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The role of zeolite in the Fischer – Tropsch synthesis over cobalt – zeolite catalysts

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The review deals with the specifics of the Fischer – Tropsch synthesis for the one-stage syncrude production from CO and H_2 in the presence of cobalt – zeolite catalytic systems. Different types of bifunctional catalysts (hybrid, composite) combining a Fischer – Tropsch catalyst and zeolite are reviewed. Special attention focuses on the mechanisms of transformations of hydrocarbons produced in the Fischer – Tropsch process on zeolite acid sites under the synthesis conditions.
The bibliography includes 142 references.

Contents

I. Introduction 1176
II. Specifics of the Fischer – Tropsch synthesis 1177
III. Catalysts for the one-stage production of syncrude from CO and H_2 1177
IV. Conclusion 1185

I. Introduction

Currently, oil is still the main source of hydrocarbons. Development of alternative methods for the preparation of hydrocarbons from the non-oil raw materials is becoming an increasingly urgent problem due to the continuous rise in oil prices, as well as because of its limited resources.[1 – 3] One of such methods is the XTL technology intended to produce high-quality synthetic liquid fuel. This technology combines three separate methods using different feedstocks:[4 – 7]

— GTL (Gas-to-Liquids) — the feedstock is gas (natural gas, associated gas, shale gas, *etc.*);

— CTL (Coal-to-Liquids) — the feedstock is coal or other solid fossil fuels;

— BTL (Biomass-to-Liquids) — the feedstock is biomass.

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The commercially implemented XTL processes include three stages: production of syngas (conversion of the initial carbon-containing feedstock into a mixture of carbon monoxide and hydrogen); production of hydrocarbons from CO and H_2 (the Fischer – Tropsch synthesis), and processing (hydrocracking and/or hydroisomerization) of the products obtained at the second stage of synthesis.

The technological solution of the first stage is determined by the nature and composition of the feedstock that should be treated and the H_2 : CO ratio, which is dictated by the next stage. Relevant engineering solutions have been realized in industry for several decades, and any of them can be used in XTL technology as a standard component for designing the process flow diagram optimal in energy consumption.

The technological solution of the second stage depends on the character of the synthesized product. The Fischer – Tropsch synthesis affords either a mixture of only hydrocarbons or a mixture of hydrocarbons with oxygen-containing compounds; the composition of the mixture is determined by the nature of the catalyst and synthesis conditions.

The technological solutions of the third stage are widely known, implemented, and readily available in the technology market. This stage involves hydrotreating of high-molecular-weight products obtained in the Fischer – Tropsch synthesis into liquid hydrocarbons of the gasoline, kerosene and diesel ranges and bases for oils.

In the case of direct synthesis of liquid hydrocarbons (so-called syncrude, a mixture of hydrocarbons with the boiling point < 450 °C free of sulfur and nitrogen com-

pounds) from CO and H_2, the hydrotreating stage is unnecessary, and the flow diagram of the process is reduced.

Thus, it is evident that the efficiency of XTL technology is, on the whole, dictated by the stage of synthesis of hydrocarbons from CO and H_2 — the Fischer–Tropsch synthesis. It is impossible to improve the process of syngas conversion without development of new catalytic systems efficient and selective for production of syncrude from CO and H_2 in one stage. At the same time, design and optimization of such catalytic systems requires a deep understanding of the processes that occur on their surface, in particular, the role of the zeolite — the essential component of the catalyst for the direct production of syncrude from syngas.

Despite the fact that in the past decade the one-stage production of syncrude from CO and H_2 has attracted the attention of many scientists all over the world, there are no recent reviews where basic results of studies in this area would be systematized. One of the recent reviews in a related field was published by Lapidus and Krylova in 1998.[8] In the modern literature, reviews devoted to certain areas are available, in particular, to process design solution of the Fischer–Tropsch synthesis,[5,6] as well as to the transformations of hydrocarbons on acid sites of zeolites.[9–11] The present review covers the literature devoted to all aspects of design of catalytic systems combining the functions of the Fischer–Tropsch catalyst and the catalyst of hydrocarbon transformations. In addition, the mechanisms of possible reactions and their contribution to the composition of syncrude are discussed.

II. Specifics of the Fischer–Tropsch synthesis

The Fischer–Tropsch synthesis is a complex catalytic process, which proceeds on heterogeneous catalysts containing Group VIII metals (iron, cobalt, nickel or ruthenium) and involves a complex set of consecutive and parallel transformations. The synthesis mainly gives alkanes and alkenes, and their yield and composition depend on the nature of the catalyst and synthesis conditions. The process is accompanied by a large number of side reactions, the water gas shift reaction and hydrogenation of CO to methane being basic among them. In addition, the synthesis is complicated by diffusion limitations and high heat release (160–180 kJ mol^{-1}), which can be responsible for the uncontrolled heating-up and can have an effect on the composition of reaction products. As a rule, the local overheating of the catalyst reduces the selectivity to the target products because of the increase in the contribution of methane formation through the hydrogenation of CO.

Currently, catalysts containing cobalt or iron as the active metal are most attractive for commercial-scale application. The choice between iron and cobalt depends, first of all, on the desired composition of products. The most selective catalysts for the synthesis of fuel hydrocarbons by the Fischer–Tropsch method are believed to be cobalt-containing catalysts since they almost do not catalyze the formation of oxygenates and aromatic compounds. Cobalt is active in hydrogenation reactions and, hence, produces smaller amounts of unsaturated hydrocarbons and oxygenates;[12,13] in addition, it can promote the hydrocarbon chain growth reactions involving alkenes, which leads to the increase in the content of branched hydrocarbons.[14–16] Cobalt catalysts are superior to iron catalysts in that they are more active under milder conditions and have a longer service life.[17] As a rule, the active metal is supported on oxides, mainly on aluminium, silicon, titanium or zinc oxides.

The deactivation of cobalt catalysts of the Fischer–Tropsch synthesis is well understood and explained by several factors. One of them is the decrease in the amount of accessible cobalt active sites because of the accumulation of heavy hydrocarbons (waxes) on the catalytic surface.[18] It should be noted that, according to Egiebor *et al.*,[18] the presence of a cocatalyst exhibiting acid properties elongates the service life of the Fischer–Tropsch catalyst, which is explained by the cracking of the resulting high-molecular-weight products on the acid sites of the cocatalyst.

The molecular-weight distribution of the Fischer–Tropsch synthesis products obeys the Anderson–Schulz–Flory polymerization model, which imposes constraints on the selectivity of the formation of particular hydrocarbons. Therefore, in the presence of conventional catalysts, the selective formation of hydrocarbons of the desired fraction and group composition cannot be achieved. In this context, as long ago as in the mid-1970s, the idea was put forward to combine the Fischer–Tropsch catalyst and an acid catalyst, in particular, a zeolite, in order to overcome the obedience to the Anderson–Schulz–Flory distribution. In the presence of such dual catalysts, the hydrocarbons that are formed from syngas on the metal sites or their intermediates can be further transformed at the acid sites of the support, for example, of the zeolite,[8,9,19–23] which leads to deviations from the Anderson–Schulz–Flory distribution. The composition of synthesis products is determined by relative reaction rates at the acid and metal sites.

A combination of the Fischer–Tropsch catalyst and zeolite in a common system has led to the creation of so-called bifunctional catalysts,[24–65] which are often referred to as hybrid catalysts[9,25,27,28,30,49,50] and which also include composite systems.[31,32,51–53,63–65] Bifunctional catalysts enable the one-stage selective production of syncrude from CO and H_2 free of heavy hydrocarbons (waxes), which obviates the necessity of the hydrotreating stage and makes XTL technology much more promising.

III. Catalysts for the one-stage production of syncrude from CO and H_2

In the presence of bifunctional (hybrid, composite) catalysts, long-chain hydrocarbons formed from CO and H_2 at metal sites can be subjected to hydrocracking at acid sites of the zeolite to give liquid hydrocarbons of the gasoline and diesel fractions.[8,9,19–23] At the same time, at the acid sites of zeolites, isomerization and alkylation to produce branched alkanes can occur, which increases the octane number of the products.[9,19,20,23,66]

Zeolites have a special pore structure, which is a system of communicating channels.[67,68] In addition, owing to their acid properties, zeolites are active catalysts of hydrocracking and hydroisomerization.[66] For example, the HZSM-5 zeolite is commercially used in reactions of acid-catalyzed cracking and promotes low-temperature isomerization reactions.[19] These characteristics of zeolites are responsible for their use as an essential component of Fischer–Tropsch catalysts intended for the one-stage production of syncrude from CO and H_2.

Among the secondary reactions on zeolite-containing Fischer–Tropsch catalysts, hydrocracking and hydroisomerization are discussed most frequently,[19,21,22] while alkylation[66] and oligomerization,[9] as well as cracking and isomerization, are less widely discussed.[9,23–26] However, it is worth noting that, in petroleum refining processes, isomerization of high-molecular-weight hydrocarbons is carried out at lower temperatures (200–250 °C) than hydrocracking (400–550 °C).[8,69]

It has been reported[70] that cracking and isomerization reactions are more probable on the acid sites of zeolites under Fischer–Tropsch synthesis conditions (210–260 °C), since the synthesis temperature is insufficiently high for hydrocracking to occur, and the $H_2:C_{5+}$ hydrocarbons ratio in the reaction products is <0.5, which is insufficient for the active hydrotreating process. It is also worth noting that some authors make no difference between hydrocracking and cracking and between hydroisomerization and isomerization and describe them as one process.[9,19]

In the reactions of hydrocarbons that occur on zeolites, an important role is played by carbocations.[8,20,22,69] On bifunctional catalysts, carbocations can be generated as a result of hydrogen activation at metal sites with subsequent hydrogen transfer to Brønsted acid sites and proton transfer from the acid site to the alkene that was formed on the surface of the metal phase.[27,28] When describing the mechanism of transformations on the zeolite, some authors consider carbenium and carbonium ions as well; however, the more general term carbocation is often used. Carbocation can be involved in reactions of skeletal isomerization, double bond shift, alkylation of alkenes or other carbocations and oligomerization of alkenes with an internal double bond, which proceed on zeolite acid sites.[8,20,69,71,72] In addition, H-zeolites are active in hydrogen transfer reactions,[73,74] which can stabilize acid sites or increase their strength. These reactions lead to an increase in the content of alkenes, isoalkenes and isoalkanes in reaction products, while the molecular weight of the products decreases. It has been demonstrated[75–77] that the rates of secondary hydrocarbon transformations depend on both the strength of zeolite acid sites and the zeolite pore structure.

It has been suggested to combine the Fischer–Tropsch synthesis and the upgrading of its products, which is carried out in a consecutive dual reactor system.[78–83] In the upper reactor, a physical mixture of the Fischer–Tropsch catalyst Co/SiO_2 and zeolite (HZSM-5, HB, Pd/HB, HY, HMOR) catalyzes the formation of syncrude, which, according to the authors, should be upgraded. The lower reactor is loaded with the hydrocracking–hydroisomerization catalyst (Pd/HB, Pt/HB or Pd/SiO_2) mixed with zeolite (HZSM-5, HB, HY, HMOR). The composition of the products is close to that of syncrude produced in the presence of hybrid catalysts placed into one reactor. The authors note that the dual reactor system allows one to independently vary and optimize the conditions of both processes; however, on the other hand, it can lead to an increase in sophistication of process design and to a rise in its cost, which other researchers try to avoid by combining the Fischer–Tropsch catalyst and the hydrotreating catalyst in a single reactor.

It has been suggested[24] to divide bifunctional Fischer–Tropsch catalysts into three groups: (1) physical mixtures [as a rule, a mixture of powders (more rarely, pellets) of the Fischer–Tropsch catalyst and zeolite often diluted with an inert material];[25–29,31] (2) capsule catalysts (a zeolite shell covers the Fischer–Tropsch catalyst);[24,33,35–39] (3) impregnated catalysts (zeolite is a support onto which cobalt is deposited, as a rule, from solutions of its salts).[32,40–62,77,84–86] In the present review, we suggest completing this classification by assigning composite catalysts to a separate group: (4) composite catalysts (finely dispersed cobalt and zeolite are blended with other components, including binders, and pelletized, which increases, as compared with physical mixtures, the probability of contact of the Fischer–Tropsch products with zeolite acid sites, but without decreasing the mass exchange rate, unlike encapsulation).[31,32,51,63–65]

III.1. Physical mixtures of catalysts

Physical mixtures combine the functions of the Fischer–Tropsch catalyst and the acid catalyst (zeolite) by mere physical mixing or layer-by-layer arrangement of powders of initial components or catalyst pellets. When loaded into a reactor, mixtures of powders are almost always diluted with an inert material to avoid excessive compacting of the catalyst bed.

A three-component hybrid catalyst has been developed for one-stage direct synthesis of isoalkanes *via* modified Fischer–Tropsch synthesis.[27] The catalyst consists of three mixed components: Co/SiO_2 (as the Fischer–Tropsch catalyst), ZSM-5 zeolite (as a hydrocracking and hydroisomerization catalyst) and Pd/SiO_2 (for extending the service life of the zeolite catalyst). The component mass ratio was $Co/SiO_2:Pd/SiO_2:ZSM\text{-}5 = 4:1:4$. For comparison, a mixture with $Co/SiO_2:SiO_2:ZSM\text{-}5 = 4:1:4$ was used. The synthesis was carried out at 230–250 °C and 1.0 MPa ($H_2:CO = 3$ or 2). In the presence of the $Co/SiO_2:SiO_2$:ZSM-5 mixture, syncrude free of heavy hydrocarbons was formed, mainly consisting of C_4-C_{10} isoalkanes and alkanes, as well as of some amounts of alkenes. The authors believe that long-chain hydrocarbons are more readily hydrocracked on zeolite acid sites. The introduction of the Pd/SiO_2 catalyst instead of SiO_2 led to a significant decrease in the yield of alkenes, and under hydrogen excess ($H_2:CO = 3$), the formation of alkenes was completely suppressed. The introduction of Pd/SiO_2 also led to a decrease in selectivity to methane from 18% to 11%. The authors have explained this fact by assuming that methane is formed not only *via* the Fischer–Tropsch synthesis but also through hydrocracking of α-alkenes produced from CO and H_2. In the presence of Pd, such alkenes are actively hydrogenated, which suppresses the formation of excessive methane. In addition, the introduction of Pd extended the service life of the hybrid catalyst: a 100-h test did not reveal a decrease in activity or a change in the fractional composition of synthesis products. This has been explained[87] by hydrogen activation in the presence of Pd, which can promote the appearance of new acid sites of the zeolite (the spillover effect).

The behaviour of hybrid catalysts Co/SiO_2 + zeolite (HZSM-5, HY, HMOR) + Pd/SiO_2 has been studied in the course of production of light isoalkane-rich syncrude at 240–300 °C, 0.5–2 MPa and $H_2:CO = 1.8-3$.[28] The authors believe that the introduction of Pd/SiO_2 modifies the reaction mechanism: in the absence of Pd/SiO_2, secondary cracking reactions on zeolite yield methane, alkenes and isoalkanes, while the introduction of Pd initiates hydrocracking, almost suppressing the formation of alkenes and significantly increasing the content of isoalkanes. The

authors also explain the contribution of Pd/SiO_2 by the activation of gaseous hydrogen and its transfer to acid sites of the zeolite (spillover effect).[88,89] As a result, saturated hydrocarbons are activated, and intermediate carbenium ions are stabilized, which promotes isomerization. Hybrid catalysts prepared by deposition of palladium directly on zeolite HB have been studied.[29] This catalyst affords C_4-C_{10} isoalkanes from syngas with high selectivity (>60%).

The effect of acidity and pore structure of zeolites on the activity and deactivation of hybrid catalysts has been studied for a physical mixture of the Fischer–Tropsch catalyst Co/SiO_2 and zeolite (HY, HB, HMOR or HZSM-5) active in cracking and isomerization reactions under typical Fischer–Tropsch synthesis conditions (250 °C, 2.0 MPa, $H_2:CO = 2$).[25] The use of such catalytic mixture improves the selectivity to C_5-C_{12} hydrocarbons and leads to a sharp increase in the amount of branched hydrocarbons. In addition, the yield of C_2-C_4 hydrocarbons increases, which is explained by the cracking of primary products of the Fischer–Tropsch synthesis. As observed by the authors, the activity of zeolites in cracking did not correspond to the amount and strength of Brønsted acid sites: in particular, the most active catalyst turned out to be the catalyst containing HZSM-5 zeolite, which was characterized by significantly weaker acid sites (according to the pyridine adsorption test) than the HY and HMOR samples. These results have been explained by the effect of water on the zeolite activity and different mechanisms of formation of carbonaceous compounds. An additional experiments with n-$C_{16}H_{34}$ as a model molecule has shown that, under the Fischer–Tropsch synthesis conditions (250 °C, 2.0 MPa), the HZSM-5 zeolite actually promotes the cracking of hydrocarbons. It has been found[25] that the presence of water in the reaction zone decreases the zeolite activity (by ~10%) but does not deteriorate its stability since polar water molecules compete with n-$C_{16}H_{34}$ for adsorption onto the Brønsted acid sites of the zeolite, thus decreasing the number of the sites accessible for cracking. A similar suggestion has been put forward in one more study.[90] In addition, it has been shown that the interaction with water is stronger for a more hydrophilic zeolite (with a lower Si:Al ratio). However, it is more logical to assume that water has an effect on the deactivation of Lewis acid sites,[91,92] whose participation in hydrocarbon transformations is hard to deny.[70,93,94]

The influence of zeolites with channels formed by 10-membered rings (ZSM-5, MCM-22, IM-5, ITQ-2) on the behaviour of the Co/SiO_2 catalyst in the Fischer–Tropsch synthesis (250 °C, 2.0 MPa, $H_2:CO = 2$) has been studied.[30] All zeolites have the same Si:Al ratio (15). The introduction of the zeolite leads to an increase in the content of monosubstituted branched hydrocarbons and in selectivity to gasoline-range hydrocarbons (C_5-C_{12}) by 20%–50% depending on the type of zeolite (MCM-22 ≈ IM-5 < ITQ-2 ≪ ZSM-5). It has been noted that, although the cracking of branched hydrocarbons can give methane, the introduction of the zeolite does not improve the selectivity to methane. According to the authors, this is explained by cracking *via* β-scission mechanism, which does not yield additional methane amounts.

The loss of activity of a catalytic mixture of Co/SiO_2 with different zeolites has been observed.[25] The degree of deactivation and its rate depended on the zeolite structure

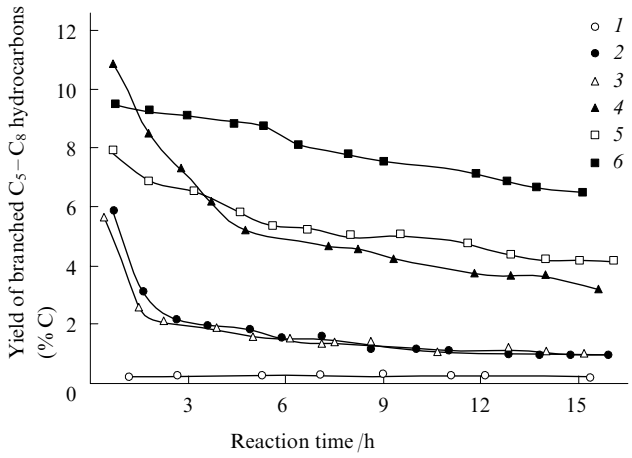


Figure 1. Yield of branched C_5-C_8 hydrocarbons as a function of reaction time in the presence of different catalysts: Co/SiO_2 (*1*) and Co/SiO_2 mixtures with zeolites HY-500 (*2*), HY-720 (*3*), HB (*4*) HMOR (*5*), HZSM-5 (*6*).[25]
Reaction conditions: 250 °C; 2 MPa; $H_2:CO = 2$; gas flow rate, 13.5 litre g^{-1} cat h^{-1}.

and did not correlate with the strength of the Brønsted acid sites. The deactivation rate (and the amount of deposited coke) decreases in the order HY-720 ≈ HY-500 > HB > HMOR > HZSM-5 (Fig. 1). The HY and HB zeolites with large pores and a 3D system of communicating channels and cages were deactivated due to coking more rapidly than the HMOR zeolite, which containes a 1D system of 12-membered channels. Medium pore-size zeolite HZSM-5 turned out to be most resistant to deactivation. Despite significantly different Brønsted acidities, zeolites HY-720 and HY-500 show almost identical time dependences of deactivation (Fig. 1). According to the authors, this result demonstrates that, under Fischer–Tropsch synthesis conditions, the zeolite structure is more responsible for its deactivation than the strength of its acid sites. From analysis of carbonaceous deposits, the authors have concluded that different types of coke are deposited on zeolites with different structures. Carbonaceous deposits of type I formed in the presence of HZSM-5 are located near the outer surface of zeolite crystals and consist mainly of long-chain n-alkanes, primary products of the Fischer–Tropsch synthesis. Carbonaceous deposits of type II are formed in large pores of the HMOR, HB and HY zeolites and consist mainly of naphthalenes and phenanthrenes with the number of carbon atoms from 13 to 20. Formation of polyaromatic coke is believed to be a result of cracking of the primary products of the Fischer–Tropsch synthesis through the stage of oligomerization of alkenes with subsequent cyclization and dehydrogenation, as has been suggested.[95,96] Such reactions involve larger intermediate molecules (as compared with the cracking reactions),[97] which cannot be accommodated in narrower channels of the HZSM-5 zeolite.

The behaviour of a mixture of the Pt/ZSM-5 hydroprocessing catalyst and the cobalt- or iron-containing Fischer–Tropsch catalyst in a fixed-bed reactor at 1 MPa has been studied.[26] The catalyst was used either in dual-layer arrangement or in uniform mixture. It has been shown that the introduction of the Pt/ZSM-5 catalyst leads to a

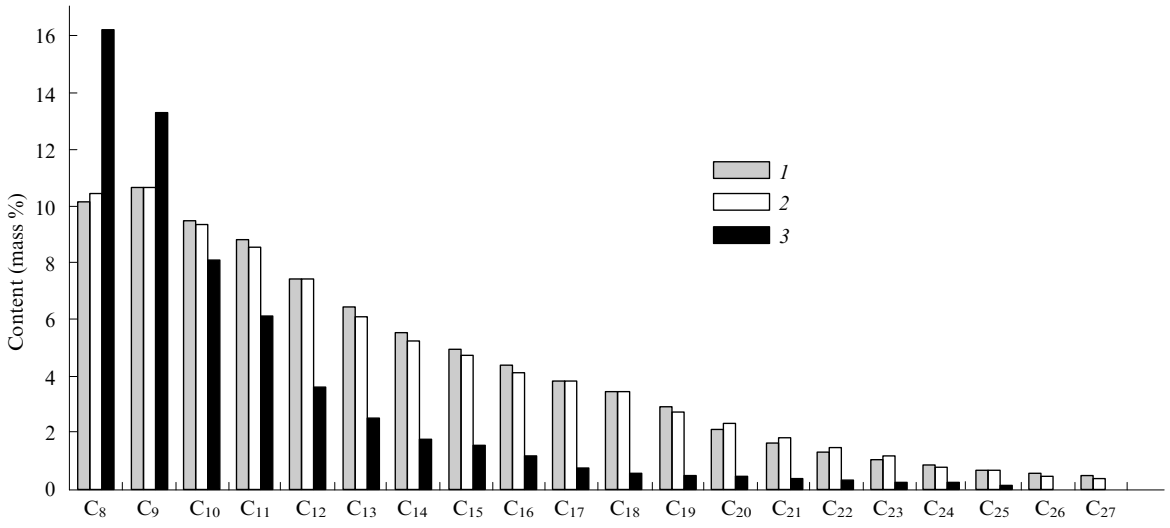


Figure 2. Influence of the composition of the catalytic mixture on the molecular-weight distribution of C_8-C_{27} hydrocarbons at 2 MPa, 251 °C for Co sample (*1*), 258 °C for samples Co – Z (*2*) and Co + Z (*3*) and the syngas hourly space velocity (GHSV) of 3000 h^{-1} (Ref. 31).

change in the composition of the Fischer–Tropsch synthesis products since it promotes hydrogenation, hydrocracking and isomerization reactions. As a result, the selectivity to long-chain hydrocarbons (C_{21+}) is reduced, the content of isoalkanes of the gasoline (C_5-C_9) and diesel ($C_{10}-C_{20}$) ranges increases, and alkenes are nearly completely hydrogenated. The authors have observed no catalyst deactivation in the experiment with a duration of 1 month.

Recently,[31] our team has studied the role of the zeolite in the synthesis of hydrocarbons from CO and H_2 in the presence of catalytic mixtures containing finely dispersed skeletal cobalt as the Fischer–Tropsch catalyst and a zeolite HB powder promoting hydrocarbon transformations. The behaviours of such mixtures have been compared depending on the arrangement of catalytically active components: the layer-by-layer arrangement of cobalt and zeolite (Co – Z, Fig. 2) or their uniform mixture (Co + Z, Fig. 2). It has been noted that when zeolite is added to cobalt as a separate layer (the Co – Z catalyst), the yield of methane increases from 31% – 37% to 35% – 39%, whereas the decrease in the distance between cobalt and zeolite particles from several tens to a few micrometres in the uniform mixture (the Co + Z catalyst) leads to a decrease in the yield of methane to 28% – 32%. The yield of C_3 hydrocarbons also increases when the zeolite is added to the cobalt as a separate layer and decreases when it is mixed with the cobalt. Similar trends have also been reported.[26, 98–100] The introduction of the zeolite as a separate layer leads to a noticeable (more than twofold) decrease in the yield of n-butene, which is likely due to that it undergoes conversions *via* the carbocation mechanism to give branched products. Mixing cobalt with the zeolite leads to a noticeable increase in the content of n-butane and a decrease in the content of n-butene, isobutane and isobutene. The authors believe that alkenes forming through cracking on the zeolite[3, 24, 76, 101, 102] are readsorbed on metal sites where they can be hydrogenated, as well as where they can be involved in initiation of hydrocarbon chain growth from CO and H_2.[14, 15, 102, 103] Despite the very close distributions of C_8-C_{27} products obtained in the presence of cobalt (Co) and a two-layer mixture (Co – Z) (Fig. 2), the fraction of C_{11+} hydrocarbons decreases by 20% – 30% when the zeolite layer is added. The synthesis over a uniform mixture of cobalt and zeolite powders (Co + Z) leads to an essentially different molecular-weight distribution of C_8-C_{27} hydrocarbons: the content of hydrocarbons with boiling point < 170 °C increases, while the content of hydrocarbons in the diesel range decreases. No products with a molecular weight above C_{26} have been observed in the presence of uniformly mixed cobalt and zeolite, which has been explained by assuming that the hydrocarbons formed from CO and H_2 on a metal site are cracked on acid sites of the zeolite. As in other studies,[14, 15, 102, 103] it has been suggested[25] that cracking occurs *via* the carbocation mechanism leading to the formation of shorter hydrocarbon chains, as well as alkenes and isoalkanes. The higher the molecular weight of a hydrocarbon, the more readily it undergoes cracking.

In addition, it has been indicated[31] that the depth of secondary transformations of high-molecular-weight products of the Fischer–Tropsch synthesis increases with a decrease in distance between the metal and zeolite particles, which has also been observed.[32]

III.2. Capsule catalysts

When a bifunctional catalyst as a physical mixture is used, syngas is converted into linear hydrocarbons on the Fischer–Tropsch catalyst (catalyst A); some of these hydrocarbons find themselves on the zeolite (catalyst B) where they are hydrocracked and isomerized to give light isoalkanes (Fig. 3 *a*). However, a part of the Fischer–Tropsch synthesis products leaves the catalytic zone without transformations on the zeolite, which leads to low selectivity to light branched products.[33]

Tsubaki and co-workers[33, 35] have suggested a special structure of a combined catalyst — a core–shell capsule catalyst (Fig. 3 *b*) in which the Fischer–Tropsch catalyst (catalyst A) is coated with a membrane shell of the zeolite (catalyst B). In this case, all the products (linear hydro-

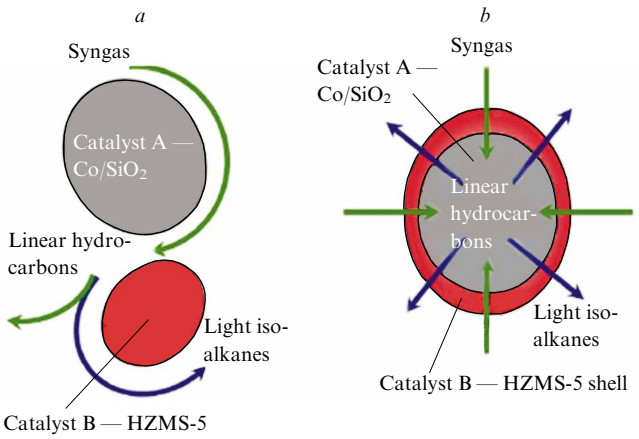


Figure 3. Schematic representation of the combined catalytic process in the presence of a bifunctional catalyst of different structure: physical mixture (*a*) and the core–shell capsule catalyst (*b*).[33]

carbons) generated from syngas on catalyst A pass through the membrane shell and are thus converted on the zeolite to give light isoalkanes with high selectivity.

For producing isoalkanes from syngas, the most efficient catalysts contain the active sites of the Fischer–Tropsch synthesis and acid sites,[81] on which successive transformations syngas (I) → n-alkanes (II) → isoalkanes (III) take place. Active sites of one type promote the I → II reaction, and those of the other type promote the II → III reaction. The principal factor that affects the selectivity of the process is the possibility of migration of the products formed on the active sites of the Fischer–Tropsch catalyst to the acid sites of hydrocracking and isomerization.[34] According to the authors, the active sites of both types are randomly distributed over the surface of a common (impregnated) bifunctional catalyst, which leads to the independent and random occurrence of two reactions, even though the distances between different active sites are small. This means that the products formed on the active sites of the first type can leave the catalytic zone without reacting with acid sites. Capsule catalysts are intended precisely to increase the probability of migration of the Fischer–Tropsch synthesis products to the acid sites of the zeolite.

The behaviour of a capsule catalyst in the direct conversion of syngas into isoalkanes has been studied.[36] Preformed Co/SiO_2 pellets have been used as a core, which is coated with a monolithic shell of the HZSM-5 zeolite. Syngas penetrates through the zeolite membrane to the catalyst core where hydrocarbons are generated; after desorption from the active sites of the Fischer–Tropsch catalyst, the latter are caught in zeolite channels and undergo hydrocracking and isomerization. The resulting distribution of hydrocarbons does not obey the Anderson–Schulz–Flory model. In this case, as distinct from a physical mixture of Co/SiO_2 and HZSM-5, the formation of C_{10+} hydrocarbons is completely suppressed. It should be noted that hydrocarbons with a longer carbon chain spend more time inside the zeolite, thus leading to the increase in their cracking depth. The molecular-weight distribution of hydrocarbons depends on the zeolite membrane thickness, which makes it possible to control the composition of the resulting hydrocarbons.

The same researchers[37] have focused on the size of preformed Co/SiO_2 pellets and capsules based on them. It has been noted that the capsule catalyst with the smallest pellets is characterized by a higher CO conversion and a higher selectivity to C_5 – C_{10} isoalkanes (up to 49%). Treatment of the zeolite shell of the capsule catalyst with palladium metal made it possible to reduce the content of the resulting alkenes from 27% to 15% owing to their active hydrogenation on palladium.[38, 39] It has been suggested[33] that α-alkenes generated in the Fischer–Tropsch synthesis can be readsorbed on the zeolite surface and can be involved in formation of light hydrocarbons, as described.[84, 104–106] It is believed that there is a competition between the isomerization and cracking reactions on the zeolite sites. Isomerization is preferable; however, the excess of acid sites (over cobalt sites) stimulates cracking to give alkenes. In addition, the decrease in the methane content is observed when the capsule catalyst is used, which can be explained either by dilution of the catalytic bed because of the larger volume of the capsule catalyst as compared with Co/SiO_2 pellets or by the thermodynamically favourable combination of the exothermic Fischer–Tropsch synthesis that occurs at the centre of the capsule and endothermic cracking and isomerization reactions that occur in its shell.[33] In both cases, it can be assumed that the local warming-up of the catalyst responsible for the increased methane formation becomes less probable. At the same time, in the studies dealing with the carbocation mechanism of cracking on zeolites,[27, 63, 93, 94, 107, 108] the low yield of methane is attributed to the fact that the formation of the primary carbocation leading to methane is thermodynamically unfavourable.

The behaviour of the $HB/Co/Al_2O_3$ capsule catalyst in synthesis of isoalkanes from CO and H_2 (260 °C, 1.0 MPa, $H_2:CO = 2$) has been studied.[34] The zeolite membrane (20 mass % HB) was coated onto the pellets of the impregnated catalyst 10 mass % Co/Al_2O_3. For comparison, the 10 mass % Co/Al_2O_3 catalyst and a physical mixture of the 10 mass % Co/Al_2O_3 catalyst with 20 mass % zeolite HB were used. In the presence of the Co/Al_2O_3 catalyst, linear hydrocarbons were basically generated. When the physical mixture was used, the distribution of the products deviated from the Anderson–Schulz–Flory distribution, and selectivity to isoalkanes and alkenes increased. However, there were C_{20+} hydrocarbons among the reaction products. In the presence of the capsule catalyst, the formation of C_{12+} hydrocarbons was almost completely suppressed. In addition, in this work, as in Ref. 37, it has been noted that the capsule catalyst is characterized by the lower selectivity methane (14% as compared with 22% in the presence of Co/Al_2O_3 and 17% in the presence of the physical mixture). However, in this case, this fact has been explained by hydrophilicity of the zeolite, which increases with a decrease in $Si:Al$ ratio.[109] It has been revealed that the $SiO_2:Al_2O_3$ ratio in the zeolite membrane of the capsule catalyst is nonuniform, the aluminium content near the Al_2O_3 support being somewhat higher, which implies high hydrophilicity.[34] According to the solubility rule, the presence of water can promote the accumulation of CO,[110] which can reduce the $H_2:CO$ ratio in the catalyst bulk and, hence, the selectivity to methane. In addition, some isoalkanes and alkenes formed in the channels of the zeolite membrane can diffuse

in the opposite direction to the surface of the Fischer–Tropsch catalyst and react there with the CH_2 intermediates located on the surface of the Co/Al_2O_3 catalyst.[111] The concentration gradient is favourable for the occurrence of this process, which can also suppress the formation of methane as a product of hydrogenation of CH_2 intermediates. However, in many works dealing with cracking on zeolites,[27, 63, 93, 94, 107, 108] the low yield of methane and ethane is explained by the thermodynamic disadvantage of formation of the primary and secondary carbocations.

Sartipi *et al.*[24] agree with the authors of many other studies [32, 36, 112, 113] in that the efficiency of the bifunctional catalyst is explained by tight contact between the metal sites active in the Fischer–Tropsch synthesis and the acid sites of the zeolite. In this case, unsaturated hydrocarbons formed in the Fischer–Tropsch synthesis can be sorbed on the zeolite and cracked or isomerized before they will be hydrogenated on a neighbouring metal site.[114] Thus, we can conclude that small distances between hydrogenating–dehydrogenating and acid sites is favourable for secondary transformations of hydrocarbons.[19]

The behaviour of the impregnated catalyst Co/H-ZSM-5 and the Co/SiO_2 catalyst coated with the H-ZSM-5 zeolite has been compared with the behaviour of Co/SiO_2 and a physical mixture of this catalyst with H-ZSM-5.[24] In the presence of the capsule catalyst, as in the presence of the impregnated catalyst, C_{12+} hydrocarbons are not formed. However, the core–shell catalyst exhibits low activity in the formation of gasoline-range synthetic hydrocarbons because of strong transport hindrances for diffusion of the products and initial components through the zeolite shell; therefore, it is believed that the impregnated catalyst supported on mesoporous HZSM-5 is preferable for direct synthesis of C_5-C_{12} hydrocarbons enriched in isoalkanes.

III.3. Impregnated catalysts

In impregnated catalysts, zeolite acts as a support, and the active metal is applied to the support by impregnation. Active sites of two types are in tight contact with each other; however, interactions of metal sites with the support become of crucial importance. Using the zeolite support allows one to obtain catalytic systems differing in metal dispersity and in the strength of metal interaction with the support surface. The pore type, structure and size, as well as the zeolite Si : Al ratio, have an effect on the catalytic characteristics of the system. Catalysts of this type have attracted the greatest interest and have been most fully described in the papers of different research teams.

It has been shown that the use of the bifunctional impregnated catalyst Co/HZSM-5 in the Fischer–Tropsch synthesis at 220–240 °C, 2.0 MPa and the ratio $H_2:CO = 2$ leads to an increase in selectivity to liquid hydrocarbons and to a decrease in the content of high-molecular-weight hydrocarbons (waxes).[40] The CO conversion is reduced with increasing the Si : Al ratio. (For the catalysts studied, the increase in the Si : Al ratio is accompanied by a decrease in the surface area, volume and average pore size.) It has been suggested that the increase in the specific surface area and pore size of the zeolite support promotes the formation of smaller cobalt particles, which are more readily reduced. This is favourable for the increase in conversion and the decrease in the rate of deactivation caused by coking or wax deposition.[41] However, other researchers [42, 43] have arrived at the conclusion that formation of cobalt clusters in micropores is undesirable since cobalt clusters < 6 nm in size are not optimal for the design of an active and selective Fischer–Tropsch catalyst. The increased methane formation in the presence of the Co/HZSM-5 catalyst is attributed to the strong cobalt–zeolite interaction responsible for the appearance of coordinatively unsaturated metal sites.[40]

It has been demonstrated that using the nanosized HB zeolite as the support for the cobalt catalyst makes it possible to synthesize significant amounts of isoalkanes even at 220 °C, whereas zeolites, as a rule, exhibit low isomerizing activity at such temperatures.[44] This work has focused on the effect of the cobalt content deposited by impregnation on the HB zeolite, as well as of the size of Co_3O_4 crystallites and Brønsted acidity, on the properties of the Co/HB catalyst and the composition of reaction products. A conclusion has been made that the catalyst properties depend on the amount of active sites of the Fischer–Tropsch synthesis (which is directly related to the size of cobalt crystallites) and the degree of their interaction with the zeolite acid sites determining its acidity. This conclusion is based on the observation that catalysts containing 10 mass % and 15 mass % cobalt are characterized by a smaller crystallite size (7–9 nm) and lower Brønsted acidity (26–47 mmol g^{-1}) but are nevertheless distinguished by the higher conversion of CO (21%–30%) and lower yield of isoalkanes (27%–32%). Conversely, catalysts with large Co_3O_4 crystallites (16–28 nm) and higher acidity (55–72 mmol g^{-1}) are less active in CO conversion (13%–20%) and more active in the formation of isoalkanes (41%–42%). It is likely that such a conclusion is somewhat hasty since the increase in the content of isoalkanes in the presence of the catalyst containing 20% cobalt can be associated with the decrease in the content of alkenes (more precisely, isoalkenes) in the products due to hydrogenation on cobalt.[44]

The results of tests of 10% Co/HZSM-5 catalysts in the Fischer–Tropsch synthesis (220–240 °C, 1.5 MPa, $H_2:CO = 2$), which made it possible to overcome the constraints imposed by the Anderson–Schulz–Flory distribution on the composition of the products, have been discussed.[45–47] The authors have demonstrated that the zeolite pore size plays a crucial role for the efficient conversion of hydrocarbons since small pores (micropores) prevent the transfer of large molecules. Creation of mesoporous zeolites can largely remove the diffusion limitations. Figure 4 shows transmission electron microscopy (TEM) images where the spongy morphology of Co/mesoHZSM-5 is seen as distinct from Co/HZSM-5, which is due to the mesoporous structure of the former. On the outer surface of HZSM-5 crystals (Fig. 4 *a*), large clusters of cobalt oxide can be seen. By contrast, in mesopores of mesoHZSM-5, small cobalt oxide agglomerates can be identified (Fig. 4 *b*). According to the authors of this and some other works,[75, 76] the activity of secondary transformations of the Fischer–Tropsch products depends on both the degree of mesoporosity of the zeolite and the strength of acid sites. It has been stated [46] that only strong acid sites lead to the deviation from the Anderson–Schulz–Flory distribution. In addition, the content and distribution of mesopores in the support have an effect on the dispersity of cobalt and the distance between the Fischer–Tropsch synthesis sites and zeolite acid sites.[45–47] Tight contact between the acid and metal sites makes it possible to increase the efficiency of a

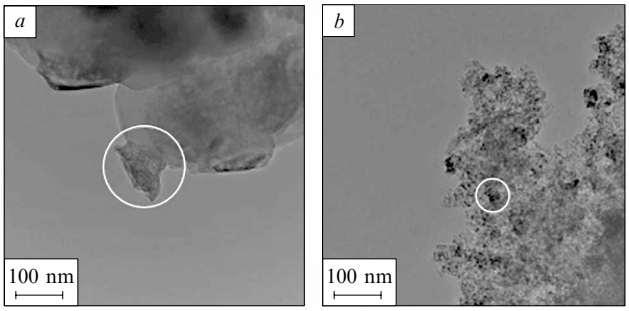


Figure 4. TEM images of Co/HZSM-5 (*a*) and Co/mesoHZSM-5 (*b*) before activation.[47]
Circles mark cobalt oxide clusters.

bifunctional catalyst by increasing the probability of sorption of unsaturated hydrocarbons on acid sites for secondary transformations.[114]

The effect of the mesostructured zeolite HB on the behaviour of the powder cobalt catalyst of the Fischer–Tropsch synthesis has been studied.[48] It has been shown that when the common zeolite HB is replaced by the mesoporous zeolite, the specific surface area of the catalyst decreases, while the size of Co_3O_4 crystallites increases. In the presence of the mesoporous zeolite, methane formation is reduced, and the alkenes : alkanes ratio decreases.

Catalysts in which 20 mass % cobalt was deposited on completely delaminated ITQ-2 and ITQ-6 zeolites have been studied.[49] The catalytic properties in the Fischer–Tropsch synthesis were determined at 220 °C, 2 MPa and the ratio $H_2 : CO = 2$ and compared with the properties of Co/SiO_2 and mesoporous Co/MCM-41. The Co/ITQ-6 and Co/ITQ-2 catalysts were more selective to C_{5+} hydrocarbons than Co/SiO_2 and Co/MCM-41. The authors have suggested that the higher concentration of coordinatively unsaturated Co^0 sites, characterized by the absorption band at 1897 cm^{-1} in the IR spectrum of adsorbed CO, is responsible for the enhanced selectivity of catalysts based on delaminated zeolites to C_{5+}. They believe that such a type of active site having enhanced electron density can stabilize surface intermediates, which is favourable for the carbon chain growth.

Catalytic performance of cobalt-based catalysts supported on SiO_2, Al_2O_3, montmorillonite and zeolites HY, HZSM-5 or MCM-22 in the slurry-phase Fischer–Tropsch synthesis has been studied at 230 °C and 1.0 MPa.[84] When a microporous acid support was applied, the formation of heavier hydrocarbons was retarded and the average number of carbon atoms in a molecule (carbon number) was reduced, since, according to the authors, micropores limited the hydrocarbon chain growth. In the presence of zeolite supports, the molecular-weight distribution of hydrocarbons was shifted toward the gasoline range. In addition, the selectivity to isoparaffins was considerably improved owing to the microporous structure and acidity favourable for the isomerization reaction. With decreasing aluminium content in the zeolite (*i.e.*, with increasing Si : Al ratio), the activity of the catalysts was enhanced and the selectivity to methane and isoparaffins decreased.

A commercially viable pelletized catalyst for the one-stage production of syncrude from CO and H_2 has been reported.[50] This is an impregnated cobalt/ruthenium catalyst supported on zeolite pellets (ZSM-5, ZSM-12). The cobalt content is 7.5 mass %, and the ruthenium content is 0.19 mass %. It is emphasized that the use of the pelletized catalyst (pellet size, 0.8–1.6 mm) is of crucial importance for subsequent commercial implementation of the process: in particular, the pressure drop across the catalyst bed is avoided. The Fischer–Tropsch synthesis is carried out at 205–235 °C, 0.5–3.0 MPa and the ratio $H_2 : CO = 1–2$. The ZSM-5 supported catalyst affords larger amounts of $C_1–C_4$ hydrocarbons, and the average molecular weight of the products noticeably decreases. Since the authors of this study have been interested most of all in diesel range hydrocarbons ($C_9–C_{19}$) rather than in gasoline range products ($C_5–C_{10}$), the ZSM-12 zeolite has been chosen for commercial implementation. The selectivity to methane in the presence of the hybrid catalyst is enhanced since the $C_2–C_3$ alkenes initiate the hydrocarbon chain growth reaction. The authors invoke the results of earlier works,[26,98–100] where it has been shown that, in the case of the layered arrangement of the Fischer–Tropsch catalyst and zeolite, hydrocracking of hydrocarbons gives C_{3+} hydrocarbons, which should not lead to an increase in methane formation. In addition, it follows[14] that the introduction of 5 mass %–20 mass % ethylene into a mixture of CO and H_2 does not contribute to the increase in the methane yield.

Another interesting observation[50] suggests that the formation of alcohols from CO and H_2, often observed in the presence of traditional Fischer–Tropsch catalysts, is suppressed in the presence of the hybrid catalyst because of their dehydration on zeolite acid sites.

The design of a high-performance catalyst for the one-stage production of syncrude from CO and H_2 has been reported.[51,52] The catalyst is cobalt deposited by impregnation on a multicomponent support containing the HB zeolite. In the presence of such a catalyst, the productivity of 450 g kg^{-1} cat h^{-1} has been achieved for C_{5+} hydrocarbons. Partial replacement of cobalt from nitrate by skeletal cobalt increased this characteristic to 600 g kg^{-1} cat h^{-1} (Refs 32, 51 and 52).

The effect of the zeolite nature in the composite support of a high-performance cobalt catalyst on the composition of hydrocarbons synthesized from CO and H_2 has been studied.[53,64] Zeolites (HB, HY, HMOR, HZSM-5) were introduced at the stage of preparation of a multicomponent support. Cobalt was deposited from an aqueous nitrate solution by impregnation. The synthesis was carried out in a flow-type fixed-bed reactor at 170–245 °C, 2 MPa, the GHSV 3000–5000 h^{-1} and the ratio $H_2 : CO = 2$. All catalysts exhibited high activity in synthesis (the CO conversion was 70%– 85%) and ensured the productivity of 400–450 g kg^{-1} cat h^{-1} with respect to C_{5+} hydrocarbons, the syncrude composition being determined by the zeolite nature. First of all, the effect of the type of zeolite is evident. In particular, whatever the Si : Al ratio and acidity, the presence of HY leads to hydrocarbon mixtures of similar composition containing large amounts of alkenes and small amounts of isoalkanes, and the resulting hydrocarbons are characterized by similar chain growth probabilities. This zeolite contains communicating cavities of large diameter. The pores in the other zeolites are open-ended linear channels of medium and large diameter. The composition of syncrude obtained in the presence of these zeolites correlates well with the Si : Al ratio: as the Si : Al

ratio decreases, the content of isoalkanes increases and the content of n-alkanes decreases. According to Koklin *et al.*,[54] this is due to the fact that a lower Si : Al ratio corresponds to a larger amount of Brønsted sites active in isomerization on zeolites.

The effect of the alkaline treatment of the cobalt ion-exchanged zeolite Co/HY on the synthesis of hydrocarbons at atmospheric pressure and the ratio $H_2 : CO = 1$ has been studied by Koh *et al.*[55] The CO conversion over this catalyst was no higher than 4%. It has been shown that decreasing acidity, determined by temperature-programmed desorption (TPD) of ammonia, leads to a decrease in the yield of branched hydrocarbons. At the same time, the yield of $C_{10}-C_{20}$ hydrocarbons increases. It is believed that the increase in the chain growth probability is due to the fact that the intermediates are entrapped deep in zeolite pores, while secondary isomerization and cracking of n-alkanes and α-alkenes occur on the acid sites of the zeolite.

Opposite results were obtained by Bessell,[77] who studied the effect of the type of zeolite (HZSM-5, HZSM-11, HZSM-12 or HZSM-34) on the properties of an impregnated cobalt catalyst in the Fischer–Tropsch synthesis at 240 °C, 2 MPa, the syngas GHSV 1000 h^{-1} and the ratio $H_2 : CO = 2$. It has been shown that the decrease in zeolite acidity, determined by TPD of ammonia, leads to a decrease in the yield of n-alkanes and in the average molecular weight of hydrocarbons. Since the structure and size of pores and channels of the selected zeolites were different, a conclusion has been made that not so much the strength and amount of acid sites as their accessibility is important for secondary transformations of Fischer–Tropsch synthesis products.

There are studies[56–58] dealing with optimization of conditions for catalyst activation and Fischer–Tropsch synthesis in the presence of the impregnated catalyst Co/HZSM-5 to achieve maximal selectivity and yield of the target product — C_{5+} hydrocarbons. At the same time, the authors do not pay attention to the mechanisms of reactions that occur on bifunctional catalysts.

In some works, zeolite has been used as the support of the Fischer–Tropsch catalyst with the aim to obtain cobalt clusters of definite size and study the effect of cluster size on the catalyst properties.[59–62] The mechanisms of reactions on a bifunctional catalyst has also remained beyond the scope of these studies. In particular, the surface reactions of H_2 and CO in the presence of the Co/NaY catalyst prepared by decomposition of cobalt carbonyl mixed with the NaY zeolite have been studied.[60] The authors have discussed specific features of the arrangement of small cobalt clusters inside the cages of the NaY zeolite and large cobalt metal aggregates on the external surface of the zeolite. The catalyst having most of cobalt metal clusters inside the zeolite cages is more selective to C_3 and C_4 hydrocarbons. It is suggested that the low hydrogenating ability of cobalt induces the enhanced chain propagation and the chain growth is terminated on the surface sites of cobalt clusters.

The effect of the Co particle size in an ion-exchanged catalyst based on the NaX and NaY zeolites on the behaviour of the catalyst in Fischer–Tropsch synthesis at 250 °C, 2.0 MPa, $H_2 : CO = 2$ and the gas flow rate 20 $cm^3\ min^{-1}$ has been studied.[61,62] According to the authors, cobalt particles of 1–2 nm in size inside the faujasite supercages make it possible to obtain a unique catalyst selective to C_5-C_{20} hydrocarbons, the content of C_{21+} hydrocarbons being minimal not exceeding 1.7%.

III.4. Composite catalysts

Composite catalysts in which fine skeletal cobalt and zeolite powders are introduced into a multicomponent catalyst have been suggested as catalysts for the one-stage production of syncrude from H_2 and CO.[32,51–53,63,64] In addition to the active components promoting transformations of syngas and hydrocarbons, composites contain an aluminium metal powder to increase heat conductivity and alumina as a binder. Such pelletized systems are of special interest for commercial implementation of the process since they exhibit good heat conductivity and strength sufficient for use in a multitube reactor. In addition, large pressure drop across the catalyst bed, as observed in physical mixtures of active powders, can be avoided; moreover, physical mixtures should be diluted, which decreases the free useful volume of a reactor.

Comparison of the physical mixture of the composite components and the pelletized composite prepared from this physical mixture with adding a liquid phase in the synthesis of hydrocarbons from CO and H_2 shows[31] that formation of the physical mixture leads to a considerable increase in CO conversion (~1.2 times) and to a 1.5-fold decrease in the yield of methane. Pelletizing the mixture of cobalt and zeolite have no significant effect on the composition of C_{5+} hydrocarbons: only an insignificant increase in the content of isoparaffins is observed, due to the decrease in the content of n-paraffins, and an insignificant decrease in the content of C_{11+} hydrocarbons. A conclusion is made that the effect of the zeolite on the synthesis of hydrocarbons from CO and H_2 in the presence of skeletal cobalt is determined not only by the acid properties of the zeolite but also by the arrangement of metal and zeolite particles with respect to each other, namely, by the distance between them, which is consistent with the results obtained by other researchers.[24,36,112–116] It is evident that this leads to an increase in the degree of secondary transformations; as a result, the average molecular weight of the products decreases, which facilitates mass exchange in a pellet.[32]

The effect of the type of cobalt (deposited from an aqueous nitrate solution or finely dispersed skeletal cobalt) introduced into a pelletized composite catalyst containing the HB zeolite has been examined.[32] It has been demonstrated that the most active catalysts are not the most productive; *i.e.*, to obtain a high-productive pelletized catalyst, an optimal combination of activity and heat and mass exchange in the pellet is necessary.[65,117] It is assumed that the composition of the synthesis products is determined by relative reaction rates on acid and metal sites: with increasing syngas flow rate, mass exchange is accelerated, the residence time of alkenes inside liquid-filled pores is reduced, and, hence, the probability of their secondary transformations on the zeolite component of the composite decreases. In the presence of composites with finely dispersed cobalt, the content of C_{5+} isoalkanes in the products decreases with increasing syngas flow rate, whereas it slightly depends on the contact time when an impregnated cobalt catalyst is used. The authors believe that this is due to the larger number of contacts between the zeolite and impregnated cobalt as compared with skeletal cobalt and, hence, is due to the higher probability of isomerization of alkenes on the zeolite acid sites.

The effect of the type of zeolite (HB, HY, HMOR or HZSM-5) on the behaviour of the cobalt composite catalyst in the Fischer–Tropsch synthesis has been studied.[52] It has been revealed that the content of n-alkanes in C_{5+} hydrocarbons decreases with increasing zeolite acidity, the content of isoalkanes and alkenes increases, whereas the chain growth probability depends only slightly on this characteristic of zeolite.

The composition of the Fischer–Tropsch synthesis products generated in the presence of the composite catalyst based on fine skeletal cobalt and the HB and KA zeolites has been studied.[63] It has been demonstrated that the HB-based composite is distinguished by the higher CO conversion, specific activity and productivity and the lower selectivity to methane as compared to the KA-based composite. Major differences were observed in the composition of the resulting hydrocarbons: the existence of strong Brønsted sites in the HB zeolite, which were not found on the surface of the Co/KA catalyst, promotes the formation of C_{5+} hydrocarbons enriched in C_5-C_{10} alkenes (including isoalkenes) and isoalkanes, the chain growth probability of the n-alkanes being lower in this case. Comparative analysis of the synthesized products and literature data made it possible to assume that the role of the H-form zeolite is related to the generation of carbenium ion through cracking of C_{5+} hydrocarbons formed from CO and H_2 on the active surface of skeletal cobalt. According to the literature data, skeletal cobalt in the synthesis from CO and H_2 catalyzes the formation of long-chain hydrocarbons with a chain growth probability of >0.9; and containing 90% of linear alkanes.[118]

The same authors[64] have found that the introduction of the HB zeolite into a pelletized composite catalyst containing skeletal cobalt improves the CO conversion and productivity with respect to C_{5+} hydrocarbons. The introduction of the zeolite leads to an increase in the content of alkenes and isoalkanes among the C_{5+} products. At the same time, the chain growth probability decreases, whereas increasing zeolite content in the composite leads to an increase in this characteristic. Similar trends have been observed in the presence of the supported Co/HB catalyst with different cobalt contents.[44]

It has been reported that promotion of the Fischer–Tropsch catalyst with alkali and alkaline earth metals increases the CO adsorption[119] and chain growth probability.[120] However, their influence on the catalyst activity is still debatable: some researchers believe that alkali metals are poisons for the Fischer–Tropsch catalysts,[34, 121–124] whereas other researchers use them to enhance the catalyst activity.[125, 126] However, all authors agree that promotion of the Fischer–Tropsch catalysts with alkali and alkaline earth metals leads to the formation of larger amounts of α-alkenes and increases the chain growth probability (*i.e.*, results in the formation of a heavier product). In the presence of the Co catalyst based on the KA zeolite, a relatively high chain growth probability but a low yield of alkenes were observed.[63] This allowed the authors to suggest another, not bimolecular, carbocation mechanism of secondary transformations, namely, the radical one.

In addition, the authors[63] found that the activity of the catalyst based on the KA zeolite was reduced after 90 h of operation, while the activity of the composite based on the HB zeolite was not reduced even after 120 h of operation. According to the authors, this can be due to the differences between the structures of the above zeolites: the sizes of the channels and cages of the HB zeolite are insignificantly different; therefore, the cracking products generated in the cage can escape from this cage. By contrast, in the hydrocarbon transformation reactions, only the external surface of the KA zeolite is working, so that it is rapidly coated with high-molecular weight products of the Fischer–Tropsch synthesis, and catalyst degradation is observed.

IV. Conclusion

It is evident from the above data that the use of cobalt—zeolite catalysts for one-stage production of syncrude from CO and H_2 is topical and reasonable. It follows from analysis of the literature data that all available types of such catalytic systems — physical mixtures of the Fischer–Tropsch catalyst and zeolite, the Fischer–Tropsch catalysts encapsulated into a zeolite shell, conventional impregnated and composite catalysts ensuring intense mass exchange in a pellet — are of applied and theoretical interest and occupy their own niches.

In particular, capsule catalysts make it possible to control the conversion in both processes — the Fischer–Tropsch synthesis and secondary transformations of hydrocarbons on zeolites — and, thus, to vary the composition of the products; the composite systems make it possible to intensify the heat and mass exchange in the pellet, which enhances the catalyst productivity. Studying the behaviour of physical mixtures of the Fischer–Tropsch catalyst and zeolite is important for understanding the mechanism of the one-stage synthesis of hydrocarbons from CO and H_2. In addition, the layered arrangement of Fischer–Tropsch catalyst and zeolite pellets as a kind of physical mixture can be successfully implemented on a commercial scale. Pelletized zeolite-supported catalysts are simple in preparation and, hence, are relatively inexpensive, and this should be taken into account when scaling up the process.

In addition, it is evident that cobalt/zeolite Fischer–Tropsch catalysts are bifunctional: cobalt active sites catalyze the synthesis of hydrocarbons from CO and H_2, which then undergo transformations on the acid sites of zeolites; *i.e.*, the contribution of acid-catalyzed reactions to the composition of Fischer–Tropsch synthesis products is rather significant. To assess this contribution, one should invoke the literature data on the mechanisms of transformation of hydrocarbons over solid acids, namely, zeolites. The most frequently considered mechanisms of transformations of hydrocarbons on zeolite acid sites[93, 94, 107, 108, 10, 127, 128] include the bimolecular mechanism *via* the formation of carbenium and carbonium ions suggested for the first time in 1934[129] and the monomolecular, or protolytic, mechanism considered for the first time in 1984.[130]

Corma and Orchillés[94] have described the carbocation mechanism of alkene transformations on acid sites as a chain mechanism consisting of three steps: initiation, chain propagation and termination. Initiation involves the attack of the initial alkene molecule at the Brønsted acid site to form active complexes, namely, carbocations. Chain propagation is hydride ion transfer from the reactant molecule to the adsorbed carbenium ion, and chain termination involves the desorption of the carbenium ion as alkene and the recovery of the initial active site. The authors note that the carbocation can both participate in further transformations

without skeletal isomerization and form a branched carbocation. For the transformations of alkanes on zeolite acid sites to occur by this mechanism, at least traces of alkenes are necessary for generation of the first carbocation. However, initiation can occur when a proton of the Brønsted site attacks a C–C bond of alkane to form a surface active complex, *i.e.*, *via* the protolytic, or monomolecular, mechanism.[127] Supporting this mechanism, some researchers[131–133] believe that, in the presence of Lewis acid sites (electron acceptors) the dehydrogenation of alkanes is promoted to give alkenes, while other researchers[134,135] assume the formation of a radical cation on electron-accepting sites of the zeolite. According to Weitkamp,[136] the mechanism of cracking through the formation of a pentacoordinate carbonium ion explains not only the chain propagation without involving the primary carbocation, but also the high yield of isoalkanes in the cracking of alkanes. Theoretically, carbenium and carbonium ions can be intermediates in acid-catalyzed reactions — skeletal isomerization, monomolecular cracking of alkanes, alkylation and dehydrogenation.

When studying the isomerization and cracking of pentane, cyclohexane and branched C_5–C_6 hydrocarbons over zeolites, Wakayama and Matsuhashi[70] have made a conclusion that bimolecular reactions require weaker acid sites than the isomerization reactions. In addition, bimolecular reactions require an induction period for generation of carbonium ions by the monomolecular mechanism. In particular, selective isomerization of pentane by the monomolecular mechanism occurs only at the early stage of reaction, and the more branched the alkane used as a feedstock, the shorter the induction period.

The possibility of generation of alkenes, which are necessary for transformations by the bimolecular mechanism, at the early stage of reaction by the monomolecular mechanism has been discussed.[127] It is assumed that for the protolytic cracking to occur, high temperatures, low partial pressure of the initial feedstock and low conversions are required.[107] In addition, transformations by the monomolecular mechanism are distinguished by the absence of the induction period.

It is assumed[107] that alkanes can be activated by both mechanisms — monomolecular and bimolecular. The monomolecular mechanism dominates for zeolites with pores of moderate size (ZSM-5), a high Si : Al ratio and strong proton sites with low density. The major products of monomolecular cracking are alkanes, including methane and ethane, while those of bimolecular cracking are low-molecular-weight hydrocarbons with a predominance of alkenes (methane, ethane and ethylene are not formed).[93,108] It should be noted that pelletizing the physical mixture of skeletal cobalt and HB zeolite leads to a considerable decrease in the yield of methane and in the chain growth probability, which is explained by intensification of bimolecular cracking on zeolite acid sites as the distance between them and the Fischer–Tropsch synthesis site decreases.

The possibility of the cracking of n-hexane by the bimolecular and oligomerization mechanisms is discussed.[137] The basic specific feature of the oligomerization mechanism is that alkenes alkylate each other to form products with a larger molecular weight than the initial reactants. In addition, the authors believe that it is precisely the oligomerization mechanism that is responsible for the deactivation of the catalyst. Dimerization and oligomerization through the formation of intermediate carbenium or alkylcarbenium ions have also been reported.[127,138,139]

It is suggested[10] that transformations of hydrocarbons on zeolite acid sites first occur on Lewis sites and then on Brønsted sites. This is the essence of the bifunctional character of catalysis over zeolites. The radical mechanism of transformations of hydrocarbons on zeolites is discussed: transformations occur on electron-acceptor sites and lead to dehydrogenation of alkanes to give alkenes, which are then converted on Brønsted sites. The source of electron-acceptor sites can be defects of the zeolite crystal lattice.

Some researchers[93,140,141] consider that the mono- and bimolecular mechanisms are too simplified and, for a more complete understanding of the mechanism of acid-catalyzed transformations of hydrocarbons over zeolites, an intermediate complex that can be formed by carbocations with the zeolite surface should not be ignored. In particular, based on quantum-chemical calculations, Kazansky[140] has arrived at the conclusion that there are intermediates, namely, covalently bonded alkoxides or surface ethers that form through partial cleavage or stretching of the C–O bond. This leads to charge separation and formation of the carbenium ion-like transition state of alkyl moieties. However, other researchers[142] argue that reactions through carbocations are energetically more favourable.

Thus, the mechanism in which the active intermediate is a carbonium ion formed on the Brønsted sites of the zeolite should be considered the most accepted mechanism for cracking in the presence of zeolites in the H-form. In the Fischer–Tropsch synthesis, the alkene capable of initiating bimolecular transformations can be formed from CO and H_2 on the cobalt metal. The alkene adds a proton on a strong Brønsted site of the zeolite to generate the carbenium ion active in reactions of skeletal isomerization, double bond shift, hydrogen transfer, alkylation of alkenes or other carbocations and oligomerization. These reactions lead to an increase in the content of alkenes, isoalkenes and isoalkanes and to a decrease in the molecular weight of the products.[32,50] In addition, the possible readsorption on cobalt metal of the products of transformations on zeolite acid sites should not be ignored; there, they can be hydrogenated and hydrocracked or can be involved in the chain growth reaction. The number of readsorption events of the Fischer–Tropsch synthesis products and reactions on acid sites of the zeolite depends on the distance between the cobalt and zeolite active sites and the rates of each process determined by synthesis conditions. Thus, both the Fischer–Tropsch synthesis products and the products of secondary transformations of hydrocarbons can be repeatedly readsorbed on both the cobalt and zeolite sites lying in the path of hydrocarbon molecules. In so doing, these molecules can undergo a series of successive, including cyclic, transformations with both the elongation of the hydrocarbon chain and the cleavage of C–C bonds. The products can be desorbed from any site after any number of events or cycles of repeated readsorption. As a result, a mixture of alkenes and saturated and branched hydrocarbons almost free of high-molecular-weight products and usually referred to as syncrude is formed (Fig. 5).

In some cases,[63] another mechanism of secondary transformations of hydrocarbons formed from CO and H_2 is evident. The synthesis products contain mainly saturated hydrocarbons,[93,108] and the mechanism can be either mono-

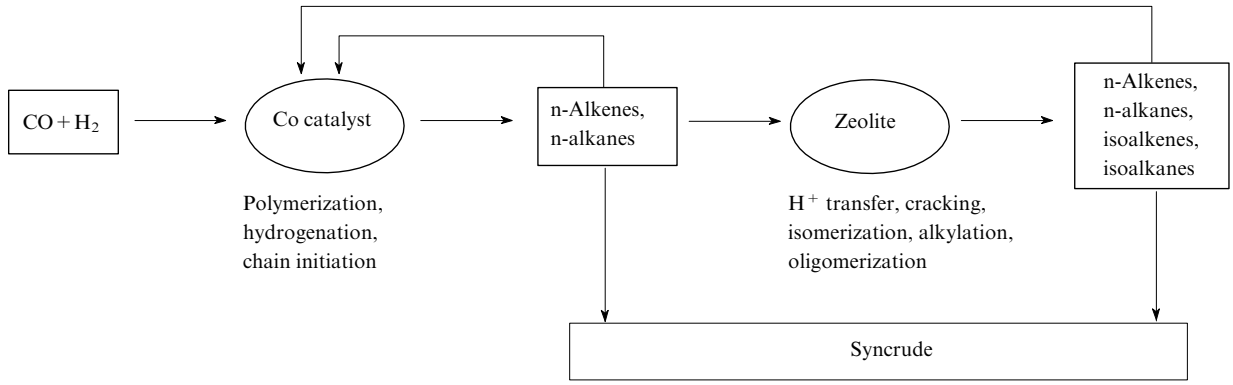


Figure 5. Scheme of one-stage production of syncrude from CO and H_2 in the presence of a zeolite-containing catalyst.

molecular or radical one initiated on electron-acceptor sites; the source for the latter can be defects of the zeolite crystal lattice. The existence of Lewis sites in the reaction medium of the Fischer–Tropsch synthesis, where one of the basic products is water, is hardly probable.[92]

Hence, the basic role of zeolite in the Fischer–Tropsch synthesis over cobalt catalysts is to decrease, on acid sites, the average molecular weight of hydrocarbons formed from CO and H_2. Transformations on zeolites in the H-form lead to the increase in the content of isoalkanes, isoalkenes and n-alkenes in the reaction products. The overall composition of the products depends on the type of zeolite (*i.e.*, the system and size of channels and cages) and its acidity; the accessibility of acid sites for hydrocarbon products of the Fischer–Tropsch synthesis is more important than their strength. By changing the type of zeolite in the presence of the same catalyst of synthesis of hydrocarbons from CO and H_2, one can produce syncrude of different composition. In addition, in some cases, the introduction of the zeolite into cobalt catalysts of the Fischer–Tropsch synthesis reduces deactivation rate and sometimes improves the catalyst bed performance.

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