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Catalytic synthesis of isoalkanes and aromatic hydrocarbons from CO and H_2

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Abstract. Characteristic features of the synthesis of isoalkanes and arenes from CO and H_2 in the presence of oxide, metallic and zeolite-containing catalysts are considered. Primary attention is paid to cobalt – zeolite systems. The bibliography includes 96 references.

I. Introduction

Nowadays, petroleum is the main source of hydrocarbons. However, since petroleum resources are limited, development of methods for production of hydrocarbons from coal, natural gas, oil shales, plant biomass, *etc*. becomes a topical task. One of these methods is the Fischer–Tropsch synthesis, which includes three stages: (1) production of synthesis gas (a mixture of hydrogen and carbon monoxide) by gasification of solid raw materials (coal, peat, biomass, *etc*.) or reforming of natural gas; (2) synthesis of hydrocarbons from synthesis gas; (3) upgrading (hydrocracking, hydroisomerisation) of the resulting mixture giving commercial products. The term 'Fischer–Tropsch synthesis' is often used in the literature to denote only the second stage of the process, that is, production of a mixture of liquid and solid hydrocarbons from synthesis gas. It is in this sense that we use this term in this review.

The synthesis of hydrocarbons from carbon monoxide and hydrogen in the presence of Group VIII transition metals is a widely employed polymerisation reaction on heterogeneous catalysts. This process yields mostly alkenes and alkanes the yields and composition of which depend on the nature of the catalyst and the reaction conditions.

In some countries, iron and cobalt catalysts are used in industrial syntheses of hydrocarbons from non-petroleum raw materials. At present, catalysts of this type are preferred because they are highly selective in relation to the formation of paraffins the proportion of which in the synthesis products usually exceeds 90%.

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Cobalt catalysts are traditionally used to produce linear alkanes. These products can be separated to give petrol ($C_5 - C_{10}$) and diesel ($C_{11} - C_{18}$) fractions of liquid hydrocarbons and a wax fraction (synthetic ceresin C_{19+}).

Mixtures of liquid hydrocarbons are mostly needed to produce components of engine fuels, detergents, solvents and some medicines and perfumes. At present, production of fuels is the predominant field of application of the Fischer – Tropsch products.

The hydrocarbon mixtures synthesised from CO and H_2 are not finished liquid fuels. However, the main characteristics of the diesel fraction obtained on Co catalysts conform to those required of diesel fuels (for example, its cetane number is greater than 50). In contrast, the substantial amount of linear alkanes (70% or more) present in the petrol fraction considerably reduces the possibility of using it directly in internal combustion engines.

Figure 1 presents the plots for the octane numbers of individual hydrocarbons of various homologous series.[1] It can be seen

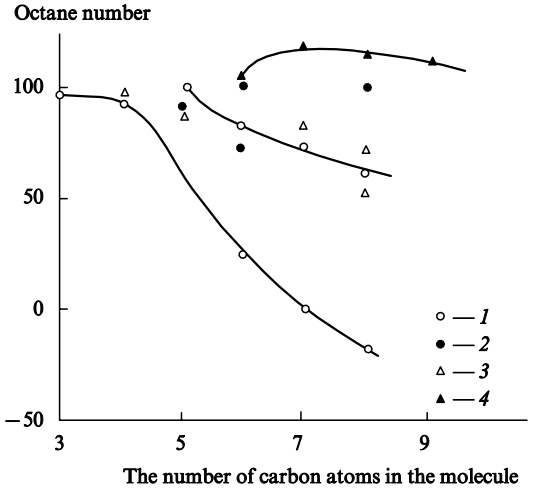


Figure 1. Octane numbers of individual hydrocarbons of various homologous series.
(*1*) saturated hydrocarbons (paraffins and naphthenes); (*2*) isoparaffins; (*3*) olefins; (*4*) aromatic hydrocarbons.

that aromatic compounds possess the highest octane numbers and that the octane numbers of isoalkanes are markedly higher than those of the corresponding linear alkanes (especially when the number of carbon atoms in the molecule is large). Thus, isoparaffins, aromatic compounds and cycloalkanes, which are formed in relatively small amounts in the Fischer–Tropsch synthesis in the presence of traditional Co catalysts, are the desirable components of high-octane petrols. These compounds can be produced from linear alkanes by isomerisation, cyclisation and cracking; aromatics can also be obtained by dehydrogenation.

At present, it is considered expedient to use branched alkanes for increasing the octane numbers of petrols, because these substances give less harmful exhausts into the atmosphere upon transformations in internal combustion engines than do aromatic hydrocarbons, which are also used to improve the quality of petrol. A fairly promising method is direct production of hydrocarbon mixtures with increased contents of isoalkanes from synthesis gas. This can be accomplished using oxide and metal-containing catalysts.

II. Oxide catalysts

Let us consider synthesis of branched hydrocarbons from CO and H_2 in the presence of oxide catalysts.[1] For example, the process catalysed by TiO_2, ZrO_2 or CeO_2 (375–475 °C, 30–60 MPa) gives isobutane as the major product, its yield being 20–50 g m^{-3} of synthesis gas.†

The synthesis of branched hydrocarbons from CO and H_2 in the presence of oxide catalysts includes apparently the following stages: formation of methanol and dimethyl ether, hydrocarbon chain growth, dehydration of higher alcohols and hydrogenation of alkenes to give isoalkanes.[2,3]

In the presence of mixed oxide catalysts such as TiO_2–Al_2O_3, ThO_2–ZnO and ZnO–Al_2O_3 at 400–450 °C and 2.5 MPa, synthesis gas is converted into hydrocarbons in a yield of 105 g m^{-3} at a degree of CO conversion of 70%–80%. Liquid hydrocarbons (C_{5+}) account for about 57 g m^{-3} of the products formed.[3] At temperatures above 450 °C, gaseous hydrocarbons are mainly produced (up to 50–70 g m^{-3} of isobutane), whereas below 375 °C alcohols are formed as the major products. In addition to isoparaffins, the reaction products contain unsaturated aliphatic hydrocarbons (more than 90% of which are branched), and small amounts of aromatic hydrocarbons and naphthenes.

To produce high-quality petrols from CO and H_2, catalysts consisting of aluminium, tungsten, zirconium, uranium and lanthanide oxides with ZnO, Cr_2O_3 and CuO present as additives have been developed. These catalysts are active at >10 MPa and at temperatures above 350 °C.[4] A two-stage process for production of olefins and high-octane petrol from synthesis gas in the presence of iron and oxide catalysts has also been proposed.[5] The first stage is carried out over the Fe_3O_4 (96.8%)–Al_2O_3 (2.4%)–K_2O (0.8%) catalyst at 310 °C and at 1–3 MPa and affords a mixture of alkenes in a yield of 171 g m^{-3}. In the second stage catalysed by ThO_2, the remaining CO and H_2 are converted at 400–450 °C and 28–30 MPa into petrol (yield 137 g m^{-3}).

The process of selective production of branched hydrocarbons from CO and H_2 on oxide catalysts has not yet found practical application, because it usually requires relatively drastic conditions. In addition, most often, the yield of the main products of this synthesis in the presence of oxide catalysts is rather low. Therefore, hybrid or bifunctional metal-containing catalysts, which are active under milder conditions, are considered to be more promising for the synthesis of branched hydrocarbons. These catalytic systems combine the properties of hydrogenating catalysts (to convert CO and H_2 into hydrocarbons) and catalysts for hydrocarbon transformations (in particular, isomerisation).

It is known[6–9] that hydrocarbons can undergo various transformations in the presence of solid acids. Mixed oxides (for example, amorphous aluminosilicate) and zeolites belong to this class of catalysts. Deposition of metal salts onto solid acids or introduction of reducible cations into zeolites by ion exchange gives (after reduction of the metal cations) bifunctional catalysts, which combine the properties of metallic and acidic contacts.

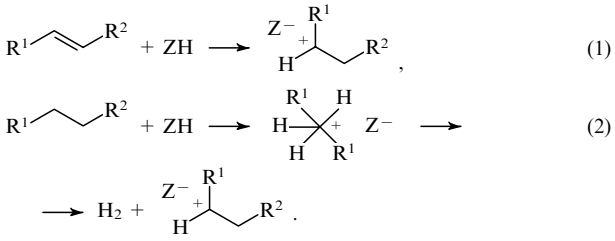
Hydrocarbons or intermediates formed from CO and H_2 with participation of the metallic component of the catalyst can undergo secondary transformations on the oxide (acid) surface. The majority of these transformations resemble homogeneous catalytic reactions occurring in the presence of strong acids. Therefore, it is usually assumed that the mechanisms of these processes are similar.

III. Transformations of hydrocarbons on acidic catalysts

In reactions occurring on solid acidic catalysts (as well as in homogeneous acid-catalysed reactions), carbocations play an important role. These species are generated on bifunctional catalysts upon proton transfer from a Brønsted acid site to an alkene formed on the metallic phase.

Carbocations can be classified into carbenium and carbonium ions. Carbenium ions contain a positively charged carbon atom coordinated to three alkyl groups or three hydrogen atoms (R_3C^+). Carbonium ions are based on a pentacoordinated positively charged carbon atom surrounded by the same substituents, at least one of them being hydrogen (R_4C^+H).

The formation of carbocations on solid acids Z (in particular, on zeolites) includes the following reactions:[9]

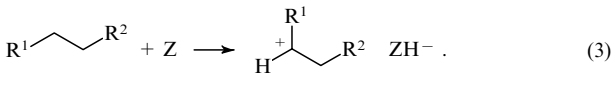


(1)

(2)

According to reaction (1), a zeolite proton reacts with an alkene to give a carbenium ion. Reaction (2) describes protonation of alkanes resulting in a carbonium ion. The latter is then converted into a smaller carbenium ion upon elimination of an alkane molecule or molecular hydrogen. Both reactions occur on Brønsted acid sites. It should be noted that process (1) occurs more rapidly and at lower temperatures than process (2).

Transformations with hydride ion transfer can also occur on Lewis acid sites.



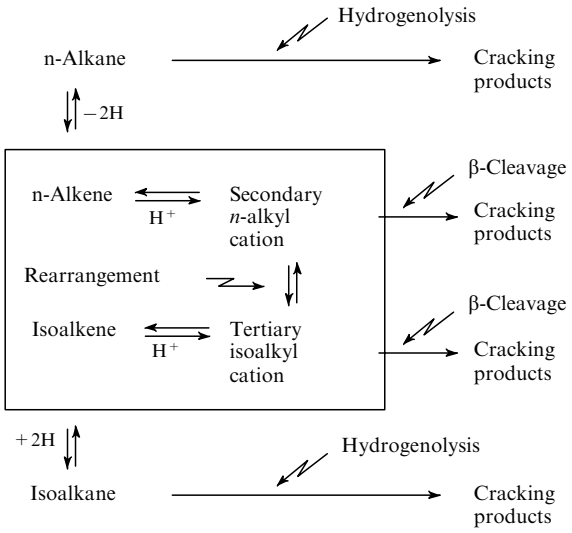
(3)

The formation of carbenium ions on bifunctional metal-containing catalysts occurs mostly by reaction (1), *i.e.* these ions result from the transfer of a proton from a Brønsted acid site to an alkene formed on the metallic phase. The proton transfer is terminated as a result of fast hydrogenation of unsaturated fragments on metal particles. The presence of a metal permits the reaction temperature to be decreased by ~100 °C.[9] Simultaneously, isomerisation and cracking of isomerised hydrocarbons occur on acid sites. The rearrangements and cleavage of alkylcarbenium ions are the rate-determining steps.

In bifunctional catalysts, a metal ensures the occurrence of hydrogenation–dehydrogenation reactions, whereas the role of a solid acid (zeolite or a mixed oxide) consists in the formation of

† The activity of catalysts in the Fischer–Tropsch synthesis is usually estimated based on the yield of hydrocarbons produced from 1 m^3 of synthesis gas under normal (or standard) conditions (s.t.p.). The maximum theoretical yield of hydrocarbons amounts to 208.5 g m^{-3} (s.t.p.).

carbocations on acid sites. These cations undergo isomerisation and destruction and then they are desorbed, mostly as alkenes. The latter are converted into alkanes upon hydrogenation on the metal component of the catalyst. The classical transformation chart can be represented as follows:



In accordance with this scheme, carbenium ions result from protonation of alkenes. These ions can rearrange and be desorbed as isomers, or they can be cracked (β-cleavage). Thus, cracking and isomerisation are competing processes. In the general case, isomerisation of alkanes with high molecular masses occurs at lower temperatures than hydrocracking.[9]

Alkylcarbenium ions can participate in the following transformations:[9] intramolecular hydride shift, skeletal isomerisation, intermolecular transfer of a hydride ion from a carbenium ion to a substrate molecule to give a new carbenium ion and an alkene (this is normally the slowest step occurring on the strongest acid sites of the catalyst),[10] alkylation by alkenes resulting in the formation of longer alkylcarbonium ions, β-cleavage yielding shorter alkylcarbenium ions and alkene fragments and deprotonation (chain termination). All alkylcarbenium ions formed from both neutral molecules and various intermediates can enter into the above reactions.

In the presence of bifunctional catalysts, lower alkanes participate in more complex processes, namely, dehydrogenation and oligomerisation of 'internal alkenes' (those with an internal double bond) followed by cracking of the oligomers.[11]

IV. Zeolite-containing catalysts

In recent years, studies have been started on bifunctional catalysts that combine the properties of traditional Fischer–Tropsch catalysts (redox function) and selective zeolite catalysts (acid–base function). Both types of catalytic sites are involved in consecutive and parallel transformations.[12] Alkenes formed from CO and H_2 on the metal-containing component of the catalyst are converted on the zeolite into aromatic and branched aliphatic hydrocarbons, while alkanes are cracked, which increases the petrol fraction.

The catalytic sites for acid–base reactions are hydroxy groups of the zeolites or water molecules dissociated in the cation field.[13] The zeolite hydroxy groups can result from the following processes:

(a) hydrolysis

$$Na^+\text{-zeolite} + H_2O \rightleftharpoons NaOH + H^+\text{-zeolite}$$

(since the sodium form of a zeolite is the salt of a weak acid and a strong base, this equilibrium is shifted to the right, and aqueous suspensions of zeolites are normally alkaline);

(b) decomposition of the ammonium form of a zeolite

$$[Al\begin{smallmatrix}ONH_4^+\\ \diagdown\\ Si\end{smallmatrix}] \rightleftharpoons [Al\begin{smallmatrix}OH^+\\ \diagdown\\ Si\end{smallmatrix}] + NH_3;$$

(c) heterolytic dissociation of water molecules in the field of a polyvalent cation and the zeolite framework atoms

$$[Al\begin{smallmatrix}OM\\ \diagdown\\ Si\end{smallmatrix}] + H_2O \rightleftharpoons [Al\begin{smallmatrix}OH^+\\ \diagdown\\ Si\end{smallmatrix}] + MOH,$$

where M is metal.

The aluminium atom has a vacant *p* orbital; occupation of this orbital results in withdrawal of the electron density from oxygen in the [Al–O(H)–Si] group and thus in polarisation of the O–H bond. Thus, the OH group in the [SiOH] fragment, which exhibits weakly acidic properties when incorporated in silica gel, behaves as a strong Brønsted acid site in the presence of aluminium atoms.

Bifunctional catalysts are usually prepared on the basis of HZSM-5 zeolite. This choice is due to the following reasons:[8] the average size of the zeolite pores is 5.5 Å, which facilitates selective formation of molecules containing less than 10 carbon atoms, *i.e.* hydrocarbons of the petrol fraction; the strong acid sites of HZSM-5 are responsible for oligomerisation, cracking and aromatisation; this zeolite is stable against coking, because the presence of medium-size pores prevents the formation of coke precursors; the zeolite is stable under hydrothermal conditions and resistant against dealumination, which is possible under the Fischer–Tropsch synthesis conditions because this reaction yields a substantial amount of water.

The high selectivity of zeolites of the HZSM-5 type towards the formation and subsequent transformations of light hydrocarbons is determined by their structure. In the pores containing strong acid sites, organic molecules are adsorbed according to the 'tail-to-tail' pattern.[14] In the majority of cases, only alkenes and/or carbonium ions containing five or fewer carbon atoms are able to participate in reactions occurring in zeolite channels with a size of ~9 Å; therefore, the oligomers formed in these reactions contain not more than 10 carbon atoms. In addition, HZSM-5 zeolites 'control the movement of molecules': the reactants enter the zeolite structure through sinusoidal channels, whereas the products are removed through linear channels. As this takes place, alkenes, which slowly diffuse through the pores, are transformed into branched alkanes. The absence of back diffusion is a crucial factor determining the use of HZSM-5 zeolites in catalytic transformations.

The use of HZSM-5 and other high-silica zeolites as supports for the catalysts for the synthesis of hydrocarbons from CO and H_2 has been started quite recently.[15–17] To increase the content of aromatic hydrocarbons or isoalkanes in the synthesis products, two types of catalysts are usually employed, namely, hybrid systems comprising an oxide catalyst for methanol synthesis and a zeolite (for example, Zn/HZSM-5 and Zn–Cr/HZSM-6)[16] and also bifunctional systems based on metallic catalysts of the Fischer–Tropsch synthesis and zeolites. Both types of catalysts have advantages and drawbacks. Systems of the former type permit selective and highly efficient synthesis of mixtures of aromatic hydrocarbons; however, they are insufficiently stable (the period between catalyst regenerations varies from one to several months). Systems of the latter type are characterised by a lower productivity but they are suitable for the synthesis of both aromatic hydrocarbons and branched paraffins.

V. Synthesis of aromatic hydrocarbons and isoalkanes on zeolite-containing catalysts

Zeolite-containing catalysts based on Group VIII transition metals are usually prepared by co-precipitation or ion exchange followed by activation with hydrogen. The transition metal cations occur initially within the zeolite structure and on its surface and can be reduced almost completely.[13] In the general

case, the degree of reduction depends on the method of cation activation with hydrogen, the nature of these cations and the reactivity of their oxygen environment in the zeolite. In addition, it depends on the degree of dispersion of the initial compound containing the transition element and on the diffusion processes in the zeolite during reduction.

The Co–O bond of an isolated cobalt species in a zeolite framework is ionic.[18] The reduction of cations in the coordination sphere of these zeolites occurs at temperatures above 450 °C,[19] cation-exchange zeolites behaving as ordinary salt systems.

The mechanism of reduction of transition metal cations in zeolites differs from the mechanism of reduction of the corresponding metal oxides.[20] The latter is irreversible, the hydrogen that has reacted being removed as water. On the contrary, in zeolites, the protons are retained by the framework where they form hydroxy groups.

$$[M^{n+}Z^-] + (n/2)\,H_2 \rightleftharpoons [n\,H^+Z^-, M^0],$$

$$[n\,H^+Z^-, M^0] \longrightarrow [n\,H^+Z^-] + M^0.$$

Cations located in different crystallographic positions have different electrostatic environments and, therefore, different reducibilities.[21] The reducibility depends also on the silicon to aluminium ratio in the zeolite framework,[22] *i.e.* on the Si–O bond length, the residual charge on the framework, and the effective charge on the cation itself.

The character of localisation of cations and their reducibility depend appreciably on the catalyst pretreatment conditions. In particular, dehydration leads to the destruction of aqua complexes of transition metal cations; the cations migrate to positions with higher degrees of coordination unsaturation, which decreases their reducibility.[23]

After reduction, transition metals can occur in zeolite-containing catalysts as separate atoms, clusters or crystallites with a size of $\geqslant 100$ Å located on the external surface of the zeolite.[13] It should be noted that decationised zeolites contain large amounts of strong proton-releasing and electron-withdrawing sites. Thus, the use of a zeolite support makes it possible to prepare catalytic systems differing in the degree of metal dispersion and in the strength of its interaction with the surface.

The activity of the most widely used Co catalysts for the Fischer–Tropsch synthesis is determined to a large extent by the nature of the zeolite support.[24] Thus the yield of liquid hydrocarbons on the Co catalysts supported on X and Y zeolites is higher than those on similar specimens based on zeolite A and mordenite. The highest yield of liquid products (166 g m^{-3}) over this series of specimens, attained on the Co–MgO/NaX catalyst, was 1.3 times higher than that on the Co–MgO/kieselguhr catalyst with the same component ratio (the latter catalyst was close in composition to the commercial one).

The nature of synthetic zeolites has a substantial influence on the polymerising and isomerising properties of Co catalysts for the Fischer–Tropsch synthesis.[25] An increase in the $SiO_2 : Al_2O_3$ ratio in a zeolite results in an increased content of high-boiling products in the catalysate and in an increased proportion of normal aliphatic hydrocarbons in these products.

Catalysts containing A, X, Y or M zeolites in the H-form or with exchangeable Ca^{2+}, Mg^{2+} and ZrO^{2+} cations are less active in the synthesis of hydrocarbons from CO and H_2 than catalysts containing zeolites in the Na-form.[25] The highest yield of liquid hydrocarbons (125–130 g m^{-3}) was achieved on catalysts containing NaX and NaY zeolites ($SiO_2 : Al_2O_3 = 2.8–5$).[26] When more acidic catalysts were used, the proportion of iso hydrocarbons reached 50 mass %.

The composition of the products is substantially influenced by the nature of the exchangeable cation.[27] Thus introduction of Mg^{2+} by ion exchange into NaX zeolite used as a support increases the yield of liquid products 1.5-fold. Simultaneously, the proportions of branched hydrocarbons and alkenes in the catalysate decrease.

The catalytic properties of metal zeolite systems depend on the methods of their preparation and modification and on the operation conditions.[6] For example, the cobalt particles in the Co/HZSM-5 catalyst prepared by impregnation of the zeolite with an aqueous solution of cobalt nitrate[28] are 3 times larger than those in the specimen prepared using dicobaltoctacarbonyl $Co_2(CO)_8$.[29]

The initial system used to produce the 9.5 mass % Co/HZSM-5 catalyst contains cobalt nitrate as amorphous particles with a size of ~ 20 Å.[30] After calcination in a flow of air, the nitrate is converted into the oxide Co_3O_4. The reduction in a flow of hydrogen at 350 °C affords cobalt crystallites with a size of ~ 300 Å, which remain virtually unchanged during the Fischer–Tropsch synthesis, and the cobalt oxide CoO (~ 90 Å). The ratio of these components, equal to 4, remains approximately the same after treatment with synthesis gas, *i.e.* the catalyst is not reduced during the synthesis.

The Co/HZSM-5 catalysts prepared by impregnation contain cobalt in two states: exchangeable non-reducible Co^{2+} ions within the zeolite structure and crystalline Co_3O_4 on its external surface.[15] The latter can be reduced with hydrogen to metallic cobalt and CoO. Specimens containing only exchangeable cobalt ions do not exhibit catalytic activity in the synthesis of hydrocarbons from CO and H_2.

After preliminary reduction with hydrogen of the 30 mass % Co/HZSM-5 catalyst prepared by mixing basic cobalt carbonate with the support, the degree of Co reduction is 52%–58%.[31] The rest of the cobalt occurs as Co^{2+}. Treatment of the catalyst with synthesis gas results in partial oxidation of the metal on the catalyst surface: the degree of Co reduction decreases to 31%–35% and Co_3O_4 (14%–17%) is formed. As the Si : Al ratio in the zeolite increases, the Co^0 surface concentration somewhat decreases, resulting in a decrease in both the total catalyst activity and the yield of liquid products.

Catalysts produced by impregnation or mixing and containing a metallic cobalt phase on the surface of HZSM-5 zeolite crystals are fairly active in the Fischer–Tropsch synthesis (the degree of CO conversion reaches 60%).[15] At 280 °C, these catalysts permit the synthesis of aromatic hydrocarbons, the yield and composition of which depend on the composition of the catalyst and the method by which it was prepared. Thus the hydrocarbon mixtures obtained on the 8.5 mass % Co/HZSM-5 catalyst prepared by mechanical mixing of the components contained up to 49 vol. % of aromatic compounds, whereas the content of aromatics in the products of synthesis on 7.5 mass % Co/HZSM-5 catalyst prepared by impregnation was not more than 20 vol.%.

A number of Co/HZSM-5 catalysts containing from 3 mass % to 9 mass % of the metal and prepared by various methods have been studied.[32] The following methods were used: decomposition of $C_5H_5Co(CO)_2$ on the zeolite (specimen **I**), impregnation of the support by an aqueous solution of cobalt nitrate (specimen **II**) and mechanical mixing of cobalt oxide with the zeolite (specimen **III**). The conversion of synthesis gas at 2.1 MPa and 280 °C on any of these speciments increased with an increase in the cobalt loading. When the Co concentration was 9 mass %, the highest yield of liquid hydrocarbons C_{5+} (74%) was attained on catalyst **I**. This specimen contained much less ion-exchangeable cobalt than catalyst **II**. The rest of the cobalt in **I** occurred as Co_3O_4 on the external surface of the zeolite. Catalyst **III** did not contain exchangeable cobalt ions at all. Thus, the metallic component had no influence on the acidic properties of HZSM-5 zeolite, and this catalyst was best suited for the synthesis of aromatic hydrocarbons from CO and H_2. The concentration of aromatics in the liquid products obtained on this catalyst was ~ 51 vol. %. The liquid products produced on specimens **I** and **II** were enriched in alkenes (their content was 14 vol. % and 22 vol. %, respectively).

The Co/HZSM-5 catalysts employed for the synthesis of aromatic hydrocarbons are prepared conventionally by mechanical (dry) mixing of Co_3O_4 and the zeolite to keep the latter in the H-form. Mixtures formed in the presence of these catalysts

contain up to 70 mass % of aromatic hydrocarbons.[15, 25, 33] However, the yield of the products is not more than 10–20 g m^{-3}, which is largely due to the low porosity of the catalyst samples. The yield of liquid aliphatic hydrocarbons in the presence of analogous catalysts prepared by co-precipitation (using basic cobalt carbonate) and promoted by magnesia reaches 150–170 g m^{-3}.[25, 34] It has been found[35] that the nature of the initial cobalt compound used to prepare the Co/HZSM-5 catalyst influences the yield and the composition of the liquid products formed. The syntheses were carried out at a pressure of 0.1 MPa, a temperature of 220–280 °C, volume ratio $H_2:CO = 1$ and a gas hourly space velocity of 100 h^{-1}. The use of basic cobalt carbonate makes it possible to increase the catalyst porosity (the specimen is loosened during reductive decomposition of the carbonate) and increases the yield of liquid products (up to 42 g m^{-3}) and the selectivity of their formation (up to 44%). However, simultaneously the content of aromatic hydrocarbons decreases markedly (to 42%).

The introduction of 0.4 mass % to 1.5 mass % of ThO_2 into the 9 mass % Co/HZSM-5 catalyst prepared by mechanical mixing of the components substantially increases the degree of conversion of synthesis gas (up to 74%) and the selectivity of the formation of the petrol fraction of hydrocarbons (to 70%).[32] The proportion of aromatic compounds in the liquid products decreases to 26% but, nevertheless, the octane number of the products is 90. It has been shown by IR spectroscopy that when the Co/HZSM-5 catalyst contains ThO_2, the relative concentration of the Brønsted acid sites in the zeolite diminishes; this accounts for the lower yield of aromatic compounds. A ^{59}Co NMR study has shown the presence of α- and β-cobalt phases in the Co/HZSM-5 catalyst.[33] The reduced $Co-ThO_2$/HZSM-5 specimen contained no hexagonal cobalt. In addition, upon the introduction of ThO_2, the size of the cobalt particles arising decreased from 40 to 10 nm;[32, 36] this facilitated adsorption of synthesis gas and ensured higher product yields.[32] However, after treatment of the catalyst with synthesis gas for 48 h at 280 °C, the size of Co crystallites again increased (apparently, due to sintering of metal particles) and the yield of aromatic hydrocarbons decreased. A similar decrease in the content of aromatic hydrocarbons in the liquid products of the synthesis on Co/HZSM-5 catalysts prepared using $CoCO_3$ has been observed upon introduction of 2%–3% of Mg, Zr or La oxides into the catalysts.[32]

The synthesis carried out under relatively mild conditions (0.1 MPa, 250–280 °C) in the presence of the $Co-Ni-ZrO_2$/HZSM-5 catalyst gave aromatic hydrocarbons with a selectivity of 30 mass %–35 mass %.[37] A decrease in the space velocity, an increase in the temperature or an increase in the zeolite proportion in the catalyst resulted in a higher content of aromatic hydrocarbons in the C_{6+} fraction.

A study dealing with the adsorption properties of bifunctional cobalt–zeolite catalysts prepared by mechanical (dry) mixing of the components has shown that the adsorption isotherm deviates noticeably from the corresponding curve for the initial zeolite.[35] This implies destruction of the zeolite during the catalyst preparation, the degree of destruction being dependent on the duration of the mechanical impact on the specimen.

The hydrogenating activity of cobalt can be decreased by introducing Cu into the catalyst. The yield of methane on a mechanical mixture of 4% Co/SiO_2 and HZSM-5 zeolite is 1.7 times higher than that on the 4% Co/SiO_2 specimen itself (2.1 MPa, 280 °C, $H_2:CO = 1$). However, the proportion of methane formed in the presence of the 6% Co–0.05% Cu/SiO_2 + HZSM-5 specimen under similar conditions is only 1.2 times higher than that on 6% Co–0.05% Cu/SiO_2. Thus, the addition of copper decreases somewhat the efficiency of methane formation.[38]

When developing and employing bifunctional catalysts, one should bear in mind that the rate of synthesis of aromatic hydrocarbons on these catalysts at a given temperature and at the optimum activity of HZSM-5 cannot be higher than the rate of formation of alkenes on the metallic component of the catalyst (the Fischer–Tropsch component).[8] The temperature for the synthesis of aromatic compounds is normally 280 °C. At this temperature, zeolite is active towards aromatisation of alkenes, and methane formation on the Fischer–Tropsch component is not too pronounced. The maximum rate of formation of aromatic hydrocarbons from alkenes at 280 °C is 0.084 g (g of HZSM-5)$^{-1}$ h^{-1}.[8] At the same time, a catalyst for the Fischer–Tropsch synthesis (for example, 4% Co/SiO_2) can ensure formation of 0.123 g of alkenes per hour under similar conditions. It is the ratio of 0.084 to 0.123 that determines the ratio of the components in the bifunctional 4% Co/SiO_2 + HZSM-5 catalyst.

The main problem associated with the use of bifunctional zeolite catalysts is their deactivation during the interaction with synthesis gas. The deactivation is due to the following factors:[8] deposition of inactive carbon on the metallic component, sintering of metal particles and coking of the zeolite component. The first and the second processes result in a gradual decrease in the overall rate of the synthesis gas conversion. The third process diminishes the selectivity of formation of aromatic hydrocarbons due to a decrease in the number of active sites capable of converting alkenes.

An attempt has been made to regenerate the $Co-ThO_2$/HZSM-5 catalyst by conducting redox cycles, because oxidative treatment favours the removal of the carbon deposits. However, in each regeneration cycle, cobalt particles sintered, and this retarded the reforming of synthesis gas. In order to suppress metal sintering during the oxidative regeneration of bifunctional zeolite-containing catalysts, the use of oxygen enriched in ozone was proposed.[40]

Synthesis of branched alkanes from CO and H_2 can also be carried out in the presence of bifunctional catalysts containing Group VIII noble metals.[41] Most often, these catalytic systems exhibit low activities. Conversely, Co/HZSM-5 catalysts are highly active: at an atmospheric pressure and a temperature of 175–200 °C, they permit production of liquid hydrocarbons (C_5-C_{10}), containing 60%–80% of isoparaffins, in 46%–59% yield with respect to the converted CO.[42]

In the presence of 10% Co–6% MgO/HZVM catalysts ($SiO_2:Al_2O_3 = 30-104$) prepared by co-precipitation and containing high-silica zeolites, analogues of HZSM-5, the degree of conversion of carbon monoxide is 70%–100% at 175–200 °C.[43] On these catalysts, liquid hydrocarbons enriched in isoalkanes can be synthesised selectively in 70%–90% yield. The C_5-C_{10} fraction prepared on a catalyst supported on a zeolite with a silica modulus (the $SiO_2:Al_2O_3$ ratio) of 30–68 contains 36%–46% of isoalkanes. The zeolite silica modulus has an influence on the yield of isoalkanes, the highest yield being attained at $SiO_2:Al_2O_3 = 68$. An increase in the reaction temperature from 175 to 220 °C permits selective synthesis of C_5-C_{10} hydrocarbons containing more than 50% of isoalkanes.

The influence of the synthesis conditions on the formation of isoalkanes on Ru–Pt catalysts has been studied.[41] It was found that the shorter the contact time, the higher the yield of branched hydrocarbons. When the $W:F$ ratio (W is the mass of the catalyst, and F is the space velocity of synthesis gas through the catalyst) was proportional to the residence time and was equal to 7 (g of the catalyst) h mol^{-1} (2% Ru–2% Pt/HY, 240 °C, 1.5 MPa, $CO:H_2 = 2:3$), the iso to normal ratio (iso/n) for C_4 and C_5 hydrocarbons was an order of magnitude higher than that expected from the thermodynamic viewpoint (this ratio cannot be achieved upon hydroisomerisation of linear alkanes). As the residence time increased, the iso/n ratio reached the theoretical (thermodynamic) value. This means that the ratio of branched to linear alkanes is controlled by kinetic factors, and an increase in the residence time leads to gradual hydroisomerisation of branched alkanes into linear alkanes.

It was found[41] that the Fischer–Tropsch synthesis on Ru/zeolite catalysts yields alkenes as the primary products. The predominant formation of branched alkanes in the initial reaction

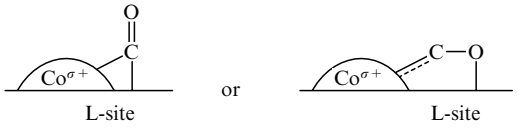
stage may be due to transformation of alkenes on the zeolite acid sites followed by hydrogenation on ruthenium. It can be expected that the ratio of the synthesis products would be determined by the relative reaction rates on the acidic and metallic sites. Since raising the temperature usually enhances the hydrogenating activity of a catalyst, the iso/n ratio simultaneously decreases. A decrease in pressure results in lower iso/n ratios, because hydrogenation is facilitated at low partial pressure of CO. The highest iso/n ratio (ranging from 10 to 40 for various C_{4+} hydrocarbons) on the 2% Ru–2% Pt/HY catalyst was attained at a pressure of 1.5 MPa.[41] As the pressure increased, this ratio substantially decreased. The $W:F$ ratio remains constant upon a pressure increase, whereas the real residence time (*i.e.* the residence time of hydrocarbons in a catalyst layer) becomes longer, and this causes a decrease in the iso/n ratio. It was found that this ratio is inversely proportional to the selectivity of methane formation.

When the reaction is carried out on the 2% Ru–2% Pt/HY catalyst, the iso/n ratio in the C_{4+} hydrocarbons depends on the nature of the support and increases in the order AS < CaY < DAHY < HY (where AS is a synthetic amorphous aluminosilicate, and DAHY is dealuminised HY).[41] As the Si : Al ratio in the zeolite increases, the degree of CO conversion diminishes, whereas the selectivity of CH_4 formation grows. The H-forms of zeolites with higher silica moduli give lower yields of isoalkanes. These results are inconsistent with those obtained in other studies,[44,45] according to which Ru/zeolite catalysts with higher Si : Al proportions give products characterised by greater iso/n ratios. This inconsistency may be due to the fact that the iso/n ratio is determined by the relationship between the rates of various steps involved in the synthesis of isoalkanes from CO and H_2, which depend on the nature of the metal and the type of the zeolite used. To elucidate the general regularities of the synthesis of hydrocarbons from CO and H_2, it is necessary to study systematically various catalysts under identical conditions.

VI. The mechanism of the Fischer–Tropsch synthesis

The surface of supported Co catalysts contains two types of metal-containing active sites **A** and **B** (Scheme 1).[46–49] Sites of type **A** are metallic cobalt crystallites; on these sites, CO undergoes dissociative adsorption giving surface carbon, which is hydrogenated yielding methane. Thus, sites **A** are responsible for CO methanation. On the same type of sites, as a result of CO dissociation, adsorbed oxygen appears, which is able to react with carbon monoxide to give CO_2 (or with hydrogen to give water). Type **B** sites comprise metallic cobalt and an oxide component. They might be located at the Co–oxide interface.[50] The oxide component can be represented by cobalt oxide resulting from incomplete reduction of the initial cobalt salt, by an oxide support or by a surface mixed oxide formed upon interaction of cobalt, the support and an oxide promoter during high-temperature pretreatment of the catalyst (calcination and/or reduction).

On the metallic part of site **B**, reagents are activated giving intermediates of the type COH_x or CH_x; these species spill over to the oxide part of the site on which they polymerise. The oxide part of site **B** is normally a Lewis acid site (L-site). It affects the neighbouring metallic cobalt in such a way that some of the electron density shifts from the metal to the support[51] yielding $Co^{\delta+}$. Carbon monoxide is adsorbed on site **B** in the molecular form; apparently it binds simultaneously to both components of the site.



It is also possible that CO is adsorbed on the interface in such a way that its oxygen atom binds to the oxide component of the active site.[52,53] In this case, the Lewis acid site located near the Co–oxide interface weakens the C–O bond in the carbon monoxide molecule and increases the rate of its hydrogenation.[54]

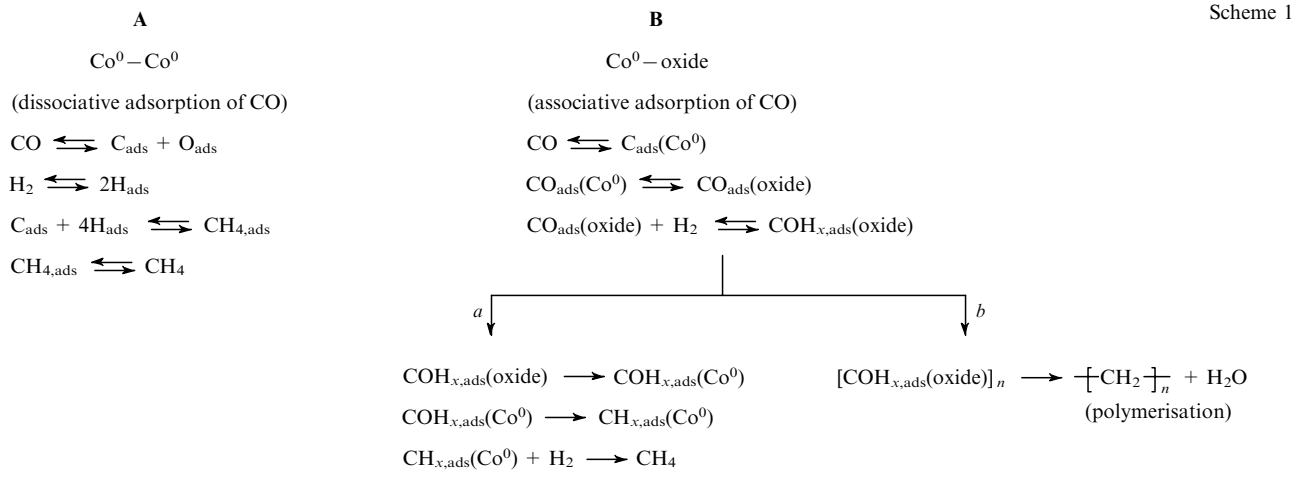
The role of metallic cobalt in active site **B** is not limited to adsorption of CO (which is also adsorbed efficiently by cobalt oxide); cobalt also ensures hydrogen activation and transport to the polymerisation site. In the case where hydrogen can be delivered to the polymerisation site without participation of the metal (for example, by dissociative adsorption of C_2H_2 on an oxide[55]), CH_x radicals can polymerise directly on the oxide.

It should also be noted that in addition to the two types of metal-containing active sites mentioned above, the surface of Co catalysts for the Fischer–Tropsch synthesis contains Lewis and Brønsted acid sites of various strengths, which are located on the oxide surface and are able to participate in secondary transformations of the intermediates formed from CO and H_2. In addition, the energetic characteristics of sites of a particular type (**A** or **B**) can differ owing to the inhomogeneity of the catalyst surface.

VII. Distribution of the products of the Fischer–Tropsch synthesis

The process of formation of hydrocarbons from CO and H_2 is an example of catalytic hydropolymerisation. The distribution of the products formed in this reaction can be described using the Schulz or Flory equations, which virtually coincide for high chain growth rates.[56] In particular, the Schulz equation is written as follows

Scheme 1



(*a*) Proposed by Bartholomew in 1989; (*b*) proposed by Lapidus in 1991.

$$g_n = (\ln^2\alpha)n\alpha^n ,$$

where g_n is the weight fraction of a product containing n carbon atoms, and α is a factor of the hydrocarbon chain growth characterising the ratio of the probabilities of chain growth and chain termination.

In some cases, the distribution of the products of the Fischer–Tropsch synthesis does not conform to the classical Schulz–Flory distribution; this is due to the fact that there are at least two centres of chain growth on the catalyst surface, polymerisation on which occurs by different mechanisms.[57–59] For example, it has been suggested [60] that hydrocarbons, the chain growth of which is characterised by factors α_1 and α_2, can arise in the following way:

$$(CO)_{ads} \begin{cases} \longrightarrow (CH_xO)_{ads} \longrightarrow \alpha_1\text{-products} \\ \longrightarrow (O)_{ads} + (C)_{ads} \longrightarrow \alpha_2\text{-products.} \end{cases}$$

The ratio of the α_1- to the α_2-products is determined by the hydrogen pressure.

It has been assumed [61] that on different active sites of the surface, different intermediates can be formed, which are converted, in their turn, into different surface compounds. According to these views, all the reactions occurring on the surface including the formation of the primary complex are reversible.

VIII. Secondary transformations in the Fischer–Tropsch synthesis

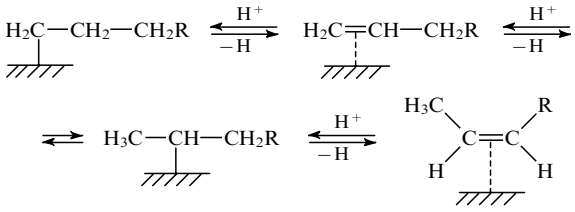
The deviation of the product composition from the Schulz–Flory distribution can also be explained by assuming that the alkenes formed from CO and H_2 are adsorbed once again on one or several active surface sites.[62, 63] In particular, the readsorption of alkenes substantially decreases the overall rate of the surface chain termination by changing the direction of the hydrogen elimination step, which leads to alkenes with a double bond located at the end of the molecule (terminal alkenes).[64]

Study of the compositions of the products formed on the Fe/SiO_2 catalyst has demonstrated that there are two types of distribution, namely, a 'classical' distribution obeying the Schulz–Flory law and a 'non-classical' distribution, which does not obey this law.[65] The non-classical distribution appears because the primary reaction products can be rapidly converted into isomeric secondary products on the acid sites of the catalyst. The secondary transformations include double bond shift, *cis–trans* isomerisation, cyclisation and aromatisation.

There exists a direct correlation between the content of silica gel in a precipitated iron catalyst and the selectivity of this catalyst towards the formation of internal alkenes and branched hydrocarbons.[66] The content of alkenes with an internal double bond increases with an increase in the proportion of silica gel in the catalyst. Terminal alkenes are known to isomerise on silica gel,[67] alumina [68] and zeolites.[69] In the presence of these catalysts, alkenes undergo the following transformations (listed in order of increasing difficulty of transformation): *cis–trans* isomerisation, double bond shift, skeletal isomerisation, cyclisation, hydrogen transfer and polymerisation. These reactions occur on Brønsted and Lewis acid sites.

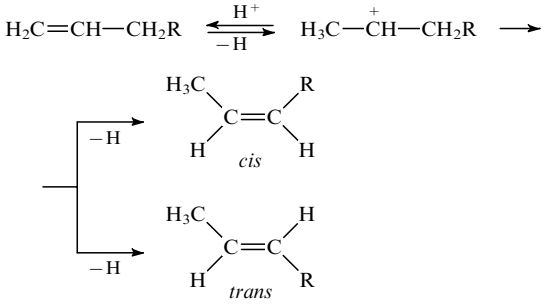
It is generally believed that termination of a growing alkyl chain upon elimination of a β-hydrogen atom yields terminal alkenes, whereas termination occurring by interaction of hydrogen with the α-carbon atom in the chain affords linear alkanes.[70] The formation of small amounts of *cis*- and *trans*-alkenes as the primary products occurs apparently in those rare cases where the growing carbon chain comes in contact with the active site of the catalyst through its β-carbon atom, the chain being terminated upon elimination of δ-hydrogen.

As the content of SiO_2 in the support of the Fe catalyst increases, the yield of alkenes with an internal double bond increases, whereas the amount of terminal alkenes simultaneously decreases; therefore, it can be concluded that internal alkenes result from isomerisation of terminal alkenes on silica gel, which occurs according to the following scheme:[66]



This mechanism implies that isomerisation proceeds on the same sites on which hydrocarbons are synthesised from CO and H_2 and that the two hydrogen atoms attached to the third carbon atom can be removed with equal probabilities to give *cis*- and *trans*-isomers in a ratio close to unity. This mechanism explains adequately the composition of the products formed on Fe catalysts supported on a material devoid of SiO_2.

In the presence of silica gel, the probability of isomerisation of terminal alkenes increases, because this support contains Brønsted acid sites. In this case, the scheme of formation of the *cis*- and *trans*-isomers can be represented as follows:[71]



The interaction of an acid site proton with the double bond of an alkene yields a carbenium ion. Elimination of a hydrogen atom from the adjacent carbon gives rise to a *cis*- or *trans*-alkene. This mechanism accounts for the predominance of the *cis*-isomers in the reaction products, since it is known that on acidic catalysts (which include SiO_2) *cis*-isomers are formed predominantly.[72]

The secondary transformations of the hydrocarbons produced from CO and H_2 have been studied using the precipitated catalysts 14% Co/SiO_2 (**I**) and 15% Co/SiO_2 + HZSM-5 (**II**).[38] In addition, a two-stage process was carried out using two consecutively connected reactors, one of which (the first stage) contained the 14% Co/SiO_2 catalyst, while the other one (the second stage) contained HZSM-5. The tests were carried out at a pressure of 2.1 MPa, a temperature of 280 °C, and the ratio $H_2:CO = 1$. The degree of conversion of CO on specimen **I** reduced at 350 °C reached 50%, and the content of C_{5+} hydrocarbons in the carbon-containing products of the synthesis was 72%. The C_{5+} fraction consisted of alkanes (63%), alkenes (34%) and aromatic compounds (3%). In the case of the two-stage process with catalyst **I** in the first stage and the zeolite at the second stage, the yield of liquid hydrocarbons somewhat decreased (to 65%). However, the $C_2–C_4$ alkenes formed in the first stage (~8%) were converted almost completely on HZSM-5. As a consequence, the content of aromatics in the liquid products increased to 33%. The proportion of $C_3–C_4$ alkanes markedly increased (from 7% to 21%), that of methane remained virtually unchanged (14%) and the content of C_{5+} hydrocarbons diminished to 65%. When the 14% Co/SiO_2 catalyst was mixed with HZSM-5 (specimen **II**) and the synthesis was carried out in one stage, the methane formation was enhanced (up to 25%), whereas the yield of C_{5+} hydrocarbons and the content of aromatics in them barely changed with respect to those attained in the two-stage process. This led to the assumption that methane is formed in a secondary reaction (apparently, hydrogenolysis of light alkanes) occurring on metallic cobalt. This assumption is supported by the fact that the yield of $C_2–C_4$

alkanes on catalyst **II** is lower than that in the two-stage process (15% and 21%, respectively). This type of side reaction proceeds to a noticeable extent only on catalyst **II** in which cobalt particles occur in tight contact with HZSM-5 zeolite.

Hybrid catalysts RuNaY + SO_4^{2-}/ZrO_2 consisting of a mechanical mixture of ion-exchange RuNaY zeolite and sulfidised zirconium oxide have been studied.[73] It was found that under the synthesis conditions (0.1 MPa, 250 °C, $H_2:CO = 1:1$), the propene formed initially on the Fischer–Tropsch component (RuNaY) undergoes two subsequent transformations on the sulfidised zirconium oxide, which behaves as a superacid, namely, hydrogenation through hydrogen transfer to give propane and transformations giving C_{4+} alkanes. The formation of C_{4+} hydrocarbons from propene follows an oligomerisation–cracking mechanism with hydrogen transfer.[11]

$$C_3H_6 \longrightarrow [C_3H_7]^+ \longrightarrow [C_6H_{13}]^+ \longrightarrow [C_9H_{19}]^+ ,$$

$$[C_9H_{19}]^+ \longrightarrow C_4H_8 + [C_5H_{11}]^+ \longrightarrow [C_8H_{17}]^+ \longrightarrow$$

$$\longrightarrow C_4H_8 + [C_4H_9]^+$$

$$\longrightarrow [C_3H_7]^+ + C_5H_{10} .$$

Propene is formed on the Fischer–Tropsch component and is readsorbed on the acid sites of the hybrid catalyst where it oligomerises to give heavier products. The resulting C_4 fragments can be converted into C_4 and C_5 surface groups, which, in turn, react with propene giving rise to C_7 and C_8 hydrocarbons, respectively. The probability of interaction with propene for the C_5 fragments is higher than that for C_4, since heavier hydrocarbons are more readily adsorbed and more difficultly desorbed.[74,75]

The formation of branched oligomeric intermediates during the conversion of alkenes on zeolites depends appreciably on the concentration and the strength of acid sites.[76] A higher concentration and a higher strength of acid sites lead to more branched oligomeric alkene intermediates. Oligomers synthesised on strong acid sites form larger amounts of isoalkanes.

The transformations of linear alkenes on acid sites of the catalysts can follow two routes:[73] (1) alkenes undergo direct skeletal isomerisation to isoalkenes and subsequent hydrogenation *via* hydrogen transfer; (2) oligomers formed on acid sites decompose. The fact that the amount of isobutane produced is larger than its equilibrium amount [77] indicates that isoalkanes are mainly formed *via* reaction (2).

It should be noted that hydrogen transfer is also catalysed by acid sites.[78–80] Upon the hydrogen transfer reactions, some of the alkene molecules are saturated with hydrogen at the expense of other alkene molecules and/or oligomers attached to the catalyst surface. Consequently, oligomers giving off hydrogen become more unsaturated. Polymerisation of these highly unsaturated fragments results in the formation of coke precursors.[73]

The presence of the metallic component in the hybrid catalyst stabilises its activity towards isomerisation of hydrocarbons.[75,81,82] This can be explained in the following way. Molecular hydrogen is adsorbed on the metallic phase of the catalyst and undergoes homolytic dissociation. The atomic hydrogen thus formed spills over to the support, migrates to a Lewis acid site and then gives off an electron, being thus converted into H^+. The interaction of the proton with oxygen located near the L-site affords a Brønsted site, which is also capable of participating in acid-catalysed reactions. This is accompanied by weakening of the L-site which has accepted the electron. Thus, the catalyst is deactivated to a lesser degree. Another possible explanation is neutralisation of carbocations on the catalytic surface by hydride ions, which result from heterolytic dissociation of hydrogen on the metal.[73] The appearance of hydride ions decreases the lifetime of intermediates and prevents their subsequent transformations.

The compositions of the products obtained upon cracking of oct-1-ene on DAHY zeolite and upon the Fischer–Tropsch synthesis on the 2% Ru–2% Pt/DAHY bifunctional catalyst were found to be similar.[83] However, the products of catalytic cracking contain larger amounts of branched alkanes in the C_4 and C_5 fractions (especially in the initial stage of the reaction). This is explained by the increase in the lifetime of a carbenium ion due to the low reactivity of hydrogen in the absence of a metal, which results in a higher probability of isomerisation of the carbenium ion before it is desorbed. The presence of a metallic component in the catalyst favours hydrogenation of alkenes to alkanes;[84,85] this promotes the formation of large amounts of linear saturated hydrocarbons and accelerates the spillover of hydrogen to acid sites. Therefore, to equalise the functions of hybrid catalysts, it is necessary that they contain similar numbers of metallic and acid sites.

The distribution of the Fischer–Tropsch synthesis products formed on the 2% Ru–2% Pt/zeolite catalyst shifts towards lighter hydrocarbons in the series NaY < HY < DAHY.[83] The number of strong acid sites of the zeolites determined by the method of temperature-programmed desorption of NH_3 (T_{max} > 350 °C) increases in the same sequence. Among the products of the synthesis catalysed by the DAHY-containing material, mono- and di-branched alkanes predominate. This is due to the fact that relatively strong acid sites are unsuitable for skeletal isomerisation.[86]

Under conditions of the Fischer–Tropsch synthesis, the growing linear chain is chemically bound to the surface. This bond ruptures upon elimination of β-hydrogen from the hydrocarbon yielding a terminal alkene or upon α-hydrogenation giving rise to a linear alkane.[87] The latter is inert under the Fischer–Tropsch reaction conditions;[88] therefore, it does not participate in secondary transformations. Meanwhile, terminal alkenes can be partly hydrogenated or involved once again in the hydrocarbon chain growth after readsorption.[89,90] Upon the repeated adsorption of alkenes, the possibility of chain termination as a result of hydrogenation decreases, resulting in a higher probability of chain growth and a greater alkane : alkene ratio.[62,91]

The probability of secondary reactions involving terminal alkenes substantially increases with an increase in the number of carbon atoms in the molecule.[92,93] Correspondingly, the alkane : alkene ratio [94,95] and the probability of chain growth [62,95] also increase. The probability of secondary transformations of alkenes is normally assumed to be proportional to the contact time. Some investigators [63,93] believe that the contact time increases appreciably as the chain becomes longer, because hydrocarbons with longer chains are better soluble in heavy products of the Fischer–Tropsch synthesis, which fill the catalyst pores. However, the dependence of the solubility on the chain length cannot be determined or calculated; therefore, this parameter is difficult to use as a quantitative characteristic. In addition, this interpretation does not seem to be fully justified because the presence of a liquid phase does not influence the chemical potential and, hence, the secondary transformations.[62] The dependence of the chain length on the residence time might also be due to transport limitations (*i.e.* diffusion). When there are no transport limitations, the components of the gas and liquid phases of the reaction system are in thermodynamic equilibrium. Therefore, in this case, neither the residence time of the products in the reaction area nor the kinetic driving force (volatility or chemical potential) depend on the presence of the liquid phase.[62] The secondary transformations of hydrocarbons are not influenced by the liquid phase either. When there are external-diffusion limitations, the number of carbon atoms in the molecules being formed depends on the factor of the hydrocarbon chain growth α and on the concentration of alkenes. In this case, the residence time of hydrocarbons in the pores filled with a liquid increases and, hence, the probability of secondary transformations also increases.

An attempt has been made [88] to elucidate the reason for the dependence of the rate of secondary reactions on the hydrocarbon chain length using cobalt foil as a model catalyst. Diffusion

limitations were modelled using a foil coated preliminarily by wax. When a non-coated foil was used, there were no such limitations. Below we consider the results of this study in more detail.

The ratio of the rates of hydrogenation and repeated involvement of readsorbed alkenes in the chain is determined by a large number of parameters, in particular, CO and H_2O pressures.[62] Under the conditions studied (0.1 MPa, 220 °C, $H_2:CO = 1$, polycrystalline cobalt), virtually all readsorbed alkenes should be hydrogenated. Thus, the distribution of hydrocarbons up to C_{14} cannot deviate from the Schulz–Flory distribution, *i.e.* it cannot depend on secondary transformations. The chemisorbed intermediates which undergo hydrogenation differ from those involved once again in the chain growth.

To be repeatedly involved in the synthesis, an alkene should be chemisorbed on a vacant site on the catalyst surface. Under the conditions of the Fischer–Tropsch synthesis, vacant sites are scarce, because the surface is occupied almost completely by various fragments.[95] In order to occupy a growth site which has become vacant, an alkene should compete with CO and H_2. It is unlikely that an alkene molecule that has moved far away from a vacant active site would reach it before it is occupied again. Of all the alkenes present in the reactor, only those located in the close vicinity of a site have a chance to be readsorbed.

Thus, the probability of the repeated involvement of alkenes in the chain is intimately connected with their concentration at the interface in the physically adsorbed layer and with their average concentration over the whole reactor (*i.e.* the contact time). The alkene concentration at the interface is influenced, in addition to the transport limitations, by the preferred physical adsorption and solubility. Chemisorption of alkenes is a non-activated process. On passing from a physically adsorbed state to chemisorption, there is no competition between the reactions. Thus, the rate of readsorption is controlled only by the effective 'rate of collisions', which depends on the concentration of the molecules in the physical adsorption region at the interface, *i.e.* on the total contact time in the physically adsorbed layer and on the alkene concentration in wax. The chemisorbed phase occurs in a steady state; however, there is no equilibrium between the physically and chemically adsorbed phases.

As a consequence, at low degrees of CO conversion on the Co foil, the alkane/alkene ratio grows exponentially as the chain is lengthened. The coating of the foil with wax results in lower yields of alkanes and a less pronounced dependence of the alkane/alkene ratio on the chain length. These findings can be explained by the fact that the rate of readsorption of alkenes increases exponentially with chain length. A model was proposed which assumes competitive participation of alkenes in the readsorption, so that the readsorption rate is proportional to the alkene concentration at the catalyst–wax interface. Thus, the dependence of the alkane/alkene ratio on the chain length is determined by the solubility of hydrocarbons and by diffusion limitations; the latter, in turn, are caused by the predominant physical adsorption in the boundary layer. Under normal synthesis conditions (when the degree of CO conversion is high), the transport limitations are more significant.

IX. Conclusion

The foregoing leads to a number of general conclusions concerning the current state of the problem of catalytic synthesis of isoalkanes and aromatic hydrocarbons from CO and H_2.

The transformation of CO and H_2 on oxide catalysts giving mainly isoalkanes ('iso-synthesis') normally requires high pressures.[96] In this case, the yield of liquid hydrocarbons is low, and the overall catalyst activity is not sufficiently high.

A more promising method is the synthesis of isoalkanes as mixtures with linear alkanes on catalysts containing high-silica zeolites together with Group VIII metals. Apparently, either intermediates or alkenes which undergo skeletal isomerisation serve as the source of isoalkanes. Aromatic hydrocarbons can also be formed on these catalysts but this requires higher temperatures.

The zeolite component of the catalyst ensures the occurrence of isomerisation and aromatisation processes. Isomerisation occurs on the Brønsted and Lewis acid sites. Isomerisation of alkenes is more efficient on bifunctional metal-containing catalysts. Thus, the transformation of CO and H_2 on the Co–MgO/HZVM catalyst affords hydrocarbons (yield 70%–90%) containing 36%–40% of isoalkanes.[40]

The 'two-sites' model for the Co catalysts for the Fischer–Tropsch synthesis that we proposed previously makes it possible to divide all the active sites on the catalyst surface into three main types, namely, methanation sites (Co^0), hydrocarbon chain growth sites ($Co^{\delta+}-M_xO_y$) and isomerisation and cyclisation sites (acid sites).

The deviation of the product composition from the Shulz–Flory distribution is due to the repeated adsorption of alkenes on one or several active sites. Readsorption of alkenes and their involvement in growing chains results in an appreciably decreased total rate of hydrocarbon chain termination and in a change in the step of hydrogen elimination giving terminal alkenes. Thus, readsorption of alkenes followed by their skeletal isomerisation and hydrogenation ensure the formation of isoalkanes. Yet another pathway to isoalkanes is decomposition of unsaturated branched oligomers on acid sites and subsequent hydrogenation.

Of course, it is as yet impossible to draw ultimate conclusions about the true mechanism of the formation of isoalkanes and aromatic hydrocarbons under the Fischer–Tropsch synthesis conditions. However, in all probability, a fairly important role in the processes catalysed by cobalt-containing catalytic systems is played by unsaturated intermediates and by their subsequent readsorption with involvement in the growing hydrocarbon chain or their oligomerisation and isomerisation.

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