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THE DEVELOPMENT OF CATALYTIC SYNTHESES OF ORGANIC COMPOUNDS FROM CARBON MONOXIDE AND HYDROGEN

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INTRODUCTION

The catalytic synthesis of hydrocarbons and oxygen-containing compounds from carbon monoxide and hydrogen, particularly on an industrial and semi-industrial scale (Fischer–Tropsch hydrocarbon synthesis, synthesis of alcohols), is of great practical and theoretical interest[1-7]. The most recent reviews in this field were published by one of us in 1950–1951.[1,2] In the present review the main

advances during the past decade in the development of syntheses based on the catalytic reduction of carbon monoxide are considered†.

I. FISCHER–TROPSCH SYNTHESIS OF HYDROCARBONS

The object of the synthesis of hydrocarbons from carbon monoxide and hydrogen, discovered in Germany in 1925 and adopted there industrially at the end of the 1930's, was to obtain liquid fuel[5,8,9]. Between 1936 and 1942 more than fifteen plants were set up in different countries (Germany, Japan, France) in which cobalt catalysts were used, mainly at atmospheric pressure[10]. In the post-war years intensive study of the process continued in the United States, Great Britain, West Germany, Japan, and India and also in the Soviet Union, Poland, East Germany, and China. A number of new plants were constructed, for example in South Africa and the United States, in which valuable chemical products (compressed gas, alcohols, solvents, paraffin wax) were obtained, in addition to liquid fuel, at moderate pressures in the presence of cobalt and iron catalysts[11–16]. At the same time new methods of obtaining cheap starting materials and highly productive and stable catalysts were developed, and new technological schemes of synthesis appeared[11,17–23].

1. Iron Catalysts

Iron catalysts have a number of advantages over cobalt catalysts: they are cheap and readily available, and they enable the synthetic process to be intensified by factors of 10–20; they are active and stable over a comparatively wide range of temperature and pressure with different H_2 : CO ratios in the starting gas.

(a) Methods of preparation. The first iron catalysts were prepared by the thermal decomposition of nitrates, and they contained activating copper and alkali additives[24,25]. However, *precipitated* iron catalysts were found to be considerably more active, especially when they contained activating additions of copper, alkalis (K_2CO_3, KOH, Rb_2CO_3), alkali-metal borates and silicates, several difficultly reducible oxides (MnO, MgO, Al_2O_3, ThO_2, CaO, TiO_2), and also cobalt and nickel[1,26–34]. The mechanical strength of the carriers was increased by depositing magnesium oxide, silica, kieselguhr, pumice, dolomite, diatomite, infusorial earth, and activated charcoal on them[16,35]. On the best iron catalysts (100 Fe, 5–25 Cu, 0.08–2 alkalis) at 200–280° and 1–30 atm, a CO–H_2 mixture (0.5–2 : 1) at a space velocity of ~ 100 h^{-1} gave, per cubic metre at s.t.p., 100–130 g of liquid products, with a total yield of all products of 140–160 g m^{-3}. The hydrocarbons obtained at 10 atm and 212–218° in the presence of iron-copper catalysts promoted by silicates (10–20% on the Fe content), with a total yield of 131–134 g m^{-3} consisted of 52–55% of solid paraffins with boiling points above 300°.[36] Active catalysts for the synthesis of the lower hydrocarbons were prepared on carriers of finely ground natural minerals containing over 10% of soluble silicates[37].

In recent years, in connection with the development of highly efficient synthetic processes, fused, sintered, and cemented iron catalysts have been intensively studied[1,16,38].

Fused catalysts are prepared by roasting powdered electrolytic iron or iron carbonyl vapour in oxygen with the subsequent addition of activators to the melt, or by fusing magnetic iron oxide with these activators[39–43]. Fused iron catalysts of the contact type used in ammonia syntheses began to be employed in the synthesis of hydrocarbons as early as the 1930's.[3,44] Later in Germany the Synthol process was developed in which a similar catalyst of composition 100 Fe : 4.9 Al_2O_3 : 0.9 K_2O : 2.9 CaO was used; this had an activity approaching that of precipitated iron catalysts. Similar catalysts were also developed in the United States[16]. After reduction with hydrogen at 450–500°, they gave yields of hydrocarbons of up to 114–117 g × × m^{-3} at 247–254°, 7–8 atm, and a space velocity (1 CO : 1 H_2) of 100–300 h^{-1}. However, all these catalysts were unstable.

Bashkirov and his coworkers found that fused iron catalysts, promoted by alumina, silica, and potassium carbonate, and reduced with hydrogen and carbon monoxide at 900–1150°, have higher activity and stability than those reduced at lower temperatures[40–43,45]. At 300–310°, 20–25 atm, and a space velocity (1 CO : 1 H_2 mixture) of 1500 h^{-1}, 85% conversion was achieved with a total hydrocarbon yield of 140–150 g m^{-3}. The most active catalyst had the composition Fe_3O_4 + 4–7% Al_2O_3 + 4–6% SiO_2 + + 1–1.4% K_2CO_3; it was necessary to introduce the potassium carbonate in such a way that reaction with the silica was avoided. The stability increased sharply when 0.3–1% of chromium, vanadium, or titanium, or of both chromium and vanadium, was introduced into the catalyst; the duration of the working cycle reached 600 h. The addition of 0.5% of molybdenum or 1% of manganese had no effect on the activity, and the addition of silicon and tungsten had a deactivating effect.

Sintered and cemented catalysts are prepared by sintering iron or its oxides with binding additives — $Al_2(NO_3)_6$, $Na_2B_4O_7$, Na_2SiO_3, etc.[3,16,46–50] — and also by sintering precipitated iron–alumina catalysts[51]. Catalysts sintered in a hydrogen atmosphere are active at 20 atm and 300° without preliminary activation. A catalyst of 100 Fe + + 10 Al_2O_3 remained active for more than 1000 h; in the range of space velocities of 100–300 h^{-1}, the degree of conversion of carbon monoxide reached ~ 98%, and the mean total yield of hydrocarbons 140–145 g m^{-3}.

(b) Physical properties and preliminary treatment. Unreduced precipitated iron–copper catalysts have the structure of an iron oxide gel with small pores and a large surface area (up to 300 $m^2\ g^{-1}$)[35,52–54], but unreduced fused and sintered iron catalysts have a magnetite structure[16,54] with a very small surface area (< 1 m^2 × × g^{-1}), and consist, according to X-ray analysis, of the oxides FeO and Fe_3O_4.[42] Promoters are uniformly distributed in the melt[40,42]; this is apparently due to the formation in the fusion process of iron aluminates, silicates, and possibly aluminosilicates, partly dissolved in the iron oxides and partly concentrated as crystals or amorphous layers between the grains of solid solution[40,42,55]. Thermomagnetic results show that the alkali-metal oxides also form solid solutions with magnetite[56], but there is evidence against this: over 70% of the surface is covered by alkali, which can be easily removed from the catalyst, and the properties of the catalyst are independent of whether the alkali has been added before or after fusion[16].

† The mechanism of these processes will be considered in a separate review.

Before use in synthesis the precipitated iron–copper catalysts are usually treated with hydrogen, carbon monoxide, ammonia, or mixtures of carbon monoxide and hydrogen. The method of treatment has no effect on the activity (Table 1), but materially affects the duration of further development of the catalyst, its selectivity, and its stability[3,16,57,58]. According to some data, when iron oxides are treated with hydrogen at 230–250° they are almost completely reduced to the metal; but according to other data[35] no metallic iron, or at most 1–2%, is observed after such treatment, and the catalysts consist to the extent of 50–60% of FeO and compounds of the spinel type — $FeO.Fe_2O_3(Fe.Fe_2O_4)$, $CuO.Fe_2O_3(Cu.Fe_2O_4)$, $MgO.Fe_2O_3$, or $MnO.Fe_2O_3$ [59] — which is evidently explained by differences in the degree of reduction of the iron oxides depending on the duration of reduction. Treatment with carbon monoxide or a mixture of carbon monoxide and hydrogen gives magnetite and Hägg's carbide, and treatment with ammonia gives magnetite and iron nitrides[54]. Catalysts treated with hydrogen and particularly with ammonia promote the formation of products of lower molecular weight (and also considerable quantities of alcohols) than do catalysts treated with a mixture of carbon monoxide and hydrogen. Nitrided catalysts were less stable than those treated with hydrogen or a mixture of carbon monoxide and hydrogen. The greater the alkali content and the lower the copper content of catalysts, the higher the temperature and the longer the time required for reduction. When the starting gas contained carbon monoxide, the temperature and duration of treatment could be decreased[57]. Reduction by a gas containing carbon dioxide, and particularly water vapour, had a deleterious effect on activity. Treatment with a mixture of carbon monoxide and hydrogen gives catalysts that are insensitive to sulphur compounds[60]. After precipitated catalysts have been treated with a mixture of hydrogen and carbon monoxide, their surface area has decreased from ~300 to ~20 $m^2 g^{-1}$,[35,53,61] but the surface area of catalysts precipitated on a carrier evidently remains unchanged or slightly increases[10].

Fused catalysts are reduced by hydrogen at 375–500° in 25–60 h,[16,62-64] or at ~1000° in 1.5–6 h[41-43,65-67] at atmospheric or higher pressure (up to 10 atm). In this case also water vapour or carbon dioxide has a deleterious effect on the activity of the catalysts[63]. In reduction at 450° the surface area of the catalysts and the volume of the pores increase linearly with the degree of reduction up to ~80% reduction[62]. Pores with a mean diameter of ~333 Å are formed. With a degree of reduction of over 80% the surface area increases more rapidly than the pore volume. With reduction between 99.5% and 100% there is some decrease in the surface area. At 550° catalysts having a mean pore diameter of 830 Å are formed. With reduction in the range 400–650°, the particle size of the catalyst does not change; the porous structure is formed by removal of the oxygen from the iron oxides. The volume of the pores increases and the surface area decreases[62,64]. The reduction process becomes more rapid with increasing temperature. The surface area of reduced fused catalysts is 1–50 $m^2 g^{-1}$.[10,62] Promoters stabilise the structure produced on reduction, but they do not prevent diminution in the surface area with increasing temperature. In the course of reduction the promoters are extruded on to the surface of the α-iron crystals, in which they are insoluble[42,68]. α-Iron, α-quartzite, γ-alumina, and compounds of the andalusite type have been detected in reduced samples of fused catalysts. Extraction with hot water improved the activity of sintered catalysts; the improvement is due to the removal of sulphur compounds present as impurities and to the formation of a finely dispersed highly active iron oxide by decomposition of the ferrites formed in the preparation of the catalysts[49,50].

TABLE 1. The effect of preliminary treatment at 250° on the activity of precipitated iron–copper catalysts[16].

Preliminary treatment	Duration of treatment, h	Activity of catalyst	
		temp. of synthesis, °C	contraction of gas, %
No treatment	—	251	64
With nitrogen	24	250	65
With natural gas	16	250	67
With hydrogen	17	250	65
With carbon dioxide	21	250	69
With air	16	248	67

The thermal conductivity of precipitated iron–copper catalysts is 2–3 times that of cobalt–thoria catalysts[69], and the conductivity of fused catalysts is greater than that of precipitated catalysts. The thermal conductivity of all catalysts approximately doubles in operation, as a result of saturation with reaction products. This is important because when a reactor is being brought into operation, the temperature and the gas charge must be increased slowly for effective removal of the heat of reaction. Only when the catalyst has become saturated with the reaction products (paraffin is sometimes poured over it for this purpose) and its thermal conductivity has been increased can the synthesis function under normal conditions.

(c) Development. Fused iron catalysts, reduced at ~1000°, are inactive immediately on reduction, and acquire a high activity only after the starting gas has been passed over them for 7–50 h.[65-67] Precipitated and fused catalysts are at once activated at 375–500°, but it is only in the process of synthesis that the active catalyst surface is formed; its structure and phase composition are changed as a result of the chemical reaction of iron compounds with starting reagents and reaction products[35,70-72]. Metallic iron, iron carbides, and iron oxides do not separately catalyse the synthesis of organic compounds from carbon monoxide and hydrogen[65,72]. In the initial period of the synthesis a number of competing reactions occur on the catalyst surface between its components and the gases in the reaction mixture; these include carbidation of the iron, hydrogenation of carbides, oxidation of the iron by water, reduction of the iron oxides by carbon monoxide and hydrogen, etc. Dynamic equilibrium is established between the surface phases[70,73-77]. In the course of these reactions, proceeding at the interphase boundaries of the surface, molecules of carbon monoxide and hydrogen are activated and, when the necessary geometrical relationship with the surface arises, they interact[66,72]. To acquire such properties, catalysts reduced at 375–500°, either carbided[78-80] or nitrided[80-86], do not require a long activation process. The formation of their active surface apparently consists in the rapid production of the phase combination necessary for the synthesis. In the formation of the surface and then in the synthesis, water vapour and carbon dioxide have a deleterious effect on the activity and selectivity: oxidative deactivation occurs with change in the phase composition[70,73,76,87,88].

(d) Catalysts based on natural ores. Work has been carried on for a long time on the use of natural

minerals or ores containing iron or its oxides as catalysts in the reduction of carbon monoxide. After reduction with hydrogen at 450° these proved to be active at 230–300° and 7 atm with a space velocity of starting gas ($CO_2 + H_2$, 1 : 1) of ~ 1000 h^{-1}.[3,16,89-92] Krivorog ochre haematite ($79Fe_2O_3$, $7Al_2O_3$, $1.0SiO_2$), Khallilovo ore ($56Fe_2O_3$, $12Al_2O_3$, $10SiO_2$), red mud, a by-product of the aluminium industry ($55.4Fe_2O_3$, $20.3Al_2O_3$, $12.5SiO_2$, $4.8CaO$), titanomagnetite ($50Fe_2O_3$. $.24FeO.3Al_2O_3.3SiO_2.13TiO_2$), and magnetic iron ore ($60Fe_2O_3.14FeO.3Al_2O_3.6SiO_2.6CaO + MgO$) have been used[93]. After reduction at 800–1000° and saturation with potassium carbonate or sodium borate solution, the catalysts work stably at 20–40 atm, 300–320°, and a space velocity of 500–1500 h^{-1} (with a 1 : 1 mixture of carbon monoxide and hydrogen), giving a yield of liquid products up to 90 g m^{-3}. For catalytic activity, iron ores must have a high content of iron oxides and an alkali additive. Oxides in the ore that are difficult to reduce serve as structural promoters. The catalytic properties of iron ores are improved by fusion, which leads to a more uniform distribution of the oxide promoters and the removal of some compounds that lower activity. Such catalysts are active in the same way as ordinary fused catalysts, but they are rapidly destroyed by the deposition of carbon.

(e) Industrial methods of synthesising hydrocarbons from carbon monoxide and hydrogen in the presence of iron catalysts. The intensive investigation of iron catalysts led to the development of a highly efficient process accomplished by different technological methods (Table 2).[46,94-99] The earliest of these, in which the process was carried out *in the gas phase* with stationary precipitated iron–copper catalysts, was inefficient. Its disadvantages were: (1) low efficiency because of the low space velocity of the starting gas necessitated by the difficulty of removing the heat of reaction; (2) the narrow temperature range of the reaction; (3) non-uniform distribution of temperature and composition of the reaction mixture along the layer of catalyst, which led to choking up by coke formation and oxidation of the catalyst by water vapour; and (4) the ratio in which hydrogen and carbon monoxide were consumed differed from the ratio in the starting gas, and this led to a decrease in the theoretical yield of product. The problem of effectively removing the heat of reaction was partly solved by the use of fused, sintered, or cemented catalysts, operating at high degrees of conversion of the gas and over a wide range of space velocities, and also by recirculating the effluent gases. When recirculation is used, the reaction, which ordinarily proceeds at constant temperature and pressure in the region of kinetic control, passes to the external diffusion region, because of changes in the concentrations of carbon monoxide and hydrogen in the gas, its linear velocity, and the hydrodynamic conditions[35,97,100,101]. When the coefficient of recirculation is greater than unity, the reaction passes into the internal diffusion region. With recirculation[102,103], or increase in the linear velocity of the starting gas[13], the productivity of the process is increased 6–8 times and the yield of products approaches the theoretical. On fused catalysts the optimal consumption ratio of H_2 : CO establishes itself at a space velocity of 100–50 000 h^{-1} and a recirculation coefficient of 0–50.[102]

The best removal of heat is achieved with a *fluidised bed* of catalyst suspended in the gas phase. With this method the efficiency is 2–4 times that achieved with a stationary layer, there is a high degree of conversion of the starting gas, and the catalyst can be easily replaced or regenerated (Table 2).[1,46,63,104-107] Fused and sintered catalysts of particle size 2–100 μm are used; they are active for more than 350 h without regeneration. Such a process is operated at a works in South Africa. The precipitated catalyst ($86.6Fe + 5Cu + 8Mg + 0.4K_2O$) in a fluidised layer worked at a lower temperature and pressure, but its activity, selectivity, and stability were less than those of fused catalysts[63,107]. Catalysts in a fluidised

TABLE 2. Characteristics of processes for the synthesis of hydrocarbons from carbon monoxide and hydrogen on iron catalysts.

Process	Synthesis in gas phase on stationary catalyst			Synthesis in gas phase on fluidised catalyst		Synthesis in liquid phase with suspended catalyst	Synthesis in liquid phase with suspended catalyst	
Catalyst	pptd. Fe–Cu	fused NH_3-synthesis type	pelleted on powdered steel	pptd. Fe–Cu	fused NH_3-synthesis type	fused NH_3-synthesis type	pptd. Fe–Cu	fused NH_3-synthesis type
References	22, 35	94, 104	97	63, 107	46, 104–107	108, 109	35, 111–115	104, 110, 116
Pressure, atm	1–10	21–42	30	5–15	20–30	20	8–20	21–42
Temperature, °C	175–230	250	230–310	250–320	300–340	255–265	220–290	265–305
Space velocity, h^{-1}	~100	up to 1045	300–1000	600–1200	500–2200	~300	~230	up to 1000
H_2 : CO in starting gas	0.67–2	2	0.83–1.2	1.35–1.9	1.95–2.5	1–1.3	0.65–1.5	0.7–2.0
Recirculation coefficient	0–9	2–2.5	2–3.5	nil	1.5–13	1–2	nil	up to 6
Conversion, %								
CO	90–96	up to 96	69	92–97	90–98	—	91	up to 96
CO + H_2	50–60	up to 85	61	70–77	80–93	70	89	up to 93.5
H_2 : CO consumed	0.63–1.52	1.56–1.88	—	0.99–1.04	1.7	0.99–1.22	—	1–1.57
Yield, g m^{-3} (at s.t.p.)								
C_1	7–15	15–37		10–34	20–63	~14		12.7–22.6
C_2			12–23			11–12	3–12	
$C_3 + C_4$	22–51	34–59	11–27	40–70	55.8–64		4–48	37–38
Petrol (up to 200°)	23–87					72	13–102	57–58
Oil (200–320°)	17–45	75–95	69	20–50	38–72	11–12	10–45	11.3–13.4
Paraffin wax (>320°)	17–60					16–23	2–150	16–30
Overall yield of hydrocarbons, g m^{-3} (at s.t.p.)	157–186	140–170	93–119	140	159–170	124–135	162–182	125–139
Yield of oxygen-containing compounds, g m^{-3} (at s.t.p.)	23–41	5–16	6	—	5–19	14–15	2–3	8–15
Efficiency, kg m^{-3} of catalysts per day	—	1250	1970	—	up to 4320	—	770–1000	—
Cooling surface in reactor, m^2 per 1000 m^3 of converted gas per h	—	235	—	—	~30	—	50	—

bed must have high mechanical strength. Polymeric products must not be formed, as their deposition on the surface of the catalyst would bring about defluidisation, so that a higher temperature is also required. However, this may greatly accelerate side-reactions of carbon monoxide with water (the water-gas reaction) and carbon formation, and lead to a decrease in the selectivity and stability of the catalysts. These undesirable effects may be prevented by carrying out the synthesis with hydrogen-enriched gas ($H_2 : CO = 1.95–2.5$) and by using circulation.

Highly active, selective, and stable nitrided catalysts are of considerable interest in this process[63]. Synthesis on these takes place at 260–275° and 15–25 atm with a starting gas consisting of $H_2 : CO = 1.2–1.3$. They had a working cycle without regeneration of over 1500 h.

In *liquid-phase* synthesis, precipitated and fused iron catalysts are used both stationary[108,109] and suspended in oil[35,104,110–116]. Hydrocarbon fractions of b.p. 200–450° and 300–450° were used as medium. The heat of reaction went to heat the circulating oil and evaporate its lighter components. The rise in temperature of the oil did not exceed 50 deg. Precipitated iron catalysts were very active, but were rapidly destroyed by the circulating oil. The less active and more stable fused catalysts (Table 2), however, did not work for more than 2–3 months, because of cementation and a sharp rise in hydraulic resistance. This disadvantage is eliminated when a catalyst of 6–20 mesh particle size forms a circulating or stationary suspension in the oil. According to the conditions of synthesis and the catalyst, the product may consist mainly of gasoline, diesel oil, or solid paraffins. The solubility of the gases and reaction products in the liquid phase plays an important part[112]. The process is characterised by good heat removal, high selectivity, flexibility, uniform loading of the catalyst, ease and simplicity of plant layout, and high efficiency.

Processes using a stationary layer of iron catalyst with circulating gas, but particularly in the liquid phase with the iron catalyst suspended in oil, are most selective (lowest yield of methane) and are characterised by high stability and productivity, good heat exchange, comparatively low reaction temperatures and pressures, and also great flexibility. Gasoline as the main product, or gasoline with diesel fuel, or solid paraffins can be obtained from gases with an $H_2 : CO$ ratio of 0.6–2.0, and consequently from effluent gases of a number of plants (Table 3). Considerable amounts of oxygen-containing compounds, mainly alcohols, are formed on fused and sintered catalysts[11,117–125]. The gasolines have much better engine characteristics than those obtained from carbon monoxide and hydrogen on cobalt catalysts.[3,11,21,118,126] After the addition of R-9 or polymer motor fuel (0.5–1.5 ml kg^{-1}) or after thermal treatment in the presence of alumina, commercial A-66 or A-70 motor fuels are obtained. Diesel fuel obtained on

TABLE 3. Composition and characteristics of products of industrial processes in semi-works trials of the synthesis of hydrocarbons from carbon monoxide and hydrogen on iron catalysts.

Process	Synthesis in gas phase with stationery catalyst			Synthesis in gas phase on fluidised catalyst	Synthesis in liquid phase with suspended catalyst		
	at atmospheric pressure	at moderate pressure					
Catalyst	pptd. Fe–Cu		fused NH_3-synthesis type	fused NH_3-synthesis type	pptd. Fe–Cu		
	I	II			I	II	III
References	35	22, 35, 117–119	118,120–123	46, 124	35, 112		
Yield, wt. % on total CH_2							
C_1	5.1	4.5–8.1	8.9	13.4–15.8			
C_2	7.1		7.8	12.2–12.3	6.2	1.7	1.6
$C_3 + C_4$	6.1	15–30	29.8	24.5–25.1	17.0	6.8	2.2
Petrol (190°)	34.8	15–50	41.0	29–31	63.8	39.4	7.0
Diesel fuel (190–310°)	24.4	10–30	6.2	3–4	10.2	25.4	8.1
Soft paraffin (310–450°)	13.1				2.3	18.0	32.6
Hard paraffin (>450°)	9.4	10–40	6.3	1.6–2.6	0.5	8.9	48.5
Unsaturated compounds, %							
$C_3 + C_4$	—	50	up to 83	85–86		70–92	
Petrol	26	42–53	74–87	44–49		62–95	
Diesel fuel	—	25.4	73–76	—		30–80	
Paraffin (>310°)	—	—	75	—		10–60	
Engine characteristics							
1. Petrol							
Octane No. (engine method)	35	55–61	58	73.8		73	
After treatment with Al_2O_3	—	—	—	74.9		81	
With addition of R-9, mg kg^{-1}							
0.5	—	67.0–68.3	—	—		—	
1.0	—	71.7–73.2	—	—		—	
1.5	—	73.8–77.0	68	—		—	
2. Diesel fuel							
Cetane rating	—	85	50	—		70	
Pour point, °C	—	—4	—24	—		—11	
Content of oxygen compounds in reaction water, %							
Acids	—	0.31–0.47	1.2–1.3	3.1–3.9		—	
Alcohols	—	6.1–14.7	4.3–9.2	9.1–10.4		—	
Aldehydes	—	0.129	0.1–0.6			—	
Ketones	—		0.6–2.2			—	

iron catalysts is of low quality, and can be used only as a component of high-quality diesel fuels [126].

A gas-phase process on fluidised iron catalysts is used for the preparation of high-quality motor fuels, although it is less selective than the previous two, and requires higher temperatures and pressures and the use of a hydrogen-enriched starting gas [46].

The synthesis of hydrocarbon fuels from carbon monoxide and hydrogen is of definite value for countries that have no, or very limited, natural oil sources [11,18,19,21,127]. However, it is more expedient to obtain from these gases raw materials for organic synthesis in the form of unsaturated hydrocarbons and oxygen-containing compounds [45,118,128]. For the synthesis of C_2–C_4 unsaturated hydrocarbons [129] or a mixture of liquid and gaseous olefins [130–134], iron catalysts in a stationary or fluidised layer are recommended, with addition to the starting gas of halogens, hydrogen halides, or organic halogen compounds that give hydrogen halides on dissociation. The catalyst may be promoted with iron halides or alkali-metal halides [134], with lead [135,136], and also by the addition of 0.02–0.5 wt.% of sulphur [129,137,138]. The process operates at high pressure, 295–400°, and a space velocity of starting gas (2.25 CO : 1 H_2) of 3100 h^{-1}.

2. Oxide Catalysts

(a) Metal oxides. Oxides that are difficult to reduce — ThO_2, Al_2O_3, SiO_2, ZnO, etc., — are known as promoters of nickel, cobalt, and iron catalysts in the synthesis of hydrocarbons from carbon monoxide and hydrogen. Pichler and Ziesecke found that, at temperatures of ~450° and pressures of over 100 atm, liquid and gaseous aliphatic hydrocarbons, mainly with branched structures, can be synthesised from carbon monoxide and hydrogen on these oxides [139–142]. Thoria, zirconia, and ceria were found to be active [139,143,144], as were also the mixed catalysts ThO_2–Al_2O_3, ThO_2–ZnO, and ZnO–Al_2O_3. [143] In the presence of these catalysts at 400–450° and 250 atm, 70–80% conversion of carbon monoxide was achieved; the total yield of hydrocarbons was 105 g m^{-3}, of which up to 57 g m^{-3} represented liquid hydrocarbons. At 30 atm the degree of conversion of carbon monoxide and the yield of products were small. At increased temperatures (above 450°) the gaseous products increased, and below 375° alcohols were mainly formed. When potassium carbonate, kieselguhr, or iron was added to ThO_2 or ThO_2–Al_2O_3, the activity of these catalysts was diminished and methane formation was increased [143]. The reaction products contained large amounts of unsaturated aliphatic hydrocarbons, over 90% of which had branched structures; small amounts of aromatic hydrocarbons and naphthenes were found. Catalysts consisting of the oxides of aluminium, tungsten, zirconium, uranium, and the rare earths, with the addition of zinc oxide, chromic oxide, or copper, have been proposed for the preparation of high quality motor fuel from carbon monoxide and hydrogen; they are active at pressures above 100 atm and temperatures above 350–400°. [145] On oxides of molybdenum, tungsten, chromium, manganese, vanadium, and magnesium promoted with 1–5% of potassium carbonate the degree of conversion of carbon monoxide at 30 atm and 400–470° was 87–92%, but gaseous products were mainly formed. Oxides of titanium and strontium, and also metal oxides that are easily reduced, e.g. PbO, SnO_2, and CdO, were inactive [146,147]. Catalysts prepared from bauxites by impregnation or fusion with potassium carbonate and borax, and containing Fe_3O_4, are active at 280° and 20 atm with a gas mixture (1CO : 1H_2) at a space velocity of 1250 h^{-1}; these operated for more 120 h without loss in activity, giving a yield of C_2 and higher hydrocarbons up to 110 g m^{-3}. [148]

(b) Silicic acid catalysts. Promoted silicic acid catalysts form a large group of oxide catalysts for the reduction of carbon monoxide; they are prepared both from soluble silicates and from natural silicate-containing minerals [144]. Silicon dioxide with 2% of potassium carbonate, potassium hydroxide, or sodium borate is active at 350–450° and 20–40 atm after preliminary treatment [146,148]. The degree of conversion of carbon monoxide with a gas mixture (1 CO : 1 H_2) at a space velocity of 100–300 h^{-1} was 80–95%; the yield of hydrocarbons was 110–130 g m^{-3}, up to 65 g m^{-3} being liquid. At temperatures above 450° more liquid products and much gas were obtained, and at 500° methane was the main product. The addition of small quantities of alumina promoted the reaction, but the oxides of magnesium, calcium, tungsten, and thorium were inactive [144].

Natural silicate minerals are active at 350–470°, pressures above 20 atm, and a space velocity (1 CO : 1 H_2) of 100–300 h^{-1}. [149,154] Alkaline additives (potassium and sodium carbonates, potassium hydroxide) generally increased the activity and promoted the formation of hydrocarbons of higher molecular weight. The minerals rhodonite (Mn, Ca)$[Si_2O_6]$, kaolin $Al_2[Si_2O_5](OH)_4$, montmorillonite (Mg, Ca)O.Al_2O_3.5SiO_2.7H_2O, nontronite $H_2Fe_2Si_2O_5.H_2O$, and microcline $K[AlSi_3O_8]$ were virtually inactive. The minerals beryl $Be_3Al_2[SiO_3]_6$, dumortierite $HBAl_8Si_3O_{20}$, spodumene (Li, Na)$Al[Si_2O_6]$, and albite $Na[AlSi_3O_8]$ gave methane as the main product with a high conversion of carbon monoxide. Liquid hydrocarbons were formed only in the presence of almandite $Fe_3Al_2[SiO_4]_3$, diopside $CaMg[Si_2O_6]$, actinolite $Ca_2(Mg, Fe)_5[Si_4O_{11}](OH)_2$, gedrite, anthophyllite (Mg, Fe)$_7[Si_4O_{11}]_2(OH)_2$, talc $Mg_3[Si_4O_{10}](OH)_2$, biotite K(Mg, Fe)$_3[Si_3AlO_{10}](F, OH)_2$, and kieselguhr.

The most active minerals were talc and kieselguhr; these gave yields of liquid products of 75 and 95 g m^{-3} with total yields of 130 and 140 g m^{-3} respectively. The reaction started only at 320°. The optimum temperature of the reaction was 350–450° on kieselguhr, and 415–450° on talc. Above 450° methane formation and coking up sharply increased. At atmospheric pressure the reaction did not occur even at temperatures above 450°; the optimum pressure was 20–40 atm. Increasing the pressure to 200 atm reduced the yield of liquid hydrocarbons, and increased the formation of oxygen-containing products and coke.

Alkaline additives (K_2CO_3, Na_2CO_3, KOH, $Na_2B_4O_7$, etc.) and also the salts KNO_3, $KMnO_4$, etc. are activators. With salts the efficacy of the cations diminished in the order K > Na > Li. Carbonates, nitrates, and fluorides were the most effective, but chlorides, bromides, and sulphates deactivated the catalysts. The degree of conversion of carbon monoxide and the total yield of hydrocarbons increased continuously as the potassium carbonate content increased from 0 to 10%. With further increase up to 50%, the yield of products decreased and the stability of the catalyst diminished. The activity of talc catalysts depends largely on preliminary thermal treatment. The best results are obtained by preliminary heating to 600°. According to X-ray analysis, this promoted the removal of all adsorbed interplanar and interstitial water without destroying the

structure of the talc. At 850–1000° the structure was destroyed, and the surface area was reduced by a factor of 2–3. Talc roasted at 600° together with an alkaline additive had a low activity, apparently because of sintering of the particles and reduction of the surface area.

The maximum total yield and also yield of liquid hydrocarbons were observed with 54–60% of CO in the starting gas. As the space velocity is increased in the range 100–1650 h^{-1}, the efficiency of the catalysts continuously increases, but its stability falls sharply. Silicate catalysts are regenerated by air at 450°. Gaseous and liquid hydrocarbons, oxygen-containing compounds, water, and carbon dioxide are formed on silica catalysts. The content of oxygen-containing compounds, mainly alcohols and carbonyl compounds, in the products of the reaction on kieselguhr catalysts is small (5–8%); on talc it reaches 80%. The hydrocarbons, which are mostly volatile below 170°, contain 60–70% of unsaturated compounds and consist mainly of aliphatic hydrocarbons with branched structures. The content of aromatic hydrocarbons does not exceed 6–10%. The octane number of the motor fuel obtained from carbon monoxide and hydrogen on silicic acid catalysts reaches 76–81.

A characteristic feature of natural silicate minerals is their crystalline structure, which is based on different arrangements in space of $[SiO_4]^{4-}$ tetrahedra. Only lower, mainly gaseous hydrocarbons are formed on silicates with single or double tetrahedra, but liquid hydrocarbons are formed on silicates with a layer structure.

Oxide catalysts therefore constitute a new class of catalyst for the reduction of carbon monoxide. They form neither carbides nor carbonyls with the latter, but decompose it, promoting its conversion by water vapour. They are not oxidised by water and carbon dioxide, but under the conditions of the synthesis they may perhaps react with carbon dioxide to form carbonates. The reduction of carbon monoxide on oxide catalysts proceeds at high temperatures (350–500°) and pressures (20–600 atm) with the formation of hydrocarbons, mainly with branched structures.

According to the semi-contact hypothesis on the hydrogenation of carbon monoxide to branched hydrocarbons [155], oxide catalysts are not capable of activating hydrogen directly, which leads to an increased concentration of CHOH groups together with CH_2 groups on the surface of the catalyst. Branched compounds are formed by catalytic dehydration and condensation, in which the hydroxy-groups on the secondary carbon atoms react with hydrogen atoms of the hydrocarbon chain.

II. DIRECTED SYNTHESES OF ORGANIC COMPOUNDS FROM CARBON MONOXIDE AND HYDROGEN

The Fischer–Tropsch synthesis of hydrocarbons from carbon monoxide and hydrogen on catalysts based on iron, cobalt, and nickel is not selective [5]. For this reason, the directed syntheses of valuable chemical products from carbon monoxide and hydrogen are of great interest.

1. Synthesis of Higher Hydrocarbons

(a) Ruthenium catalysts. As early as 1938, a yield of hydrocarbons of 140–150 g m^{-3} (60–70% solid paraffin) was obtained from a mixture of $1CO + 2H_2$ on finely divided metallic ruthenium at 180–200° and 100–800 atm. [156,157] At the present time, in connection with the development of radio-electronic and other processes, the demand for synthetic paraffins with a number of properties superior to those of petroleum paraffins has greatly increased. New work has been done on the synthesis of solid paraffins in the presence of ruthenium catalysts [158–160]. It was found that, as the temperature increased in the range 165–275°, the degree of conversion of the starting gas continuously increased, but the yield of paraffins passed through a maximum at 170–180°. Increasing the total pressure to 1500 atm and reduction of the contact time promoted the formation of solid paraffins, their content in the reaction products reaching up to 65%. At the same time the optimum reaction temperature was lowered. The maximum yield of solid and liquid hydrocarbons was obtained from a 1 : 2 mixture of carbon monoxide and hydrogen. More liquid and gaseous hydrocarbons were formed on ruthenium with the addition of 20% of thorium, aluminium, and magnesium oxides. However, it was later shown that the addition of small amounts of metal oxides, for example 1.5% of magnesium oxide, led to a sharp increase in the yield of solid hydrocarbons. Preliminary treatment of the catalysts with hydrogen at 220–420° led to a 20% reduction in activity, but sharply increased the selectivity, apparently by the formation of a definite microstructure with pores of 400–1000 Å diameter and a total surface area of 7–15 $m^2\ g^{-1}$. Catalysts containing traces of alkali and having a pore diameter of 1200–1600 Å were much less selective. Catalysts nitrided at 250–300° with the formation of ruthenium nitrides gave mainly liquid and gaseous hydrocarbons, but catalysts nitrided at 400–450° had high selectivity and stability to oxygen and gave products containing 93–95% of solid paraffins.

Therefore the conditions for activating ruthenium catalysts for very selective synthesis of solid paraffins having m.p. 50–140° have now been established.

(b) Modified cobalt catalysts. Thorium dioxide in cobalt catalysts for the synthesis of hydrocarbons from carbon monoxide and hydrogen may be replaced by zirconium or titanium dioxide [161]. Such catalysts, after preliminary reduction with hydrogen at 400° for 12 h, operated at 190° and atmospheric pressure with yields of liquid hydrocarbons of 150–170 g m^{-3} of starting gas (1 CO : 2 H_2). With a pressure of 10 atm on catalysts of composition 100Co : $6ZrO_2$, or TiO_2 : 10MgO: 200 kieselguhr, the reduction of carbon monoxide in the first 144 h proceeded, as at atmospheric pressure, with the formation mainly of liquid hydrocarbons. Then solid paraffins began to be mainly formed having m.p. 70–98°, with an average yield of ~92 and a maximum yield of 116 g m^{-3}. The catalysts worked for over 800 h with no loss in activity [162].

(c) Molybdophosphoric catalysts. Solid paraffins are obtained from mixtures (10 : 1 to 1 : 5) of carbon monoxide and hydrogen at 125–350° and 450–500 atm in the presence of molybdophosphoric acids $P_2Mo_xO_y$ (x = 20–24 and y = 31–60) and their salts $M_yP_2Mo_xO_z$ (M is a metal — Li, Na, K, Rb, Cs, Cu, Ag, Au, Zn, Cd, Hg, Al, Ga, In, Mg, Mn, Fe, Co, Ni — y = 2–10, x = 20–26, and z = 37–65). [163,164] The following acids and salts have been used as catalysts $P_2Mo_{22}O_{39}$, $P_2Mo_{21}O_{47}$, $P_2Mo_{22}O_{48}$, $Ni_2P_2O_5(Mo_2O_5)_{11}$, $Co_3P_2O_5(Mo_2O_5)_{22}$, $Fe_3P_2O_5(Mo_2O_5)_{10}$, $Cu_3P_2O_5(Mo_2O_4)_{12}$, and $Zn_3P_2O_5(Mo_2O_3)_{12}$. The catalyst, used in 1.5–30% quantities, was first reduced in hydrogen at 400° for 17–19 h. The synthesis was carried out in cyclohexane, methanol,

decahydronaphthalene, tetrahydronaphthalene, aromatic hydrocarbons, or cyclohexanone as diluents.

2. Synthesis of Ethylene

Ethylene is a valuable raw material for organic synthesis in industry [165], and for this reason, attempts have been made to prepare it from carbon monoxide and hydrogen [166-170]. This synthesis was first carried out by Orlov in 1908 at 95–100° and atmospheric pressure on nickel–palladium catalysts [171,172]. According to modern patent information, ethylene is formed on iron catalysts promoted by compounds of copper, titanium, manganese, chromium, molybdenum, aluminium, thorium, cerium, and zirconium, and containing 20–50% of aluminium, magnesium, and zinc silicates. The reaction occurs at atmospheric or slightly increased pressure, 470–600°, and a space velocity of circulating gas mixture of 500–5000 h^{-1} ($CO : H_2$ 1 : 1–2, circulation coefficient 0.5–5). It is necessary to add to the reaction zone small amounts of ammonium chloride or fluoride or other compounds that form hydrogen halides under the reaction conditions [166]. The following catalysts have also been proposed [168]: (1) zinc and chromic oxides with the addition of magnesium oxide; the chromic oxide may be replaced by the oxides of vanadium, niobium, tantalum, molybdenum, or tungsten, and the zinc oxide by oxides of cadmium, copper, or silver; (2) one of several metals in Group VIII of the Periodic System or their compounds; (3) the oxide or hydroxide of aluminium and/or the oxides of silicon, titanium, zirconium, hafnium, thorium, cerium, vanadium, or rare-earth elements; and finally (4) carbonates, oxides or hydroxides of the alkali metals. The catalysts may be deposited on a carrier of kieselguhr, silica gel, or clay. On a catalyst of composition $51Zn + 0.13Cr_2O_3 + 0.64Co + 0.04K_2O + 100Al_2O_3$ at atmospheric pressure, a temperature of 430°, and a space velocity of 350 h^{-1}, 25 litres of C_2H_4 and 2 litres of C_2H_6 were obtained per cubic metre of gas (1 $CO : 1\ H_2$). A catalyst of 3% CuO on Al_2O_3 is active at 20–40 atm and 250°. [169] Ethylene is also formed by passing a gas mixture (1–3 $CO : 1\ H_2$) at 350–550° and atmospheric pressure through a copper tube at a space velocity of 370–2500 h^{-1}. [170]

3. Synthesis of Alcohols

As early as 1913 it was discovered in the Badische Anilin- und Soda-Fabrik that a mixture of alcohols, aldehydes, ketones, and acids with a small admixture of hydrocarbons is formed from carbon monoxide and hydrogen at 300–400° and 100–200 atm in the presence of cobalt and osmium oxides deposited on asbestos and activated by alkalis [173]. Fischer and Tropsch set up the Synthol process operating at 400–450° and 100–150 atm in the presence of iron oxide promoted by alkali; this gave a complex mixture of alcohols, aldehydes, ketones, and acids from carbon monoxide and hydrogen [174]. Later, in Germany the Synthol process with fused iron catalysts, of the type used in ammonia synthesis, at 190–220° and 20 atm was used to obtain a liquid product (yield 170–180 g m^{-3}) containing 60–70% of alcohols from a $1\ H_2 : 1–1.3$ CO mixture [5,175,176]. The products obtained on precipitated iron–copper catalysts at 180–220° and 30 atm also contained a large amount of oxygenated compounds, comprising 75–80% of alcohols and ethers and 25–20% of carbonyl compounds, or under slightly different conditions, 80% of alcohols and 20% of ethers and carbonyl compounds [177]. The alcohols were primary with only a small amount of branching.

An important step forward in the synthesis of alcohols from carbon monoxide and hydrogen was the development of zinc–copper and zinc–chromium catalysts, in the presence of which methyl alcohol is selectively formed [178-181]. Methanol is synthesised industrially at 300–325 atm, 325–375°, and a space velocity of circulating gas (1 $CO : 2\ H_2$) of 10 000 h^{-1}. When the starting gas contained stoichiometric proportions of carbon monoxide and hydrogen, difficulty was encountered in controlling the reaction temperature. The process was considerably improved by reducing the concentration of carbon monoxide in the circulating gas to 5–6%. [182,183] It was found possible to combine the synthesis of methanol with degradative hydrogenation processes in vapour and liquid phases and with the ammonia synthesis; this made the product cheaper.

The synthesis of higher alcohols from carbon monoxide and hydrogen is thermodynamically more favoured than the synthesis of methanol [5,184]. Displacement of the reaction towards the production of higher alcohols is promoted by a higher temperature (above 400°), a lower space velocity of starting gas, and alkaline additives in the catalyst. Higher alcohols were formed at 380–490°, 150–250 atm, and a space velocity (of $H_2 : CO = 5–1 : 1$) of 2000–20 000 h^{-1} on modified oxide catalysts. [184] The alcohol content of the reaction product reached 60% with methanol and primary isobutanol predominating [184-185]. At lower temperatures the reaction product contained up to 20% of ethanol. Selective catalysts for the synthesis of ethanol are obtained on the basis of Group VIII metals [186-191].

In the presence of fused iron catalysts [188-191], promoted by oxides that are difficult to reduce (ZrO_2, Al_2O_3, ZnO, TiO_2, V_2O_5, Cr_2O_3) and alkaline additives, at 150–180°, 200 atm, and a space velocity of 300–2000 h^{-1}, a yield of liquod product of 160–170 g m^{-3} was obtained from a 1 CO : : 2 H_2 gas mixture. The product contained 85–100% of oxygen-containing compounds, 80–90% of which were normal alcohols and 5–10% carbonyl compounds. Ethanol and unsaturated hydrocarbons have been synthesised from a $3\ CO_2 : 1\ H_2$ gas mixture at 200–350 atm, 335–370°, and a space velocity of circulating gas of 10 000–20 000 h^{-1} on fused iron catalysts with oxide (K_2O, Al_2O_3, SiO_2, MnO, etc.) additives [190].

Natural mineral talc with the addition of barium aluminate and potassium carbonate may be used as catalyst in the synthesis of oxygen-containing compounds [149-154,192]. The reaction product obtained at 430°, 30 atm, and a space velocity of 500 h^{-1} with a mixture (1 : 1) of carbon monoxide and hydrogen contained up to 80% of alcohols and carbonyl compounds. After supplementary hydrogenation it consisted of a mixture of alcohols with n-propyl and isopropyl alcohols predominating.

III. KÖBEL–ENGELHARDT SYNTHESIS OF ORGANIC COMPOUNDS FROM CARBON MONOXIDE AND WATER VAPOUR

The synthesis of hydrocarbons from carbon monoxide and water vapour, discovered by Kölbel and Engelhardt in connection with a study of the mechanism of the Fischer–Tropsch synthesis on iron catalysts, proceeds according to the following overall reaction [35,70,193]

$$3CO + H_2O = 2CO_2 + CH_2 + 58.4\ \text{kcal mole}^{-1}. \quad (1)$$

This discovery became practicable after it had been shown experimentally that the formation of carbon dioxide is due to a secondary water-gas reaction[87,88]

$$CO+H_2O \rightleftarrows CO_2+H_2+9.5 \text{ kcal mole}^{-1}. \quad (2)$$

Water is formed by the primary reduction of carbon monoxide:

$$CO+2H_2=CH_2+H_2O+39.4 \text{ kcal mole}^{-1}. \quad (3)$$

On examination of the thermodynamics of the reduction of carbon dioxide to higher hydrocarbons[194-196]

$$CO_2+3H_2=CH_2+2H_2O+29.9 \text{ kcal mole}^{-1} \quad (4)$$

of the Fischer–Tropsch synthesis with the separation of water (3) or CO_2

$$2CO+H_2=CH_2+CO_2+48.9 \text{ kcal mole}^{-1}, \quad (5)$$

and of the interaction of carbon monoxide and water vapour by reaction (1), it was found that at 200–250° conditions are much more favourable for the formation of hydrocarbons from carbon monoxide and water vapour (1) than for the Fischer–Tropsch reaction (3). All the reactions examined are formally derived from the Fischer–Tropsch reaction (3), when account is taken of the water-gas reaction (2). The formation of hydrocarbons from carbon monoxide and water is possible at temperatures up to ~500°.

Kölbel–Engelhardt catalysts have as basis metals of Group VIII — iron, cobalt, nickel, or ruthenium — and they do not differ in composition and method of preparation from Fischer–Tropsch catalysts[113,197-202]. Optimum conditions for the synthesis of hydrocarbons from carbon monoxide and water vapour are given in Table 4. In addition to the formation of hydrocarbons, side-reactions also occur: these include the water-gas reaction, the decomposition of carbon monoxide

$$2CO \rightarrow C+CO_2, \quad (6)$$

methane formation

$$CO+3H_2 \rightarrow CH_4+H_2O, \quad (7)$$

and oxidation of iron present in the catalyst. These side-reactions can be kept to a minimum by changing the conditions of the process and the composition of the catalysts.

TABLE 4. Conditions and yield of products in synthesis of hydrocarbons from carbon monoxide and water vapour.

Conditions	Catalyst based on				
	Fe		Co	Ni	Ru
	stationary layer	liquid-phase synthesis			
Temperature, °C	220—240	240—280	200—240	190—205	160—199
Pressure, atm	1—100	15—20	1—10	2.5	50—110
Space velocity of initial vapour–gas mixture, h^{-1}	10—100	—	10—50	—	16—48
Initial $CO:H_2O$ ratio	3:1—2:1	3:1,15	3:1—1:1	2:1	—
Degree of conversion of CO, %	92—98	93	86—97	50—60	34—71
Yield, g m^{-3} CO					
C_1	4—12	} 22	2—4	25.0**	} 2.8—4.4
C_2	11—14		} 204	0.3	
C_3 and higher	140—190	160		74.7	66—142
Total hydrocarbons	160—210	182	206—208	100	70—145

* Duration of reaction, h.

** Composition of products of synthesis, %.

The addition of alkaline agents to the catalyst considerably diminishes methane formation, and the addition of oxides that are difficult to reduce prevents the formation of carbon[194-196]. In the presence of iron and cobalt catalysts the formation of hydrocarbons proceeds most smoothly in the temperature range 200–240°, 93–98% of the carbon monoxide being converted into liquid products. At temperatures below 200° only the water-gas reaction occurs. At temperatures above 240° the formation of methane and carbon is accelerated, and the proportion of carbon monoxide that goes to form liquid products decreases[195,203,204]. Increasing the space velocity at atmospheric pressure leads to a decrease in side-reactions and in the total yield of liquid hydrocarbons. It has been found that, in general, the maximum space velocity, expressed in $hour^{-1}$ with 90% conversion of carbon monoxide, should be 9–12 times the total pressure expressed in atmospheres. In contrast to the Fischer–Tropsch synthesis, increasing the total pressure leads to an increase in catalyst efficiency and to a weakening of side-reactions. To ensure normal operation of the synthesis it is necessary to adhere to a stoichiometric $CO:H_2O$ ratio in the gas mixture of 3:1 for the preparation of hydrocarbons and of 2:1 for the synthesis of oxygen-containing compounds. An excess of carbon monoxide leads to an increase in coke formation, especially at atmospheric pressure[203], and an excess of water vapour leads to oxidation and deactivation of the catalysts[195,203,205,206]. Iron catalysts are the most easily oxidised, and for these the $CO:H_2O$ ratio should not be less than 2:1. The stability of the catalysts is increased by treating them with a 3 CO : 1 H_2 mixture at 220°; cobalt catalysts are treated at 200° and a space velocity of 80 h^{-1}, or with ammonia at 200° and 300 h^{-1}.[206]

The reaction products obtained under optimum conditions are saturated and unsaturated aliphatic hydrocarbons mixed with small quantities of oxygen compounds. The reaction products obtained on iron and cobalt catalysts contain 50–70% of olefins. On nickel catalysts the main products are saturated hydrocarbons[207,208]. When the partial pressure of the water vapour is increased, the molecular weight of the products and their content of unsaturated compounds decrease; a total pressure up to 16 atm with a 1 CO : 1 H_2O mixture as starting gas has no effect on the degree of saturation of the reaction products[203]. An increase in pressure to 100 atm promoted the formation of ~30% of oxygen-containing compounds, mainly alcohols. In the presence of ruthenium catalysts[209], as in Pichler's synthesis[156,157], solid paraffin hydrocarbons with a mean molecular weight of 500–7000 are formed. Gases, free from catalyst poisons, containing even small amounts of carbon monoxide, such as blast-furnace and other industrial gases, may be used as raw materials in the synthesis of hydrocarbons from carbon monoxide and water vapour[194-196,210]. The synthesis is carried out on a very large scale in the presence of iron catalysts in the liquid phase with a space efficiency of 272 kg of hydrocarbons (C_3 and higher) per day per cubic metre of reaction space[113]. Petrol, diesel fuel, or solid paraffin can be obtained as the main product according to the conditions of the process and the composition of the catalyst. In all cases the products contained 70–80% of unsaturated hydrocarbons.

As kinetic measurements have shown, the process by which hydrocarbons are synthesised from carbon monoxide and water vapour consists of a series of very fast successive water-gas (2) and carbon monoxide reduction (3) reactions[208,211-214]. When the time of contact with iron, cobalt, and nickel catalysts is increased, the content of carbon

dioxide and hydrocarbons in the reaction mixture increases, while that of carbon monoxide and water vapour falls continuously. The hydrogen content passes through a maximum, which decreases as pressure increases, and increases with increase in the $H_2O:CO$ ratio. In the region of high partial pressures of carbon monoxide and water vapour, the rate of formation of hydrogen according to Eqn. (2)

$$r_1 = k_1 P_{CO}^a P_{H_2O}^b, \quad (8)$$

predominates over the rate of its disappearance by reaction (3)

$$r_2 = k_2 P_{CO}^c P_{H_2}^d. \quad (9)$$

As the partial pressures of carbon monoxide and water vapour decrease, the rate of formation of hydrogen decreases, but the rate at which it enters into reaction increases. The two rates become equal when the reaction products contain the maximum amount of hydrogen as a function of the time of contact. As the partial pressures of carbon monoxide and water vapour are further decreased, r_2 becomes greater than r_1. The numerical values of the exponents of the partial pressures — a, b, c, and d — in Eqns. (8) and (9) depend mainly on the surface concentrations, and differ little with iron, cobalt, and nickel catalysts (Table 5),

The rate constants k_1 and k_2 are determined by adsorption factors and differ from one another in different ways with different catalysts. With iron catalysts $k_1 > k_2$, with cobalt catalysts $k_1 \simeq k_2$, and the ratio of the rate constants of the hydrogen formation and consumption reactions decrease in the sequence

$$\left(\frac{k_1}{k_2}\right)_{Fe} > \left(\frac{k_1}{k_2}\right)_{Co} > \left(\frac{k_1}{k_2}\right)_{Ni}. \quad (10)$$

After hydrogen has been formed by reaction (2) it is desorbed into the gas phase to the extent of two-thirds on iron catalysts, one-third on cobalt catalysts, and one-sixth on nickel catalysts. The synthesis of organic compounds from carbon monoxide and hydrogen has many features in common with the synthesis from carbon monoxide and water vapour; they are both based on the catalytic reduction of carbon monoxide by hydrogen. They occur on the same catalysts, they are accompanied by the same side-reactions, and their apparent activation energies are closely similar. The reaction products from the two processes have virtually the same fractional composition, but the products of the carbon monoxide and water vapour synthesis contain more olefins and oxygen-containing compounds. The temperature in the synthesis from carbon monoxide and water vapour is ~30 deg higher than in the Fischer–Tropsch synthesis. Material advantages of the synthesis of hydrocarbons and oxygen-containing compounds from carbon monoxide and water vapour are the insignificant amount of methane formation and the possibility of using cheap technical and effluent gases containing small amounts of carbon monoxide and large admixtures of inert gases.

TABLE 5. Reaction order of formation and consumption of hydrogen on iron, cobalt, and nickel catalysts in the synthesis of hydrocarbons from carbon monoxide and water vapour.

Catalyst	Total pressure, atm	Reaction $CO+H_2O=H_2+CO_2$, $r_1=k_1 P_{CO}^a P_{H_2O}^b$		Reaction $CO+2H_2=CH_2+H_2O$, $r_2=k_2 P_{CO}^c P_{H_2}^d$	
		a	b	c	d
Fe	11	0.5	0.2	0.2	1.5
Co	21	1.0	0.3	−0.3...+0.3	1.0
Ni	5	0	0.6	0	0.6

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The synthesis of hydrocarbons and oxygen-containing compounds has thus been further developed in the last ten years. New technological schemes have been worked out, and cheap, readily obtainable, and effective catalysts have been developed on the basis of iron. A new method of reducing carbon monoxide with water vapour has been worked out; with this process effluent gases can be used and valuable products can be obtained. Interesting results have been obtained in putting into practice directed synthesis of oxygen compounds, mainly alcohols, macromolecular solid paraffins, and ethylene.

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SOME REGULARITIES IN THE POLYMERISATION OF BIFUNCTIONAL MONOMERS

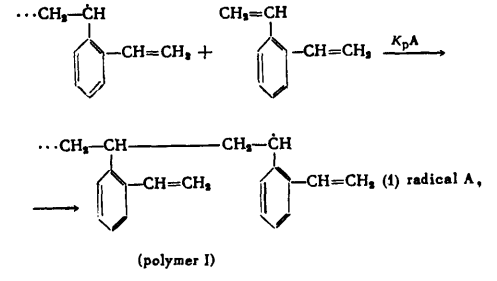
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The development of processes of linear and stereospecific polymerisation, which has considerably extended the range of polymerisable compounds and opened up new possibilities for controlling the growth of macromolecules, has given rise to a natural interest in the polymerisation of bifunctional monomers. Several new regularities have been discovered in the polymerisation of these monomers, which are of scientific and practical importance.

In the polymerisation of the simplest symmetrical bifunctional monomer, butadiene, either 1,2- or 1,4-addition is possible. A polymer chain of desired structure can be obtained by using a definite type of catalyst. The polymerisation of bifunctional compounds in which the two carbon–carbon double bonds differ in electron density is still more influenced by the type of catalyst (cationic or anionic) and by the solvent.

If a bifunctional compound containing a heteroatom attached to one of the double bonds is used as monomer, the structure of the resulting polymer depends not only on the nature of the catalyst and the solvent but also on the temperature of polymerisation. In spite of several investigations published in the literature, these questions are still far from being completely elucidated.

The polymerisation of bifunctional compounds containing two double bonds in the *ortho*-position has been studied with *o*-divinylbenzene as example [1]. This monomer was polymerised by a radical mechanism (with $\alpha\alpha'$-azoisobutyronitrile as initiator) in benzene solution. The resulting soluble polymer still contained double bonds, as was confirmed by their spectra and by bromination in carbon tetrachloride. Therefore the following three reactions can be assumed for growth of the polymer chain:



(polymer I)