ +\\ \mathrm{M{-}O}\end{matrix}$$

The reaction of the metal-hydroxy intermediate MOH or MOR ($\mathbf{I}_4$, $\mathbf{I}_{36}$) (or the metal formyl intermediate, which is less probable) with the carbonyl group of aldehyde or ketone can result in the hydroxyalkoxide intermediate[223,245]:

$$\mathrm{M{-}OH + XYC{=}O \rightleftharpoons M{-}O(XY)C{-}OH.} \tag{28}$$

The back reaction is β-elimination of the OH groups.

T7:



$$\begin{matrix}\mathrm{O}\\ |\\ \mathrm{M}\end{matrix} + \begin{matrix}\mathrm{C}\\ |\\ \mathrm{H}\end{matrix} \rightleftharpoons \begin{matrix}\mathrm{O{-}C}\\ +\\ \mathrm{M{-}H}\end{matrix}$$

The insertion of the carbonyl group into the M—H bond to give alkoxy ($\mathbf{I}_{36}$) is a typical step in hydrogenation of aldehydes to alcohols in solutions of Rh and Ru hydride complexes.[352] The formation of the methoxy species from formaldehyde has been confirmed indirectly for reactions on the heterogeneous ruthenium catalyst at high pressures.[353] The insertion of the formyl group

$$\mathrm{MH + O{=}CHM \rightleftharpoons MOCH_2M} \tag{29}$$

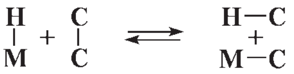
is one of the key steps of chain initiation in the Pichler—Schulz insertion mechanism.[223] The forward step was simulated by transformation of the Os complex with formaldehyde in the metal formyl group.[354] The hydrogen β-elimination step in the decomposition of alkoxy complexes is typical of oxidation and dehydrogenation of alcohols. The sequence of steps of CH_2O insertion into the M—H bond followed by cleavage of the O—CH_3 bond was demonstrated in relation to Ta complexes.[355]

$$(\eta^5\text{-}C_5Me_5)_2TaH(CH_2O) \rightarrow$$
$$\rightarrow (\eta^5\text{-}C_5Me_5)_2TaOCH_3 \rightarrow (\eta^5\text{-}C_5Me_5)_2Ta(O)CH_3 \tag{30}$$

The methathesis of σ-bonds within the framework of transform **T7** was considered as a pathway to methane from the methoxy species[275,276] and proposed in Fischer—Tropsch mechanisms.[118,356]

$$MO\text{—}CH_3 + M\text{—}H \rightarrow MO\text{—}M + CH_4 \tag{31}$$

T8:



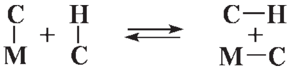
$$\begin{matrix}H\\|\\M\end{matrix} + \begin{matrix}C\\|\\C\end{matrix} \rightleftarrows \begin{matrix}H\text{—}C\\+\\M\text{—}C\end{matrix}$$

The step of olefin insertion and elimination has been proven experimentally for reactions on the surfaces of various metals including Ni[357] and Fe;[358] this step is reversible.[11,13]

$$M\text{—}H + R'CH{=}CHR'' \rightleftharpoons R'CH_2\text{—}CHR''(M) \tag{32}$$

The possibility of back elimination of (R′ = OH) has been noted.[4] The existence of enol intermediates on the surface was established for hydrogenation of ketones to alkanes.[359] No examples of **T8** type reactions with the formation or cleavage of C—C σ-bonds was found.

T9:



$$\begin{matrix}C\\|\\M\end{matrix} + \begin{matrix}H\\|\\C\end{matrix} \rightleftarrows \begin{matrix}C\text{—}H\\+\\M\text{—}C\end{matrix}$$

Methathesis of M—C and C—H σ-bonds takes place in reactions of organometallic compounds; even in the case of alkynes, this proceeds without preliminary coordination to scandium:[360]

$$(C_5H_5)_2ScCH_3 + H\text{—}C{\equiv}CR \rightarrow (C_5H_5)_2ScC{\equiv}CR + CH_4. \tag{33}$$

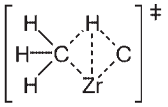
Reactions of this type are considered[343] as the key steps of alkane metathesis on a surface containing Ta hydrides.

$$[Ta]\text{—}CH_3 + CH_3CH_3 \rightarrow [Ta]\text{—}C_2H_5 + CH_4 \tag{34}$$

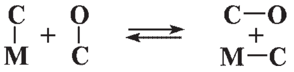
Exchange reactions were investigated[342] in relation to the reaction

$$Cp_2ZrCH_3^+ + {}^*CH_4 \rightarrow Cp_2Zr^*CH_3 + CH_4. \tag{35}$$

The possibility of formation of a fairly complex transition state with interacting Zr and H atoms was established.



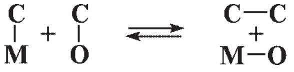
T10:



$$\begin{matrix}C\\|\\M\end{matrix} + \begin{matrix}O\\|\\C\end{matrix} \rightleftarrows \begin{matrix}C\text{—}O\\+\\M\text{—}C\end{matrix}$$

We found no examples of reactions described by transform **T10**.

T11:



$$\begin{matrix}C\\|\\M\end{matrix} + \begin{matrix}C\\|\\O\end{matrix} \rightleftarrows \begin{matrix}C\text{—}C\\+\\M\text{—}O\end{matrix}$$

The reversible insertion of alkenes and dienes into the M—OH bond (M—OR) is well-known in metal complex catalysis,[361] especially in the chemistry of Pd^{II} and Rh^{III} compounds. These steps usually proceed through the formation of alkene π-complex.

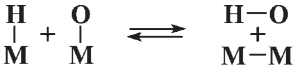
$$M\text{—}OR + CH_2{=}CH_2 \rightarrow MCH_2CH_2OR \tag{36}$$

Alkoxides and alkynes react with each other in a similar way.[362] The transition state corresponding to transform **T11** also arises in the insertion reaction of the carbonyl group into the M—C bond

$$M\text{—}R + XYC{=}O \rightarrow M\text{—}O\text{—}(XY)C\text{—}R, \tag{37}$$

which is also well-known in the chemistry of organometallic compounds. In the oxidation of olefins either by compounds having M=O bonds ($CrCl_2O_2$) or on the metal surfaces with M=O or M—O—M bonds, transform **T11** also takes place. It can be regarded as a result of olefin insertion into the M—OM bond.

T12:



$$\begin{matrix}H\\|\\M\end{matrix} + \begin{matrix}O\\|\\M\end{matrix} \rightleftarrows \begin{matrix}H\text{—}O\\+\\M\text{—}M\end{matrix}$$

The participation of the surface oxo and hydroxo species ($\mathbf{I_3}$, $\mathbf{I_4}$) in the formation of water or hydroxo groups on the surface is known for transition metal (Co, Fe[123]) catalyzed conversions:

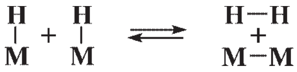
$$MO\text{—}M + H\text{—}M \rightleftharpoons M\text{—}M + MO\text{—}H, \tag{38}$$
$$M\text{—}OH + H\text{—}M \rightleftharpoons M\text{—}M + H_2O. \tag{39}$$

The formation of alcohols also involves, most likely, steps of this type.[223]

$$M\text{—}OR + H\text{—}M \rightleftharpoons M\text{—}M + ROH \tag{40}$$

The back reactions, cleavage of the O—H bonds, in particular, on Fe and Co surfaces,[294,363] have been studied more thoroughly.

T13:



$$\begin{array}{c}\mathbf{H}\\|\\\mathbf{M}\end{array}+\begin{array}{c}\mathbf{H}\\|\\\mathbf{M}\end{array}\rightleftharpoons\begin{array}{c}\mathbf{H-H}\\+\\\mathbf{M-M}\end{array}$$

The adsorption of H_2 on two surface centers is considered as a pathway to intermediate $\mathbf{I_1}$ (M—H). Theoretical investigation of the forward (reductive elimination of H_2 from the two centers) and back reactions (oxidative addition of H_2 to two linked metal atoms)[364] led to the conclusion that the reversible reaction

$$HM(L_n){-}(L_n)MH \rightleftharpoons L_nM{=}ML_n + H{-}H, \qquad (41)$$

where L is a ligand, is kinetically unfavorable (symmetry forbidden); therefore, its steps can hardly be elementary. Reaction (41) is only possible as a stepwise process with intermediate deformation of the M—H bond (vertical deviation) and formation of a weak hydrogen bond, M—H...H—M. Further movement along the reaction coordinate results in the formation and subsequent elimination of the μ-η^2-complex with molecular hydrogen. For the purpose of formal generation of Fischer—Tropsch mechanisms, transform **T13** can be considered as an elementary step with allowance for the possible decrease in the symmetry of the metal-containing center on the surface.

T14:

$$\begin{array}{c}\mathbf{C}\\|\\\mathbf{M}\end{array}+\begin{array}{c}\mathbf{H}\\|\\\mathbf{M}\end{array}\rightleftharpoons\begin{array}{c}\mathbf{C-H}\\+\\\mathbf{M-M}\end{array}$$

This transform describes many elementary reactions. It has been established reliably[4] that elimination of alkyl groups to give alkanes

$$M{-}CH_2R + M{-}H \rightleftharpoons M{-}M + RCH_3 \qquad (42)$$

is characteristic of every Fischer—Tropsch mechanism, irrespective of the features of molecular chain initiation and propagation. Numerous examples of this reaction are also known in organometallic chemistry.[148,149,222]

Hydrogenation of C_1 intermediates is postulated in the carbide mechanism of the Fischer—Tropsch synthesis [105,106,115]

$$M_x{-}CH_{3-x}{-}M + M{-}H \rightleftharpoons M_x{-}CH_{4-x} + M{-}M, \qquad (43)$$

where $x = 1$—3. The reaction reverse to (42) is, apparently, hindered kinetically and thermodynamically, and reaction (43) can also occur in the backward direction. Metal binding of the $CH_{3-x}H$ fragment in organometallic compounds usually promotes the oxidative addition of the C—H bond to the metal and formation of metallacycles.[222] Hydrogen α-elimination, resulting in the conversion of the methyl ligand into the methylene group, was confirmed by the formation of polydeuterated methane in the reaction of deuterium with a cobalt methyl complex.[11] Transform **T14** also describes the step of CO insertion into the M—H bond to give a formyl group; this step is considered to be rather probable in the Fischer—Tropsch mechanism.[223,224]

$$M_2C{=}O + M{-}H \rightleftharpoons M{-}CH{=}O + M{-}M \qquad (44)$$

Theoretical analysis of the possibility of CO insertion on one M—H center [365] showed that insertion with migration of the hydride H atom is energetically as favorable as insertion with migration of the methyl group. The step in question is regarded as reversible.[224,247] Simulation of the formyl formation on a binuclear Ta hydride complex [366] showed that this reaction occurs at −78 °C under atmospheric pressure to give a bridging formyl fragment.

$$[(Bu_3{}^tSiO)_2ClTa]_2(\mu\text{-}H)_2 + CO \rightarrow$$
$$\rightarrow [(Bu_3{}^tSiO)_2ClTa]_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}HCO) \qquad (45)$$

This stabilization of the formyl group can facilitate the formation of surface formyl intermediates ($\mathbf{I_{17}}$).

T15:

$$\begin{array}{c}\mathbf{C}\\|\\\mathbf{M}\end{array}+\begin{array}{c}\mathbf{O}\\|\\\mathbf{M}\end{array}\rightleftharpoons\begin{array}{c}\mathbf{C-O}\\+\\\mathbf{M-M}\end{array}$$

Oxidative addition of surface-coordinated CO molecule to two metal atoms can be regarded as an important step in the CO dissociation on the surface ($\mathbf{I_{16}} \rightarrow \mathbf{I_{30}}$).

$$M_2C{=}O + M{-}M \rightarrow M_3C{-}OM \qquad (46)$$

The formation of highly modified (nearly single) η^2-bonded CO group is well-known for carbonyl clusters,[367] for example, $[Co(CO)_3]_3(\mu\text{-}CO){-}AlR_2$ or $[Co(CO)_3]_3(\mu\text{-}CO){-}TiCp_2Cl$.

In addition, the insertion of the carbonyl group from formyl ($\mathbf{I_{17}}$), aldehydes, or CO_2 into the M—M bond results in the formation of intermediates with a reduced >C=O bond order ($\mathbf{I_{31}}$—$\mathbf{I_{34}}$). The attack by simple oxygen-containing intermediates $\mathbf{I_3}$ and $\mathbf{I_4}$ on the carbonyl or formyl group is also regarded as an important step of the Fischer—Tropsch synthesis. For example, the reaction of adsorbed CO and the surface O atom is a stage of CO_2 formation:[108,144,368,369]

$$M_2C{=}O + M_2O \rightarrow MC(O){-}OM + M{-}M. \qquad (47)$$

It has been suggested [256,370] that surface carboxylates are formed in the reaction

$$M_2C{=}O + M{-}OH \rightarrow MC(O){-}OH + M{-}M. \qquad (48)$$

Without any substantiation, a similar reaction has been proposed[10] for the acyl species:

$$MC(O){-}R + M{-}OH \rightarrow RC(O){-}OH + M{-}M. \qquad (49)$$

The cyclic structures of topology identifiers accepted in this work and the univalent nature of metal centers impose certain constraints on the possibility of appearance of some intermediates. For example, the linear topology of intermediate $\mathbf{I_{32}}$ makes it possible to obtain the product of C—O bond cleavage in the di-σ-bonded $CH_2{=}O$.

$$\mathrm{M{-}CH_2{-}O{-}M \rightarrow M{=}CH_2 + O{=}M}$$

$$\mathrm{M{-}C{-}O{-}M}$$

Topology identifier

However, this requires the assumption of the presence of a divalent metal center.

T16:

$$\begin{matrix}\mathrm{C}\\ |\\ \mathrm{M}\end{matrix} + \begin{matrix}\mathrm{C}\\ |\\ \mathrm{M}\end{matrix} \rightleftarrows \begin{matrix}\mathrm{C{-}C}\\ +\\ \mathrm{M{-}M}\end{matrix}$$

All the remarks made concerning transform **T13** also refer to this transform. Elimination of an alkane molecule from two neighboring M—R intermediates [364] and elimination of ethylene from σ-adsorbed ethylene (and the corresponding back reactions) are similar to the elimination of H_2. For example, elimination of ethylene from the $(CO)_4OsCH_2CH_2Os(CO)_4$ complex does not proceed at temperatures below 100 °C. The compound $Os_2(CO)_8(CH_3)_2$ decomposes with evolution of CH_4 and formation of the bridging CH_2 group.[364] The formation of intermediate $\mathbf{I_{12}}$ from ethylene on the surface is considered to be proven; therefore, in generation of the reaction network, this process, which is, apparently, a block of steps, can be regarded as an elementary step. In the modern version of the carbide mechanism,[115,150,151] reductive elimination with the formation of the C—C bond is considered to be the key step.[151]

$$\mathrm{M{-}CH_2{-}M + M{-}R \rightarrow M{-}CH_2R + M{-}M} \tag{50}$$

The steps of interaction of methylene and methylidyne groups to give C—C bonds [156] also cannot be excluded from consideration,[156] although in the case of the methylidyne fragment, the C—C bond cleavage reaction appears more likely (see the mechanism of ethane hydrogenolysis[371]):

$$\mathrm{M_2CH{-}CHM_2 + M{-}M \rightarrow M_3CH + CHM_3.} \tag{51}$$

The classical step of CO insertion in the processes of hydrocarbon chain propagation also belongs to the reaction type **T16** considered.[223,224]

$$\mathrm{M_2CO + M{-}R \rightarrow M{-}C(O)R + M{-}M} \tag{52}$$

The formation of product of reaction (52) was confirmed by IR spectroscopy.[370] This reaction was also studied by the transient response kinetic analysis.[243] Naturally, formyl can also participate in the formation of the C—C bond.

$$\mathrm{M{-}CH_2{-}M + MCHO \rightarrow M{-}CH_2CHO + M{-}M} \tag{53}$$

Step (53) was proposed to describe reactions involving the binuclear Fe cluster [257257] and assumed as the basis of the mechanism of synthesis of oxygen-containing compounds.

T17:

$$\begin{matrix}\mathrm{C}\\ |\\ \mathrm{M}\end{matrix} + \begin{matrix}\mathrm{C}\\ |\\ \mathrm{C}\end{matrix} \rightleftarrows \begin{matrix}\mathrm{C{-}C}\\ +\\ \mathrm{M{-}C}\end{matrix}$$

The reactions described by transform **T17** have been confirmed in a study of the formation and conversions of C_3 compounds. Generally, consideration of C_3 products is beyond the scope of our paper; however, some reactions of type **T17** can also proceed with C_2 compounds. Reactions of this type proceeding on Ti, Zr, and Ta hydrides ([M]—H) immobilized on the SiO_2 surface have been reported.[343] Authors assume that paraffin metathesis and catalytic cracking may include the step

$$\mathrm{M{-}CH_2CH_3 + CH_3CH_3 \rightarrow M{-}CH_3 + CH_3CH_2CH_3.} \tag{54}$$

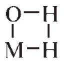
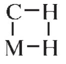
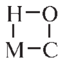
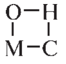
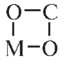
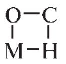
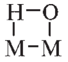
Analysis of the topology identifiers and transforms **T1—T18** they match (reaction (19)) allows one to select transforms for computer generation of the reaction network for the Fischer—Tropsch synthesis giving products containing one (C_1) or two linked (C_2) carbon atoms and to write them down in the form convenient for the ChemNet program (Table 1, 2). The numbers of transforms in the Tables consist of the number of the topology identifier (the first digit) and the number of transform matching this identifier (the second digit).

On the basis of published data, transforms **T12—T15** can be used either in the general form without constraints on the type of substituents at the carbon and oxygen atoms (X, Y, Z) or with the appropriate constraints (see Table 1). The involvement of the sp^3-hybridized carbon atom in transform **15**.1 has not yet been confirmed; however, in the successive bond cleavage in carbon monoxide, this step appears to be the most plausible pathway to the intermediates of the carbide mechanism.

Transform **T10**, which represents the exchange of the carbon fragment in the intermediate with the M—C bond, in particular, in the reaction with ROH, has not been proven experimentally. Therefore, it is not included in the initial list of transforms (see Table 1).

Generalized transform **T2** (the exchange by OR fragments) could be used in the ChemNet program but its inclusion in the process results in a substantial extension of the reaction network. Therefore, in the first variants of the computer experiment, it was excluded from the set of transforms. The same is true for **T9**, which can be used in the most general form. However, the exchange by carbon

Table 1. Transforms for the generation of the reaction network for the Fischer—Tropsch synthesis to give C_1-products

Topology identifier	Ordinal number of the transform	Transform	Variant of the use of the transform
 **1**	**1**.1	M—O + H—H → M—H + O—H	**I—IVa**
	1.2	M—H + XO—H → M—OX + H—H	**I—IVa** (**III:** X ≠ M)
 **3**	**3**.1	M—C + H—H → M—H + C—H	**I—IVa**, **VIII** (**III:** sp^3 hybridized C atoms)
	3.2	M—H + C—H → M—C + H—H	**I**, **II**, **IV**, **IVa**
 **4**	**4**.1	M—H + C=O → M—C—O—H	**I**, **II**, **IV—VIII**
	4.2	M—C(XY)—O—H → M—H + (XY)C=O	**I—VIII** (**VIII:** X = Y = H)
	4.3	M—CX + O—H → M—H + O—CX	**I—IVa**, **VI** (**I—III:** X = O)
 **5**	**5**.1	M—CX + YO—H → M—OY + XC—H	**I—IV** (**II:** X ≠ O, Y ≠ M; **III** — only sp^3 hybridized C atoms, X ≠ O, M, CH_x, Y ≠ M)
 **6**	**6**.1	M—OX + C=O → M—O—C—OX	**I—IV** (**I**, **III:** X = H)
	6.2	M—O—C—OH → M—OH + C=O	**I**, **II**, **IV**, **IVa** (**I:** X = H)
 **7**	**7**.1	M—H + XC—OY → M—OY + XC—H	**I**, **II**, **IV**, **IVa**, **VI—VIII** (**VIII:** X = H_3, Y = M)
	7.2	M—O + C—H → M—H + C—O	**I**, **II**, **IV**, **IVa**
	7.3	M—H + XC=O → M—O—CX—H	**I—IVa**, **VI—VIII** (**VIII:** X = H)
	7.4	M—O—C(XY)—H → M—H + (XY)C=O	**I—IVa**, **VI** (**VIII:** X = H, Y =M)
 **12**	**12**.1	M—H + M—O → M—M + O—H	**I—VIII**
	12.2	M—M + O—H → M—H + M—O	**I—VIII**
 **13**	**13**.1	M—M + H—H → M—H + M—H	**I—VIII**
	13.2	M—H + M—H → M—M + H—H	**I—IVa**, **VI—VIII**
 **14**	**14**.1	M—C + M—H → M—M + C—H	**I—VIII**
	14.2	M—M + C—H → M—C + M—H	**I—VIII**
 **15**	**15**.1	M—M + (XY)C—OZ → M—C(XY) + M—OZ	**I—VIII** (**VIII:** X = Z = M, Y = O)
	15.2	M—C + M—O → M—M + C—O	**I**, **II**, **IV—VIII**
	15.3	M—M + XC=O → M—CX—O—M	**I—V**, **VII**, **VIII** (**VIII:** X = O)
	15.4	M—C(XY)—O—M → M—M + (XY)C=O	**I—V**, **VII**, **VIII** (**VIII:** X = Y = M)
 **18**	**18**.1	M—M + C≡O → M—C(O)—M	**I—VIII**
	18.2	M—C(O)—M → M—M + C≡O	**I—VIII**

fragments gives rise to a multitude of steps, and this transform is not included in Table 1 either.

For transforms **T3** and **T5** related to hydrogenolysis and protolysis of the M—C bonds to give C—H bonds, constraints on the nature of the carbon atom (sp^3) and substituents X (X ≠ M, R) can be imposed. The participation of the M—C=O (X = O) fragments in these reactions in unlikely.

It is expedient to apply transform **4**.1 (**T4**) to reactions of intermediates containing a C=O group without con-

Table 2. Transforms for the generation of the reaction network of the Fischer—Tropsch synthesis to give C_2-products with C—C bonds

Topology identifier	Ordinal number of the transform	Transform
 **8**	**8**.1	M—H + C=C → M—C—C—H
	8.2	M—C—C—H → M—H + C=C
 **11**	**11**.1	M—O + C=C → M—C—C—O
	11.2	M—C—C—O → M—O + C=C
	11.3[a]	M—R + C=O → M—O—C—R
 **16**	**16**.1	M—C + M—C → M—M + C—C
	16.2	M—M + C=C → M—C—C—M
	16.3	M—C—C—M → M—M + C=C
 **17**	**17**.1[b]	M—CH_3 + C—CR → → M—CR + CH_3—C

[a] R is alkyl.

[b] R ≠ H.

straints on the nature of the substituents X and Y (reaction (24)). For the transform reverse to **4**.1, constraints on the carbon-containing intermediate can be imposed, and it can be written in form **4**.2 (see Table 1).

The transforms leading to the formation of C_2 products (**T8**, **T11**, **T16**) are presented in Table 2. In the case of **T8**, one can restrict oneself to the reversible transform including the C=C bond (reaction (32)). Generalized transform **T11** will be represented by three specific transforms related to the reactions of olefins with M—OX and carbonyl compounds with M—R (R = alkyl). It is also expedient to use generalized transforms for **T16**.

If the constraints on the number of carbon atoms in the intermediates ($m \leq 2$) are removed and transform **T17** is included, the whole set of hydrocarbon and oxygen-containing products of the Fischer—Tropsch synthesis can thus be obtained.

3. Generation of the reaction networks for the formation of C_1 compounds in the syntheses from CO and H_2 using the ChemNet program

The question of what particular set of transforms of those described above should be used to generate the reaction network and, finally, for reaction mechanisms is answered depending on the goal of the research, the particular catalyst chosen, and the experimental and theoretical possibilities of discrimination of various mechanisms. In this section, we consider the main stages of generation of simple and complex variants of the reaction network for the formation of C_1 products from CO and H_2. The size of the reaction network (the number of steps) is determined by the transforms chosen and by the constraints imposed. The main requirements to the reaction network are the following:

(1) the reaction network should describe the formation of a specified set of products (*i.e.*, they should include reactions resulting in the formation of these products);

(2) the steps in the reaction network should be elementary; the use of blocks (combinations of steps) should be a substantiated choice of the researcher;

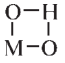
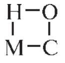
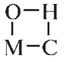
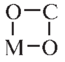
(3) the reaction network should contain a full set of intermediates stipulated by the imposed constraints.

The set of 26 transforms with the accepted constraints (see Table 1), with specified numbers of the C and O atoms in intermediates (1 and 2, respectively), and without constraints on the number of metal or hydrogen atoms in them gives rise a reaction network comprising 574 steps and containing 34 substances (not counting the initial ones) including 27 intermediates and 7 products (**P**) (variant **I**): CH_4 (P_1), CH_3OH (P_2), CO_2 (P_3), H_2O (P_4), HCOOH (P_5), CH_2O (P_6), and $CH_2(OH)_2$ (P_7). At elevated temperatures, formaldehyde hydrate P_7 can exist as CH_2O, which is formed only in the adsorbed state for thermodynamic reasons. Analysis of the reaction network corresponding to variant **I** showed that transform **5**.1 used in the most general form resulted in the generation of 280 steps. If one assumes that in transform **5**.1, oxygen cannot add to the C atom and metal cannot add to oxygen, the frequency of using this transform will decrease to 70 and the total number of steps in the reaction network will become equal to 344 (variant **II**).

Variant **III** of generation of the reaction network is devoid of transforms **3**.2 (the formation of H_2), **4**.1 (anomalous insertion of CO into the M—H bond), **6**.2 (β-elimination of the OH group), **7**.1 and **7**.2 (poorly substantiated), and **15**.2 (the formation of C—O from M—C and M—O); besides, additional constraints on transforms **1**.2, **3**.1, and **5**.1 are imposed (see Table 1). The application of the 20 remaining transforms resulted in the same numbers of intermediates (27) and products (7), while the number of steps in the reaction network decreased to 220.

The goal of the next series of experiments was to elucidate the effect of transforms that have not been used in variant **I** on the number of intermediates and steps in the reaction network, *i.e.*, to identify the upper limit of the size of the reaction network with the given constraints. We add transforms from Table 3 to transforms comprised in variant **I**. The transfer of hydrogen between M—C intermediates (**9**.1) was not used. Altogether, this

Table 3. Additional transforms for the generation of the reaction network for the Fischer—Tropsch synthesis to give C_1-products

Topology identifier	Ordinal number of the transform	Transform	Variant of the use of the transform
 $\begin{array}{c}O-H\\ \mid\ \ \ \mid\\ M-O\end{array}$ **2**	**2**.1	M—OX + YO—H → → M—OY + XO—H	**IVa**, **VI**, **VII** (**VI:** X = C, Y = H)
 $\begin{array}{c}H-O\\ \mid\ \ \ \mid\\ M-C\end{array}$ **4**	**4**.4	M—H + O—C → → M—C + O—H	**IV**, **IVa**
 $\begin{array}{c}O-H\\ \mid\ \ \ \mid\\ M-C\end{array}$ **5**	**5**.2	M—O + C—H → → M—C + O—H	**IV**
 $\begin{array}{c}O-C\\ \mid\ \ \ \mid\\ M-O\end{array}$ **6**	**6**.3	M—O + C—O → → M—O + C—O	**IV**, **IVa**
 $\begin{array}{c}C-H\\ \mid\ \ \ \mid\\ M-C\end{array}$ **9**	**9**.1	M—C + XC—H → → M—CX + C—H	**IV**, **VI**, **VII** (**VI**, **VII:** X = M)
 $\begin{array}{c}C-O\\ \mid\ \ \ \mid\\ M-C\end{array}$ **10**	**10**.1	M—C + C—O → → M—C + C—O	**IV**, **VI**

set includes 31 transforms. This gave the same 34 substances and 1647 steps in the reaction network (variant **IV**). Transforms **10**.1, **2**.1, **4**.4, and **5**.1 are used most often (~40% of steps). Elimination of these steps gives a reaction network consisting of 1069 steps (variant **IVa**).

The smallest number of transforms used in experiments was 12 (variant **V**): **4**.1, **4**.2, **12**.1, **12**.2, **13**.1, **14**.1, **14**.2, **15**.1, **15**.2, **15**.3, **15**.4, and **18**.1 (*i.e.*, only identifiers **4**, **12**, **13**, **14**, **15**, and **18** were included). The transforms taken describe one type of formation of the C—H and C—O bonds, one type of bond cleavage and cleavage of the H—H bond, and two types of cleavage and formation of C=O and O—H bonds (see Table 3). In this experiment, the same 34 substances and 150 steps were also obtained in the reaction network.

Experiments were also carried out with other combinations of transforms (variants **VI—VIII**). Variant **VI** corresponds to **I** without transforms **1**.1, **1**.2, **3**.1, **3**.2, **5**.1, **6**.1, **6**.2, **7**.2, **15**.3, and **15**.4 and with the addition of **2**.1, **10**.1, and **9**.1 (see Table 3), which have not been used in the previous versions. Finally, 542 steps and the same 34 substances were obtained for 17 transforms. Transforms **2**.1, **9**.1, and **10**.1 (exchange by fragments and hydrogen transfer), which contribute greatly to the formation of the reaction network, were used only in variant **IV** (without **9**.1). By adding two more transforms (**15**.3 and **15**.4) to variant **VI**, one can obtain 582 steps (variant **VII**). Variant **VIII** was obtained by elimination of transforms **2**.1, **4**.3, **9**.1, and **10**.1 from variant **VII** and addition of **3**.1. The transforms **7**.1, **7**.3, **7**.4, **15**.1, **15**.3, and **15**.4 were employed with substantial constraints, for example, transform **15**.1 was written as reaction (55)

$$\text{M—O—C(O)—M + M—M} \rightarrow \text{M—O—M + M—C(O)—M}. \quad (55)$$

This experiment resulted in 132 steps and the same substances (Table 4). Note that *identical sets of the same intermediates (27) and reaction products (7) are obtained in all the computer experiments.*

Analysis of the results indicates that the steps giving 27 intermediates and 7 products appeared in all the sets of transforms used. Nine transforms were used in all variants and other eight transforms are present in seven of the eight variants. Thus, the main array contains 17 transforms, five of which (**6**.1, **7**.1, **7**.2, **7**.3, and **7**.4) were present in variant **V** with the minimum number of steps. All 17 transforms are used in a rather general form.

Table 4. Results of computer generation of the reaction network for the synthesis

Variant	The number of transforms	The number of compounds	The number of steps in the reaction network	Notes
I	26	34	574	For transforms, see Table 1
II	26	34	344	**I** with a constraint **5**.1
III	20	34	220	**II** without **3**.2, **4**.1, **6**.2, **7**.1, **7**.2, **15**.2
IV	31	34	1647	**I** and **2**.1, **4**.4, **5**.2, **6**.3, **10**.1. Transforms **4**.3, **6**.1, **6**.2 without constraints
IVa	27	34	1069	**IV** without **2**.1, **4**.4, **5**.1, **10**.1
V	12	34	150	**4**.1, **4**.2, **12**.1, **12**.2, **13**.1, **14**.1, **14**.2, **15**.1, **15**.2, **15**.3, **15**.4, **18**.1
VI	17	34	542	**I** without **1**.1, **1**.2, **3**.1, **3**.2. **5**.1, **6**.1, **6**.2, **7**.2, **15**.3, **15**.4, but with **2**.1, **10**.1, **9**.1
VII	19	34	582	**VI** with **15**.3, **15**.4
VIII	16	34	132	**VII** without **2**.1, **9**.1, **10**.1, **4**.3, but with **3**.1. Transforms **7**.1, **7**.3. **7**.4, **15**.1, **15**.3, **15**.4 with constraints

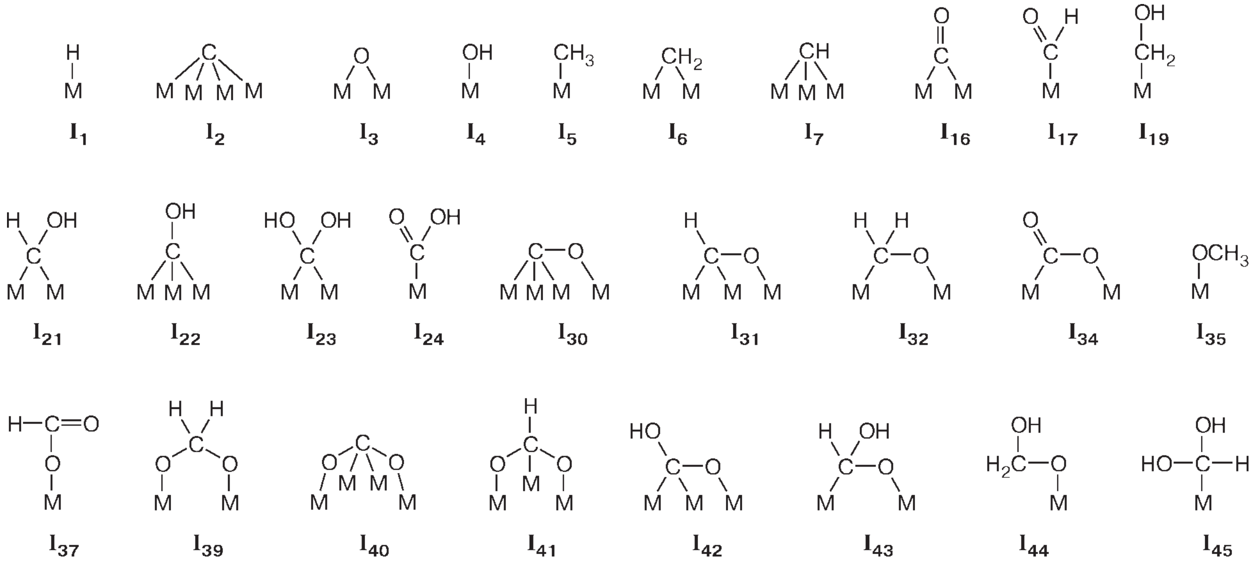


Fig. 6. Intermediates of the mechanisms of formation of C_1-products obtained in the reaction network.

4. Analysis of the reaction networks and the mechanisms of formation of C_1 products

Most of the obtained intermediates (21 of 27) are known from published data (see Section 2.1), although not all of them have been shown to exist. Six intermediates have not been described previously in the literature (Fig. 6, $\mathbf{I}_{40}$—$\mathbf{I}_{45}$). They contain adsorbed species having two C—O bonds and one to four metal atoms. Intermediate $\mathbf{I}_{45}$ is hydrated $\mathbf{I}_{17}$. All the new intermediates and $\mathbf{I}_{39}$ are the products of substitution of metal atoms for the H atoms in methylene hydrate, which can be formed from $\mathbf{I}_{44}$ or $\mathbf{I}_{45}$. Carbonate intermediate $\mathbf{I}_{38}$ was not obtained in the generated networks due to the constraint on the total number of oxygen atoms (≤2).

For detailed analysis, we chose variant **III** of the reaction network because it contains only 220 steps but includes rather general transforms. This network as a prime sequence of steps written down with designation of the reactants (**R**), intermediates (**I**), and products (**P**) by numbers is presented in Table 5.

The key objects of analysis are separate mechanisms and mechanism sub-networks, resulting in the formation of methane or methanol (without conjugation and with formation of other carbon-containing compounds) and also the pathways furnishing pairs of coupled products (CH_4 and CO_2, CH_4 and HCOOH).

4.1. Methane formation

The sub-network of steps for reaction (56) is presented in Fig. 7.

$$CO + 3\,H_2 \rightarrow CH_4 + H_2O \tag{56}$$

Some transforms involving various reactants (MH, H_2, H_2O) are marked by one arrow. The only direct precursor of CH_4 is the M—CH_3 intermediate ($\mathbf{I}_5$). The number of the possible mechanisms that can be extracted from the given network alone is rather great. In this work, we present only the most interesting pathways that result in reaction (56) with particular stoichiometric numbers of steps. Of these, we selected the pathways that either reproduce rather closely the published versions or are original (the stoichiometric numbers of steps are not given).

Pathway 1 is the classical variant of the carbide mechanism of methane formation,[106,110,243,372] which includes direct dissociation CO into adsorbed C and O atoms with subsequent stepwise hydrogenation to give methane and water, respectively. The most reliable experimental substantiation of the carbide mechanism refers to the methane formation on nickel catalysts.[110,243,372] The realization of the carbide scheme with other metallic catalysts of the Fischer—Tropsch synthesis is considered to be unlikely.[115—117,373] However, in the case of iron catalysts,[374] the formation and hydrogenation of the surface carbide gives rise to surface defects, which act as active centers in the Fischer—Tropsch synthesis.

Pathway 1

1.1. $CO + MM \rightarrow M_2CO$,
1.2. $H_2 + MM \rightarrow 2\,MH$,
1.3. $M_2CO + MM \rightarrow M_3COM$,
1.4. $M_3COM + MM \rightarrow M_4C + M_2O$,
1.5. $M_2O + MH \rightarrow MOH + MM$,
1.6. $MOH + MH \rightarrow H_2O + MM$,
1.7. $M_4C + MH \rightarrow M_3CH + MM$,
1.8. $M_3CH + MH \rightarrow M_2CH_2 + MM$,
1.9. $M_2CH_2 + MH \rightarrow MCH_3 + MM$,
1.10. $MCH_3 + MH \rightarrow CH_4 + MM$.

Table 5. Reaction network for the synthesis of C_1-products (variant **III**)

No.*	Step
1	$\mathbf{R}_1 + \mathbf{R}_3 \rightarrow \mathbf{I}_{16}$
2	$\mathbf{R}_2 + \mathbf{R}_3 \rightarrow {}_{2}\mathbf{I}_1$
3	$\mathbf{R}_3 + \mathbf{I}_{16} \rightarrow \mathbf{I}_{30}$
4	$\mathbf{R}_2 + \mathbf{I}_{30} \rightarrow \mathbf{I}_1 + \mathbf{I}_{31}$
5	$\mathbf{R}_2 + \mathbf{I}_{31} \rightarrow \mathbf{I}_1 + \mathbf{I}_{32}$
6	$\mathbf{R}_2 + \mathbf{I}_{32} \rightarrow \mathbf{I}_1 + \mathbf{I}_{35}$
7	$\mathbf{R}_2 + \mathbf{I}_{30} \rightarrow \mathbf{I}_1 + \mathbf{I}_{22}$
8	$\mathbf{R}_2 + \mathbf{I}_{31} \rightarrow \mathbf{I}_1 + \mathbf{I}_{21}$
9	$\mathbf{R}_2 + \mathbf{I}_{32} \rightarrow \mathbf{I}_1 + \mathbf{I}_{19}$
10	$\mathbf{R}_2 + \mathbf{I}_{35} \rightarrow \mathbf{P}_2 + \mathbf{I}_1$
11	$\mathbf{I}_{31} \rightarrow \mathbf{I}_1 + \mathbf{I}_{16}$
12	$\mathbf{I}_{32} \rightarrow \mathbf{I}_1 + \mathbf{I}_{17}$
13	$\mathbf{I}_{35} \rightarrow \mathbf{I}_1 + \mathbf{P}_6$
14	$\mathbf{I}_1 + \mathbf{I}_{22} \rightarrow \mathbf{R}_2 + \mathbf{I}_{30}$
15	$\mathbf{I}_1 + \mathbf{I}_{21} \rightarrow \mathbf{R}_2 + \mathbf{I}_{31}$
16	$\mathbf{I}_1 + \mathbf{I}_{19} \rightarrow \mathbf{R}_2 + \mathbf{I}_{32}$
17	$\mathbf{I}_1 + \mathbf{P}_2 \rightarrow \mathbf{R}_2 + \mathbf{I}_{35}$
18	$\mathbf{R}_3 + \mathbf{I}_{30} \rightarrow \mathbf{I}_2 + \mathbf{I}_3$
19	$\mathbf{R}_3 + \mathbf{I}_{31} \rightarrow \mathbf{I}_3 + \mathbf{I}_7$
20	$\mathbf{R}_3 + \mathbf{I}_{32} \rightarrow \mathbf{I}_3 + \mathbf{I}_6$
21	$\mathbf{R}_3 + \mathbf{I}_{35} \rightarrow \mathbf{I}_3 + \mathbf{I}_5$
22	$\mathbf{R}_3 + \mathbf{I}_{22} \rightarrow \mathbf{I}_2 + \mathbf{I}_4$
23	$\mathbf{R}_3 + \mathbf{I}_{21} \rightarrow \mathbf{I}_4 + \mathbf{I}_7$
24	$\mathbf{R}_3 + \mathbf{I}_{19} \rightarrow \mathbf{I}_4 + \mathbf{I}_6$
25	$\mathbf{R}_3 + \mathbf{P}_2 \rightarrow \mathbf{I}_4 + \mathbf{I}_5$
26	$\mathbf{I}_{30} \rightarrow \mathbf{R}_3 + \mathbf{I}_{16}$
27	$\mathbf{I}_{31} \rightarrow \mathbf{R}_3 + \mathbf{I}_{17}$
28	$\mathbf{I}_{32} \rightarrow \mathbf{R}_3 + \mathbf{P}_6$
29	$\mathbf{I}_{34} \rightarrow \mathbf{R}_3 + \mathbf{P}_3$
30	$\mathbf{I}_{39} \rightarrow \mathbf{R}_3 + \mathbf{I}_{34}$
31	$\mathbf{I}_{42} \rightarrow \mathbf{R}_3 + \mathbf{I}_{24}$
32	$\mathbf{I}_{40} \rightarrow \mathbf{R}_3 + \mathbf{I}_{37}$
33	$\mathbf{I}_{43} \rightarrow \mathbf{R}_3 + \mathbf{P}_5$
34	$\mathbf{I}_1 + \mathbf{I}_{16} \rightarrow \mathbf{R}_3 + \mathbf{I}_{17}$
35	$\mathbf{I}_1 + \mathbf{I}_{30} \rightarrow \mathbf{R}_3 + \mathbf{I}_{31}$
36	$\mathbf{I}_1 + \mathbf{I}_{17} \rightarrow \mathbf{R}_3 + \mathbf{P}_6$
37	$\mathbf{I}_1 + \mathbf{I}_{31} \rightarrow \mathbf{R}_3 + \mathbf{I}_{32}$
38	$\mathbf{I}_1 + \mathbf{I}_{32} \rightarrow \mathbf{R}_3 + \mathbf{I}_5$
39	$\mathbf{I}_1 + \mathbf{I}_{22} \rightarrow \mathbf{R}_3 + \mathbf{I}_{21}$
40	$\mathbf{I}_1 + \mathbf{I}_{21} \rightarrow \mathbf{R}_3 + \mathbf{I}_{19}$
41	$\mathbf{I}_1 + \mathbf{I}_{19} \rightarrow \mathbf{R}_3 + \mathbf{P}_2$
42	$\mathbf{I}_1 + \mathbf{I}_7 \rightarrow \mathbf{R}_3 + \mathbf{I}_6$
43	$\mathbf{I}_1 + \mathbf{I}_6 \rightarrow \mathbf{R}_3 + \mathbf{I}_5$
44	$\mathbf{I}_1 + \mathbf{I}_5 \rightarrow \mathbf{R}_3 + \mathbf{P}_1$
45	$\mathbf{I}_1 + \mathbf{I}_2 \rightarrow \mathbf{R}_3 + \mathbf{I}_7$
46	$\mathbf{I}_1 + \mathbf{I}_{34} \rightarrow \mathbf{R}_3 + \mathbf{I}_{37}$
47	$\mathbf{I}_1 + \mathbf{I}_{24} \rightarrow \mathbf{R}_3 + \mathbf{P}_5$
48	$\mathbf{I}_1 + \mathbf{I}_{39} \rightarrow \mathbf{R}_3 + \mathbf{I}_{40}$
49	$\mathbf{I}_1 + \mathbf{I}_{42} \rightarrow \mathbf{R}_3 + \mathbf{I}_{43}$
50	$\mathbf{I}_1 + \mathbf{I}_{40} \rightarrow \mathbf{R}_3 + \mathbf{I}_{41}$
51	$\mathbf{I}_1 + \mathbf{I}_{43} \rightarrow \mathbf{R}_3 + \mathbf{I}_{44}$
52	$\mathbf{I}_1 + \mathbf{I}_{23} \rightarrow \mathbf{R}_3 + \mathbf{I}_{45}$
53	$\mathbf{I}_1 + \mathbf{I}_{45} \rightarrow \mathbf{R}_3 + \mathbf{P}_7$
54	$\mathbf{I}_{22} \rightarrow \mathbf{I}_1 + \mathbf{I}_{16}$
55	$\mathbf{I}_{21} \rightarrow \mathbf{I}_1 + \mathbf{I}_{17}$
56	$\mathbf{I}_{19} \rightarrow \mathbf{I}_1 + \mathbf{P}_6$
57	$\mathbf{I}_{24} \rightarrow \mathbf{I}_1 + \mathbf{P}_3$
58	$\mathbf{I}_{42} \rightarrow \mathbf{I}_1 + \mathbf{I}_{34}$
59	$\mathbf{I}_{43} \rightarrow \mathbf{I}_1 + \mathbf{I}_{37}$
60	$\mathbf{I}_{23} \rightarrow \mathbf{I}_1 + \mathbf{I}_{24}$
61	$\mathbf{I}_{45} \rightarrow \mathbf{I}_1 + \mathbf{P}_5$
62	$\mathbf{I}_4 + \mathbf{I}_{16} \rightarrow \mathbf{I}_1 + \mathbf{I}_{34}$
63	$\mathbf{I}_4 + \mathbf{I}_{17} \rightarrow \mathbf{I}_1 + \mathbf{I}_{37}$
64	$\mathbf{I}_1 + \mathbf{I}_{30} \rightarrow \mathbf{R}_3 + \mathbf{I}_{22}$
65	$\mathbf{I}_1 + \mathbf{I}_{31} \rightarrow \mathbf{R}_3 + \mathbf{I}_{21}$
66	$\mathbf{I}_1 + \mathbf{I}_{32} \rightarrow \mathbf{R}_3 + \mathbf{I}_{19}$
67	$\mathbf{I}_1 + \mathbf{I}_{35} \rightarrow \mathbf{R}_3 + \mathbf{P}_2$
68	$\mathbf{I}_1 + \mathbf{I}_3 \rightarrow \mathbf{R}_3 + \mathbf{I}_4$
69	$\mathbf{I}_1 + \mathbf{I}_4 \rightarrow \mathbf{R}_3 + \mathbf{P}_4$
70	$\mathbf{I}_1 + \mathbf{I}_{34} \rightarrow \mathbf{R}_3 + \mathbf{I}_{24}$
71	$\mathbf{I}_1 + \mathbf{I}_{39} \rightarrow \mathbf{R}_3 + \mathbf{I}_{42}$
72	$\mathbf{I}_1 + \mathbf{I}_{42} \rightarrow \mathbf{R}_3 + \mathbf{I}_{23}$
73	$\mathbf{I}_1 + \mathbf{I}_{37} \rightarrow \mathbf{R}_3 + \mathbf{P}_5$
74	$\mathbf{I}_1 + \mathbf{I}_{40} \rightarrow \mathbf{R}_3 + \mathbf{I}_{43}$
75	$\mathbf{I}_1 + \mathbf{I}_{43} \rightarrow \mathbf{R}_3 + \mathbf{I}_{45}$
76	$\mathbf{I}_1 + \mathbf{I}_{41} \rightarrow \mathbf{R}_3 + \mathbf{I}_{44}$
77	$\mathbf{I}_1 + \mathbf{I}_{44} \rightarrow \mathbf{R}_3 + \mathbf{P}_7$
78	$\mathbf{R}_3 + \mathbf{I}_{17} \rightarrow \mathbf{I}_1 + \mathbf{I}_{16}$
79	$\mathbf{R}_3 + \mathbf{I}_{31} \rightarrow \mathbf{I}_1 + \mathbf{I}_{30}$
80	$\mathbf{R}_3 + \mathbf{P}_6 \rightarrow \mathbf{I}_1 + \mathbf{I}_{17}$
81	$\mathbf{R}_3 + \mathbf{I}_{32} \rightarrow \mathbf{I}_1 + \mathbf{I}_{31}$
82	$\mathbf{R}_3 + \mathbf{I}_{35} \rightarrow \mathbf{I}_1 + \mathbf{I}_{32}$
83	$\mathbf{R}_3 + \mathbf{I}_{21} \rightarrow \mathbf{I}_1 + \mathbf{I}_{22}$
84	$\mathbf{R}_3 + \mathbf{I}_{19} \rightarrow \mathbf{I}_1 + \mathbf{I}_{21}$
85	$\mathbf{R}_3 + \mathbf{P}_2 \rightarrow \mathbf{I}_1 + \mathbf{I}_{19}$
86	$\mathbf{R}_3 + \mathbf{I}_7 \rightarrow \mathbf{I}_1 + \mathbf{I}_5$
87	$\mathbf{R}_3 + \mathbf{I}_6 \rightarrow \mathbf{I}_1 + \mathbf{I}_7$
88	$\mathbf{R}_3 + \mathbf{I}_5 \rightarrow \mathbf{I}_1 + \mathbf{I}_6$
89	$\mathbf{R}_3 + \mathbf{P}_1 \rightarrow \mathbf{I}_1 + \mathbf{I}_5$
90	$\mathbf{R}_3 + \mathbf{I}_{37} \rightarrow \mathbf{I}_1 + \mathbf{I}_{34}$
91	$\mathbf{R}_3 + \mathbf{P}_5 \rightarrow \mathbf{I}_1 + \mathbf{I}_{24}$
92	$\mathbf{R}_3 + \mathbf{I}_{40} \rightarrow \mathbf{I}_1 + \mathbf{I}_{39}$
93	$\mathbf{R}_3 + \mathbf{I}_{43} \rightarrow \mathbf{I}_1 + \mathbf{I}_{42}$
94	$\mathbf{R}_3 + \mathbf{I}_{41} \rightarrow \mathbf{I}_1 + \mathbf{I}_{40}$
95	$\mathbf{R}_3 + \mathbf{I}_{44} \rightarrow \mathbf{I}_1 + \mathbf{I}_{43}$
96	$\mathbf{R}_3 + \mathbf{I}_{45} \rightarrow \mathbf{I}_1 + \mathbf{I}_{23}$
97	$\mathbf{R}_3 + \mathbf{P}_7 \rightarrow \mathbf{I}_1 + \mathbf{I}_{45}$
98	$\mathbf{I}_1 + \mathbf{I}_{16} \rightarrow \mathbf{I}_{31}$
99	$\mathbf{I}_1 + \mathbf{I}_{17} \rightarrow \mathbf{I}_{32}$
100	$\mathbf{I}_1 + \mathbf{P}_6 \rightarrow \mathbf{I}_{35}$
101	$\mathbf{I}_1 + \mathbf{I}_{34} \rightarrow \mathbf{I}_{40}$
102	$\mathbf{I}_1 + \mathbf{I}_{24} \rightarrow \mathbf{I}_{43}$
103	$\mathbf{I}_1 + \mathbf{I}_{37} \rightarrow \mathbf{I}_{41}$
104	$\mathbf{I}_1 + \mathbf{P}_5 \rightarrow \mathbf{I}_{44}$
105	$\mathbf{I}_1 + \mathbf{P}_3 \rightarrow \mathbf{I}_{37}$
106	$\mathbf{R}_3 + \mathbf{I}_{22} \rightarrow \mathbf{I}_1 + \mathbf{I}_{30}$
107	$\mathbf{R}_3 + \mathbf{I}_{21} \rightarrow \mathbf{I}_1 + \mathbf{I}_{31}$
108	$\mathbf{R}_3 + \mathbf{I}_{19} \rightarrow \mathbf{I}_1 + \mathbf{I}_{32}$
109	$\mathbf{R}_3 + \mathbf{P}_2 \rightarrow \mathbf{I}_1 + \mathbf{I}_{35}$
110	$\mathbf{R}_3 + \mathbf{I}_4 \rightarrow \mathbf{I}_1 + \mathbf{I}_3$
111	$\mathbf{R}_3 + \mathbf{I}_{24} \rightarrow \mathbf{I}_1 + \mathbf{I}_{34}$
112	$\mathbf{R}_3 + \mathbf{I}_{42} \rightarrow \mathbf{I}_1 + \mathbf{I}_{39}$
113	$\mathbf{R}_3 + \mathbf{P}_5 \rightarrow \mathbf{I}_1 + \mathbf{I}_{37}$
114	$\mathbf{R}_3 + \mathbf{I}_{43} \rightarrow \mathbf{I}_1 + \mathbf{I}_{40}$
115	$\mathbf{R}_3 + \mathbf{I}_{44} \rightarrow \mathbf{I}_1 + \mathbf{I}_{41}$
116	$\mathbf{R}_3 + \mathbf{I}_{23} \rightarrow \mathbf{I}_1 + \mathbf{I}_{42}$
117	$\mathbf{R}_3 + \mathbf{I}_{45} \rightarrow \mathbf{I}_1 + \mathbf{I}_{43}$
118	$\mathbf{R}_3 + \mathbf{P}_7 \rightarrow \mathbf{I}_1 + \mathbf{I}_{44}$
119	$\mathbf{R}_3 + \mathbf{P}_4 \rightarrow \mathbf{I}_1 + \mathbf{I}_4$
120	$\mathbf{R}_3 + \mathbf{I}_{17} \rightarrow \mathbf{I}_{31}$
121	$\mathbf{R}_3 + \mathbf{P}_6 \rightarrow \mathbf{I}_{32}$
122	$\mathbf{R}_3 + \mathbf{I}_{34} \rightarrow \mathbf{I}_{39}$
123	$\mathbf{R}_3 + \mathbf{I}_{24} \rightarrow \mathbf{I}_{42}$
124	$\mathbf{R}_3 + \mathbf{I}_{37} \rightarrow \mathbf{I}_{40}$
125	$\mathbf{R}_3 + \mathbf{P}_5 \rightarrow \mathbf{I}_{43}$
126	$\mathbf{R}_3 + \mathbf{P}_3 \rightarrow \mathbf{I}_{34}$
127	$\mathbf{R}_2 + \mathbf{I}_{22} \rightarrow \mathbf{I}_1 + \mathbf{I}_{21}$
128	$\mathbf{R}_2 + \mathbf{I}_{21} \rightarrow \mathbf{I}_1 + \mathbf{I}_{19}$
129	$\mathbf{R}_2 + \mathbf{I}_{19} \rightarrow \mathbf{I}_1 + \mathbf{P}_2$
130	$\mathbf{R}_2 + \mathbf{I}_7 \rightarrow \mathbf{I}_1 + \mathbf{I}_6$
131	$\mathbf{R}_2 + \mathbf{I}_6 \rightarrow \mathbf{I}_1 + \mathbf{I}_5$
132	$\mathbf{R}_2 + \mathbf{I}_5 \rightarrow \mathbf{I}_1 + \mathbf{P}_1$
133	$\mathbf{R}_2 + \mathbf{I}_2 \rightarrow \mathbf{I}_1 + \mathbf{I}_7$
134	$\mathbf{R}_2 + \mathbf{I}_{39} \rightarrow \mathbf{I}_1 + \mathbf{I}_{40}$
135	$\mathbf{R}_2 + \mathbf{I}_{42} \rightarrow \mathbf{I}_1 + \mathbf{I}_{43}$
136	$\mathbf{R}_2 + \mathbf{I}_{40} \rightarrow \mathbf{I}_1 + \mathbf{I}_{41}$
137	$\mathbf{R}_2 + \mathbf{I}_{43} \rightarrow \mathbf{I}_1 + \mathbf{I}_{44}$
138	$\mathbf{R}_2 + \mathbf{I}_{23} \rightarrow \mathbf{I}_1 + \mathbf{I}_{45}$
139	$\mathbf{R}_2 + \mathbf{I}_{45} \rightarrow \mathbf{I}_1 + \mathbf{P}_7$
140	$\mathbf{R}_2 + \mathbf{I}_3 \rightarrow \mathbf{I}_1 + \mathbf{I}_4$
141	$\mathbf{R}_2 + \mathbf{I}_4 \rightarrow \mathbf{I}_1 + \mathbf{P}_4$
142	$\mathbf{R}_2 + \mathbf{I}_{34} \rightarrow \mathbf{I}_1 + \mathbf{I}_{24}$
143	$\mathbf{R}_2 + \mathbf{I}_{39} \rightarrow \mathbf{I}_1 + \mathbf{I}_{42}$
144	$\mathbf{R}_2 + \mathbf{I}_{42} \rightarrow \mathbf{I}_1 + \mathbf{I}_{23}$
145	$\mathbf{R}_2 + \mathbf{I}_{37} \rightarrow \mathbf{I}_1 + \mathbf{P}_5$
146	$\mathbf{R}_2 + \mathbf{I}_{40} \rightarrow \mathbf{I}_1 + \mathbf{I}_{43}$
147	$\mathbf{R}_2 + \mathbf{I}_{43} \rightarrow \mathbf{I}_1 + \mathbf{I}_{45}$
148	$\mathbf{R}_2 + \mathbf{I}_{41} \rightarrow \mathbf{I}_1 + \mathbf{I}_{44}$
149	$\mathbf{R}_2 + \mathbf{I}_{44} \rightarrow \mathbf{I}_1 + \mathbf{P}_7$
150	$\mathbf{I}_4 + \mathbf{I}_{16} \rightarrow \mathbf{I}_{42}$
151	$\mathbf{I}_4 + \mathbf{I}_{17} \rightarrow \mathbf{I}_{43}$
152	$\mathbf{I}_4 + \mathbf{P}_6 \rightarrow \mathbf{I}_{44}$
153	$\mathbf{I}_7 + \mathbf{I}_{24} \rightarrow \mathbf{I}_6 + \mathbf{I}_{34}$
154	$\mathbf{I}_7 + \mathbf{I}_{42} \rightarrow \mathbf{I}_6 + \mathbf{I}_{39}$
155	$\mathbf{I}_7 + \mathbf{P}_5 \rightarrow \mathbf{I}_6 + \mathbf{I}_{37}$
156	$\mathbf{I}_7 + \mathbf{I}_{43} \rightarrow \mathbf{I}_6 + \mathbf{I}_{40}$
157	$\mathbf{I}_7 + \mathbf{I}_{44} \rightarrow \mathbf{I}_6 + \mathbf{I}_{41}$
158	$\mathbf{I}_7 + \mathbf{I}_{23} \rightarrow \mathbf{I}_6 + \mathbf{I}_{42}$
159	$\mathbf{I}_7 + \mathbf{I}_{45} \rightarrow \mathbf{I}_6 + \mathbf{I}_{43}$
160	$\mathbf{I}_7 + \mathbf{P}_7 \rightarrow \mathbf{I}_6 + \mathbf{I}_{44}$
161	$\mathbf{I}_7 + \mathbf{P}_4 \rightarrow \mathbf{I}_4 + \mathbf{I}_6$
162	$\mathbf{I}_6 + \mathbf{I}_{24} \rightarrow \mathbf{I}_5 + \mathbf{I}_{34}$
163	$\mathbf{I}_6 + \mathbf{I}_{42} \rightarrow \mathbf{I}_5 + \mathbf{I}_{39}$
164	$\mathbf{I}_6 + \mathbf{P}_5 \rightarrow \mathbf{I}_5 + \mathbf{I}_{37}$
165	$\mathbf{I}_6 + \mathbf{I}_{43} \rightarrow \mathbf{I}_5 + \mathbf{I}_{40}$
166	$\mathbf{I}_6 + \mathbf{I}_{44} \rightarrow \mathbf{I}_5 + \mathbf{I}_{41}$
167	$\mathbf{I}_6 + \mathbf{I}_{23} \rightarrow \mathbf{I}_5 + \mathbf{I}_{42}$
168	$\mathbf{I}_6 + \mathbf{I}_{45} \rightarrow \mathbf{I}_5 + \mathbf{I}_{43}$
169	$\mathbf{I}_6 + \mathbf{P}_7 \rightarrow \mathbf{I}_5 + \mathbf{I}_{44}$
170	$\mathbf{I}_6 + \mathbf{P}_4 \rightarrow \mathbf{I}_4 + \mathbf{I}_5$
171	$\mathbf{I}_5 + \mathbf{I}_{24} \rightarrow \mathbf{P}_1 + \mathbf{I}_{34}$
172	$\mathbf{I}_5 + \mathbf{I}_{42} \rightarrow \mathbf{P}_1 + \mathbf{I}_{39}$
173	$\mathbf{I}_5 + \mathbf{P}_5 \rightarrow \mathbf{P}_1 + \mathbf{I}_{37}$
174	$\mathbf{I}_5 + \mathbf{I}_{43} \rightarrow \mathbf{P}_1 + \mathbf{I}_{40}$
175	$\mathbf{I}_5 + \mathbf{I}_{44} \rightarrow \mathbf{P}_1 + \mathbf{I}_{41}$
176	$\mathbf{I}_5 + \mathbf{I}_{23} \rightarrow \mathbf{P}_1 + \mathbf{I}_{42}$
177	$\mathbf{I}_5 + \mathbf{I}_{45} \rightarrow \mathbf{P}_1 + \mathbf{I}_{43}$
178	$\mathbf{I}_5 + \mathbf{P}_7 \rightarrow \mathbf{P}_1 + \mathbf{I}_{44}$
179	$\mathbf{I}_5 + \mathbf{P}_4 \rightarrow \mathbf{P}_1 + \mathbf{I}_4$
180	$\mathbf{I}_2 + \mathbf{I}_{24} \rightarrow \mathbf{I}_7 + \mathbf{I}_{34}$
181	$\mathbf{I}_2 + \mathbf{I}_{42} \rightarrow \mathbf{I}_7 + \mathbf{I}_{39}$
182	$\mathbf{I}_2 + \mathbf{P}_5 \rightarrow \mathbf{I}_7 + \mathbf{I}_{37}$
183	$\mathbf{I}_2 + \mathbf{I}_{43} \rightarrow \mathbf{I}_7 + \mathbf{I}_{40}$
184	$\mathbf{I}_2 + \mathbf{I}_{44} \rightarrow \mathbf{I}_7 + \mathbf{I}_{41}$
185	$\mathbf{I}_2 + \mathbf{I}_{23} \rightarrow \mathbf{I}_7 + \mathbf{I}_{42}$
186	$\mathbf{I}_2 + \mathbf{I}_{45} \rightarrow \mathbf{I}_7 + \mathbf{I}_{43}$
187	$\mathbf{I}_2 + \mathbf{P}_7 \rightarrow \mathbf{I}_7 + \mathbf{I}_{44}$
188	$\mathbf{I}_2 + \mathbf{P}_4 \rightarrow \mathbf{I}_7 + \mathbf{I}_5$
189	$\mathbf{I}_{37} \rightarrow \mathbf{I}_1 + \mathbf{P}_3$
190	$\mathbf{I}_{40} \rightarrow \mathbf{I}_1 + \mathbf{I}_{34}$
191	$\mathbf{I}_{43} \rightarrow \mathbf{I}_1 + \mathbf{I}_{24}$
192	$\mathbf{I}_{41} \rightarrow \mathbf{I}_1 + \mathbf{I}_{37}$
193	$\mathbf{I}_{44} \rightarrow \mathbf{I}_1 + \mathbf{P}_3$
194	$\mathbf{I}_1 + \mathbf{I}_{24} \rightarrow \mathbf{R}_2 + \mathbf{I}_{34}$
195	$\mathbf{I}_1 + \mathbf{I}_{42} \rightarrow \mathbf{R}_2 + \mathbf{I}_{39}$
196	$\mathbf{I}_1 + \mathbf{P}_5 \rightarrow \mathbf{R}_2 + \mathbf{I}_{37}$
197	$\mathbf{I}_1 + \mathbf{I}_{43} \rightarrow \mathbf{R}_2 + \mathbf{I}_{40}$
198	$\mathbf{I}_1 + \mathbf{I}_{44} \rightarrow \mathbf{R}_2 + \mathbf{I}_{41}$
199	$\mathbf{I}_1 + \mathbf{I}_{23} \rightarrow \mathbf{R}_2 + \mathbf{I}_{42}$
200	$\mathbf{I}_1 + \mathbf{I}_{45} \rightarrow \mathbf{R}_2 + \mathbf{I}_{43}$
201	$\mathbf{I}_1 + \mathbf{P}_7 \rightarrow \mathbf{R}_2 + \mathbf{I}_{44}$
202	$\mathbf{I}_1 + \mathbf{P}_4 \rightarrow \mathbf{R}_2 + \mathbf{I}_4$
203	$\mathbf{R}_3 + \mathbf{I}_{34} \rightarrow \mathbf{I}_3 + \mathbf{I}_{16}$
204	$\mathbf{R}_3 + \mathbf{I}_{24} \rightarrow \mathbf{I}_4 + \mathbf{I}_{16}$
205	$\mathbf{R}_3 + \mathbf{I}_{39} \rightarrow \mathbf{I}_3 + \mathbf{I}_{30}$
206	$\mathbf{R}_3 + \mathbf{I}_{42} \rightarrow \mathbf{I}_3 + \mathbf{I}_{22}$
207	$\mathbf{R}_3 + \mathbf{I}_{42} \rightarrow \mathbf{I}_4 + \mathbf{I}_{30}$
208	$\mathbf{R}_3 + \mathbf{I}_{37} \rightarrow \mathbf{I}_3 + \mathbf{I}_{17}$
209	$\mathbf{R}_3 + \mathbf{P}_5 \rightarrow \mathbf{I}_4 + \mathbf{I}_{17}$
210	$\mathbf{R}_3 + \mathbf{I}_{40} \rightarrow \mathbf{I}_3 + \mathbf{I}_{31}$
211	$\mathbf{R}_3 + \mathbf{I}_{43} \rightarrow \mathbf{I}_3 + \mathbf{I}_{21}$
212	$\mathbf{R}_3 + \mathbf{I}_{43} \rightarrow \mathbf{I}_4 + \mathbf{I}_{31}$
213	$\mathbf{R}_3 + \mathbf{I}_{41} \rightarrow \mathbf{I}_3 + \mathbf{I}_{32}$
214	$\mathbf{R}_3 + \mathbf{I}_{44} \rightarrow \mathbf{I}_3 + \mathbf{I}_{19}$
215	$\mathbf{R}_3 + \mathbf{I}_{44} \rightarrow \mathbf{I}_4 + \mathbf{I}_{32}$
216	$\mathbf{R}_3 + \mathbf{I}_{23} \rightarrow \mathbf{I}_4 + \mathbf{I}_{22}$
217	$\mathbf{R}_3 + \mathbf{I}_{45} \rightarrow \mathbf{I}_4 + \mathbf{I}_{21}$
218	$\mathbf{R}_3 + \mathbf{P}_7 \rightarrow \mathbf{I}_4 + \mathbf{I}_{19}$
219	$\mathbf{I}_{16} + \mathbf{P}_4 \rightarrow \mathbf{I}_1 + \mathbf{I}_{24}$
220	$\mathbf{I}_{17} + \mathbf{P}_4 \rightarrow \mathbf{I}_1 + \mathbf{P}_5$

Note. $\mathbf{R}_1$ = CO, $\mathbf{R}_2$ = H_2, $\mathbf{R}_3$ = MM; $\mathbf{P}_1$ is CH_4, $\mathbf{P}_2$ is CH_3OH, $\mathbf{P}_3$ is CO_2, $\mathbf{P}_4$ is H_2O, $\mathbf{P}_5$ is HCOOH, $\mathbf{P}_6$ is CH_2O, $\mathbf{P}_7$ is $CH_2(OH)_2$; **I** are intermediates (see Figs. 1—4).

* The number of steps in the reaction network.

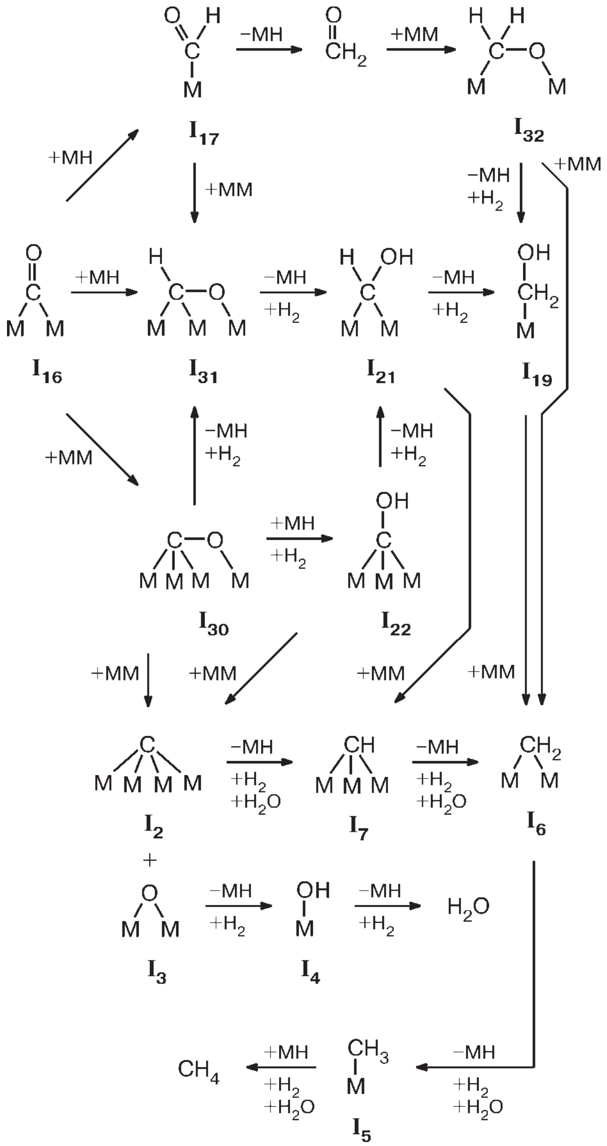


Fig. 7. Reaction network for methane formation (reaction (56)).

The reaction networks generated using the ChemNet program include large numbers of pathways to the same or several substances formed in conjugation. Each pathway can be extracted from the network and subjected to discrimination using theoretical or experimental data. In the reaction networks of the Fischer—Tropsch synthesis, groups of pathways with slight differences can be found. In some cases, they are analogs of the same literature scheme. In addition, they have differences that are rather important for the construction of kinetic equations. Pathway 2 is a good example to support this statement, as it is a carbide mechanism of methane formation, although differing by the fact that hydrogenation occurs with gaseous H_2 (by the Eley—Rideal mechanism) rather than in the traditional catalytic manner (*i.e.*, with preliminary hydrogen activation and dissociation).

Pathway 2

2.1. $CO + MM \rightarrow M_2CO$,
2.2. $M_2CO + MM \rightarrow M_3COM$,
2.3. $M_3COM + MM \rightarrow M_4C + M_2O$,
2.4. $M_2O + H_2 \rightarrow MOH + MH$,
2.5. $MOH + MH \rightarrow H_2O + MM$,
2.6. $M_4C + H_2 \rightarrow M_3CH + MH$,
2.7. $M_3CH + MH \rightarrow M_2CH_2 + MM$,
2.8. $M_2CH_2 + H_2 \rightarrow MCH_3 + MH$,
2.9. $MCH_3 + MH \rightarrow CH_4 + MM$.

Pathway 3 is a hydrolytic version of the carbide mechanism in which the conversion of the surface carbide into methane is done by water evolved during the process rather than by H_2 molecules. Steps (3.7)—(3.10) are possible both for cobalt systems in which retardation of the Fischer—Tropsch synthesis by water molecules is virtually absent[375] but also for iron catalysts on which water does exert a retarding influence on the product formation.

Pathway 3

3.1. $CO + MM \rightarrow M_2CO$,
3.2. $H_2 + MM \rightarrow 2\ MH$,
3.3. $M_2CO + MM \rightarrow M_3COM$,
3.4. $M_3COM + MM \rightarrow M_4C + M_2O$,
3.5. $M_2O + MH \rightarrow MOH + MM$,
3.6. $MOH + MH \rightarrow H_2O + MM$,
3.7. $M_4C + H_2O \rightarrow M_3CH + MOH$,
3.8. $M_3CH + H_2O \rightarrow M_2CH_2 + MOH$,
3.9. $M_2CH_2 + H_2O \rightarrow MCH_3 + MOH$,
3.10. $MCH_3 + H_2O \rightarrow CH_4 + MOH$.

Pathway 4 is a fragment of the Fischer—Tropsch mechanism that was the second to be proposed, namely, the hydroxymethylene or "enol" mechanism,[245,246] which has now been completely refuted. The question of how the surface M=CH—OH groups can oligomerize still remains obscure. The way of hydroxymethylene formation from CO and H_2 has always been considered very sketchily and represented by one symbolic step. Pathway 4 fills this gap by presenting each step of formation of the intermediate in question. It can be seen that, compared with the carbide variant, methane is formed in the same way as in the schemes considered above starting from methylidyne M_3CH (except for the steps of dissociation of the C—O bond). Pathway 4 includes combined Eley—Rideal hydrogenation by the MH intermediate and by H_2. Undoubtedly, one could also distinguish other pathways with similar formation of hydroxymethylene in which the conversion of M_3CH into methane would involve only MH or, for example, partially involve water.

Pathway 4

4.1. $CO + MM \rightarrow M_2CO$,
4.2. $H_2 + MM \rightarrow 2\ MH$,
4.3. $M_2CO + MM \rightarrow M_3COM$,
4.4. $M_3COM + MH \rightarrow M_3COH + MM$,
4.5. $M_3COH + MH \rightarrow M_2CH(OH) + MM$,
4.6. $M_2CH(OH) + MM \rightarrow M_3CH + MOH$,
4.7. $MOH + MH \rightarrow H_2O + MM$,
4.8. $M_3CH + MH \rightarrow M_2CH_2 + MM$,
4.9. $M_2CH_2 + H_2 \rightarrow MCH_3 + MH$,
4.10. $MCH_3 + MH \rightarrow CH_4 + MM$.

Pathway 5 is one more type of the hydroxymethylene mechanism that comprises other steps leading to =CH—OH and differs in the routes by which this species is converted into oxygen-free intermediates and then to methane. Owing to some features (formation of the π-coordinated formyl group in step (5.3)), the appearance of the hydroxymethyl fragment giving rise to methylene), this pathway resembles the routes based on CO insertion, which are considered below.

Pathway 5

5.1. $CO + MM \rightarrow M_2CO$,
5.2. $H_2 + MM \rightarrow 2\ MH$,
5.3. $M_2CO + MH \rightarrow M_2CHOM$,
5.4. $M_2CHOM + MH \rightarrow M_2CH(OH) + MM$,
5.5. $M_2CH(OH) + MH \rightarrow MCH_2OH + MM$,
5.6. $MOH + MH \rightarrow H_2O + MM$,
5.7. $MCH_2OH + MM \rightarrow M_2CH_2 + MOH$,
5.8. $M_2CH_2 + MH \rightarrow MCH_3 + MM$,
5.9. $MCH_3 + MH \rightarrow CH_4 + MM$.

The insertion mechanisms to give formyl type intermediates are represented by pathways 6 and 7. The former reproduces almost exactly the Pichler—Schulz mechanism [223] giving rise to formyl and π-coordinated formaldehyde, which is then cleaved to give methylene and the surface oxygen.

Pathway 6

6.1. $CO + MM \rightarrow M_2CO$,
6.2. $H_2 + MM \rightarrow 2\ MH$,
6.3. $M_2CO + MH \rightarrow MCHO + MM$,
6.4. $MCHO + MH \rightarrow MOCH_2M$,
6.5. $MOCH_2M + MM \rightarrow M_2CH_2 + M_2O$,
6.6. $M_2CH_2 + H_2 \rightarrow MCH_3 + MH$,
6.7. $MCH_3 + MH \rightarrow CH_4 + MM$,
6.8. $M_2O + MH \rightarrow MOH + MM$,
6.9. $MOH + MH \rightarrow H_2O + MM$.

Pathway 7 is an approach to another, more popular variant of the insertion mechanism, which is based almost entirely on analogies with reactions of metal complexes.[224] In terms of the reaction network variant considered here, the published scheme cannot be strictly reproduced because the direct insertion of formaldehyde weakly bound to the surface into the M—H bond giving hydroxymethyl was forbidden in the set of transforms. However, steps (7.5) and (7.6) eliminate this discrepancy and, in other respects, the literature scheme proves to be reproduced in more detail, as in the previous cases.

Pathway 7

7.1. $CO + MM \rightarrow M_2CO$,
7.2. $H_2 + MM \rightarrow 2\ MH$,
7.3. $M_2CO + MH \rightarrow MCHO + MM$,
7.4. $MCHO + MH \rightarrow CH_2O + MM$,
7.5. $CH_2O + MM \rightarrow MOCH_2M$,
7.6. $MOCH_2M + MH \rightarrow MCH_2OH + M_2O$,
7.7. $MCH_2OH + MM \rightarrow M_2CH_2 + MOH$,
7.8. $M_2CH_2 + MH \rightarrow MCH_3 + MM$,
7.9. $MCH_3 + MH \rightarrow CH_4 + MM$,
7.10. $MOH + MH \rightarrow H_2O + MM$.

Unfortunately, the variant of the reaction network considered here does not imply a mechanism for methane formation directly during the dissociation of the C—O single bond in the M—OCH_3 intermediate.[118,356] However, other sets of transforms (for example, variant **VIII** of the reaction network) do contain this mechanism.

The network also includes routes having no published analogs. Thus pathway 8 combines features of the classical set of insertion mechanisms with participation of the formyl group and the mechanisms to give hydroxymethylene.

Pathway 8

8.1. $CO + MM \rightarrow M_2CO$,
8.2. $H_2 + MM \rightarrow 2\ MH$,
8.3. $M_2CO + MH \rightarrow MCHO + MM$,
8.4. $MCHO + MM \rightarrow M_2CHOM$,
8.5. $M_2CHOM + MH \rightarrow M_2CH(OH) + MM$,
8.6. $M_2CH(OH) + MM \rightarrow M_3CH + MOH$,
8.7. $M_3CH + MH \rightarrow M_2CH_2 + MM$,

8.8. $M_2O + MH \rightarrow MOH + MM$,
8.9. $MCH_3 + MH \rightarrow CH_4 + MM$,
8.10. $MOH + MH \rightarrow H_2O + MM$.

Pathway 9 implies the intermediate formation of methanol (*via* the surface formaldehyde $MOCH_2M$), which is followed by repeated adsorption of methanol to give hydroxymethyl (apparently, these two steps could proceed on various types of surface centers).

Pathway 9

9.1. $CO + MM \rightarrow M_2CO$,
9.2. $H_2 + MM \rightarrow 2\ MH$,
9.3. $M_2CO + MH \rightarrow MCHO + MM$,
9.4. $MCHO + MH \rightarrow MOCH_2M$,
9.5. $MOCH_2M + MM \rightarrow MOCH_3$,
9.6. $MOCH_3 + MH \rightarrow CH_3OH + MM$,
9.7. $CH_3OH + MM \rightarrow MCH_2OH + MH$,
9.8. $MCH_2OH + MM \rightarrow M_2CH_2 + MOH$,
9.9. $M_2CH_2 + MH \rightarrow MCH_3 + MM$,
9.10. $MCH_3 + MH \rightarrow CH_4 + MM$,
9.11. $MOH + MH \rightarrow H_2O + MM$.

Pathway 10 is a combination of various ways of hydrogenation of the intermediates along the carbide—methane series and includes an unusual pathway to the carbide itself from coordinated CO (*via* the M_3COH intermediate).

Pathway 10

10.1. $CO + MM \rightarrow M_2CO$,
10.2. $H_2 + MM \rightarrow 2\ MH$,
10.3. $M_2CO + MH \rightarrow M_3COM$,
10.4. $M_3COM + H_2 \rightarrow M_3COH + MM$,
10.5. $M_3COH + MM \rightarrow M_4C + MOH$,
10.6. $M_4C + H_2O \rightarrow M_3CH + MOH$,
10.7. $M_3CH + MH \rightarrow M_2CH_2 + MM$,
10.8. $M_2CH_2 + H_2 \rightarrow MCH_3 + MH$,
10.9. $MCH_3 + MH \rightarrow CH_4 + MM$,
10.10. $MOH + MH \rightarrow H_2O + MM$.

Let us dwell on the scheme proposed for fused iron catalysts [374] that implies the formation of one-carbon products from a common precursor, the surface COH_2 complex, and the surface carbide C atoms. These atoms are hydrogenated, apparently, at different stages of the process giving rise to surface defects, which serve as the active sites for the Fischer—Tropsch synthesis. The reaction resulting in the formation of these defects should generally be written as follows:

$$2\ CO + 4\ H_2 \rightarrow CH_4 + 2\ H_2O + C\ (ads.). \qquad (57)$$

The pathway that reproduces this scheme[374] and is present in the reaction network can be represented in the following way.

Pathway 11

11.1. $CO + MM \rightarrow M_2CO$,
11.2. $H_2 + MM \rightarrow 2\ MH$,
11.3. $M_2CO + MH \rightarrow MCHO + MM$,
11.4. $MCHO + MH \rightarrow M_2CH(OH)$,
11.5. $M_2CH(OH) + MM \rightarrow M_3CH + MOH$,
11.6. $M_3CH + MH \rightarrow M_2CH_2 + MM$,
11.7. $M_2CH_2 + MH \rightarrow MCH_3 + MM$,
11.8. $MCH_3 + MH \rightarrow CH_4 + MM$,
11.9. $M_3CH + MM \rightarrow M_4C + MH$,
11.10. $MOH + MH \rightarrow H_2O + MM$.

Here, the surface methylidyne arising from the COH_2 fragment (step (11.5)) is converted along two opposite directions furnishing methane after stepwise hydrogenation (steps (11.6)—(11.8)) and carbide after dehydrogenation (11.9). In this case, we assume that the COH_2 species is hydroxymethylene (steps (11.4) and (11.5)), although it can be considered as coordinated formaldehyde.

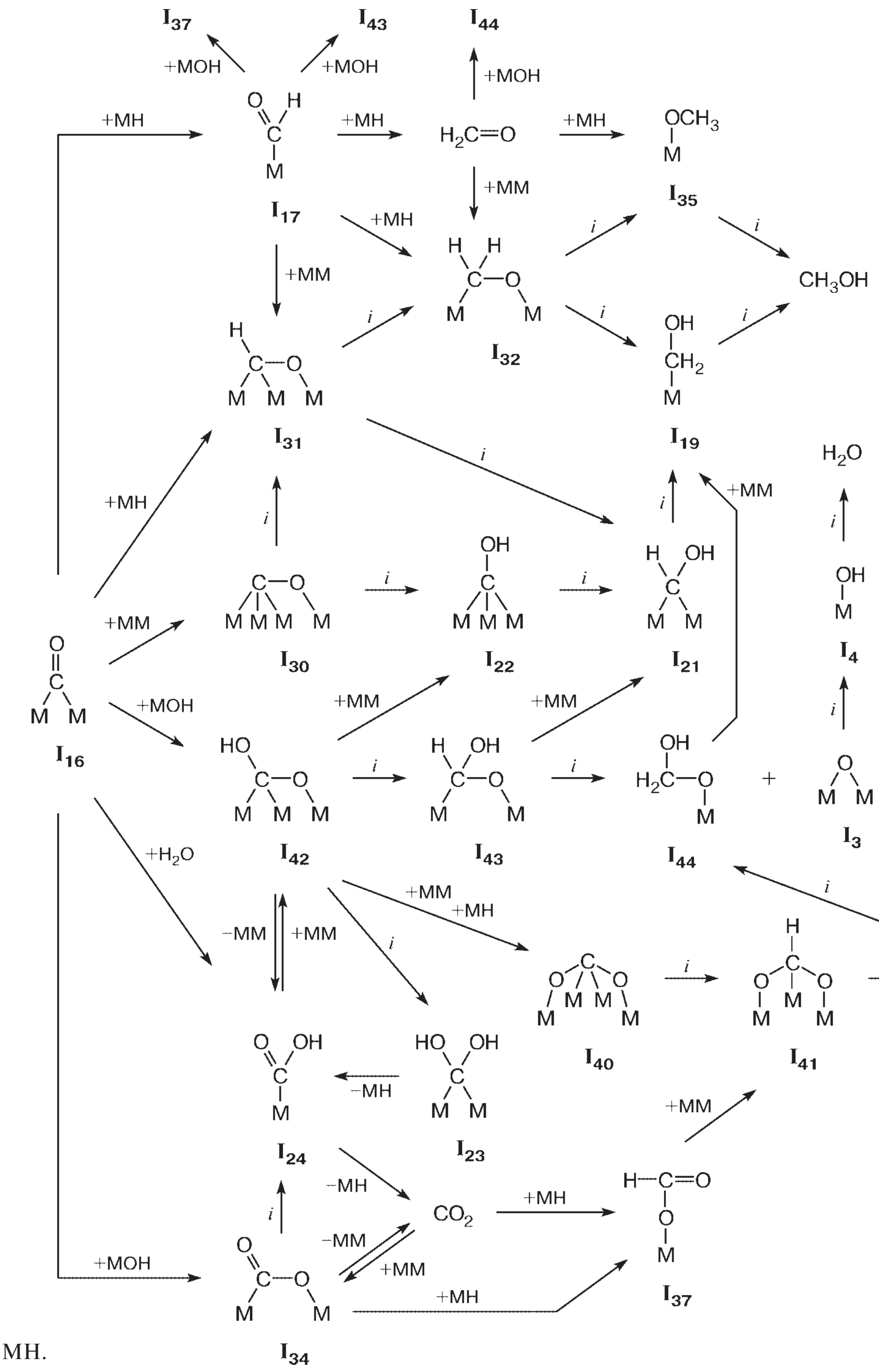
4.2. Methanol formation

Now we consider the reaction giving methanol

$$CO + 2\ H_2 \rightarrow CH_3OH. \qquad (58)$$

For this reaction, a more complicated sub-network can be distinguished (Fig. 8), which includes, in addition to the proper steps of methanol formation, a set of steps with formation and transformations of CO_2. Methanol is formed directly from two intermediates, $MOCH_3$ (**I_{35}**) and MCH_2OH (**I_{19}**). It is evident that the number of different pathways that can be derived from the given sub-network can be greater than that in the case of methane and water formation. Here, we present seven most interesting pathways selected according to the same principles as the routes resulting in methane, namely, reproduction of literature schemes and the appearance of new routes of CO transformation.

The first two pathways have been considered[11] as possible routes for the zinc-chromium catalysts. Both alternative variants of the insertion of intermediate formaldehyde into the M—H bond to give either hydroxymethyl or methoxy are presented: in the former case, formaldehyde is μ-η^2-coordinated (steps (1.4) and (1.5)), while in the latter case, it remains free (steps (2.4) and (2.5)). Pathway 1 is a part of above-described pathway 6 (see Section 4.1).[223]



i. $+H_2$, +MH.

Fig. 8. Reaction network for methanol formation (reaction (58)).

Pathway 1

1.1. $CO + MM \rightarrow M_2CO$,
1.2. $H_2 + MM \rightarrow 2\ MH$,
1.3. $M_2CO + MH \rightarrow MCHO + MM$,
1.4. $MCHO + MH \rightarrow MOCH_2M$,
1.5. $MOCH_2M + MH \rightarrow MCH_2OH + MM$,
1.6. $MCH_2OH + MH \rightarrow CH_3OH + MM$.

Pathway 2

2.1. $CO + MM \rightarrow M_2CO$,
2.2. $H_2 + MM \rightarrow 2\ MH$,
2.3. $M_2CO + MH \rightarrow MCHO + MM$,
2.4. $MCHO + MH \rightarrow CH_2O + MM$,
2.5. $CH_2O + MH \rightarrow MOCH_3$,
2.6. $MOCH_3 + MH \rightarrow CH_3OH + MM$.

The synthesis of methanol from CO on copper-containing catalysts proceeds *via* the formation of CO_2.[376,377] The mechanism of this process discussed most often in the literature assumes the successive reactions of the adsorbed CO_2 with hydrogen to give the MCO_2H_2 intermediate and then methanol and water, the latter being involved in a new catalytic cycle.[84,378] This mechanism was used, first of all, for formal-kinetics description of the process; therefore, it contains little data on the nature of intermediates. Mechanism 3 and 4 are detailed reproductions of this mechanism, which includes both the CO_2 formation and multistep transformation into methanol. The formation of CO_2 proceeds *via* either η^2-chemisorbed carbon dioxide or the surface carboxyl group. The hypothetical $CO_2H_{2\,ads}$ intermediate has the M—OCH_2O—M structure in pathway 3 or the M—OCH(OH)—M structure in pathway 4.

Pathway 3

3.1. $CO + MM \rightarrow M_2CO$,

3.2. $H_2 + MM \rightarrow 2\,MH$,

3.3. $H_2O + MM \rightarrow MOH + MH$,

3.4. $M_2CO + MOH \rightarrow MOC(O)M + MH$,

3.5. $MOC(O)M \rightarrow CO_2 + MM$,

3.6. $CO_2 + MH \rightarrow MOCHO$,

3.7. $MOCHO + MH \rightarrow MOCH_2OM$,

3.8. $MOCH_2OM + MH \rightarrow$ $\rightarrow MOCH_2OH + MM$,

3.9. $MOCH_2OH + MM \rightarrow MCH_2OH + M_2O$,

3.10. $M_2O + MH \rightarrow MOH + MM$,

3.11. $MOH + MH \rightarrow H_2O + MM$,

3.12. $MCH_2OH + MH \rightarrow CH_3OH + MM$.

Pathway 4

4.1. $CO + MM \rightarrow M_2CO$,

4.2. $H_2 + MM \rightarrow 2\,MH$,

4.3. $M_2CO + H_2O \rightarrow MC(O)OH + MH$,

4.4. $MC(O)OH \rightarrow CO_2 + MH$,

4.5. $CO_2 + MH \rightarrow MOCHO$,

4.6. $MOCHO + MM \rightarrow MOCH(M)OM$,

4.7. $MOCH(M)OM + MH \rightarrow$ $\rightarrow MOCH(OH)M + MM$,

4.8. $MOCH(OH)M + MM \rightarrow$ $\rightarrow M_2CH(OH) + M_2O$,

4.9. $M_2CH(OH) + MH \rightarrow MCH_2OH + MM$,

4.10. $MCH_2OH + MH \rightarrow CH_3OH + MM$,

4.11. $M_2O + MH \rightarrow MOH + MM$,

4.12. $MOH + MH \rightarrow H_2O + MM$.

Other mechanisms of methanol formation on copper-containing catalysts are also known.[379—381] According to one of them, methanol is formed *via* the adsorbed CH_2O (MCH_2O), which arises directly from MCO_2. In another mechanism consisting of a greater number of steps, MCO_2 is converted into MCH_2O_2, which loses one oxygen atom being thus converted into methanol *via* MCH_2O. The role of CO in both mechanisms is to decrease the number of active sites upon adsorption, while the details of formation of CO_2 from CO are not discussed. In addition, the second mechanism contains a dead-end step giving the surface XCO_3 carbonate whose further role is obscure. Pathway 5 includes another route from CO to CO_2 (*via* $MOC(OH)M_2$, which is then converted into MCOOH) and reproduces in substantial detail the first of the proposed mechanisms.[379,380] The second mechanism implies the formation of carbonate and has no step of adsorption displacement of water by carbon dioxide. Nevertheless, it is a modification of pathway 4 considered previously involving MOCH(OH)M and $M_2CH(OH)$ intermediates (XCO_2H_2 and $XCOH_2$ [84])

Pathway 5

5.1. $CO + MM \rightarrow M_2CO$,

5.2. $H_2 + MM \rightarrow 2\,MH$,

5.3. $H_2O + MM \rightarrow MOH + MH$,

5.4. $M_2CO + MOH \rightarrow MOC(OH)M_2$,

5.5. $MOC(OH)M_2 \rightarrow MCOOH+MM$,

5.6. $MCOOH \rightarrow CO_2 + MH$,

5.7. $CO_2 + MH \rightarrow MOCHO$,

5.8. $MOCHO + MH \rightarrow MCHO + MOH$,

5.9. $MCHO + MH \rightarrow MCH_2OM$,

5.10. $MCH_2OM + MH \rightarrow MOCH_3 + MM$,

5.11. $MOH + MH \rightarrow H_2O + MM$,

5.12. $MOCH_3 + MH \rightarrow CH_3OH + MM$.

Pathway 6

6.1. $CO + MM \rightarrow M_2CO$,

6.2. $H_2 + MM \rightarrow 2\,MH$,

6.3. $M_2CO + MM \rightarrow M_3COM$,

6.4. $M_3COM + MH \rightarrow M_3COH + MM$,

6.5. $M_3COH + MH \rightarrow M_2CH(OH) + MM$,

6.6. $M_2CH(OH) + MH \rightarrow MCH_2OH + MM$,

6.7. $MCH_2OH + MH \rightarrow CH_3OH + MM$.

Yet another mechanism known from the literature[381] for the given reaction network is reproduced only partially. The first half of this mechanism coincides almost completely with the second scheme (the $XCO_2 \rightarrow XCO_2H_2 \rightarrow XCOH_2 \rightarrow$ methanol sequence of transformations.)[379,380] Presumably, this is followed by the complex step

$$CH_3OH + 2\,XO \rightarrow H_2 + H_2O + CO_2 + 2\,X,$$

which, like the last step of this pathway

$$CO + XO \rightarrow CO_2,$$

is not included in the given variant of the reaction network due to exclusion of transform **15**.2.

In view of the assumption[381] of the probability of various routes for the formation of XCO_2H_2, note that this scheme corresponds to a rather large sub-network in the reaction network consisting of 220 steps. Thus, the mechanism considered is a combination of pathways, which includes, in the main, fragments of the schemes discussed previously.[84,379,380]

There are two known mechanisms[382,383] that are not reproduced in any of the variants of the reaction network because they involve carbonate groups with three O atoms as intermediates. In this study, a constraint was imposed stating that any compound should contain not more than two oxygen atoms. The final steps of these mechanisms are fairly similar. One scheme is more detailed regarding partition into steps,[382] while the other one devotes more attention to the possible structure of the catalyst active site by providing for the transformation of the carbonate intermediate into the $MHCO_2$ group (formate-containing), which is then converted into the methoxy $MOCH_3$ (*via* H_2CO_{ads}) and then into methanol.[383] This aspect for both pathways can be reproduced quite adequately by pathway 5, although their schematic character allows one to consider that several similar routes corresponding to them can be cut out from the reaction network.

As in the case of methane formation, variant **III** of the reaction network contains mechanisms having no direct analogs in the literature. Pathway 6 is a detailed hydroxymethylene ("enol") mechanism of methanol formation from CO. Finally, pathway 7, representing a compromise between pathway 6 and more up-to-date views on the methanol synthesis on copper-containing catalysts *via* CO_2, includes an interesting intermediate ($MOC(OH)M_2$) containing two oxygen atoms. The formation of free CO_2 is not envisaged. Subsequently the above-mentioned intermediate is converted into known[64,379–382] adsorbed groups of the general composition CO_2H_2 and COH_2, and then it is converted into methanol through the traditional hydroxymethyl intermediate.

Pathway 7

7.1. $CO + MM \rightarrow M_2CO,$
7.2. $H_2 + MM \rightarrow 2\,MH,$
7.3. $H_2O + MM \rightarrow MOH + MH,$
7.4. $M_2CO + MOH \rightarrow MOC(OH)M_2,$
7.5. $MOC(OH)M_2 + H_2 \rightarrow MOCH(OH)M + MH,$
7.6. $MOCH(OH)M + MM \rightarrow$
$\rightarrow M_2CH(OH) + M_2O,$
7.7. $M_2CH(OH) + MH \rightarrow MCH_2OH + MM,$
7.8. $MCH_2OH + MH \rightarrow CH_3OH + MM,$
7.9. $M_2O + MH \rightarrow MOH + MM,$
7.10. $MOH + MH \rightarrow H_2O + MM.$

4.3. Coupled formation of methane and CO_2

Now we consider the possibility of coupled formation of CH_4 and CO_2 by the reaction

$$2\,CO + 2\,H_2 \rightarrow CH_4 + CO_2. \tag{59}$$

Many possible pathways exist in the reaction network for this transform, although they mainly prove to be somewhat extended mechanisms of methane formation by reaction (58). For example, there are examples of carbide mechanisms with different routes to carbon dioxide: (1) without evolution of water and with a somewhat unusual CO_2 precursor, MOC(O)M, (2) with intermediate evolution of water and CO_2 formation *via* MCOOH. Finally, there is an original variant 3 in which the carboxyl intermediate is not converted directly into CO_2 but participates in the partial acidolysis of the surface carbide to give adsorbed methylidyne and MOC(O)M, which is already known (this variant has not been proposed previously).

Pathway 1

1.1. $CO + MM \rightarrow M_2CO,$
1.2. $H_2 + MM \rightarrow 2\,MH,$
1.3. $M_2CO + MM \rightarrow M_3COM,$
1.4. $M_3COM + MM \rightarrow M_4C + M_2O,$
1.5. $M_2O + MH \rightarrow MOH + MM,$
1.6. $M_4C + MH \rightarrow M_3CH + MM,$
1.7. $M_3CH + MH \rightarrow M_2CH_2 + MM,$
1.8. $M_2CH_2 + MH \rightarrow MCH_3 + MM$
1.9. $MCH_3 + MH \rightarrow CH_4 + MM,$
1.10. $M_2CO + MOH \rightarrow MOC(O)M + MH,$
1.11. $MOC(O)M \rightarrow CO_2 + MM.$

Pathway 2

2.1. $CO + MM \rightarrow M_2CO,$
2.2. $H_2 + MM \rightarrow 2\,MH,$
2.3. $M_2CO + MM \rightarrow M_3COM,$
2.4. $M_3COM + MM \rightarrow M_4C + M_2O,$
2.5. $M_2O + MH \rightarrow MOH + MM,$
2.6. $MOH + MH \rightarrow H_2O + MM,$

2.7. $M_2CO + H_2O \rightarrow MCOOH + MH$,
2.8. $M_4C + MH \rightarrow M_3CH + MM$,
2.9. $M_3CH + MH \rightarrow M_2CH_2 + MM$,
2.10. $M_2CH_2 + MH \rightarrow MCH_3 + MM$,
2.11. $MCH_3 + MH \rightarrow CH_4 + MM$,
2.12. $MCOOH \rightarrow CO_2 + MH$,
2.13. $2\ MH \rightarrow H_2 + MM$.

Pathway 3

3.1. $CO + MM \rightarrow M_2CO$,
3.2. $H_2 + MM \rightarrow 2\ MH$,
3.3. $M_2CO + MM \rightarrow M_3COM$,
3.4. $M_3COM + MM \rightarrow M_4C + M_2O$,
3.5. $M_2O + MH \rightarrow MOH + MM$,
3.6. $MOH + MH \rightarrow H_2O + MM$,
3.7. $M_2CO + H_2O \rightarrow MCOOH + MH$,
3.8. $M_4C + MCOOH \rightarrow M_3CH + MOC(O)M$,
3.9. $M_3CH + MH \rightarrow M_2CH_2 + MM$,
3.10. $M_2CH_2 + MH \rightarrow MCH_3 + MM$,
3.11. $MCH_3 + MH \rightarrow CH_4 + MM$,
3.12. $MOC(O)M \rightarrow CO_2 + MM$.

4.4. Coupled formation of methane and formic acid

Now we present the mechanisms of coupled formation of CH_4 and HCOOH from common intermediates ($\mathbf{I_1}$—$\mathbf{I_4}$), which have barely received attention in the literature:

$$2\ CO + 3\ H_2 \rightarrow CH_4 + HCOOH. \qquad (60)$$

Pathway 1

1.1. $CO + MM \rightarrow M_2CO$,
1.2. $H_2 + MM \rightarrow 2\ MH$,
1.3. $M_2CO + MM \rightarrow M_3COM$,
1.4. $M_3COM + MM \rightarrow M_4C + M_2O$,
1.5. $M_2O + MH \rightarrow MOH + MM$,
1.6. $M_2CO + MH \rightarrow MCHO + MM$,
1.7. $MCHO + MOH \rightarrow MOCHO + MH$,
1.8. $MOCHO + MH \rightarrow HCOOH + MM$,
1.9. $M_4C + MH \rightarrow M_3CH + MM$,
1.10. $M_3CH + MH \rightarrow M_2CH_2 + MM$,
1.11. $M_2CH_2 + MH \rightarrow MCH_3 + MM$,
1.12. $MCH_3 + MH \rightarrow CH_4 + MM$.

Pathway 2

2.1. $CO + MM \rightarrow M_2CO$,
2.2. $H_2 + MM \rightarrow 2\ MH$,
2.3. $M_2CO + MM \rightarrow M_3COM$,
2.4. $M_3COM + MM \rightarrow M_4C + M_2O$,
2.5. $M_2O + MH \rightarrow MOH + MM$,
2.6. $M_2CO + MH \rightarrow MOC(OH)M_2$,
2.7. $MOC(OH)M_2 + MH \rightarrow$
$\rightarrow MOCH(OH)M + MM$,
2.8. $M_4C + MOCH(OH)M \rightarrow$
$\rightarrow M_3CH + MOCH(M)OM$,
2.9. $MOCH(M)OM + MH \rightarrow$
$\rightarrow MOCH_2OM + MM$,
2.10. $MOCH_2OM + MH \rightarrow$
$\rightarrow MOCH_2OH + MM$,
2.11. $MOCH_2OH \rightarrow HCOOH + MH$,
2.12. $M_3CH + MH \rightarrow M_2CH_2 + MM$,
2.13. $M_2CH_2 + MH \rightarrow MCH_3 + MM$,
2.14. $MCH_3 + MH \rightarrow CH_4 + MM$.

Pathway 3

3.1. $CO + MM \rightarrow M_2CO$,
3.2. $H_2 + MM \rightarrow 2\ MH$,
3.3. $M_2CO + MH \rightarrow MCHO + MM$,
3.4. $MCHO + MH \rightarrow CH_2O + MM$,
3.5. $MCHO + MH \rightarrow MCH_2OM$,
3.6. $MCH_2OM + MH \rightarrow MCH_2OH + MM$,
3.7. $MCH_2OH + MM \rightarrow M_2CH_2 + MOH$,
3.8. $M_2CH_2 + MH \rightarrow MCH_3 + MM$,
3.9. $MCH_3 + MH \rightarrow CH_4 + MM$,
3.10. $CH_2O + MOH \rightarrow MOCH_2OH$,
3.11. $MOCH_2OH \rightarrow HCOOH + MH$.

Pathway 4

4.1. $CO + MM \rightarrow M_2CO$,
4.2. $H_2 + MM \rightarrow 2\ MH$,
4.3. $M_2CO + MH \rightarrow M_2CHOM$,
4.4. $M_2CHOM + MH \rightarrow M_2CH(OH) + MM$,
4.5. $M_2CH(OH) + MM \rightarrow MCH_3 + MOH$,
4.6. $M_2CO + MOH \rightarrow MOC(O)M + MH$,
4.7. $MOC(O)M \rightarrow CO_2 + MM$,
4.8. $CO_2 + MM \rightarrow MOCHO$,
4.9. $MOCHO + MH \rightarrow HCOOH + MM$,
4.10. $M_3CH + MH \rightarrow M_2CH_2 + MM$,
4.11. $M_2CH_2 + MH \rightarrow MCH_3 + MM$,
4.12. $MCH_3 + MH \rightarrow CH_4 + MM$.

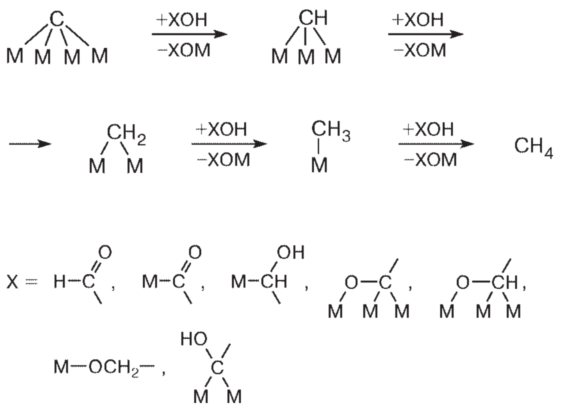


Fig. 9. Mechanism of methane formation involving protolysis steps.

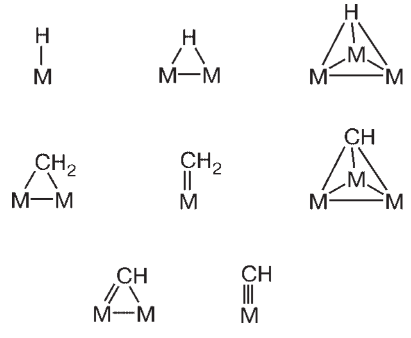
The reaction network in question proposes quite diverse ways of coupling of the formation of hydrocarbons (in this case, methane) and the formation of oxygen-containing compounds. We can construct and verify in one or another way an enormous number of hypotheses, even when we restrict ourselves to the pathways selected above. Quite interesting variants of coupling appear as a result of numerous steps of protolysis of carbon- and hydrocarbon-containing intermediates with participation of XOH (Fig. 9).

Conclusion

Prospects for the subsequent use of the reaction network

The reaction networks obtained allow one to solve theoretical and experimental problems in the investigation of mechanisms and the construction of theoretically substantiated kinetic models of the syntheses based on CO and H_2 and also to approach the problem of estimation of catalysts (selection of the optimal catalyst—mechanism pairs).

1. The reaction network is a convenient base for the theoretical analysis of the stability and reactivity of various adsorbed species with different forms and any number of active sites because generation of the reaction network ensures a full set of hypothetical adsorbed species (see Section 3). In this work, we considered linked M—M atoms and individual metal atoms as active sites. When a reaction network is available, these symbolic sites can be associated with some particular clusters, different degrees of linking of adsorbed species, and any coordination numbers of the metal acceptable for quantum-chemical calculations.



Thus, analysis of the results of semiempirical calculations of the heats of carbon adsorption[371,384] showed that they coincide with experimental values. The metallic center contained three or four metal atoms.

2. Modern methods of the calculation of the enthalpies ($\Delta H°$) and activation energies (E_a) of steps on the surface[23,24,385] allow one to use the reaction network to estimate the activity of metallic catalysts in certain processes. Various calculation schemes were employed to analyze the mechanisms of carbon dioxide conversion of methane (168 elementary reactions on the surfaces of eight metals),[25] methanol synthesis (207 elementary reactions on the surface of four metals),[386] partial oxidation of methanol to formaldehyde (30 elementary reactions on catalysts simulating the silver surface modified by O, S, Cl, Br, and I).[387] All steps of hydrogen transfer that can occur between C_1—C_2 hydrocarbon species (204 reactions on the surfaces of three metals) have been calculated.[388] These calculations require representative reaction networks, which can be gained by the above-described procedure.

3. It is natural to use the reaction network for discrimination of the Fischer—Tropsch mechanisms using experimental data. This procedure was carried out,[21,389] though with a limited set of hypotheses. The reaction networks having small sizes can also be used as a whole.[20,390] The reaction networks are especially useful for the description of coupled processes (using conjugation nodes[40,56]), in particular, syntheses from CO and H_2. We attempted to demonstrate this when analyzing the reaction networks for the synthesis of one-carbon products obtained by computer generation and by the comparison of the pathways cut out from the network with the mechanisms of CH_4, $\mathrm{CH}_3\mathrm{OH}$, HCOOH, and CO_2 formation proposed throughout the whole history of development of syntheses from CO and H_2. Noteworthy are the intermediates and steps that have not yet been used by researchers and that are described in this review and in the references. It is expedient to use the reaction network and the mechanisms cut out from it for planning chemical and physicochemical experiments aimed at substantiation of individual steps under particular conditions of the catalytic process.[64]

4. In the case of kinetic discrimination of the hypotheses and construction of the theoretically substantiated kinetic models on the basis of the reaction network or separate pathways isolated from it, it is important to pay special attention to the above-mentioned problem of us-

ing the mass action law even on a homogenous surface with simultaneous presence of multicenter and one-center adsorption, especially with slow desorption and slow diffusion of the adsorbed species over the surface (in relation to the rate of surface reactions).

It is evident that further progress in the understanding of the mechanisms of surface reactions (including Fischer—Tropsch synthesis and methanol synthesis) will depend on the research into the nature of centers, adsorbed species, the ways of their bonding to the active centers, the degree of substantiation of the generated reaction networks, and on the quality of the kinetic experiment used for the discrimination of hypotheses.

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