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HYDROGENATION OF CARBON MONOXIDE TO ALKENES. A CRITICAL REVIEW OF THEORETICAL CONSIDERATIONS AND PROCESSES

COUNCIL FOR SCIENTIFIC AND INDUSTRIAL
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CHEMICAL ENGINEERING RESEARCH GROUP

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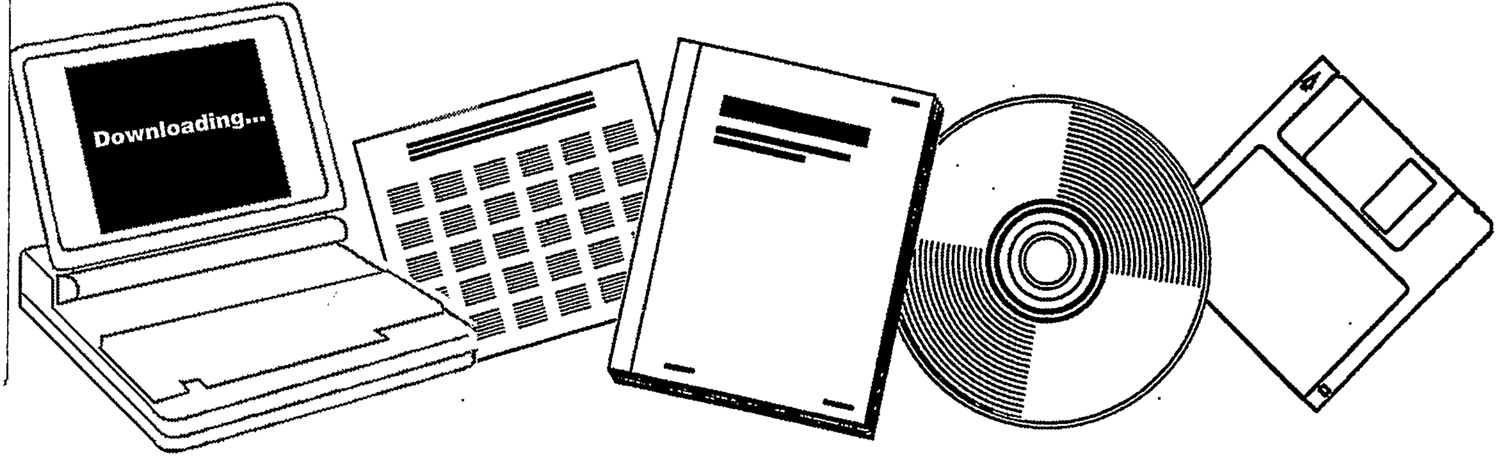

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A critical review of theoretical considerations and processes

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SYNOPSIS

The production of olefins from syngas is comprehensively reviewed. Major attention is given to fundamental aspects of the Fischer-Tropsch synthesis. Various routes and processes are examined and the areas in which research efforts are most needed are pointed out.

DIE HIDROGENERING VAN KOOLSTOFMONOKSIED TOT ALKENE
'n Kritiese oorsig van teoretiese beskouings en prosesse

SINOPSIS

'n Uitgebreide oorsig van die produksie van olefiene uit singas word gegee. Aandag is hoofsaaklik aan die basiese aspekte van die Fischer-Tropsch-sintese geskenk. Verskeie roetes en prosesse is ondersoek en die gebiede waarin navorsing die nodigste is, word aangedui.

KEYWORDS: Review, olefins, hydrogen, Fischer-Tropsch, syngas, small particles, demetallization.

File No: 660-50-2

CONTENTS

1. INTRODUCTION

The first known energy crisis occurred[1] in 1593 when the price of firewood in Europe rose by over 800 %. This makes the recent increases in the price of oil of ca 300 % look modest. The increases have, however, caused a rekindling of interest in coal as an energy source. Because of the strong need for transportation fuels, attention is increasingly being focused on the synthesis of hydrocarbons from coal.

Although there are many routes for this synthesis, only the Fischer-Tropsch process is commercially established. This process produces hydrocarbons from synthesis gas, a mixture of carbon monoxide and hydrogen, which may be derived from the gasification of coal. This type of hydrocarbon synthesis was first reported in 1902 by Sabatier and Senderens[2] who reduced carbon monoxide to methane, using a nickel catalyst. This was followed in 1913 by the first patent in respect of high-pressure operation, in which BASF disclosed a process for the production of hydrocarbons and oxygenated hydrocarbons from syngas at reaction conditions of 10 MPa to 20 MPa and 573 K to 673 K. The catalyst consisted of alkali-activated cobalt and osmium oxides supported on asbestos[3,4].

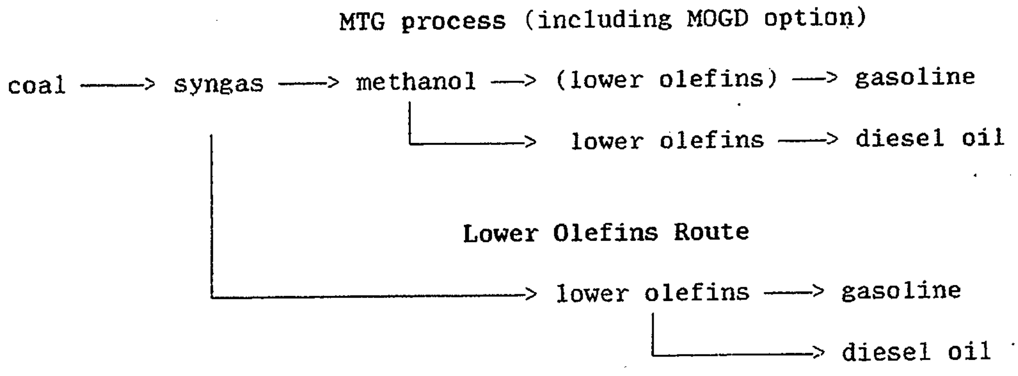
In 1923 Fischer and Tropsch published their first report[5] on "Synthol", a mixture of oxygenated hydrocarbons produced from synthesis gas at 10 MPa and 673 K in the presence of alkalized iron turnings. A major breakthrough occurred in 1925 when Fischer and Tropsch reported a process that yielded predominantly hydrocarbons[6]. The process operated at atmospheric pressure and in the temperature range 523 K to 573 K, and used an iron oxide/zinc oxide catalyst[7].

The subsequent development of the process was described in many review articles[8-11] which do not need duplication. It will suffice to mention that at present there are only three plants that utilize the process, all situated in South Africa and owned by Sasol. Commercial operation started in 1955 with the Sasol I plant at which the planned output of 223 000 tons per annum of primary products was reached two years later[12]. The production capacity was increased dramatically in 1980 when Sasol II came on stream with 1 400 000 tons of motor fuels per annum, and was boosted even further in 1982 when Sasol III came on line with the same production capacity[13-15].

One of the most severe limitations of the Fischer-Tropsch process is the poor selectivity and very broad product spectrum typically obtained. In addition, the products are largely linear and this represents a serious drawback when the aim is to produce high-octane gasoline, but is advantageous in obtaining synthetic diesel fuel. The same problems in producing gasoline are not found in the methanol-to-gasoline (MTG) process[16], which produces high-octane gasoline selectively from methanol. In addition, this process can be geared towards diesel production by using the Mobil Olefins to Gasoline and Distillate (MOGD) option[17]. In this option, the MTG process is adjusted to produce mainly lower olefins, which are subsequently fed to the MOGD process, which, run in the distillate mode, produces mainly diesel oil. As shown in Fig. 1, synthesis gas is first converted to methanol and then, in the second stage, to gasoline. Both stages show a very high selectivity[16]. However, a disadvantage of the process is the high "water" content of the methanol (CH_3OH can be seen as being composed of CH_2 and H_2O) produced in the first stage[16]. This water is liberated in the second stage, and the overall process involves the recycling of ca 60 % water. The "water recycle" increases production costs and is unnecessary on stoichiometric grounds.

It is known that the primary products of the MTG process are lower olefins[18] and it has been suggested[19,20] that these olefins react to form hydrocarbons in the gasoline range. It is also known that the primary products of the Fischer-Tropsch synthesis are the same lower olefins[21,22] and in principle the methanol synthesis could be omitted from the overall process (Fig. 1).

FIGURE 1 Routes for the selective production of motor fuels from coal



This reasoning has led to the proposal of an alternative and potentially less expensive (than MTG/MOGD) route to petrochemical feedstocks and hydrocarbons for liquid fuels, including high-octane gasoline[23]. This proposed process, termed the Lower Olefins Route, converts syngas to lower olefins which are in turn either oligomerized to diesel oil or converted to high-octane gasoline by engaging acid catalysis. This makes economically attractive (and therefore highly selective) lower olefin synthesis imperative. As a variation of this approach, the process could be geared towards gasoline production with the associated lighter products being highly olefinic. In this way a large part of the light products could be oligomerized to diesel oil.

The purpose of this review is not only to highlight the current position of research on olefin-selective Fischer-Tropsch catalysis but also to create a better understanding of all facets of the hydrocarbon synthesis, to indicate where further research is needed and, in addition, to suggest new areas of research to be explored.

2. LIMITATIONS ON THE SELECTIVE PRODUCTION OF OLEFINS FROM SYNGAS

As the broad product distribution of Fischer-Tropsch synthesis places severe limitations on its attractiveness as a commercial operation, the various underlying constraints associated with the synthesis, with respect to the selective formation of lower olefins, will now be considered in some detail.

2.1 Economic constraints

According to Kölbel and Ralek[24], 80 % of the total operating cost of a Fischer-Tropsch-based plant is the cost of producing purified synthesis gas. Shah and Perrotta[25] report a figure of 70 %. It is therefore pertinent to examine the various available gasification processes, with a view to minimizing costs.

Coal gasification processes suitable for the production of synthesis gas have recently been reviewed by Shires and Mahon[26]. They indicate that, although there are estimated to be more than 40 different coal gasifiers at various stages of development, they fall mainly into three types: fixed-bed, fluidized-bed and entrained-bed processes. The main differences lie in the acceptability of a wide range of coal types and sizes and the formation of by-products. The entrained-flow gasifier is the best choice on both accounts. Table 1 shows that the entrained-flow gasifiers of Shell and Saarberg-Otto are among those that produce a synthesis gas with a minimum of by-products. They deliver a syngas with an H_2:CO ratio of ca 0,5 at a pressure in the range of 2,5 MPa to 3,0 MPa.

Table 1 Type of coal required and product composition of various gasifiers (after ref. 26)

Gasifier	Coal type	% vol. (dry)			
		H_2	CO	CO_2	CH_4
Lurgi	bituminous	40	18	30	9
BGC-Lurgi	bituminous	28	61	3	8
Winkler	lignite	41	36	20	2
HT Winkler	lignite	35	52	9	3
Westinghouse	bituminous	32	51	10	5
U-Gas	bituminous	45	36	16	2
Koppers-Totzek	bituminous	32	55	11	-
Texaco	bituminous	38	46	12	1
Shell	bituminous	29	64	4	-
Saarberg-Otto	sub-bituminous	29	61	7	-

Shinnar[27] used differential economic analysis to show that the synthesis gas with the lowest cost has an H_2:CO ratio of less than 1,0 and possibly as low as 0,5. Gray *et al.*[28] arrived at the same conclusion. They analysed the liquid phase Fischer-Tropsch process of Kölbel and Ralek[24], which claims to accept an H_2:CO ratio of 0,67 and calculated that such a system would bring about a decrease of as much as 30 % in the production cost of gasoline. Although H_2:CO ratios of 1 or less are considered incompatible with long-term vapour-phase Fischer-Tropsch operation because of excessive carbon deposition[29], in view of the economic considerations above there is a great attraction in the development of a new generation of Fischer-Tropsch catalysts that can accept an H_2:CO ratio of ca 0,5 at a pressure of 2 MPa to 3 MPa, so that the best suitable gasification processes, such as those of Shell or Saarberg-Otto, can be employed to full advantage.

Although the hydrocarbon synthesis and subsequent refining itself comprises only 20 % to 30 % of the total operating expenditure, cost-effective operation is still of the essence. A 1980 evaluation of investment and production costs in Europe[30] suggested that ca 50 mass % of the product must consist of light olefins to obtain an economically viable process. However, this figure depends on the location of the plant and, in addition, the lower olefins route could well be economically viable with an olefin selectivity of 50 % in the C_2 to C_5 fraction, provided that the C_2 to C_{12} fraction is maximized. This will be the case when the Schulz-Flory growth probability is ca 0,7. It has been suggested that the process would be very attractive with an olefin selectivity in the range of 60 % to 70 % in the C_2 to C_5 fraction[31].

2.2 Thermodynamic constraints

Five basic reactions are involved in the Fischer-Tropsch synthesis. Equation (1) shows the basic synthesis reaction which applies particularly to cobalt catalysts. Cornils *et al.*[32] reported the change in Gibbs free energy, ΔG°_{T}, at the typical synthesis temperature of 500 K as shown below.

i) Synthesis (Co)

$$\mathrm{CO} + 2\mathrm{H_2} \rightleftharpoons (\mathrm{CH_2}) + \mathrm{H_2O} \quad \Delta G^{\circ}_{T}\ (\text{n-hexane}) = -165{,}5\ \text{kJ} \tag{1}$$

Equation (2) is a shift reaction between the water formed in Equation (1) and carbon monoxide.

ii) Shift reaction

$$\mathrm{CO} + \mathrm{H_2O} \rightleftharpoons \mathrm{CO_2} + \mathrm{H_2} \quad \Delta G^{\circ}_{T} = -40{,}0\ \text{kJ} \tag{2}$$

Both equations together yield the synthesis reaction, Equation (3), which occurs preferentially on iron catalysts.

iii) Synthesis (Fe)

$$2\mathrm{CO} + \mathrm{H_2} \rightleftharpoons (\mathrm{CH_2}) + \mathrm{CO_2} \quad \Delta G^{\circ}_{T}\ (\text{n-hexane}) = -205{,}4\ \text{kJ} \tag{3}$$

Assuming that a rapid and complete thermodynamic equilibrium is attained between carbon monoxide and hydrogen, elementary carbon and carbon dioxide should be formed according to the Boudouard reaction, Equation (4), as well as methane and water according to Equation (7).

iv) Boudouard reaction

$$2\mathrm{CO} \rightleftharpoons \mathrm{C} + \mathrm{CO_2} \quad \Delta G^{\circ}_{T} = -134{,}4\ \text{kJ} \tag{4}$$

v) Methanation

$$\mathrm{CO} + 3\mathrm{H_2} \longrightarrow \mathrm{CH_4} + \mathrm{H_2O} \quad \Delta G^{\circ}_{T} = -205{,}2\ \text{kJ} \tag{5}$$

In the temperature range 500 K to 600 K, which is typical for hydrocarbon synthesis, there is competition between the synthesis and side reactions (Fig. 2). The methanation and Boudouard reactions are clearly more favoured than the desired synthesis reaction and lower synthesis temperatures are needed.

Thermodymamic calculations[32-34] of simultaneous equilibria for several concurrent reactions indicate that, under most reaction conditions, no olefins would result on attainment of equilibrium. These calculations also indicate that the equilibrium conversion would increase with increasing pressure.

As the hydrogenation of carbon monoxide is highly exothermic (Equations 1 and 3), the synthesis equilibrium constant for Equation 1, K_p, decreases with increasing temperature (Fig. 3), suggesting that low synthesis temperatures are preferable. Another consideration is the temperature-dependence of the mass selectivity. This relationship indicates that the formation of short-chain products is favoured by high temperatures (Fig. 3). This contrasts, however, with the temperature constraints of the methanation and Boudouard reactions.

Another parameter that influences the thermodynamic equilibria is the $CO:H_2$ ratio in the feed gas. High values of this ratio favour the formation of lower olefins[32] (Table 2).

Table 2 The influence[32] of the $CO:H_2$ ratio on log K_p of Equation 1 at 0,1 MPa and 500 K

$CO:H_2$	ethene	propene	1-butene
0,5	4,85	10,09	13,67
2,0	9,09	16,45	22,15

Taking all thermodynamic considerations into account, it may be concluded that:

a) the probability for the formation of methane is always higher than that for higher hydrocarbons and increases with temperature;

b) the probability for carbon deposition is always higher than that for the formation of hydrocarbons other than methane and increases with temperature;

c) the probability for the selective formation of lower olefins increases with temperature and decreasing $H_2:CO$ ratio in the feed gas;

d) under most reaction conditions no olefins will be produced on attainment of equilibrium;

e) the equilibrium conversion will increase with pressure.

Conclusions (a) and (b) indicate that low temperatures minimize side-reactions, and conclusion (c) indicates that high temperatures favour short-chain products. Accordingly, compromise on the use of moderate temperatures is indicated.

FIGURE 2 ΔG^{o}_{T} in relation to temperature of synthesis (kcal/mol C atom for n-hexane (after ref. 32)

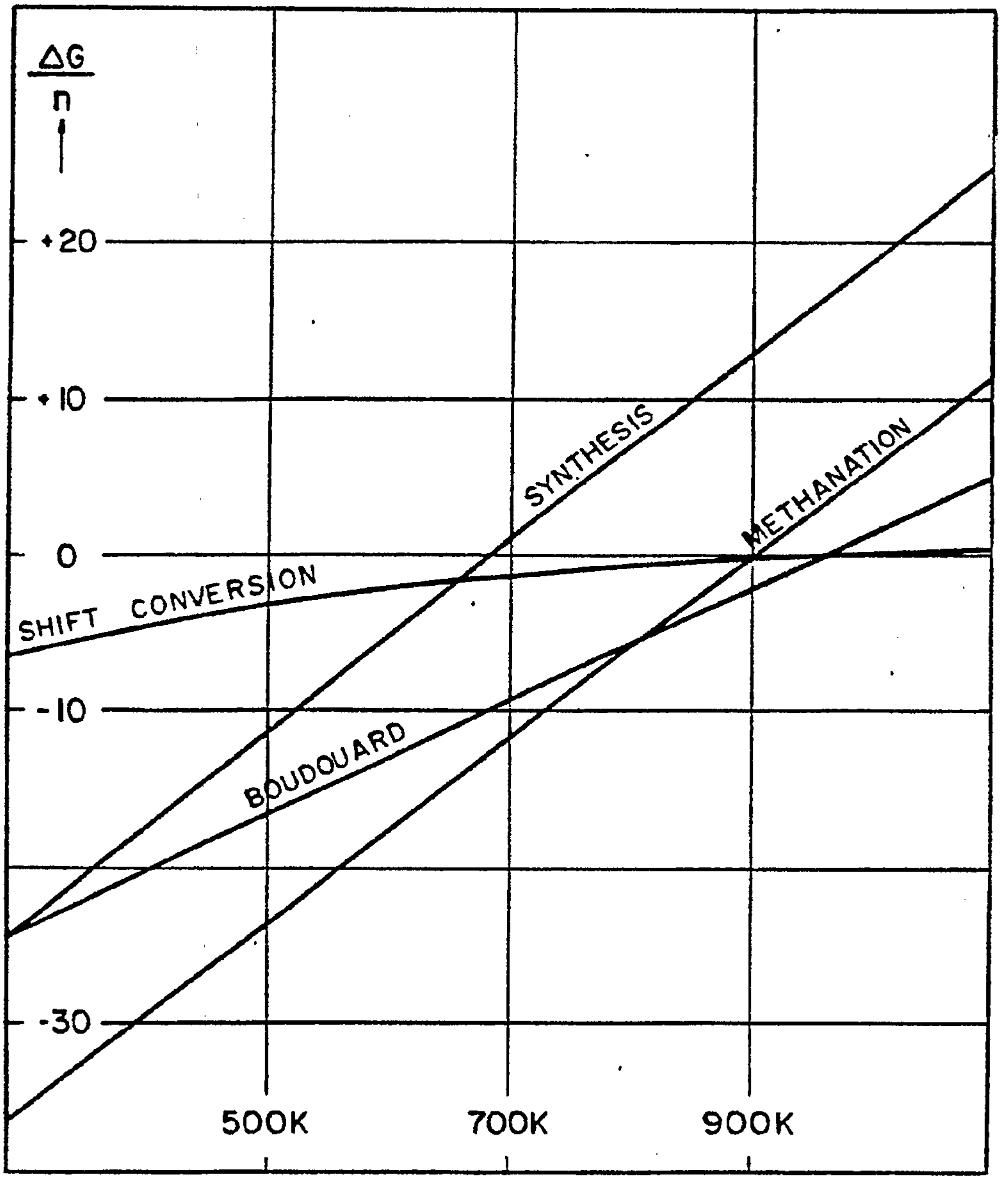
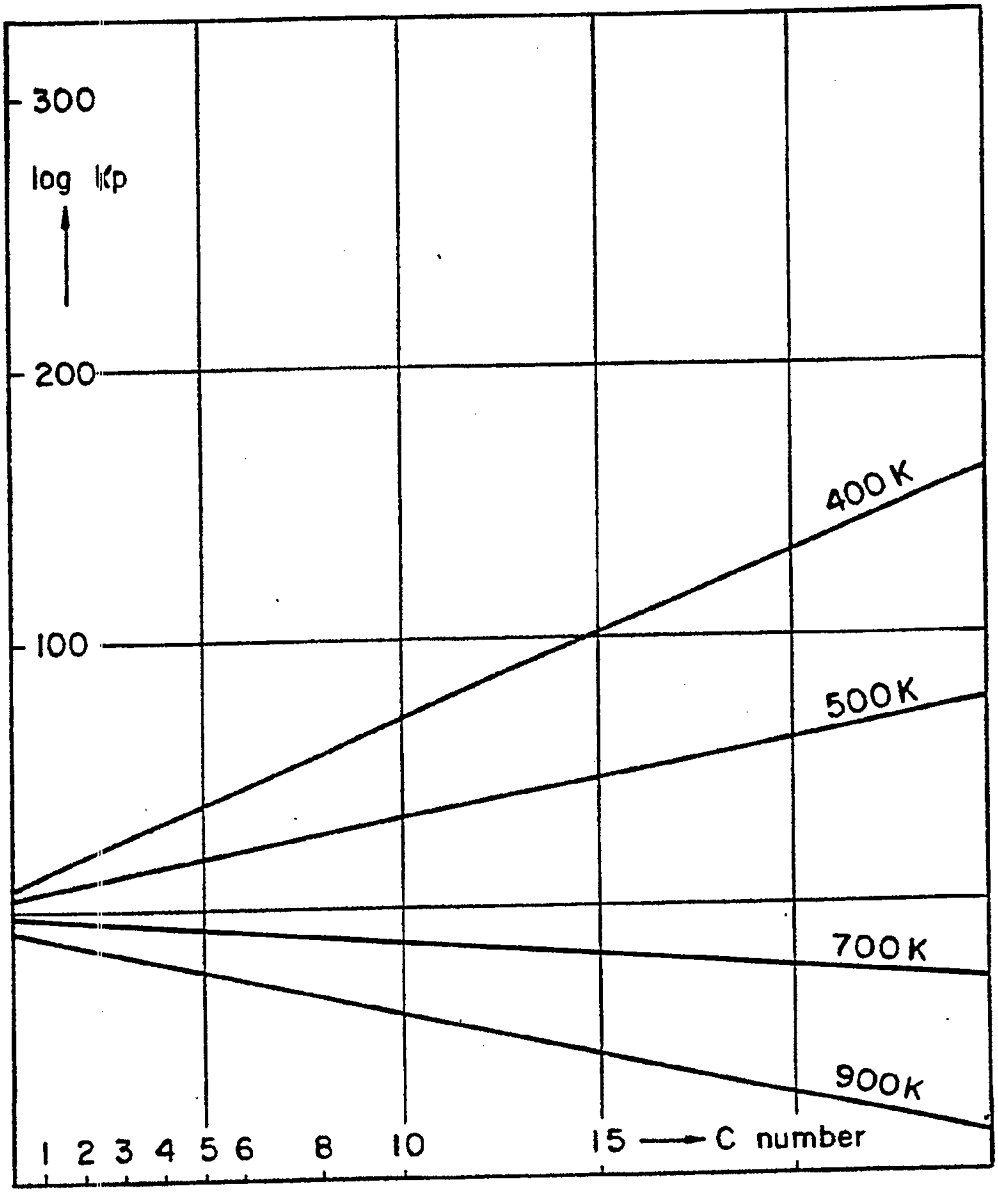


FIGURE 3 Log K_p as a function of temperature and chain length (after ref. 32)



It should, however, be borne in mind that these thermodynamic considerations refer to equilibrium conditions and that under normal conditions the equilibria in the Fischer-Tropsch synthesis are attained only slowly. Although the maximum attainable conversion is, of course, dictated by the thermodynamic equilibrium constant, under normal process conditions selectivity and activity will be governed mainly by the properties of the catalyst and by the reaction conditions employed. Our attention should therefore be focused mainly on those two parameters.

2.3 Kinetic constraints

2.3.1 Reaction kinetics

Several authors[8,35–37] have suggested that the overall synthesis rate is controlled by the temperature and by the partial pressures of carbon monoxide, hydrogen and water as follows:

$$r = \frac{k[P(H_2)]}{1 + b[P(H_2O)/P(CO)]} \qquad (6)$$

where k and b are temperature-dependent intrinsic rate constants. It has often been reported[36–40] that the term $b[P(H_2O)/P(CO)]$ can be neglected for conversions less than ca 60 % or at low to medium temperatures (e.g. for iron catalysts less than 573 K) where the rate is controlled by the temperature and the partial pressure of hydrogen:

$$r = k[P(H_2)] \qquad (7)$$

This is not unexpected since Fischer-Tropsch catalysts are known to show poor activity at atmospheric pressure. Reasonable conversions are seldom reached at pressures of less than 1 MPa.

Equation (7) is in contrast to the findings of Feimer *et al.*[41] who report that the initial synthesis rate is inhibited by carbon monoxide and that the rate may be fitted to a power-law model:

$$r = [P(H_2)\ P(CO)]^{-0.25} \qquad (8)$$

Vannice[42] reports that, under similar conditions, the exponential dependence of the methanation reaction is usually close to first order in hydrogen and between 0 and -0,5 in carbon monoxide, which is in agreement with various other reports[43-45]. In the light of these findings, the deviation of Equation (8) from Equation (7) could be explained by assuming a high methane selectivity of the reaction reported by Feimer *et al.*[41], which would decrease the power of the carbon monoxide partial pressure in the rate equations. These kinetic aspects imply that an increase in total pressure at constant H_2:CO ratio will lead to a higher activity and lower methane selectivity.

Any meaningful kinetic model should be based on mechanistic assumptions. A short consideration of the mechanism is therefore in order. Many mechanisms of the Fischer-Tropsch synthesis have been reviewed comprehensively[46-49] and there is still considerable controversy about the nature of the hydrocarbon synthesis. However, recent evidence[46,50] stresses the importance of carbon monoxide dissociation in the initiation step. Partially hydrogenated surface carbon species play a predominant role in the growth of hydrocarbon chains. In addition, a parallel route is thought to exist, which involves the insertion of undissociated carbon monoxide into a metal-alkyl bond, accounting for the formation of oxygen-containing products.

Regarding the selective production of lower olefins, only those proposed mechanisms that involve secondary reactions of these primary products need be considered in this discussion. One such mechanism has been proposed by Hugues *et al.*[51], who suggested an olefin insertion mechanism which is a variation on the surface carbide mechanism proposed by O'Donohoe *et al.*[52]. The incorporation of olefins into the growing chain involves a metallo-cyclobutane transition state followed by β-H transfer to form an α-olefin. Since the formation of these longer-chain compounds is an undesirable reaction, short contact times are indicated to preclude this and other types of secondary reaction of the primarily formed lower olefins. This may be effected by either increasing the gas flow rate or decreasing the catalyst concentration.

The rate-determining step is still the subject of some controversy. However, results obtained by several independent research groups[24,53,54] indicate that the kinetics of the Fischer-Tropsch synthesis on iron, as well as on cobalt, catalysts may be explained by an initiation step which proceeds via carbon monoxide dissociation and the formation of an intermediate surface carbene species $CH_{2,ads}$. The formation of this intermediate is generally seen as the rate-determining step.

In the last decade, studies of carbon monoxide hydrogenation kinetics[55-57] have for the first time included chemisorption measurements, so that the reduced metal surface area could be quantified. Thus for the first time specific activities and turnover frequencies were calculated for the synthesis reactions. The turnover frequency is defined by the IUPAC[58] as the number of molecules reacting per active site in unit time. In Fischer-Tropsch studies the number of active sites is generally determined by carbon monoxide adsorption on the reduced catalyst. This implies that a site for carbon monoxide adsorption would also be an active site in the Fischer-Tropsch synthesis. Kieffer[30] very justly questions this approach, for there is no evidence that the number of adsorption sites on the reduced catalyst precursor is really an indication of the number of active sites on the catalyst during synthesis. For the Fischer-Tropsch synthesis with iron catalysts, this method would be particularly questionable, since the reduced α-iron phase is converted to iron carbide under synthesis conditions with modification of the surface properties[59].

The turnover frequency, which is based on the population of catalytically active sites - the number of which may be only a fraction of the total number of surface sites - will have an upper limit which is determined by the number of adsorption sites for carbon monoxide. In summary, there need be little relation between the number of chemisorption sites for carbon monoxide on the reduced catalyst precursor and the number of active sites on the carbided catalyst. It is conceivable that reported turnover frequencies are far lower than the true turnover frequencies, but in certain cases they might be correct. A typical example is the reported activities over different metals. Turnover frequencies of 0,03 molecules site^{-1} s^{-1} for cobalt, 0,16 for iron and 0,33 for ruthenium have been reported[56]. These values seem to indicate that iron catalysts display a far higher catalytic activity than cobalt catalysts, but in fact cobalt is far more active than iron. Reported turnover frequencies should therefore be treated with care.

It has been suggested[30] that the concept of active site may have to be enlarged. Lankhuijzen[60] introduced the following differentiation between surface elements:

- active site
- active centre
- active ensemble
- active aggregate.

In the Fischer-Tropsch synthesis one could distinguish between the adsorption of hydrogen atoms on active sites, the adsorption via multiple bonds of species such as surface carbene and carbon monoxide on active centres and the reaction, during each of the reaction steps, of the synthesis on active ensembles. All the active sites, centres and ensembles required to make a product from the reactant gases will form a single active aggregate.

The use of such definitions would certainly contribute to the determination of the true turnover frequency. If there were also a method for the unambiguous determination of the number of active ensembles and sites under synthesis conditions, there would be less ambiguity in the literature, such as claims[30,61] that the number of sites required for the formation of hydrocarbons is anything between 5 and 20.

2.3.2 Polymerization kinetics

If the Fischer-Tropsch synthesis is seen as starting from a single carbon unit which is gradually built up in molecular size by the repeated addition of single carbon units, then the product distribution can often be described by the probability of propagation (P) and the competing probability of termination (1-P). Both probabilities are assumed to be independent of the length of the oligomer chain attached to the surface.

The first mathematical descriptions of the Fischer-Tropsch product distribution were reported by Herrington[62] and were used by Friedel and Anderson[63,64] to develop the first formal Fischer-Tropsch product statistics. They showed that, although the nature of the monomer unit may be an object of considerable controversy, it does not affect the mathematical description of the chain-growth process.

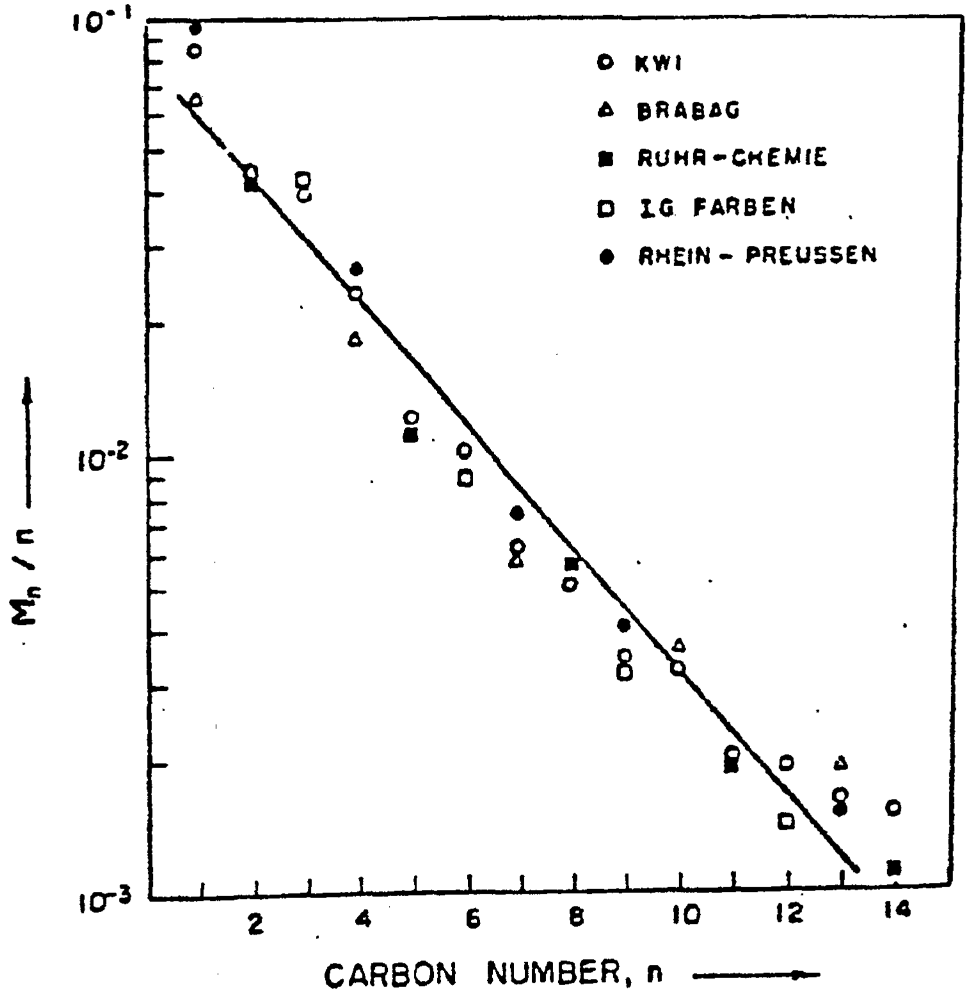
Henrici-Olivé and Olivé[65,66] pointed out that the same statistics are applicable to the radical polymerization of vinyl-monomers, which was reported by Dostal and Mark[67] and by Schulz[68,69] in 1935 and 1936, and to the linear polycondensation of polymers as described by Flory[70] in 1936. The product statistics therefore became known as the Schulz-Flory distribution, represented by[10]:

$$\ln(M_n/n) = n\ln P + \ln[(1-P)^2/P] \tag{9}$$

where M_n is the mass fraction of the product hydrocarbons with n carbon atoms.

This equation is widely used and served as the basis for King *et al.*[71] to plot the product distribution of commercial Fischer-Tropsch data (Fig. 4).

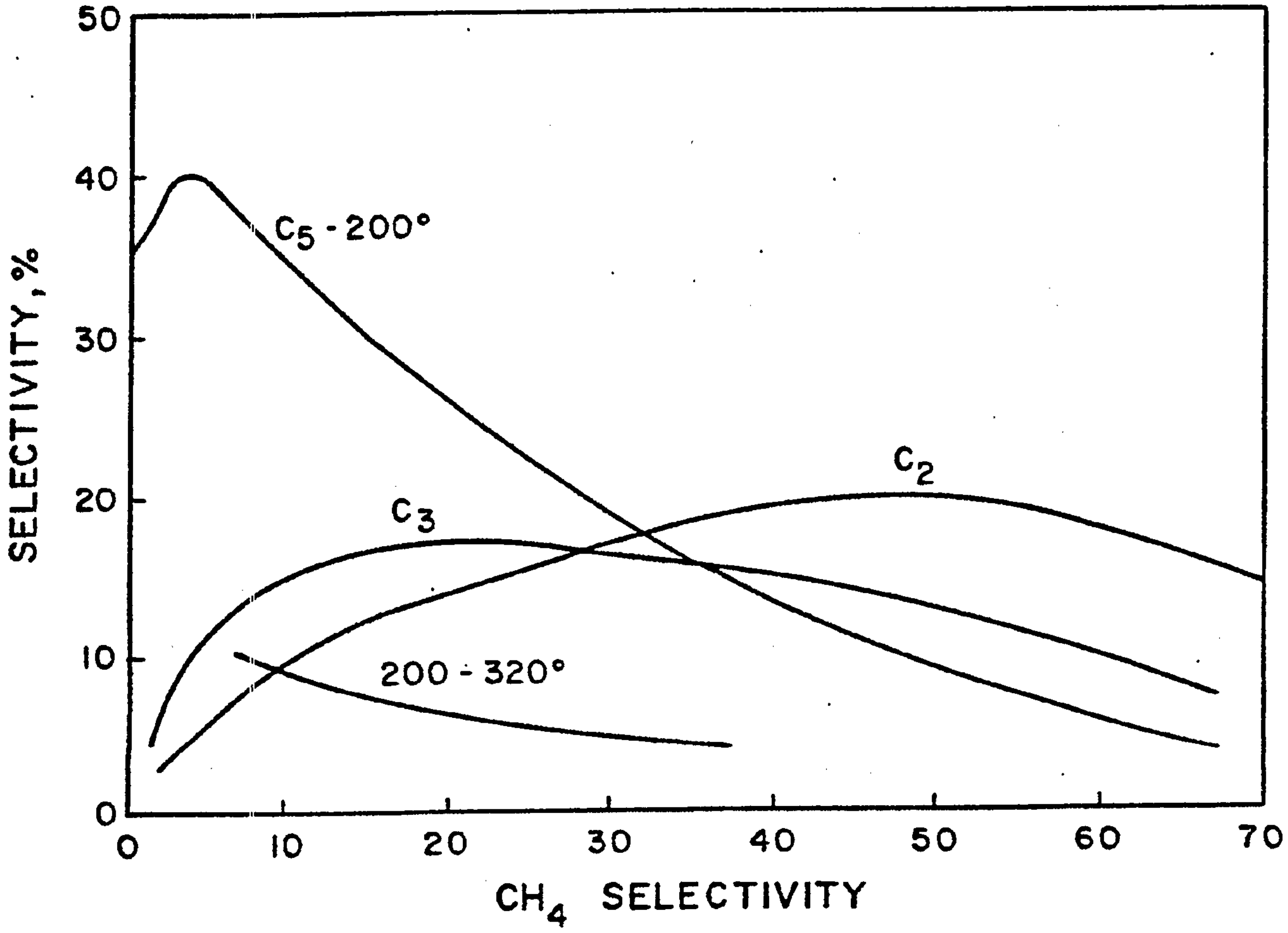
FIGURE 4 Hydrocarbon distributions for commercial iron catalysts, plotted[7i] according to Equation (9)



Product statistics of this type are characterized by only one parameter, P, the value of which may be calculated from a Schulz-Flory plot. If the product distribution follows Schulz-Flory statistics, then a plot of $\ln(M_n/n)$ as a function of n should yield a straight line, where both the slope and intercept give the same calculated value of P. The data in Fig. 4 provide strong evidence for the validity of the Schulz-Flory distribution.

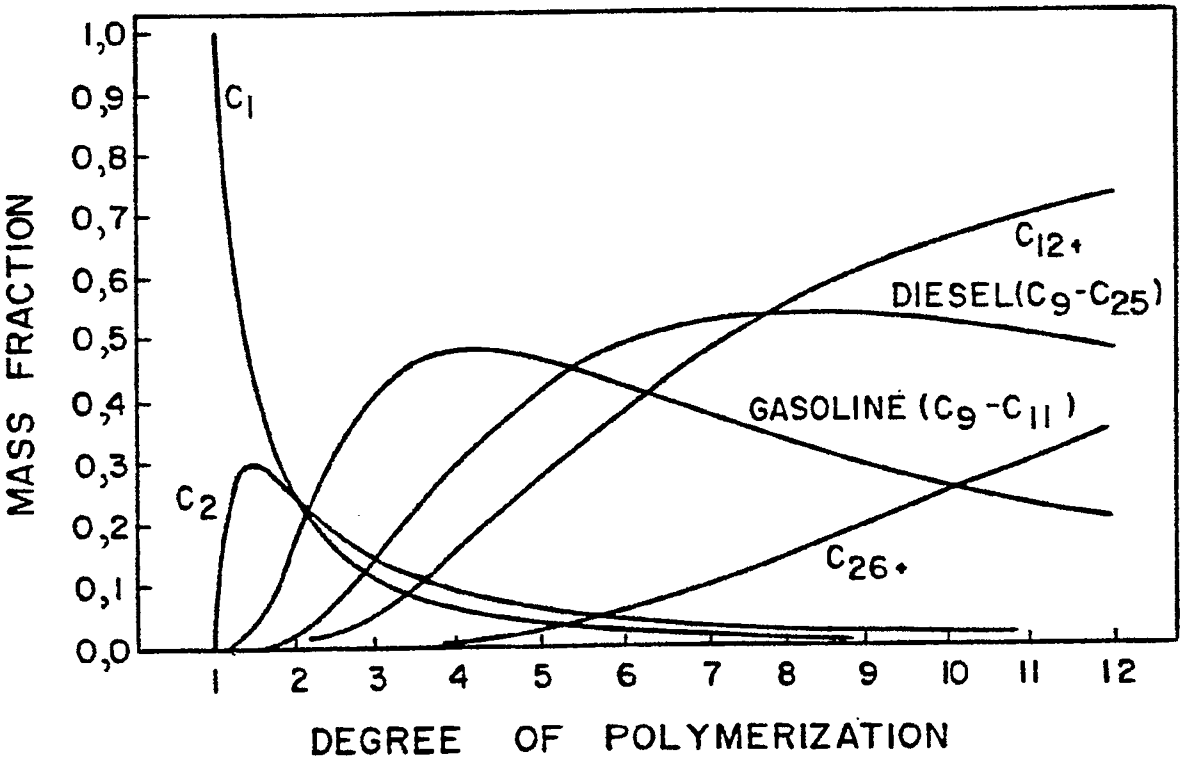
King *et al.*[71] show very clearly that the consequences of Equation (9) are profound, for it suggests that, once P is fixed, the entire product distribution is fixed. This view is supported by commercial data from Sasol[72] in which a strong interdependence of selectivity is observed (Fig. 5).

FIGURE 5 The interdependence of the product selectivities with Fischer-Tropsch catalysts.
Data[72] are the average for a variety of Sasol Fe catalysts at 470 K to 610 K and 0,5 MPa to 4,0 MPa



If the mass fraction is plotted as a function of the degree of polymerization D, which is given by $(1-P)^{-1}$, the impact of the chain-growth mechanism on the selectivity becomes even clearer (Fig. 6). This plot indicates that C_5 to C_{11} hydrocarbons (gasoline) cannot be produced with a selectivity greater than 50 % and the same holds true for C_9 to C_{25} hydrocarbons (diesel oil). Only single carbon species, such as methanol and methane, can be produced with a selectivity of 100 %. These facts set a very real limit on the highly selective production of lower olefins.

FIGURE 6 Selectivity limitations on Fischer-Tropsch synthesis as determined by Schulz-Flory statistics[71]



Many Schulz-Flory-type kinetic models that explain the product distribition have been proposed. For example, Dautzenberg *et al.*[73] report a simple kinetic model, which they claim describes the product distribution well. In addition, they report that the rate of propagation is very low on ruthenium. With two differently prepared Ru/Al_2O_3 catalysts they found that the chains grow at a rate of about one CH_2 group per 60 seconds. The low rate is attributed to the very low intrinsic activity of the exposed ruthenium atoms. A low propagation rate is also reported for iron catalysts in a kinetic study by Kieffer[30] who, in addition, concludes that on iron catalysts the rate of propagation is not rate-determining.

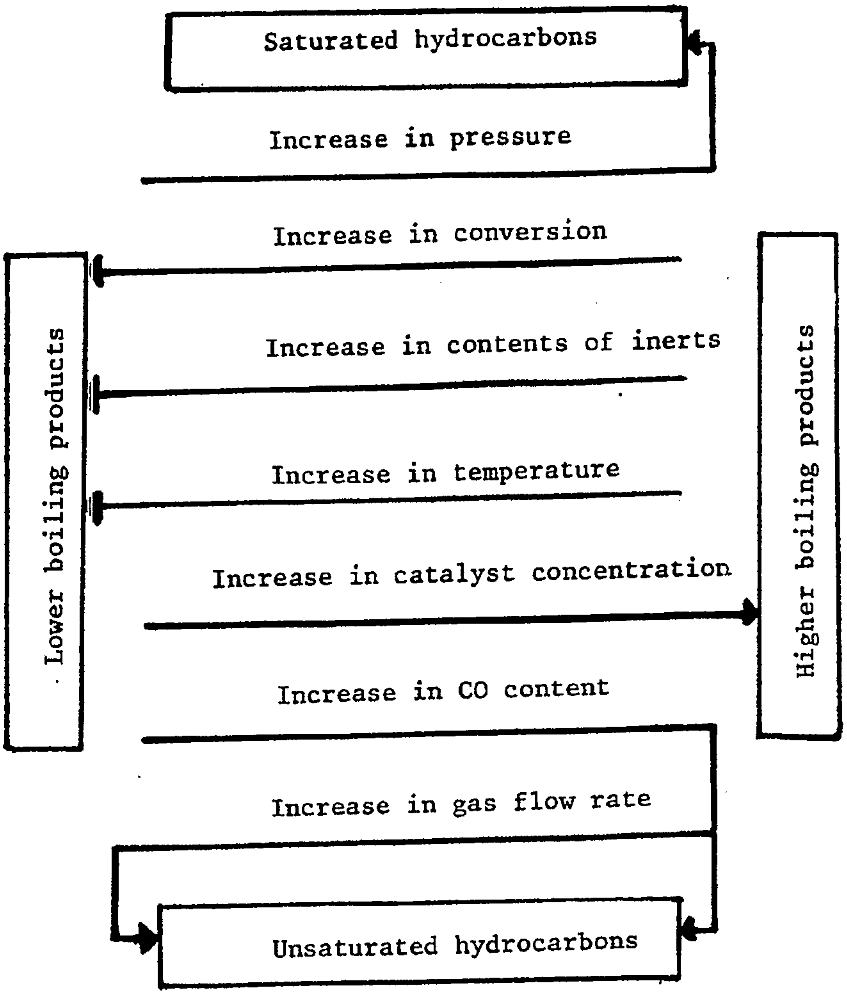
Several kinetic models, which do not obey Schulz-Flory statistics, have been reported recently. Nijs and Jacobs[74] propose an extended Schulz-Flory model to describe the product distribution which includes the metal particle size of the catalyst. On metal particles greater than a certain size, normal Schulz-Flory polymerization kinetics are obeyed, but smaller sizes limit the chain growth. Gaube *et al.*[75] and Schliebs[76] report two different polymerization probabilities, one for the lower molar mass products and one for the higher, each involving different kinetics. An interesting aspect was reported by Baerns and Bub[77] who claim that the probability of chain growth depends on the partial pressure of carbon monoxide:

$$P = k[P(CO)]^{0.11} \qquad (10)$$

This implies that the formation of light hydrocarbons is favoured by low H_2:CO ratios of the synthesis gas.

The combined effects of thermodynamic and kinetic constraints are summarized diagramatically[32] in Fig. 7.

FIGURE 7 Effects of thermodynamic and kinetic constraints on the product composition[32]



2.4 Constraints caused by methanation and carbon deposition

For the highly selective production of lower olefins from syngas, the occurrence of side-reactions must be restricted. The suppression of side-reactions such as methanation and the Boudouard reaction is not easy since they are thermodynamically more favourable than the synthesis reaction (Fig. 2).

Some solace may be found in kinetic considerations since the methanation reaction is known to be slightly suppressed by the use of short contact times and low temperatures.

Another factor is the hydrogenation ability of the catalyst. For example, catalysts such as nickel and platinum are well known for their strong hydrogenation activity and produce mainly methane in the Fischer-Tropsch synthesis. To retard attainment of thermodynamic equilibrium, use of a poor hydrogenation catalyst is indicated.

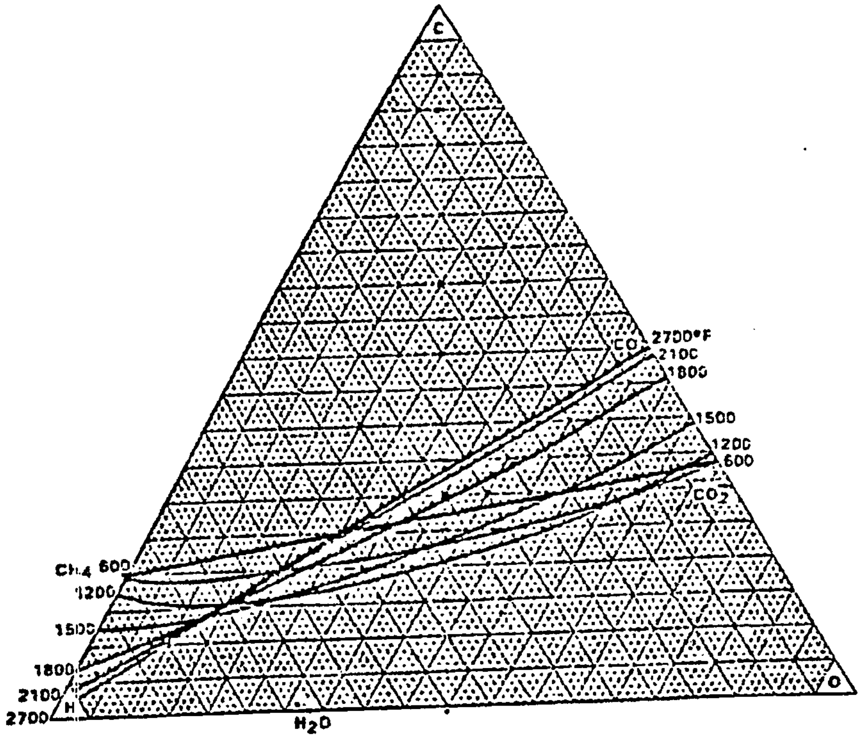
Dry[36] claims that the controlling parameters are different for different catalysts and process conditions. Thus for fixed-bed operations the H_2:CO ratio is the dominant factor. Here methanation is favoured by a high H_2:CO ratio. For fluidized-bed reactors the H_2:CO ratio seems to be of no consequence and the methanation is inversely proportional to the partial pressure of carbon dioxide at the reactor entrance.

A further cause of methanation is carbon deposition, since some types of carbon are readily hydrogenated to methane[78]. The deposition of carbon occurs mainly because of the disproportion between carbon monoxide [the Boudouard reaction, Equation (4)] and carbon dioxide and elemental carbon. This process causes major problems: it may lead to excessive methane formation, catalyst deactivation, destruction of the catalyst pellet and increased attrition and physical plugging of the reactor in the case of iron catalysts. Two types of carbidization may be discerned, the bulk and surface types.

The conditions under which elemental carbon can be deposited on the catalyst are well known from thermodynamic considerations. A rapid assessment of these conditions is made possible by White *et al.*[79] who constructed extremely useful ternary diagrams (Fig. 8).

Carbon is deposited in the form of multiple layers and this deposition is generally seen as one of the major reasons for the deactivation of iron catalysts. These multilayers are formed after the iron has been carbided to compounds with an average composition of Fe_2C. During synthesis some of this carbon is removed again, giving rise to a steady state in which the removal of carbon by a small, but very active, portion of the surface just compensates for the deposition. Major parts of the surface of iron catalysts are covered with unreactive carbon deposits which coexist with the true reaction intermediates[80].

FIGURE 8 Carbon formation. Equilibrium isotherms at 2,6 MPa total pressure[79]



The nature of this surface carbon has been studied by many research groups. Kieffer[30] and Kieffer and Van der Baan[81] distinguished three types of carbon on iron catalysts after hydrocarbon synthesis, using the technique of temperature-programmed surface reaction to show different reactivities towards hydrogen. The first type, referred to as a-carbon, is readily formed during coadsorption and is thought to be responsible for methane formation. It is claimed to lower the hydrocarbon production by encapsulating active sites. This type of carbon is thermally unstable and is easily converted to a less reactive form of carbon, referred to as b-carbon. It has been suggested that this type of carbon diffuses into the bulk and thus causes disintegration of the catalyst particles. It is further claimed that the formation of type a can be inhibited by the addition of 0,4 mass % ferric sulphate to the catalyst, thereby suppressing methane formation. Type b formation can be suppressed by the addition of 3 mass % ferric sulphate to the catalyst, although this lowers the catalyst activity. The third type, a'-carbon, is very reactive towards hydrogen and produces both methane and higher hydrocarbons. It is speculated that this carbon species is one of the reaction intermediates that has a major influence on the catalytic activity.

Bonzel and Krebs[82] also identified three types of carbon in the carbonaceous layer on iron, using Auger and photoelectron spectroscopy. The first type is formed during the first stages of the synthesis and is extensively hydrogenated carbidic carbon. It is thermally unstable and converts readily to carbidic carbon. The second type is formed only after longer periods of synthesis. It has also been identified as hydrogenated carbidic carbon, but it contains less hydrogen than the first type. The occurrence of such hydrogenated carbon entities is not limited to iron surfaces but has also been reported for nickel, cobalt and ruthenium catalysts[83]. Such carbon species are thought to play a major role in the hydrogenation of carbon monoxide over these metals. The third type has been identified as graphitic carbon, which is unreactive towards hydrogen under normal synthesis conditions. The conversion of carbidic carbon to the graphitic form is thought to be responsible for the deactivation of iron catalysts after prolonged periods.

Partially hydrogenated carbon, originating from the hydrogenation of surface carbon, has often been reported to participate in the hydrocarbon synthesis, thereby influencing the selectivity and activity[84–87]. Biloen *et al.*[88] suggest that elemental surface carbon takes part in the synthesis, and Rabo *et al.*[78] as well as McCarty and Wise[89] recognize up to four different types of carbon, of which they identify two as amorphous carbon: a, a chemisorbed carbon, and b, a loosely bound carbon. They report that nickel surfaces are covered with a carbon and b carbon species with a ratio of 2:1 after exposure to carbon monoxide at a temperature of 550 K. At this temperature the a state is hydrogenated to methane at a substantial rate. It is not clear whether these species, the a- and b-type carbon reported by Kieffer[30] and the first two types of carbon identified by Bonzel and Krebs[82], are identical. Elemental carbon is, however, formed not only by the disproportionation of carbon monoxide, but also by the decomposition of chemisorbed hydrocarbons. This type of carbon deposition has been reported for both iron[90] and cobalt catalysts[91].

Swift *et al.*[92] suggest that metallic nickel is responsible for initiating and propagating the deposition of carbonaceous residues on nickel catalysts and that these reactions could be eliminated by adding to the feed a compound capable of sulphiding metallic nickel as soon as it is formed. This idea is in line with the views of Kieffer[30].

Dry[35] investigated the kinetic parameters that govern the rate of carbon deposition in entrained-bed reactors at high temperature. He found this rate to be proportional to the factor $P(CO)/P(H_2)^3$. A higher hydrogen pressure helped to reduce the problem to some extent, but it is not yet possible to operate normal fluidized-bed reactors at such pressures. Entrained-bed operation is still necessary to extend the life of the catalyst particle to only a few weeks. Although this eases the operation of the process, significant problems remain and, in addition, production costs are increased since the H_2:CO ratio has to be increased dramatically. Some of the underlying factors are known. Dry[36] has noted that as the basicity of the catalyst increases, the carbon deposition rate first decreases and, after having reached a minimum value, increases again. This is in good agreement with the views of Kölbel and Giering[93,94], who reported the same observation thirteen years earlier and showed, in addition, that the minimum rate of carbon deposition is reached at a potassium carbonate concentration of 0,2 mass %. Bearing in mind Kieffer's results with sulphate[30], it might be speculated that at the molecular level there is an electronic effect influencing the rate of carbon deposition.

Kölbel and Ralek[24] seem to have circumvented the carbon deposition constraint of having to work at high H_2:CO ratios. They reported a liquid phase process operating at an H_2:CO ratio of 0,67 which allows a very long catalyst life. This achievement could result from the H_2:CO ratio at the catalyst surface being substantially higher than 0,67. Heinemann *et al.*[95] showed that the H_2:CO ratio in the liquid phase of a slurry reactor is a sensitive function of differences between the solubilities and mass transfer coefficients for hydrogen and carbon monoxide, and that the H_2:CO ratio of the syngas in the liquid phase can differ substantially from that of the gas fed to the reactor.

The research group of Vannice[96-100] reports a carbon-supported iron catalyst that is able to accept a low H_2:CO ratio, produces a hydrocarbon mixture with a high olefin-to-paraffin ratio and has good activity maintenance during Fischer-Tropsch synthesis. They attribute these qualities to the very small size of the iron crystallite present. The role of the carbon support is not considered, but the reaction between the iron and carbon surface may well stabilize the small iron and iron carbide crystallites, or the support may even take part in the synthesis reaction.

Schay and Guczi[101] concluded from their study of mixed iron-ruthenium carbonyl clusters in the hydrogenation of carbon monoxide that three different types of carbon are included in the mechanism. The first type is active in methane formation and the second type plays a role in catalyst deactivation; this agrees well with the reports discussed before. The third type is claimed to be active in the formation of olefins. It was suggested that this type of surface carbon, together with metallic sites, is required for the formation of olefins.

Related to the deposition of carbon on catalytic surfaces is the formation of bulk carbon. There are known to be several types of bulk carbide. During Fischer-Tropsch synthesis under normal conditions (480 K to 573 K), α-Fe is converted to Fe_2C and then to Hägg carbide[102], FeC_2. At higher temperatures (598 K), α-Fe is converted directly to Hägg carbide[78,103]. Stanfield and Delgass[104] reported three carbidic phases for silica-supported iron catalysts: Fe_x, ϵ'-$Fe_{2.2}C$ and χ-Fe_5C_2. Matyi *et al.*[105] observed that on these catalysts the iron carbide crystallites transformed from the ϵ' phase to the more stable χ-carbide when synthesis gas was replaced by helium. Van Dijk[106] noted four iron carbides, adding θ-Fe_3C to the list. The Fe_xC carbide had a composition intermediate between that of α-Fe and that of χ-Fe_5C_2. This intermediate carbide has often been wrongly classified as the Hägg carbide.

It is sometimes suggested[86,107] that the extent of carburization of the catalyst is closely connected with the catalytic activity, although it has never been conclusively proved that bulk carbon is directly involved in the synthesis reaction. Stanfield and Delgass[104] reported that ϵ-carbide is a possible intermediate for methane formation, and Niemantverdriet and van der Kraan[108] suggest that there is competition between bulk carbidization and hydrocarbon synthesis. Raupp and Delgass[86] observed that the rate of synthesis reaction on silica-supported iron catalysts was linked to the extent of bulk carbide formation and suggested that the concentration of active surface sites is controlled by the incorporation of carbon into the iron particles. Ott *et al.*[109] report that unsupported iron catalysts accept carbon into the bulk during the initial 24 h on stream, along with a slow build-up of carbon on the surface. Carbide formation results in a temporary increase in the hydrocarbon synthesis activity as well as a decrease in the olefin selectivity. The mass selectivity, however, remains unchanged until the carbon build-up on the surface is large, after which it shifts towards lower-mass products.

Matsumoto and Bennet[80] suggest that the rate-controlling step in the hydrogenation of carbon monoxide over iron catalysts is the hydrogenation of a carbon intermediate, the concentration of which depends on the extent of catalyst carburization. This implies that this carbon species is the intermediate for both bulk carbide formation and hydrocarbon synthesis, supporting the competition model of Niemantverdriet and van der Kraan[108]. Further support is provided by the observation[80] that a catalyst having a clean iron surface on a carbidic bulk is immediately active in Fischer-Tropsch synthesis, since the active carbon intermediate is readily available for hydrogenation. Further support for the competition model is provided by Ott *et al.*[109], who noted that Fe-Ru alloys with an iron content of 3 % catalyse the Fischer-Tropsch synthesis reaction at an uniform rate per surface atom. In this case there is no competition since the alloys do not form bulk carbides during reaction. Therefore, the hydrocarbon synthesis activity does not depend on the rate at which the intermediate converts to bulk carbides and the synthesis reaction rate is uniform. In conclusion, it seems that bulk carbides are unlikely to be intermediates in the hydrocarbon synthesis.

If the competition model is correct, then the transition of the active carbon intermediate to bulk carbide constitutes a most undesirable side-reaction, leading to deactivation of the catalyst and disintegration of catalyst particle pellets. This remains one of the major problem areas in the iron-based Fischer-Tropsch synthesis and, although some information has become available on this subject, it remains an important area in which much more research is needed.

3. CHEMISORPTION OF THE COMPONENTS OF SYNGAS

As Sachtler pointed out recently[110], the opening act of the Fischer-Tropsch reactions on reduced Group VIII metals is the adsorption and dissociation of hydrogen and carbon monoxide. Therefore, detailed knowledge of this part of the surface chemistry is a prerequisite for selective manipulation of the reactions.

3.1 Bonding interactions in syngas chemisorption

The hydrogenation of carbon monoxide occurs by means of interaction between the reaction components in the adsorbed state, hence an understanding of the chemisorptive behaviour of hydrogen and carbon monoxide on Fischer-Tropsch-active metals is crucial.

3.1.1 Chemisorption of hydrogen and carbon monoxide on transition metal surfaces

Hydrogen may adsorb dissociatively[111] on transition metals by the withdrawal of electron density from the metal surface[8] to form a bond that is partly ionic and partly covalent. The ionic component of this bond is often disregarded, but an increase in the work function of electrons in a metal at low hydrogen pressures has been demonstrated on Fe[112] and Pd[113]. The hydridic character of the metal-hydrogen bond is evidenced by the ease with which many transition metal hydride complexes are formed[114].

In contrast, carbon monoxide has two competing adsorption states. Both associative and dissociative adsorption modes are possible on transition metal surfaces[115-119]. The type of adsorption encountered depends on the temperature, the pressure and the enthalpies of adsorption into associatively and dissociatively adsorbed states[120]. At low temperatures mainly associative adsorption is observed. Dissociative adsorption is favoured when its enthalpy is less than or equal to the enthalpy of molecular adsorption[120,121].

Carbon monoxide is a highly versatile ligand. It can bond to monoatomic, diatomic, or triatomic ensembles, apparently with equal ease[122,123]. This also makes the ligand very mobile. The bonding is usually effected through the carbon atom but, in addition, interaction may occur via the oxygen atom, which can act both as an electron acceptor and as an electron donor. In the latter capacity it may formally supply either two or four electrons.

Wade[123] discerns five main ways in which carbon monoxide can attach to metal surfaces, which are all more or less perpendicular to the surface through the carbon end of the molecule[124] (Fig. 9):

a) A linear carbon-metal bond to a monoatomic metal site. The M-C-O unit is almost linear with an M-C-O angle of 165° to 180°.

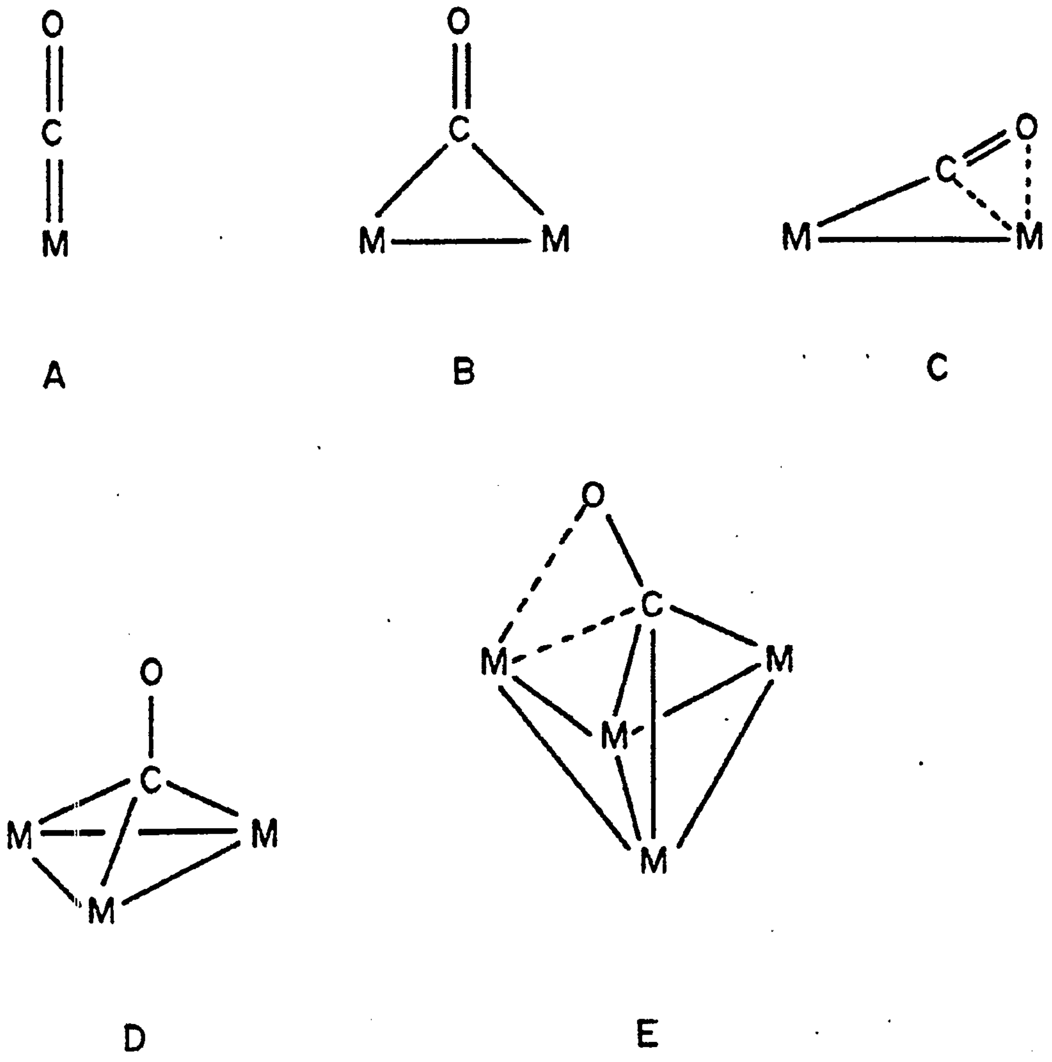
b) A doubly bridged bond between the two metal atoms of a diatomic metal ensemble monohapto through the carbon atom. The C-O axis is perpendicular to the M-M axis.

c) A doubly bridged bond between the two metal atoms of a diatomic metal ensemble and the carbon atom in a dihapto coordination with some M....O bonding.

d) A triply bridged bond between three metal atoms of a triatomic metal ensemble and the carbon atom, the C-O axis being perpendicular to the M_3 plane.

e) A triply bridged bond between three metal atoms of a quadroatomic metal ensemble, with a coordinating dihapto to the fourth atom.

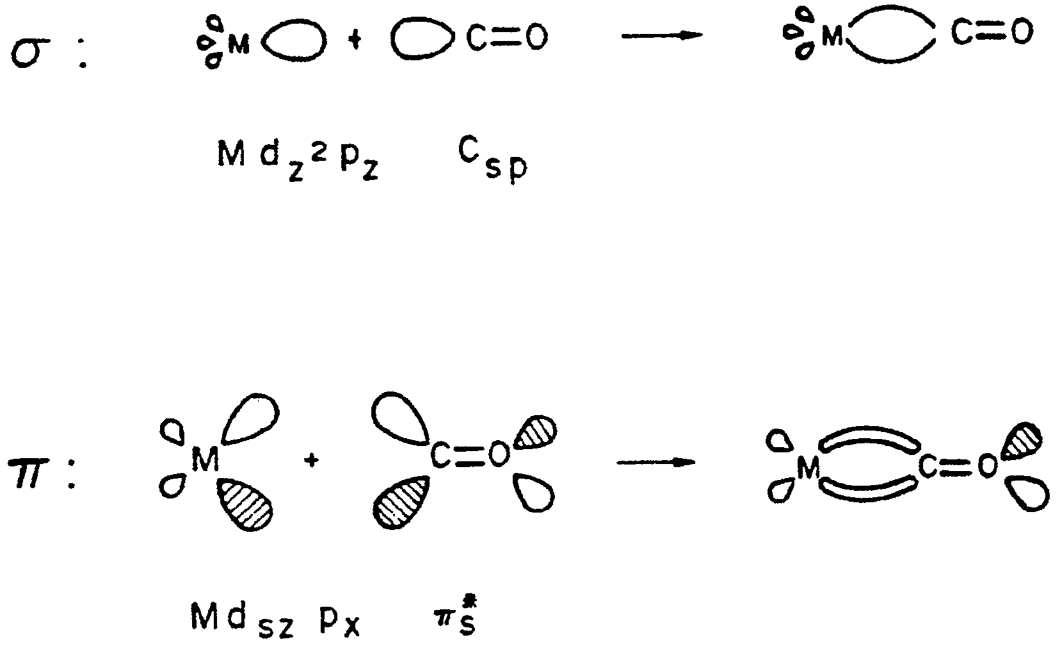
FIGURE 9 Ways in which carbon monoxide may attach to metal surfaces



Coordination is also possible in ways that are intermediate between the five main types. The bonding interactions that allow this versatility will be considered briefly.

The linear bond (a). According to the Hückel molecular orbital theory[125], the metal-carbon bond in chemisorbed carbon monoxide can be seen as consisting of two parts[124]. This theoretical consideration is supported by experimental observation with ultraviolet photoelectron spectroscopy[117]. The first part of the metal-carbon bond arises from the overlapping electron orbitals of a carbon monoxide 5σ carbon lone-pair and the essentially unoccupied d orbitals of the metal (Fig. 10). This overlap can result in the donation of electrons from carbon monoxide to the metal. The other part of the metal-carbon bond is formed by back-donation of electrons from other metal orbitals to the empty 2π* orbitals of carbon monoxide. It is generally believed that no appreciable bond forms between the carbon 4σ and 1π orbitals and the metal surface[126,127].

FIGURE 10 σ and π bonding interactions of a carbonyl ligand when bonding linearly to a monoatomic metal site



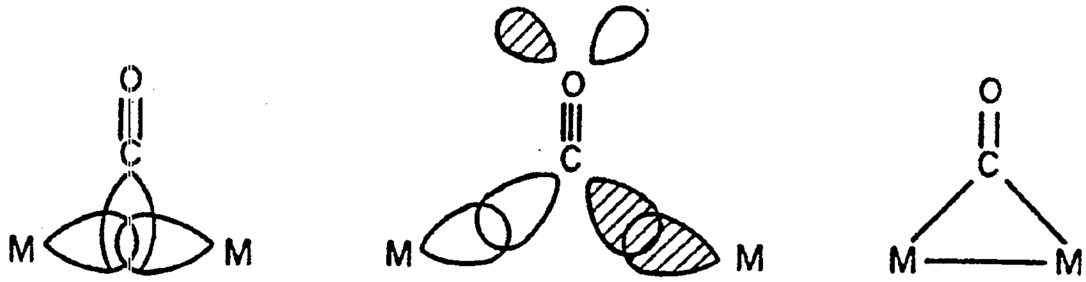
The synergistic nature of the bonding allows each component to reinforce the other. It is therefore commonly assumed that the adsorbed carbon monoxide molecule remains essentially neutral. However, studies of the orbitals involved have revealed that the carbon monoxide ligand acquires a significant negative charge[128-131]. This charge effect is caused by a much stronger charge transfer in the π back-donation than is commonly supposed, whereas the σ donation from ligand to metal involves less charge transfer than it is generally thought to do. Since the lone-pair electrons on the carbon atom of carbon monoxide occupy an orbital that is essentially a carbon sp hybrid non-bonding orbital, the effect of electron donation from this orbital on the strength of carbon monoxide bonding is actually very small.

The back-donation into the empty 2π* orbitals of the carbon-oxide bond results, however, in significant electron transfer to the ligand since the acceptors involved, the ligand π* MOs, have a substantial oxygen p-orbital character and so require the electron density on the oxygen atom to be increased. There are, moreover, two such π* orbitals.

The result of the weak donation and strong back-donation is therefore the formation of a metal-carbon bond with simultaneous weakening of the carbon-oxygen bond. The oxygen atom will acquire a significant negative charge, while the metal will be charged positively.

The monohapto doubly bridged bond (b). When coordinating monohapto to two metal atoms, the carbonyl ligand can still overlap its lone-pair orbital on carbon with a suitable metal-metal bonding combination of filled metal orbitals (Fig. 11).

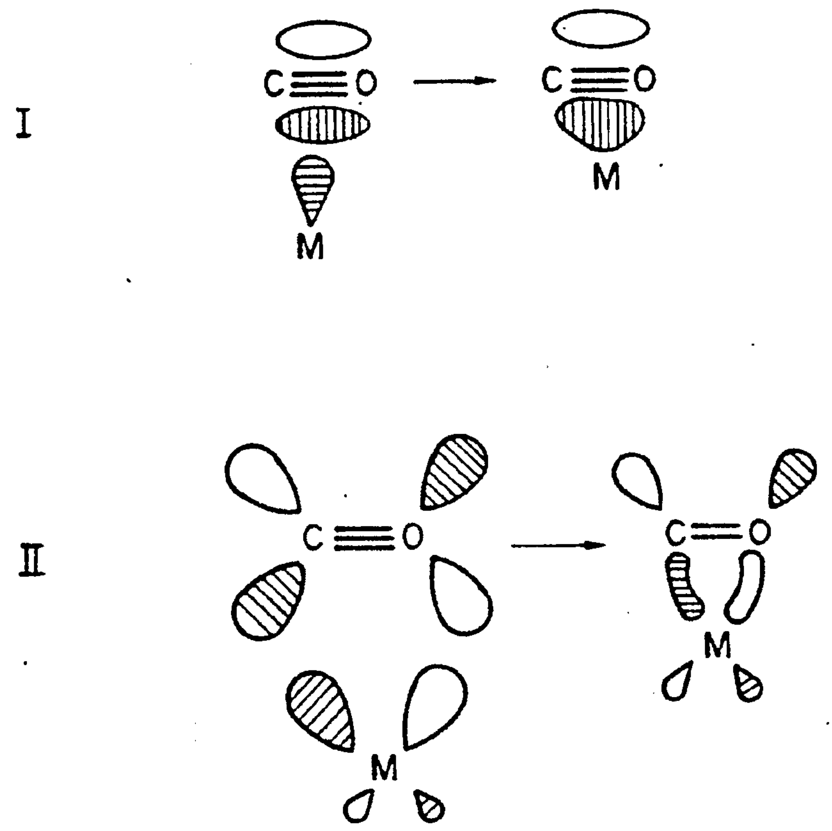
FIGURE 11 Bonding interactions of a carbonyl ligand when bonding monohapto doubly bridged to a diatomic metal ensemble



A metal anti-bonding combination of filled metal orbitals can back-donate electrons into the carbon monoxide $2\pi^*$ orbital. This results in a situation similar to that found with the linear bond[132]. This conclusion is supported by the ease with which carbonyl ligand scrambling occurs between the two types of site[133].

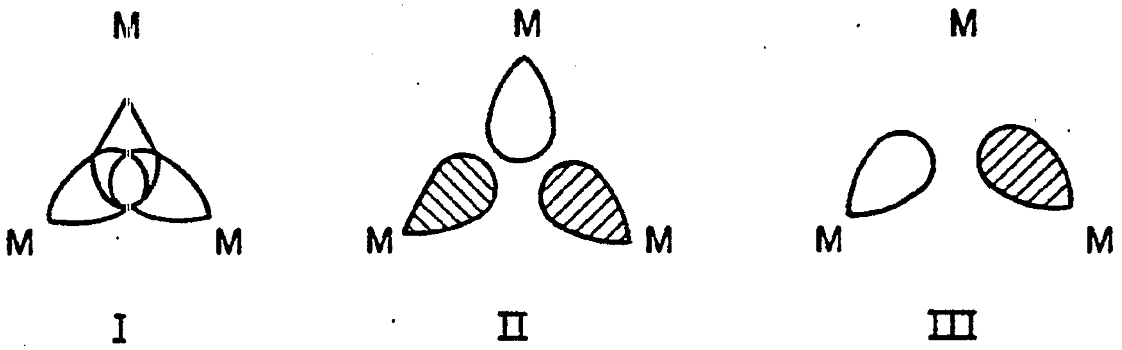
The dihapto doubly bridged bond (c). In this coordination the carbonyl ligand is effectively linearly bound to one metal atom while coordinating dihapto to another (Fig. 12). This carbonyl ligand thus contributes four electrons (twice as many as a linear or monohapto coordinated ligand) to the metal, two to the valence band of each metal atom. This type of bonding is therefore much stronger than the linear or monohapto doubly bridged type.

FIGURE 12 Bonding interactions of a carbonyl ligand when bonding dihapto to one of the metal atoms of a diatomic metal ensemble; (I) electron donation from the ligand π MO to the metal and (II) electron donation from the metal to the ligand π* MO



The triply bridged bond (d). Like the monohapto doubly bridged bond, this coordination can also attach carbonyl ligands to metal atoms by overlapping the lone-pair 5σ carbon orbital with a suitable combination of metal orbitals (Fig. 13-I). Electron back-donation then occurs from suitable ε-symmetry combinations of metal orbitals (Figs 13-II and III).

FIGURE 13 Bonding interactions of a carbonyl ligand when bonding triply bridged to a triatomic metal ensemble; (I) lone-pair interaction, and (II) and (III) π^* interactions



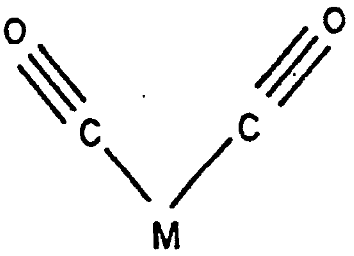
In this coordination of the carbonyl ligand, six electrons are involved, two with each of the three metal atoms. This type of bonding is therefore even stronger than the three types discussed earlier.

The dihapto triply bridged bond (e). This type of bonding combines a triply bridged bond of a carbonyl ligand to three of the metal atoms of a quadroatomic metal ensemble with a dihapto bond to the fourth metal atom. Slightly more then six electrons are involved in this bond and hence it is the strongest of the five main types. The increased electron density in the metal-carbon bond results in a weakening of the carbon-oxygen bond. The bond order is in effect reduced from 2,4 to 2,8 in a linear carbonyl ligand to formally 1 in triply bridged carbonyls, as indicated by the stretching frequencies and force constants[134,135].

In addition to these bonding interactions, multi-carbonyl bondings are possible. In this coordination two or more carbonyl groups are attached through their carbon atoms to a monoatomic metal site (Fig. 14). Dicarbonyl bonding is known to exist for transition metals of the second and third periods, such as ruthenium[136], rhodium[137] and iridium[138]. Quaternary carbonyl bonding has been reported for ruthenium[139,140] under certain conditions.

These metals are also known to coordinate with two hydrogen atoms. Multi-ligand bonding of metals with carbon monoxide is weaker than linear bonding. As may be expected from the higher electron density in the C-O bonds, this type of ligand bonding is characterized by a much higher dissociation energy. This is supported by the observation[136] that ruthenium sites that adsorb two carbon monoxide molecules per site were catalytically inactive in the Fischer-Tropsch synthesis, indicating associative rather than dissociative adsorption.

FIGURE 14 Dicarbonyl bonding of two carbonyl ligands monohapto to a monoatomic metal site



From this consideration of the bonding interactions of carbon monoxide with transition metal surfaces, it can be concluded that during progression from the linear bond (as often occurs on clusters and distorted surfaces) to triply bridged bonds (as normally occur on bulk iron surfaces) there is a strong increase in the metal-carbon bond strength and a decrease in the carbon-oxygen bond strength. These changes result in the dissociation energy of carbon monoxide decreasing, the metal surface acquiring an increasingly positive charge, and the oxygen end of the carbonyl group being charged negatively.

3.1.2 Influence of additives

Since adsorbed species as well as catalyst promoters may change the electron work function of the catalyst, the use of additives may also influence the chemisorption of hydrogen and carbon monoxide.

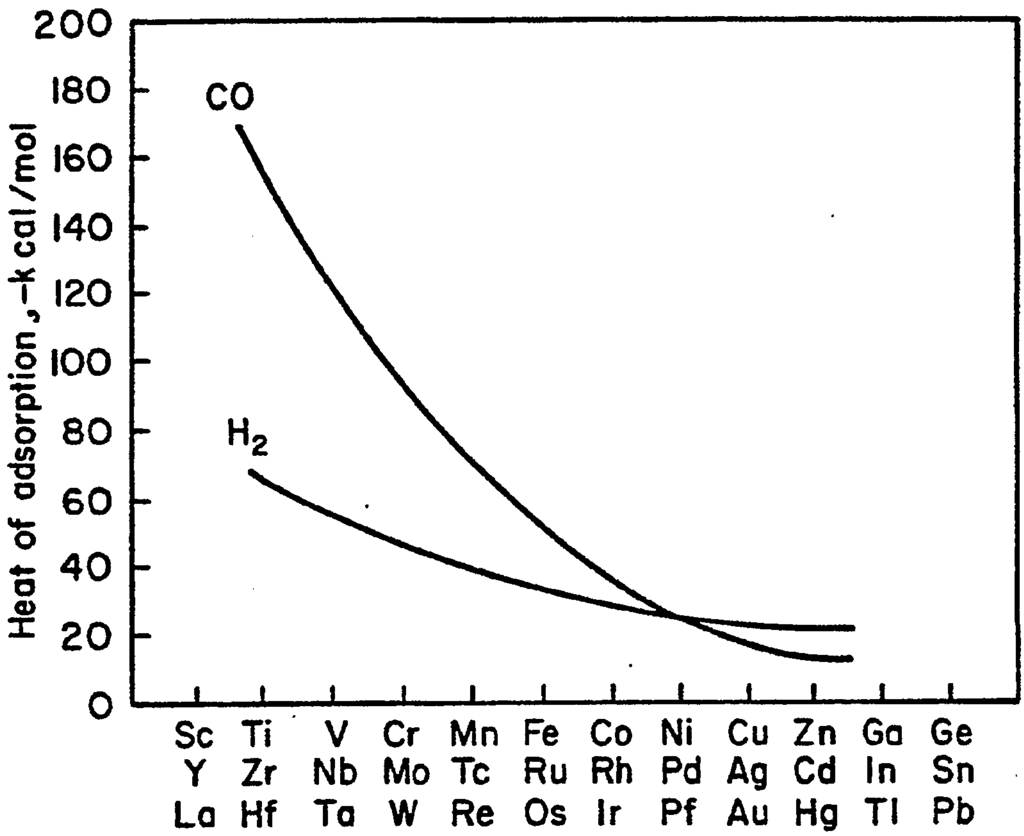
Adlayers of carbon[140,141], nitrogen[142], oxygen[115,140,141], sulphur[140,141,143–146], phosphorus[140,143], chlorine[143,147] and bromine[147] on transition metal surfaces are reported to reduce the strength of adsorption of both hydrogen and carbon monoxide. Moreover, they inhibit carbon monoxide dissociation. The phenomena are readily explainable in terms of ligand bonding. On adsorption, electron acceptors withdraw electron density from the metal surfaces in the immediate vicinity, thereby hampering the electron back-donation of the metal to adsorbed carbon monoxide species; this in turn inhibits the dissociation of the carbon-oxygen bond. This effect, known as the electron withdrawal ligand effect, increases with the electronegativity of the additive[147].

The electron transfer between coadsorbed species, discussed above, is a collective property of all the metal surface atoms and may therefore be considered as a long-range effect. In addition, Queau *et al.*[147] note a short-range effect in the localized oxidative demetallization of some metal atoms due to metal-metal bond cleavage following halogen chemisorption. These metal atoms will then have lost the collective properties of the surface and will constitute specific catalytic sites. A similar phenomenon has been observed in consequence of the chemisorption of sulphur or oxygen atoms on various metals[148]. In addition, the promotion of metal catalysts with Lewis acids may also lead to demetallization of the surface. Halogen *ions*, however, are, in electronic terms, sufficiently stable to be unlikely to interact in such a manner. But they may exert a structural effect, for example by reducing the size of the ensembles available for carbon monoxide adsorption, which may result in a lower metal-carbon bond order and hence in a decrease in the heat of adsorption.

The reduction in the metal-hydrogen bond strength upon promotion with Lewis acids may also be similarly explained by the electron withdrawal ligand effect. A study of this reduction by means of co-chemisorption of nitrogen[149] revealed that nitrogen selectively blocks strongly adsorbed hydrogen, while the more weakly chemisorbed hydrogen remains unaffected. This effect is in line with other adsorption data.

Toyoshima and Somorjai[150] compiled adsorption data, including data on the adsorption of hydrogen and carbon monoxide on polycrystalline transition metal surfaces (Fig. 15). It is evident that the heat of adsorption of both hydrogen and carbon monoxide decreases from Mn to Ni, a region in which the electron work function of the metals increases. Since the chemisorption of electronegative elements involves the withdrawal of electrons from the metal surface, this is not unexpected.

FIGURE 15 Heats of adsorption of hydrogen and carbon monoxide on polycrystalline metal surfaces[150]



The effect of alkali metals, notably potassium, on the adsorption of carbon monoxide is well known. These promoters cause an increase in the metal-carbon bond strength and a simultaneous weakening of the carbon-oxygen bond[11]. This effect has been confirmed by recent spectroscopic studies of carbon monoxide adsorption on potassium-promoted Fe(110) surfaces[151], as well as by calorimetric[152] and work function studies[113] on the same metal.

There is some controversy about the mechanism of this promoter effect. The mechanism is usually explained in terms of the electron donor properties of the alkali metal[11]. The promoter is assumed to donate electrons to the catalyst, resulting in an increased back-donation to the carbonyl group. This argument does not take into account the fact that the alkali metal is normally introduced to the catalyst in the oxide form. XPS studies[153] indicate that potassium is likely to be present as the hydroxide during the synthesis reaction. Since the ionization potential of K^+ is very large (3,04 MJ) compared with that of elemental potassium (0,42 MJ), it is highly unlikely that the potassium ion has electron donor properties. In fact, when the promoter is introduced by means of the action of alkali vapours on previously reduced transition metals, superbasic systems are obtained[154], indicating that K has a far more pronounced influence in elemental form than in ionic form.

Ozaki *et al.*[155] have suggested that the electron donor properties of the potassium complex as a whole should be considered, regardless of the form of this complex. If the alkali metal is present in the oxide or hydroxide form, electron transfer is very likely to involve the oxygen ion.

A different approach is suggested by Henrici-Olivé and Olivé[156] who argue that the potassium ion is not an electron donor but an electron acceptor. In their view it is more likely that potassium will react through the electron-rich oxygen of the carbonyl group, thereby weakening the carbon-oxygen bond. Electron transfer could then occur from the oxygen ion of potassium oxide to the catalyst metal, thereby strengthening the metal-carbon bond. This theory has the advantage that the coordinatively unsaturated oxygen atom of the carbonyl group is stabilized. Similar ideas have recently been expressed by Sachtler *et al.*[157].

Although the exact form in which potassium is present on the surface of iron and the mechanism of the promoter effect are still largely unexplained[158], the results of a recent study of alkali promotion of silica-supported palladium catalysts by Rieck and Bell[159] indicate that the valence state of the alkali metal and its promoting action are strongly influenced by the conditions of catalyst pretreatment. If reduction takes place below 573 K, alkali addition shows little influence on the distribution of hydrogen adstates, and the carbon monoxide adstate distribution shifts towards a higher proportion of linearly adsorbed species and a lower proportion of bridge-bound species. This pattern was attributed to ensemble effects in which bridge sites are blocked by the promoter. As a result, dissociation of carbon monoxide occurs less readily on an alkali-promoted catalyst that is reduced at a temperature of 573 K or lower.

Reduction at higher temperatures negates the promoter effect and there is very little difference in the distribution of either the hydrogen or carbon monoxide adstates on promoted and unpromoted catalysts. However, the carbon monoxide dissociation activity of the promoted catalysts does increase because of the participation of alkali species in the rupture of the carbon-oxygen bond. The alkali is partly reduced, the extent of reduction depending on the temperature used, allowing interaction between the slightly positively charged alkali metal atom on the metal surface and the slightly negatively charged oxygen atom of the adsorbed carbonyl ligand.

The strength of adsorption of hydrogen on iron surfaces has been reported to increase slightly upon promotion with potassium[141]. This is in line with the current views on the promotional effect of potassium, which is thought to have an electron enrichment effect on the catalyst metal. As hydrogen adsorption involves withdrawal of electron density from the metal surface, a stronger metal-hydrogen bond is indicated by a decrease in the electron work function. This agrees with the adsorption data discussed earlier (Fig. 15).

It also follows from Fig. 15 that a decrease in the work function of iron will result in a much more pronounced increase in the heat of adsorption of carbon monoxide than is the case for hydrogen. This comparatively small increase in the metal-hydrogen bond as a result of a decrease in the work function allows a better understanding of the results reported by Kölbel and Müller[112]. Their work function measurements on pure and alkalized iron films indicated that the metal-hydrogen bond was little influenced by potassium promotion.

3.1.3 Co-adsorption of hydrogen and carbon monoxide

Although a study of the adsorption properties of the two components of synthesis gas offers useful information, it is not immediately relevant to actual synthesis conditions since the adsorbates influence one another. A recent study of the simultaneous adsorption of both gases on iron surfaces using UPS[160] confirmed that these two gases interact in the adsorption layer at temperatures as low as 298 K.

At temperatures below 325 K, pre-adsorbed carbon monoxide inhibits the chemisorption of hydrogen on reduced metal surfaces, whereas carbon monoxide adsorption is not influenced by hydrogen pre-adsorption[142,152]. This result agrees well with reports by Subramanyam and Rao[161] showing that adsorbed hydrogen is partly displaced by carbon monoxide at those temperatures. This chemisorption behaviour may be explained on the basis of competition for the withdrawal of electrons from the surface. Because of its higher electron affinity and heat of adsorption, carbon monoxide is able to displace hydrogen.

At higher temperatures, this competition decreases and under synthesis conditions hydrogen is not displaced by carbon monoxide[161].

An additional effect associated with co-adsorption is an increase in the number of adsorption sites. It has been observed that the total adsorption from synthesis gas mixtures on iron catalysts is greater than the sum of the adsorptions of the individual components[161,162]. Similar observations were made by Ritschel[163] who reported that more carbon monoxide chemisorbs from a 1:1 syngas mixture than from pure carbon monoxide. At 370 K the H_2:CO ratio in the adsorbed phase varied between 0,7 and 1,6 on promoted iron, as the initial H_2:CO ratio in the gas phase varied between 0,5 and 2. The reason for this increase in the number of adsorption sites is not clear, but it could be speculated that hydrogen coordinates with the lone-pair electrons of the electron-rich oxygen end of the carbonyl ligand, thereby decreasing the electron density in the metal-carbon bond. The possibility that the oxygen atom of carbonyl ligands coordinates with electron acceptors has been demonstrated by Wade[123]. The decrease in the metal-carbon bond order may then result in a lower metal coordination and hence in an increase in the number of sites available for carbon monoxide chemisorption.

Promotion with potassium has been observed to decrease the H_2:CO ratio in the adsorbed phase on iron catalysts to 0,5 for all mixtures[161]. This decrease is in line with the influence of potassium on the heat of adsorption of both gases.

3.2 The role of the electronic interaction principle and geometric principle in the chemisorption behaviour of syngas

The chemisorption of synthesis gas is sensitive to the properties of the catalyst surface. The understanding of this relationship may be facilitated by considering it in terms of two heuristic principles: the electronic interaction principle, and the geometric principle. The former principle involves all electronic aspects of chemisorption, and the latter aspects such as coordination and ensemble size.

The chemisorption of synthesis gas on transition metal surfaces will now be considered in terms of both principles.

3.2.1 Catalyst basicity

One of the best-documented promoters in the Fischer-Tropsch synthesis is potassium. Since this element is electropositive and its catalytic effect is usually explained in terms of electron donation to the catalyst, this type of promotion is often described as being due to an increase in the catalyst basicity. Such explanations are derived from the premise that potassium is present in elemental form on the catalyst. However, as discussed before, under synthesis conditions this is unlikely to be the case. Nevertheless, since there is a direct relation between the basicity of an oxide and the electron work function of the parent metal, the use of the electron work function in attempts to rationalize catalytic behaviour is justified[164].

Consideration of the influence of the catalyst work function on the chemisorption behaviour of the componenents of syngas (Fig. 15) has indicated the importance of the catalyst basicity. This general observation may be used for specific chemisorption manipulation when the nature of the work-function-dependent chemisorption is understood. Such an understanding may be furthered by considering the relationship between the heats of adsorption of hydrogen and carbon monoxide on metals and the electron work function of the surface involved.

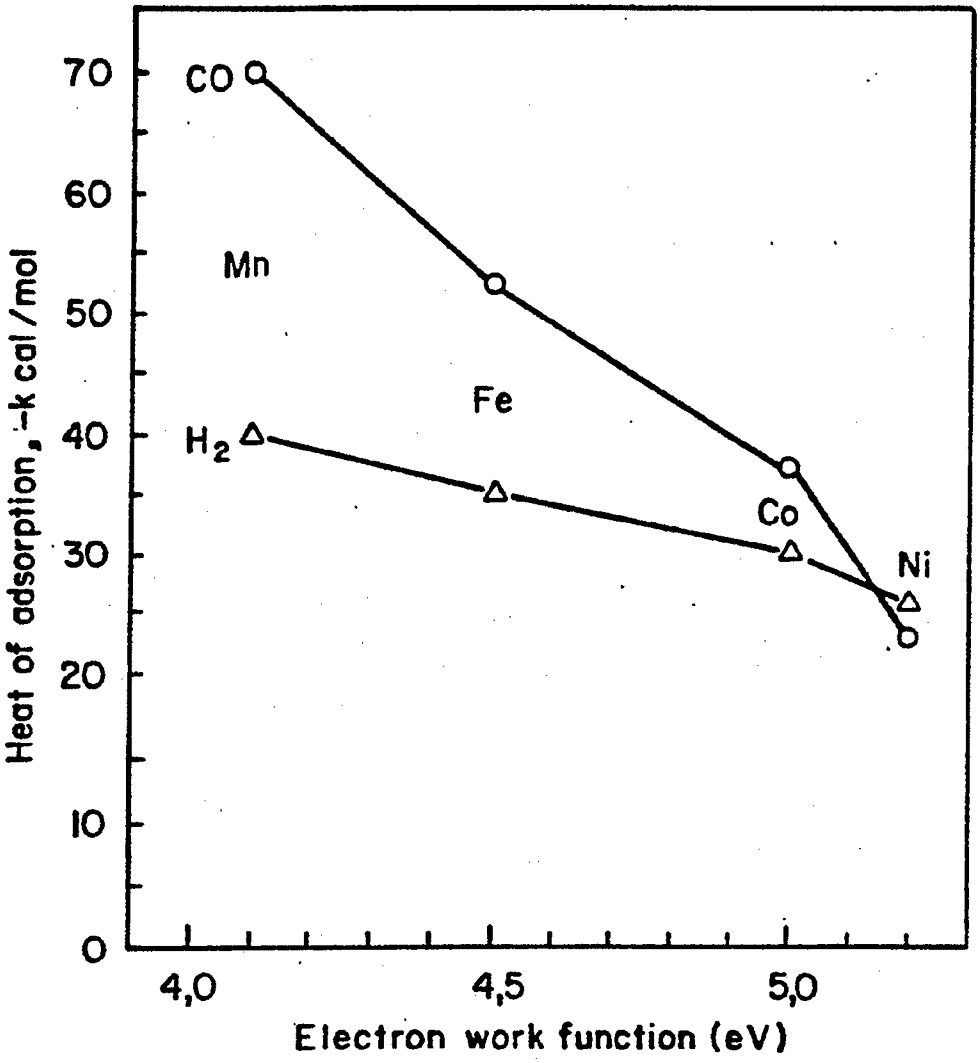
Transition metals of the second and third period are not included in this discussion since carbon monoxide can be coordinated in different ways. Weak multi-carbonyl bonding, which does not occur on metals of the first period, requires such a high dissociation energy of the carbon monoxide bond that in practice no dissociation occurs[136-139]. This type of bonding effectively results in a partial poisoning of the surface.

When plotted against the values of the work functions[165] of the metals Mn, Fe, Co and Ni, the adsorption data of Toyoshima amd Somorjai[150] show an interesting relation (Fig. 16). If the value of the work function of a metal is decreased, two effects occur simultaneously as a result of an increase in the heats of adsorption of both components of synthesis gas.

The first effect concerns carbon monoxide. A higher heat of adsorption arises from a stronger metal-carbon bond. This means that carbonaceous species have a longer surface life, resulting in increased catalyst carburization and hydrocarbon products with a higher molar mass. The high electron density in the metal-carbon bond, resulting from increased back-donation, weakens the carbon-oxygen bond, and dissociation occurs readily, which implies increased catalytic activity.

The second effect concerns hydrogen. Here a higher heat of adsorption means that less of the weakly bound, active hydrogen will be available on the surface and hence hydrogenation activity will be lower. This will cause a decrease in the production of hydrogen-rich methane and a higher content of olefins in the hydrocarbon product. In contrast to the first effect, the decreased hydrogenation activity predicts lower catalytic activity.

FIGURE 16 Dependence on the electron work function of the heats of adsorption of carbon monoxide and hydrogen on transition metal surfaces of the first period. Data from refs 150 and 165



Which of the two effects will dominate cannot be predicted. Catalytic results show that in the case of iron the effect of the lower carbon-oxygen bond dissociation energy (as a result of the decreased work function) dominates and a slightly higher catalytic activity is observed[166]. In the case of cobalt the effect of the decreased hydrogenation activity dominates, resulting in an observed decrease in the catalytic activity[167,168]. The observed behaviour with iron remains puzzling, but some unknown geometric effect may be responsible.

However, all other effects discussed before are the same for both elements[166-168]. In addition, a work function decrease in either of the metals causes a higher concentration of oxygen ions on the catalyst surface. Under the conditions that prevail with lower hydrogenation activity, only part of this surface oxygen can be reduced to water. The rest either diffuses into the lattice of the catalyst or combines with carbonaceous surface species to form carbon dioxide or oxygenated hydrocarbons that are formed in addition to those which may be formed by carbon monoxide insertion.

If these results are combined, an increase in basicity (a move to lower values of the work function) is expected to result in a decrease in catalytic activity (with the exception of iron where a small increase in activity occurs), a decrease in methane formation and an increase in the average molar mass of the products and in the content of olefins and oxygenates in the product. At extremely low values of the work function, for instance in Mn, the heat of carbon monoxide adsorption is so high that the high strength of the metal-carbon bond precludes any Fischer-Tropsch activity.

A decrease in basicity (an increase in the work function) will have opposite effects. The heat of adsorption of both hydrogen and carbon monoxide decreases, resulting in smaller amounts of chemisorbed hydrogen and carbon monoxide. However, the fraction of active weakly bound hydrogen will be higher, implying higher activity. Carbon monoxide will chemisorb with markedly weaker metal-carbon bonds and hence the carbon-oxygen bond will remain much stronger, resulting in increased dissociation energy, and implying lower activity. As discussed earlier, the effect of the stronger carbon-oxygen bond dominates for metals that have a lower work function value than that of iron. In all other cases the effect of hydrogen dominates. The increased hydrogenation activity also predicts an increase in the formation of water and paraffins (especially methane), accompanied by a decrease in the formation of carbon dioxide and olefins.

A decrease in the heat of adsorption of carbon monoxide may also be expected to result in less strongly bound surface carbonaceous species and hence in a decrease in the rate of carbon deposition on the catalyst. In the case of nickel the heat of adsorption of carbon monoxide is even lower than that of hydrogen. A very short surface life for carbonaceous species together with a high hydrogenation activity indicates the production of methane only.

3.2.2 Electron withdrawal ligand effect

When a work function increase is effected by promotion with strongly electronegative elements, a more complex situation arises depending on the type of electron acceptor used. Electronegative elements, such as halogens and sulphur, withdraw electron density mainly from the metal surface in the immediate vicinity. During coadsorption with synthesis gas, this withdrawal of electron density hampers the electron back-donation of the metal to the carbon monoxide or H ligands. This effect, known as the electron withdrawal ligand effect, increases with the electronegativity of the additive[147]. The withdrawal of electron density causes a weakening of the metal-ligand bond, and a decrease in the heat of adsorption of both gases. Furthermore, electronegative elements are then in direct competition with hydrogen and carbon monoxide for adsorption sites and act as poisons.

In the case of hydrogen, although the heat of adsorption decreases and the availability of activated hydrogen should thus increase, there is, in fact, less available hydrogen because of the competitive effect of the poison. This agrees well with experimental observations[147].

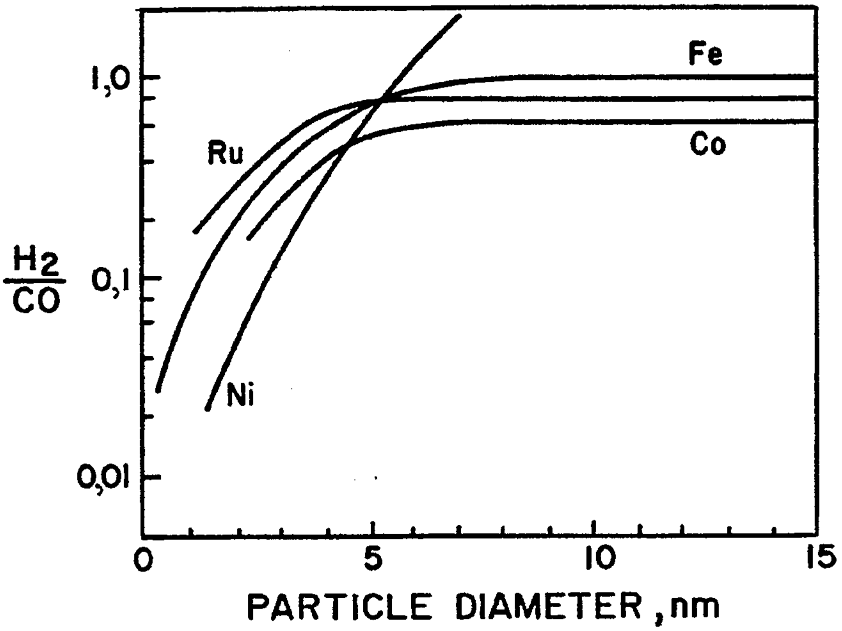
3.2.3 Catalyst dispersion

The chemisorption behaviour of hydrogen and carbon monoxide is not only a function of the catalyst basicity but is also dependent on the particle size, i.e. catalyst dispersion. When the catalyst is in a highly disperse form, hydrogen chemisorption is markedly suppressed. This has been observed for particles of iron[169], cobalt[170], nickel[171], ruthenium[172] and platinum[173,174] when the particle diameter of the metal was below 3 nm (Fig. 17).

Interestingly, all three Fischer-Tropsch metals, Fe, Ru and Co, have a constant H_2:CO ratio which is lower than, but close to, unity when the particle diameter exceeds 5 nm. In contrast, the ratio observed with Ni increases continually under the conditions studied and far exceeds unity. This finding is in line with the much higher hydrogenation activity of Ni and the fact that it produces mainly methane.

When the particle diameter is less than ca 3 nm, a different behaviour is observed and Ni exhibits very low values for the H_2:CO ratio. The low values are in agreement with reports in the literature showing that supported (and presumably well-dispersed) Ni systems are good catalysts for the formation of lower olefins[175].

FIGURE 17 Suppression of hydrogen chemisorption on various metals

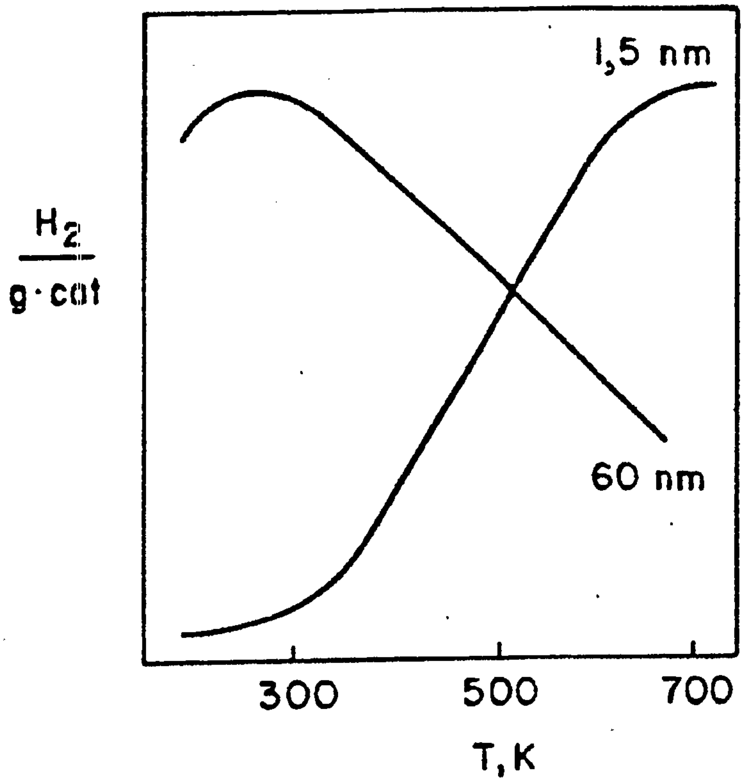


Electron microscopy and chemisorption data show that large fractions of the metal lose their ability to chemisorb hydrogen[174]. A decrease in the electron spin density of chemisorbed hydrogen has been observed by NMR spectroscopy[176], indicating a weaker hydrogen-metal bond for small particles.

Furthermore, it has been observed[169,170] that the temperature-dependence of hydrogen chemisorption on highly disperse metals is reversed with larger particles (Fig. 18). This suggests that the hydrogen adsorption process has been activated.

The chemisorption behaviour of carbon monoxide on small particles also differs markedly from that observed on larger particles. The bonding has been shown by infra-red studies[169,177] to shift from predominantly bridged bonding on bulk particles to predominantly linear bonding on very small particles. This indicates a decrease in heat of adsorption, in line with the bonding interactions discussed earlier. A microcalorimetric study[169] confirmed this decrease and, in addition, showed a coverage-dependence of the heat of adsorption of carbon monoxide. In particular, the fraction of the surface capable of strongly adsorbing carbon monoxide (i.e. the heat of adsorption was less than -125 kJ mol^{-1}) decreased with increasing dispersion, confirming reports of an increase in the amount of weakly bonded carbon monoxide with dispersion. This result is not unexpected considering the basicity effect on chemisorption of carbon monoxide.

FIGURE 18 Hydrogen chemisorption on small and large iron particles as a function of the temperature[169]



Infra-red spectroscopy studies of carbon monoxide chemisorption show a shift to higher wave numbers as the metal particle size is decreased, due to the electron-deficient nature of small metal particles. This "blue shift" has been observed for Fe[169], Ni[177-179], Ir[138,178] and Ru[172]. An unexpected shift to lower wave numbers, a "red shift", has been reported recently by Toolenaar *et al.*[180] for Ir. A similar red shift is reported for Pt and Ir by others[130]. The reason for the reported increase in heat of desorption is not clear. The anomalous increase has been tentatively ascribed to carbon monoxide bonded to metal atoms with a low coordination number which are particularly exposed on very small metal particles[180]. Because of the higher density of states in the region close to the Fermi level[181,182] carbon monoxide bonding to these sites would result in increased back-donation, resulting in a weaker carbon-oxygen bond.

The phenomenon is probably more complex since this theory does not explain why the blue shift, which is sometimes observed for transition metals of the second or third period, has never been reported for first-period transition metals. It seems likely that the different electronic structures and coordination characteristics of the higher period metals are involved.

In summary, the chemisorption behaviour of both hydrogen and carbon monoxide on small metal particles is very different from that on larger particles. In order to understand this effect and its consequences, the physicochemical properties of small metal particles will be considered briefly.

That small metallic particles have properties different from those of bulk metals, has long been known to physicists[183]. The electronic structure changes gradually as the number of atoms involved in the particle decreases. Demetallization takes place as the band structure splits into discrete levels whose spacings increase from bulk metal to single atom values[184]. Within the limit of solids, the energy gap at the Fermi level widens and effects associated with this gap, i.e. quantum size effects, occur at all levels[183]. Of particular importance for chemisorption on small particles is the decrease in the density of states associated with this wider gap. This effect, observed as a widening of the spaces between the levels of the band structure, increases with demetallization of the bulk metals.

Takasu *et al.*[185] report that small palladium particles, with a diameter less than 2 nm, have band levels far below the Fermi cut-off, indicating that they have lost their metallic character and are in fact more atomic in nature. This results in a decrease in electron density in the valence band, as evidenced by an observed increase in the ionization potential[186]. The electron deficiency of small particles is reportedly associated with those sites that have a low coordination number[187]. This suggests that both electronic and geometric factors play a part in the dispersion effect. For more detailed information on very small metal aggregates, the reader is referred to the many in-depth reviews on this subject[186,188–192].

The anomalous chemisorption behaviour of both components of synthesis gas is well explained by the increase in work function with dispersion. However, the dispersion effect causes a suppression of hydrogen chemisorption (Fig. 17) far greater than that predicted by the catalyst basicity effect. As a result, the hydrogenation activity decreases with increasing work function. This is in contrast to the basicity effect, where a work function increase results in increased hydrogenation activity because of an increase in the fraction of weakly chemisorbed hydrogen.

The influence of dispersion on the chemisorption behaviour is well explained in terms of electronic influences. However, it has been shown recently[193] that not only the ratio of linearly bonded carbon monoxide to bridge-bonded carbon monoxide decreases with the dispersion of palladium, but also the ratio of Pd(100) to Pd(111) planes on the surfaces of the palladium crystallites. It has been demonstrated[194,195] that the highest overall catalytic activity is favoured on sites to which carbon monoxide is strongly coordinated. Therefore, the observed change in the type of coordination site on the surface with changing dispersion alters the catalytic behaviour. This clearly shows an additional change in geometry, and hence in coordination, with dispersion. In conclusion, both an electronic and coordination influence are responsible for the dispersion-dependent catalytic behaviour of metals.

3.2.4 Support interactions

Supported metal catalysts have, in most cases, a high dispersion on the support. In such cases the support has many effects on the properties of the metals. It is still an unresolved question which effects are caused by the support and which by the dispersion as such. A close examination of the problem indicates that support effects are, at least, likely to occur. Ponec[196] has suggested that some of the possible effects may be classified into four different categories: the support modifies the metal causing it to have:

i) a different electronic structure and different sites;

ii) different properties because of stronger bonding by means of a charge transfer with the carrier;

iii) a built-in "charge" because of strong metal-support interactions; and

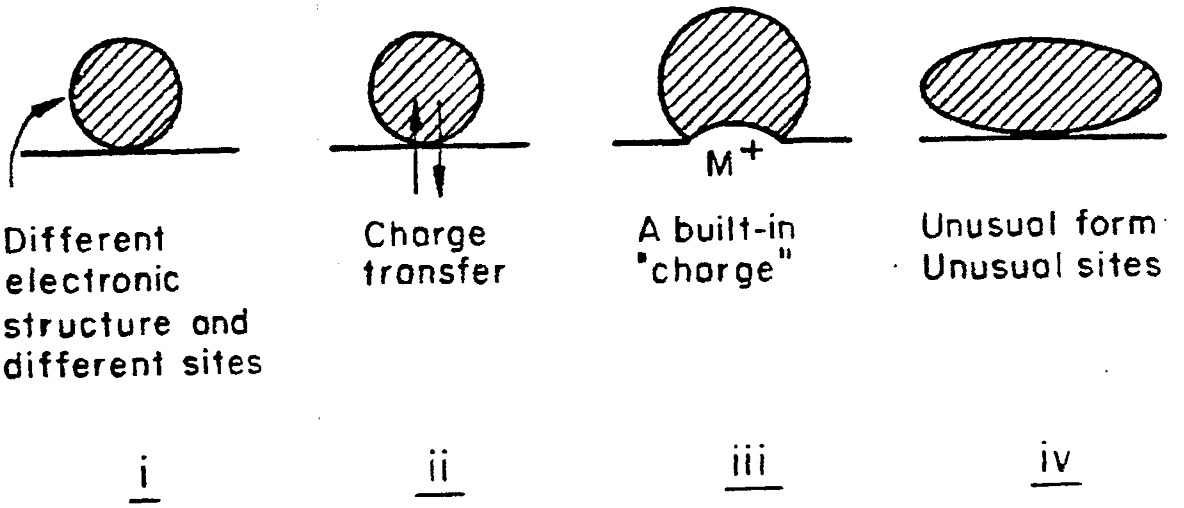
iv) unusual forms resulting in unusual sites, as shown schematically.

Effects of type (i) can be further subdivided into at least two different effects. Supports may affect the basicity or dispersion of the catalyst, resulting in a support basicity or a support dispersion effect respectively . An increase in support basicity has been demonstrated by Leith[197,198] to result in decreased hydrogenation activity, in line with the catalyst basicity effect discussed before.

A support dispersion effect, manifested by a support-dependent suppression of the amount of hydrogen chemisorbed, has been demonstrated for silica and alumina-supported iron particles[199]. This effect was more pronounced for alumina than for silica supports, which is in line with reports stating that hydrogen chemisorption is more depressed for supports having a strong Lewis acid character[172,173].

A further aspect of the support dispersion effect is that increasing support-induced dispersions are observed to be associated with stronger metal support interactions[200], indicating an additional source of demetallization.

FIGURE 19 Schematic diagram of some of the possible effects of supports on metals (after ref. 196)



Effects of type (ii) have received much attention. It has often been suggested[184.201-204] that a charge transfer between the metal and the support modifies the properties of the metal; the evidence is sometimes questionable. This type of interaction, sometimes referred to as the "Schwab" effect, is often noticed in zeolites.

Barthomeuf compares the Schwab effect with electrode phenomena[203]. He suggests that the behaviour of transition metal cations in zeolites is strongly influenced by the electrical properties, e.g. the intra-zeolite electrostatic field. The properties of the metal cations are then governed by the changes in the chemical potential of the framework ions and atoms. These solids can be considered to be "crystalline liquids" where nearly all of the framework atoms belong to the surface.

The support interaction can also result in excessive electron density on the metal crystallites. Alkaline platinum L zeolites exhibit an interesting combination of a support basicity effect (excess electron density on the metal crystallites) and a dispersion effect[201]. As a result, both extremes of carbon monoxide coordination occur. The combined effect results, unexpectedly, in a strong increase in hydrogenation activity. This anomalous catalytic behaviour is tentatively ascribed to the electrical field of the zeolite.

In highly disperse PtY systems, a transfer of electron density from the Pt to the zeolite results in an electron deficiency of the metal. Consequently, typical dispersion effects, e.g. the repression of hydrogen chemisorption, have been observed[202,204].

Effects of type (iii) are more pronounced. Under certain conditions the interactions can become quite strong. Tauster *et al.*[205] were the first to report that the sorptive and catalytic properties of supported metals depend on the strength of their interaction with the support. They prepared various noble metals supported on titania. Reduction at 473 K with hydrogen produced well-dispersed metals, which exhibited the capacity to adsorb both hydrogen and carbon monoxide. Reduction of the same material at 773 K, however, decreased hydrogen and carbon monoxide adsorption to near zero in all cases. Electron microscopic and X-ray diffraction data showed that the loss of this adsorption capacity could not be attributed to sintering since the treatment did not alter the degree of dispersion. This was confirmed by measurements of the total surface area.

It was suggested that strong metal-support interactions (SMSI) were responsible for this anomalous chemisorption behaviour. There is some evidence for the formation of semi-chemical bonds between the metal and the support[206] resulting in a "built-in" charge. It could be speculated that this bonding causes a demetallization effect.

Further evidence is presented by Bruce and Mathews[175] who, in addition, observed that the SMSI effect is support-dependent, as manifested by a different reducibility for nickel oxide on various supports. The order of ease of reduction of nickel ions on the different supports is $SiO_2 > Al_2O_3 > ZrO_2 > TiO_2$. The suppression of hydrogen and carbon monoxide chemisorption increased with metal-support interaction.

Anomalous behaviour occurs not only with Ni/TiO_2 systems, but also with titania-supported Rh, Ir, Pt and Pd[207-209]. Furthermore, titania and zirconia are not the only supports implicated in systems exhibiting SMSI effects. Oxides of vanadium, manganese and niobium are also reported to lead to these effects[206].

Recent magnetic studies[210] indicate a correlation between the suppression of hydrogen chemisorption and the Curie temperature. When metal-support interactions were induced, various supported catalysts showed an irreversible suppression of hydrogen chemisorption, as is typical of SMSI, but a significant reversible chemisorption was still evident. On these catalysts a lowering of the Curie temperature was observed. In contrast, the inducement of SMSI in TiO_2-supported catalysts showed no change in Curie temperature and no reversible hydrogen chemisorption.

To account for the SMSI effect, Baker *et al.*[211] studied the Pt/TiO_2 system using electron microscopy and concluded that platinum undergoes a structural change when brought into the SMSI state. Reduction of titania-supported platinum at 875 K initiates this state and causes platinum to assume a thin pillbox structure on which hydrogen and carbon monoxide chemisorption is suppressed. It has been suggested[212] that this pillbox is to some extent encapsulated by titanium oxide species, causing the platinum in effect to move under the titania surface. The exact nature of the surface structure under SMSI conditions is, however, still a matter of debate.

Treatment with H_2O vapour or O_2 at an elevated temperature causes three-dimensional growth of the platinum particles, and the chemisorption capacity of the metal is partially restored. This is in good agreement with a theoretical study by Horsley[213] who used the $X\alpha$ molecular orbital method to elucidate the nature of the Pt/TiO_2 system. He confirmed that electronic interactions, needed to effect SMSI, cannot take place when oxygen ions are present on the surface. The dominant interaction in the absence of oxygen ions is an ionic attraction as a result of a charge transfer from the reduced cation to an adjacent metal atom. Surface reduction is therefore imperative since it removes surface oxygen anions and reduces the surface transition metal cations. The nature of SMSI needs no further discussion as a good review on the subject exists[206].

Effects of type (iv) generally result in specific and sometimes rather unusual selectivities. It is not clear how this effect will influence the chemisorption behaviour of synthesis gas.

4. FACTORS AFFECTING THE OLEFIN SELECTIVITY

Although the need for information on the factors responsible for the selectivity behaviour of metallic catalysts was recognized long ago, almost all the information in this area has been published recently. Most of it is summarized in an excellent review by Ponec[214]. From this work he concluded that the selectivity may be influenced by two factors.

The first is often called the electronic factor and it always plays a large part in determining the activity and selectivity of metallic catalysts. This factor is a function of the electronic structure of the metal atoms in the solid.

The second factor plays a role only in reactions that require a specific ensemble size of the metal atoms involved. Such reactions could involve complexes adsorbed on the tops of several atoms or complexes adsorbed in the valleys that occur in active ensembles, hence the name geometric factor. These reactions also involve those that require the severing or forming of bonds such as C-C, C-OH and C≡O. In consequence, both factors are involved in Fischer-Tropsch reactions.

There has been a widespread tendency to relate the characteristics of the Fischer-Tropsch synthesis to various electronic factors, but this approach is now being questioned. This is quite understandable in view of Ponec's conclusion[214] that not only electronic but also geometric factors affect behaviour in the Fischer-Tropsch synthesis.

Electronic factors have been singled out by two schools of thought: the school of Dowden[215-217] and the school of those who use the semi-empirical rules related to the so-called Sabatier principle[218-220].

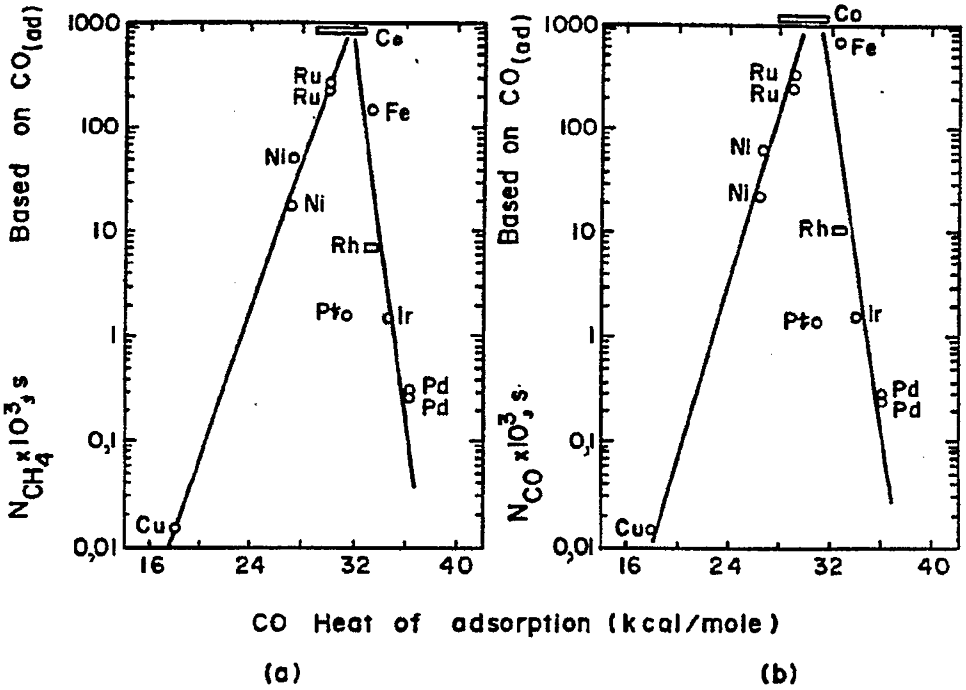
In Dowden's theory a charge transfer on the surface of the catalyst activates adsorbed molecules which then react. The faster this transfer takes place, the better the catalyst. In order to increase the speed of this transfer, the catalyst must have a high value of the density of state at the Fermi level, plus a high gradient in the densities of state near the Fermi level. The metal must also have a certain number of unoccupied energy levels of a high d-character (d-holes).

It soon became apparent that the reaction of adsorbed molecules involves more complex changes than just a simple electron transfer[221], and no clear relationship could be found between electronic structure parameters, such as the number of d-holes, electrical conductivity, work function and percentage d-character, and the chemisorption and catalytic properties[222-225]. This resulted in the ideas of Sabatier gaining popularity.

Sabatier proposed[218] as early as 1911 that reacting molecules form an intermediate compound with the catalyst. The main catalytic parameter would then be the stability of the intermediate complex. The "Sabatier principle" dictates an optimum stability, i.e. one neither too stable nor too unstable for an optimum catalytic effect. This stability principle suggests that the chemisorption bond strengths directly affect activity. This led Tanaka and Tamaru[219,226] to correlate the catalytic activity with the heat of formation of the highest oxide per metal atom, which is itself related to the chemisorption bond strength. This resulted in the well-known "volcano plots".

Using the same principle, Vannice[57,227] observed a correlation between turnover frequency in methanation and heat of adsorption of hydrogen and carbon monoxide on various metals. Although he also found a good "volcano plot" relationship (Fig. 20) between the parameters, a flaw in the theory soon became apparent. On nickel surfaces the heat of adsorption of carbon monoxide is lower than the optimum value, indicating a deficiency of carbon monoxide on the surface during synthesis. As this results in a low hydroxyl surface coverage in the theory of Vannice[57], a positive order in the carbon monoxide pressure would be expected[228]. However, as shown before, this order is negative.

FIGURE 20 Activity of methanation (a) and carbon monoxide hydrogenation (b) over silica-supported metals[227]



Although both theories have some merit, they are too simplistic for a holistic approach. This was also realized by Dowden whose more recent publications[229,230] take account of the size and geometry of the active ensembles. Although perfectly valid, oversimplified approaches have led to many inconsistencies when the terms "electronic" or "geometric" were tacitly narrowed down to imply only collective parameters.

To avoid such ambiguities Sachtler[231] used a different approach. If it is assumed that a molecule that interacts with a catalyst surface can react along different reaction paths, resulting in different products, and that each of these paths is known in every atomic detail, then it will be possible to define for each path the requirements with respect to the chemistry and geometry of the catalysing sites for the particular reaction to proceed. If the catalyst fulfils the requirements of only one of these reaction paths, it is clear that only this reaction will take place.

Since the direct use of these ideas will only be possible in the distant future, generalizations must be made for present use. The requirements relevant to catalyst selectivity may then conveniently be classified into four main categories: bond strength requirement, coordination requirement, ensemble requirement, and template requirement.

The bond strength requirement is essentially a chemical reformulation of the old electronic factor concept, since the strength of the chemisorption bond is governed by the electronic characteristics of the atoms involved. This definition may be narrowed down to a simpler relationship if the number of possible reaction paths is reduced. Using the requirement for the Fischer-Tropsch synthesis reaction over metals with similar electronic structures that differ mainly in their electron density, it should be possible to define a useful bond strength requirement in terms of heat of adsorption and electron work function only.

The basicity effect, observed for the chemisorption of both components of synthesis gas on transition metals, could well fulfil the bond strength requirement for the hydrogenation of carbon monoxide on the transition metals Mn, Fe, Co and Ni. Other transition metals have electronic structures that are sufficiently different from those of these four metals for them to be omitted from the discussion that follows.

The coordination requirement of a catalytic reaction mechanism is defined[231] as the minimum number of coordination sites per surface atom required for reaction.

The ensemble requirement of a catalytic reaction is defined[231] as the minimum number of contiguous surface atoms of the element(s) required to form bonds with the end adsorbate. It has been demonstrated that bridged coordination types involve more than one contiguous surface atom and lead to an undesirably high degree of polymerization and catalyst carburization. It follows that selective light olefin formation probably requires a low number of contiguous surface atoms.

The template requirement defines the stereochemical conditions that a catalytic centre must fulfil in order to render the reaction "shape selective" or "stereospecific". This requirement is thought not to be applicable to the selective formation of light olefins.

The chemisorption effects, discussed earlier, can be conveniently considered to result from the operation of either short-range or long-range effects. Several short-range effects have been identified, all of which seem to involve some form of demetallization. Only one relevant long-range effect has been found: the basicity effect. It involves the effect of the bulk electronic structure (expressed in terms of the electron work function) on the catalytic behaviour of metals. It should be emphasized that the catalytic behaviour of metals is governed by the combination of all the relevant short-range and long-range effects; the various effects may be complementary, or any one (or more) effect may dominate. The effects will now be considered in terms of the selectivity requirements, and the validity of the concepts will be discussed in practical terms.

4.1 Catalyst basicity effect

The consideration of the basicity effect has shown that an increase in the catalyst basicity (i.e. a decrease in the work function) results in an increase in the:

i) average molar mass of the hydrocarbon product
ii) carbon deposition and catalyst carburization
iii) formation of olefins
iv) formation of oxygenated hydrocarbons
v) formation of carbon dioxide and
vi) catalytic activity if the metal is iron,

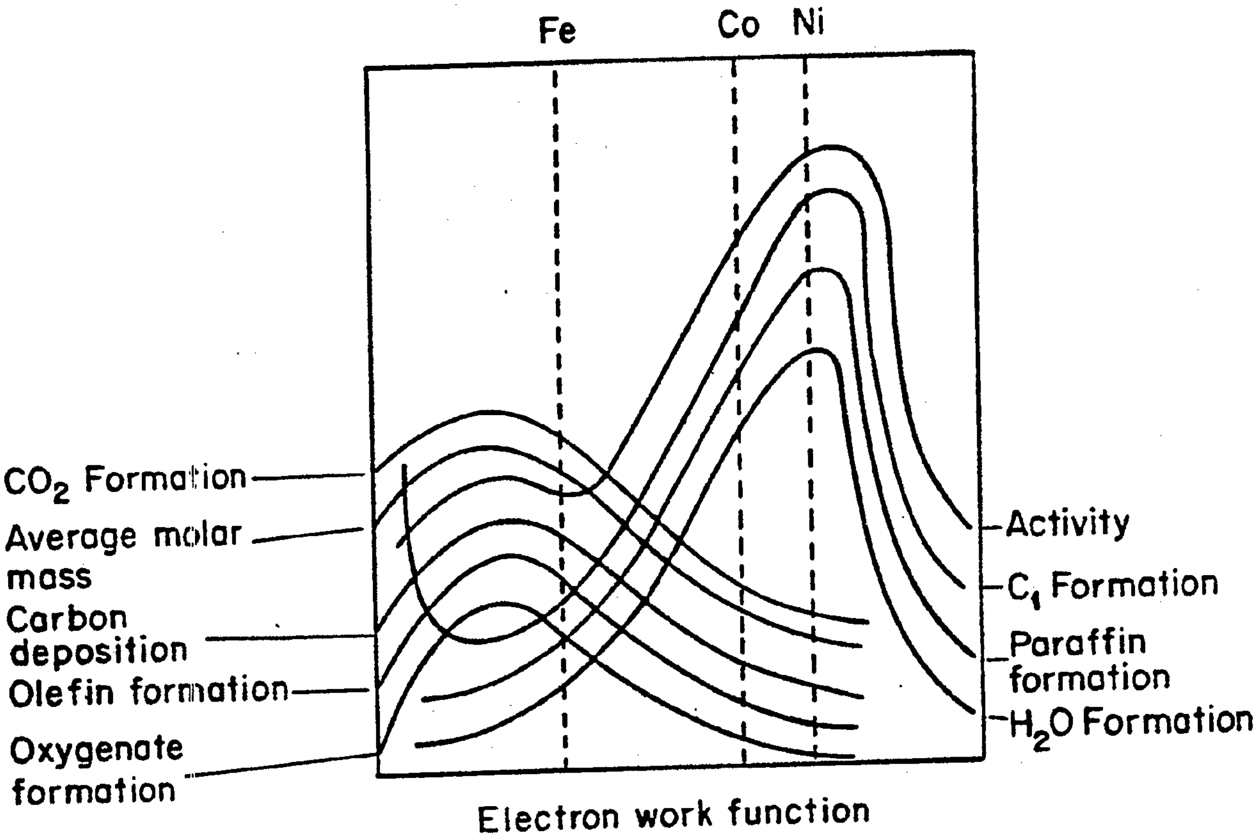
and a decrease in the
i) formation of methane
ii) formation of other paraffins
iii) formation of water and
iv) catalytic activity if the metal is cobalt.

It is predicted that a decrease in the catalyst basicity (i.e. an increase in the work function) will lead to the opposite results. In the case of nickel the heat of adsorption of carbon monoxide is quite similar to that of hydrogen (Fig. 16). This indicates a very active catalyst producing methane and water as the main products.

The rationalized activity trends are summarized graphically in Fig. 21 for the metals under discussion. It is not unreasonable to expect similar relations for transition metals of the second and third periods, but the specific coordination and electronic structure differences discussed before preclude inclusion of these metals in the rationalized scheme of relations.

Many examples of the catalyst basicity effect may be found in the literature. In an effort to prove one of the less often cited Fischer-Tropsch mechanisms, the oxygen mechanism, Sapienza *et al.*[230] promoted cobalt with more electron-deficient metals such as platinum and palladium and observed an increase of several orders of magnitude in the rate of carbon monoxide hydrogenation. As may be expected, the average molar mass of the products was low and no olefinic or oxygenated hydrocarbons were formed. Similar effects were reported for the promotion of iron with ruthenium[231] or platinum[232] and for platinum-promoted ruthenium catalysts[233,234].

FIGURE 21 Trends of the basicity effect in the first period of Group VIII metals



The influence of cobalt on iron is somewhat different[235] since a combination of effects occurs. The catalytic behaviour of this important system is discussed in Section 4.2.6 where alloys are considered.

An increase in catalyst basicity has different results. Promotion of iron with potassium results in changes in activity and selectivity in line with those expected. The degree of change depends on the magnitude of the shift in basicity. The use of highly basic materials obtained by the action of alkali metal vapours on previously reduced transition metals, referred to as superbase-ferrous metal catalysts, produces very substantial changes[154]. In general, the selectivity for long-chain hydrocarbons, as well as for olefins and oxygenates, increases, as does the production of carbon dioxide. These results are generally reported and are not the subject of any dispute.

However, in a recent study of potassium promotion on alumina-supported iron catalysts by Arakawa and Bell[236], which confirmed most of the selectivity patterns discussed earlier, a decrease in the turnover frequency for total carbon monoxide consumption was reported. This finding is somewhat unusual and could perhaps be accounted for by the values used for the turnover frequencies. The authors report that potassium promotion causes a decrease in the dispersion of the iron on the alumina surface. The measured degree of dispersion is then used to calculate the turnover frequencies. This approach presupposes that the dispersion remains constant during the reaction. However, the dispersion could change during synthesis and a potassium-dependent agglomeration of small iron particles is possible, which would explain the reported decrease in turnover frequencies.

A rather baffling situation arises when manganese is used for promotion. As it has a lower work function than iron, an effect similar to that of alkali promotion may be expected. However, a result typically associated with an electron withdrawal ligand effect is obtained. Barrault[145,237] observed that manganese and chlorine have the same effect. Both cause a decrease in chemisorption and in the extent of dissociation of carbon monoxide. These results were confirmed by Jensen[238] who reported a substantial decrease in the extent of carbon monoxide chemisorption and an even more reduced hydrogen chemisorption. The suppression of chemisorption resulted in decreased catalytic activity, less methane formation and a higher selectivity for the formation of lower olefins. The deviation from expected behaviour is probably due to the fact that, under synthesis conditions, manganese is not present in elemental form but as manganese oxide[238]. If this is the case, then SMSI effects rather than an electron withdrawal ligand effect may play a decisive role.

One of the few available examples of a basicity effect on promoting iron with the more basic manganese has been reported by Kuznetsov *et al.*[239], who prepared cluster-derived Fe/Mn bi-metallic catalysts from $(NEt_4)_2[Fe_2Mn(CO)_{12}]$. It could be speculated that because of this preparation method manganese was present in the zero-valent state. On comparing the catalytic results in carbon monoxide hydrogenation with the corresponding catalyst prepared from iron and manganese nitrates, it was found that the cluster-derived bimetallic catalyst had a decreased methane yield and an increase in the fraction of higher hydrocarbons. This increase clearly indicates a basicity effect since no other effect is known to promote a higher average molar mass of the hydrocarbon product.

One of the practical problems connected with the application of the basicity effect is the mixing-in of the promoter. It is well known that promoters may preferentially affix themselves to supports rather than to small supported-metal crystallites[240] or agglomerates to form promoter-aggregates on the catalyst surface. These problems may be overcome by mixing the promoter with the catalyst on the atomic scale. This is done by using mixed-metal clusters as precursors of promoted catalysts.

The same principle may, of course, be used for the formation of multi-metallic catalysts. Such materials will have the desired properties only when intimate mixing is fully realized. A critical test of this approach is to compare the catalytic behaviour of two isostructural cluster-derived bimetallic catalysts that have a different ratio of the two metals. Such a test was carried out by Shapley *et al.*[241] who observed sufficient difference to prove that control of the composition of individual particles of mixed-cluster-derived catalysts was possible.

A similar approach was used by Schay and Guczi[101] for the preparation of Fe/Ru catalysts from $H_2FeRu_3(CO)_{13}$ and $Fe_2Ru(CO)_{12}$. Supported on Cab-O-Sil®, these catalysts proved to be highly selective for light olefin formation in the Fischer-Tropsch synthesis. A study involving the two catalysts and a catalyst prepared from a mixture of the dodecacarbonyls of iron and of ruthenium led to the conclusion that the mechanism of the Fischer-Tropsch synthesis over such catalysts includes three different types of carbon, i.e. carbon active in methane formation, in olefin formation and in deactivation. Surface carbon and metallic sites together are required for the formation of olefins and partial decarbonylation could provide the required type of carbon-metal combination. This finding indicates an additional feature of metal carbonyl cluster-derived catalysts.

A less successful attempt at preparing bimetallic catalysts from mixed-metal clusters was reported by Choplin *et al.*[242] who prepared bimetallic silica-supported Fe/Os catalysts from the mixed cluster $H_2FeOs_3(CO)_{13}$ by reacting it with the functional groups of silica IR, and Raman spectroscopy revealed that the Fe-Os bond is cleaved by thermal treatment under Ar at 400 K. At temperatures higher than 520 K, metallic particles with a size of ca 1,6 nm resulted, which had an activity and selectivity in the Fischer-Tropsch synthesis intermediate between those of iron and osmium. It was therefore concluded that the use of such bimetallic clusters results in a segregation of the two metals.

An in-depth investigation into the use of mixed-metal clusters for catalyst preparation is reported by McVicker and Vannice[199] and concerns the preparation of supported-metal catalysts from potassium-Group VIII metal carbonyl complexes. The following catalysts were prepared and characterized: (A) 5,5 % K, 3,9 % Fe/Al_2O_3 from $K_2Fe(CO)_4.2C_4H_8O$, (B) 2,2 % K, 3,2 % Fe/Al_2O_3 from $KFe(CO)_2(C_5H_5)$, (C) 6,7 % K, 4,7 % Fe/SiO_2 from $K_2Fe(CO)_4.2C_4H_8O$, (D) 0,45 % K, 1,3 % Ru/Al_2O_3 from $K_2Ru_3(CO)_{12}$, (E) 0,3 % K, 1.4 % Ir/Al_2O_3 from $KIr(CO)_4$, (F) 5,5 % K, 3,9 % Fe/Al_2O_3 as a conventional catalyst from the nitrates, (G) conventional alumina-supported iron, (H) bulk iron and (I) K-promoted bulk iron.

Infra-red studies on the above catalysts indicated that potassium-Group VIII metal carbonyl complexes are relatively stable on partially dehydrated Al_2O_3 surfaces in the absence of oxygen. This suggests that the complexes can be supported without loss of the stoichiometry of the atomically mixed metals. It has been speculated that reductive decomposition of the three-dimensional complexes yields uniform mixed-metal particles, within which the basic metal geometry of the starting complex is retained. It can safely be assumed that an intimate contact between potassium and the Group VIII metal is achieved in this way. Chemisorption and X-ray results indicate that iron is less well dispersed on SiO_2 than on Al_2O_3.

Kinetic studies showed that potassium had a far greater influence on activity and selectivity in the hydrogenation of carbon monoxide when it was introduced into the catalyst via the mixed-cluster method (catalyst A) than via the conventional method (catalyst F), as shown in Table 3. The mixed-cluster-derived catalyst is characterized by a low methane selectivity and a high production of C_{2+} olefins. Its activity is 50 times higher (on a mass basis) than that of the conventionally prepared K/Fe catalyst. These differences cannot be explained by considering the twice-as-high Fe dispersion displayed by

TABLE 3 Comparison of the Fischer-Tropsch catalytic behaviour* of bulk and supported cluster-derived and conventionally prepared iron catalysts[199]

Catalyst	T (°C)	CO conv. (%)	Product distribution (wt %)									Activity (µmol CO min^{-1} g^{-1} Fe)
			C_1	$C_2^=$	C_2	$C_3^=$	C_3	$C_4^=$	C_4	$C_5^=$	C_5	
(A) 5,5 % K 3,9 % Fe/Al_2O_3 (complex-derived catalyst)	264	2,3	9	15	1	19	Tr	16	4	20	16	150
	271	3,5	10	14	2	26	Tr	20	4	13	11	227
(F) 5,5 % K 3,9 % Fe/Al_2O_3 (conventional catalyst)	268	0,07	44	56	0	0	0	0	0	0	0	4,5
(G) 10 % Fe/Al_2O_3 (conventional catalyst)	264	3,5	50	2	23	1	10	Tr	10	4	0	204
(H) Bulk Fe metal	264	4,9	24	5	31	7	8	Tr	16	7	2	12
(I) Bulk K/Fe	269	1,5	13	22	2	22	Tr	24		12	5	13

*H_2:CO = 3,0 101 kPa (1,0 atm) total pressure

catalyst A, but better K-Fe contact and subtle microstructural differences are expected. No major change in selectivity was observed for potassium-promoted Ru and Ir catalysts, whereas the bulk metals showed the expected effect of alkali promotion.

Similar preparation methods were used[243] for the FeCo and MnCo bimetallic catalysts[244]. These will be discussed further in Section 4.2.2, in which the dispersion effects of cluster-derived catalysts are considered.

The above discussion shows that the rationalized activity trends based on the catalyst basicity effect, summarized graphically in Fig. 21 for the first period of Group VIII metals, are indeed valid.

The trends indicated in Fig. 21 are very useful for the practical design of catalysts. However these trends should not be quantified, nor should elements in different periods be compared. Application of the catalyst basicity effect has other limitations.

The first limitation is that it lacks selectivity. For example, if methane production is to be minimized, potassium promotion can be used to increase the catalyst basicity and in this way the formation of methane will be repressed. However, a concomitant increase in the formation of oxygenates is indicated and this is a well-known problem in commercial operation.

The second limitation lies in the purely electronic nature of the basicity effect, so that geometric factors are ignored entirely. It is therefore conceivable that an increase in basicity may not have the desired effect because of geometric limitations. In fact, under certain conditions geometric effects are known to dominate (see Section 4.4, which considers support interactions).

4.2 Catalyst dispersion effect

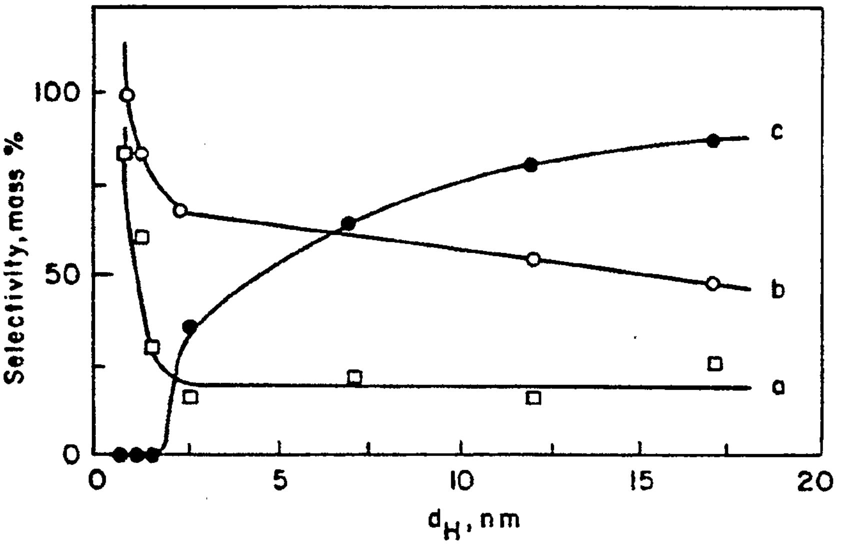
The chemisorption behaviour of both hydrogen and carbon monoxide changes gradually when the metal particle diameter is decreased. The heat of adsorption of both gases, and the amount of gas that can chemisorb, decrease with decreasing particle size, the latter being more pronounced for hydrogen than for carbon monoxide. Depending on the type of metal, these changes take effect in the particle size range 1 nm to 5 nm and are caused by a demetallization effect as manifested by a marked increase in the work function. The result of this altered chemisorption behaviour is a catalyst with entirely different activity and selectivity characteristics.

The decrease in heat of adsorption of both gases associated with an increased work function is expected to lead to the production of shorter-chain hydrocarbons, a more paraffinic product and a higher catalytic activity.

However, the last two characteristics necessarily require an increase in hydrogenation activity, which does not occur because of the marked decrease in available hydrogen. As a result, the formation of methane is strongly retarded, the overall catalytic activity decreases and the olefin selectivity increases markedly.

The decrease in available hydrogen results in rather striking changes[245] in the selectivity of hydrogen-demanding reactions as the catalyst particle diameter is decreased (Fig. 22). As far as is known, very few systematic studies involving particle dependence in the Fischer-Tropsch synthesis have yet been done (Fig. 23), but it is well established that all metals active in synthesis lose much of their hydrogenation activity when rendered into a highly dispersed form.

FIGURE 22 Changes in selectivity of platinum catalysts with particle diameter, d_H. (a) isomerization of 2-methylpentane to 3 methylpentane; (b) cyclic isomerization of n-hexane to 3-methylpentane; and (c) hydrogenolysis of methylcyclopentane (after ref. 245)



Highly dispersed catalysts may be prepared in a variety of ways. The following techniques, followed by suitable pretreatments (e.g. reduction), have been used successfully for the production of very small metal particles:

i) zeolite ion-exchange

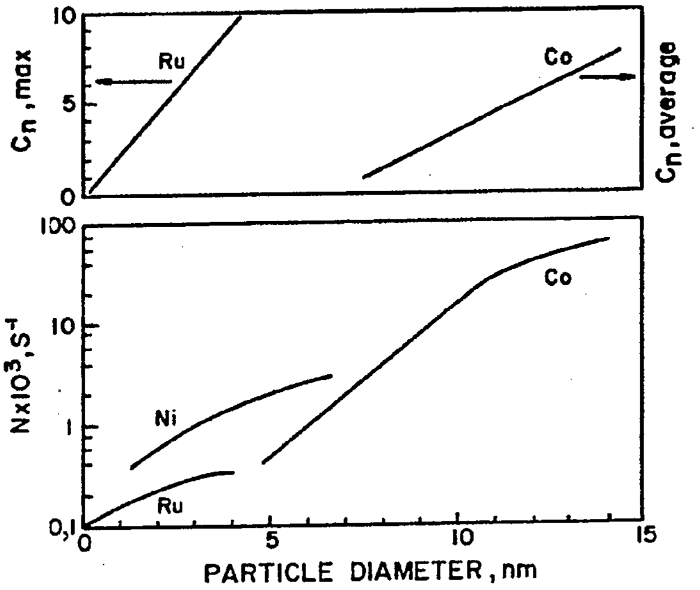
ii) decarbonylation of metal carbonyl clusters

iii) degradation of metal complexes

iv) formation of metal whiskers

v) dispersion by solvated metal atoms
vi) dispersion by alloys
vii) dispersion by support interaction.

FIGURE 23 Influence of the average particle size of Ru, Co and Ni on the turnover frequency for CO disappearance (N) and on the maximum (Ru) or average (Co) size of the F-T product (C_n) (after refs 170,171,246)



4.2.1 Zeolite ion-exchange

Zeolite-supported small metal particles prepared by the ion-exchange method[246] may have a particle size in the range 0,6 nm to 1,3 nm. The dispersion effect in RuY zeolite systems prepared by ion exchange has been thoroughly investigated by Jacobs and co-workers[246-252]. A definite dispersion effect was established for particles with a size below ca 4 nm (Fig. 23), when the activity and size of the largest Fischer-Tropsch product were directly related to the size of the ruthenium metal particles[246,248].

4.2.2 Degradation of metal carbonyl clusters

Surface organometallic chemistry can be defined as a new area of chemistry arising from the overlap between organometallic (and/or coordination) chemistry and surface science[253]. If this field is further extended to include heterogenized clusters and decarbonylated carbonyl clusters, it holds much promise for the development of new types of heterogeneous catalyst. Molecular clusters of increasing nuclearity constitute a new generation of organometallic complexes which almost fill the gap between the molecular state and the metallic state. Clusters containing up to 38 metal atoms are now known[254], and a homogeneous type of heterogenous catalysis becomes a not-too-distant possibility. Partial decarbonylation has been shown to lead to catalysts of which only a small percentage of the metal is in metallic form[255], and which display interesting catalytic features. The use of metal carbonyl clusters as precursors for small metal particles has proved to be very successful and is gaining in popularity[256].

Zeolite-supported cluster-derived Fe, Co or Ru catalysts, prepared in various different ways, have been shown to be selective for the formation of short-chain hydrocarbons[257]. However, the formation and stabilization of small metal crystallites in the supercage is still a subject of research.

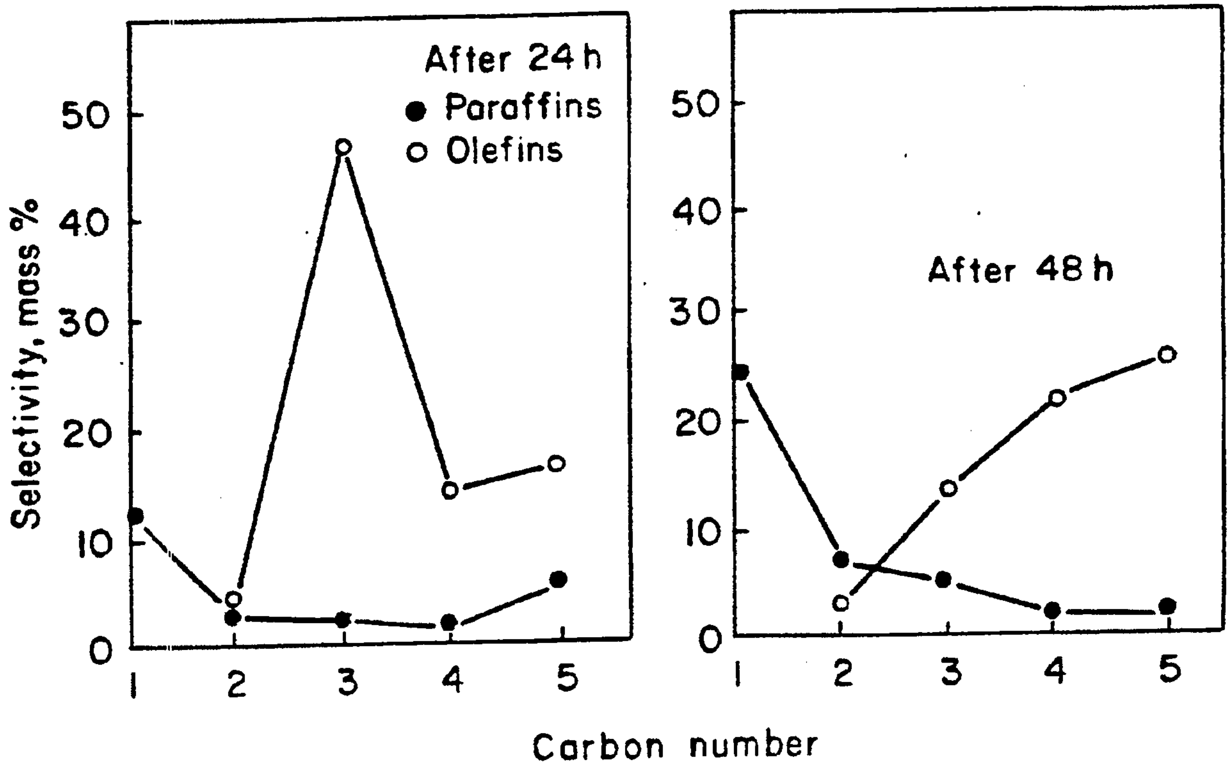
Basset and co-workers[258-265] reported that highly dispersed cluster-derived iron catalysts behave in the Fischer-Tropsch synthesis in an entirely different manner from less dispersed iron catalysts[261]. Under reaction conditions of 1 MPa and 450 K to 540 K, a hydrocarbon product with an olefinic fraction of up to 68,9 % was produced. This unusually high function selectivity was paralleled by a mass selectivity deviating strongly from that predicted by Schulz-Flory statistics and showing a maximum at C_3. The size of the iron particles was definitely less than 1,5 nm and probably less than 0,6 nm.

The unusual product spectrum obtained with these catalysts could, unfortunately, be maintained for only a short time. After 48 h on stream there was a shift to a spectrum that obeyed Schulz-Flory statistics (Fig. 24). A change in particle size was held responsible for this behaviour. Electron microscopy showed that the original size of ca 1 nm, which was still the same after 24 h on stream, had increased to 20-50 nm after 48 h on stream. The larger particles behave more like massive metal and the resulting product distribution following Schulz-Flory statistics is not unexpected.

Bruce *et al.*[266] used the mixed-cluster-adduct concept for the preparation of potassium-iron-manganese catalysts. They impregnated silica gel with a solution of K $[Fe_2Mn(CO)_{12}]$. Subsequent decarbonylation of the material yielded a silica-supported K/Mn/Fe catalyst mixed on the atomic scale in the ratio 1:1:2. This catalyst was found to be more selective for the formation of C_2 to C_4 olefins than catalysts prepared by impregnation of the corresponding nitrates. The catalyst basicity effect predicts a shift of the product spectrum to longer chains when iron catalysts are promoted with K or Mn. The observed shift to lower olefins in the product spectrum is, however, characteristic of a dispersion effect, indicating the effect of the preparation method.

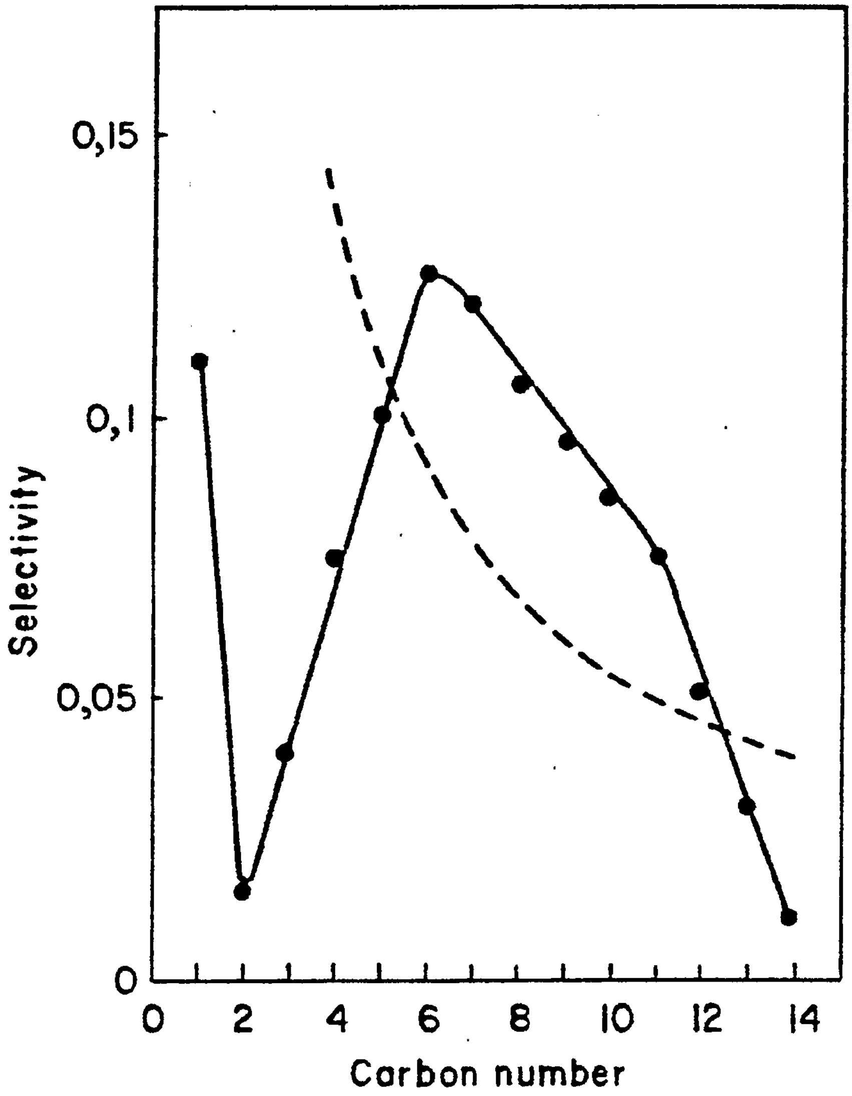
An interesting approach to the preparation of highly stable, highly dispersed bimetallic cluster-derived catalysts was followed by Hemmerich *et al.*[243.267]. They made use of acid-base reactions to anchor hydrido clusters to basic supports. The cluster chosen was $HFeCo_3(CO)_{12}$ which was supported on silica previously modified by amino donor functions. Reductive decarbonylation was effected at 473 K; the resulting catalyst was shown to be highly active in the Fischer-Tropsch synthesis, and a narrow product distribution was obtained. Methane selectivity was not higher than 12,5 % and a high alkene content was found: more than 95 % in the C_3 to C_5 range. The stability of this catalyst was excellent. Under realistic conditions (513 K, 4 MPa) the catalyst showed an almost constant activity during an operation period of up to 220 h, although a gradual change in selectivity was observed.

FIGURE 24 Selectivities observed in Fischer-Tropsch synthesis with a cluster-derived iron catalyst (after ref. 261)



Vanhove *et al.*[244] prepared manganese-cobalt catalysts from $MnCo(CO)_9$ and various mixtures of manganese and cobalt carbonyls. Unfortunately the contact times used during Fischer-Tropsch synthesis were very different, precluding a direct comparison between the catalysts derived from mixed-carbonyl complexes and those derived from mixtures of the pure carbonyls. However, the former appear to be very stable and active Fischer-Tropsch catalysts yielding a product spectrum that does not obey Schultz-Flory statistics (Fig. 25).

FIGURE 25 Selectivity of carbon monoxide hydrogenation to hydrocarbons as a function of the carbon number of the products. The dotted line represents maximum selectivity in each hydrocarbon according to Schulz-Flory statistics (after ref. 244)



McVicker and Vannice[199] showed that cluster-derived catalysts are reasonably stable in zeolite systems. Cluster-derived Ru and Ir catalysts are initially well dispersed and remain so under Fischer-Tropsch reaction conditions, in contrast to Fe catalysts. With a cluster-derived iron catalyst, a CO/Fe value of 0,063 was found after use in a Fischer-Tropsch experiment, whereas a conventionally prepared iron catalyst subjected to the same treatment showed a CO/Fe ratio of 0,037. This suggests that the complex-derived catalyst is able to maintain only a two-fold higher Fe dispersion during Fischer-Tropsch synthesis than the more conventional catalyst, prepared by incipient wetness impregnation.

Ballivet-Tkatchenko *et al.*[268,269] prepared zeolite-supported iron catalysts by the decarbonylation of iron carbonyl clusters which were first incorporated into NaY zeolites. These catalysts showed good activity under typical industrial conditions (523 K, 2MPa), with a product spectrum deviating from that indicated by Schulz-Flory statistics. The selectivity for lower olefins was remarkably high: 88 % to 98 % in the C_2 to C_4 range. Other zeolite-supported iron catalysts, stabilized in ZSM-5, mordenite and 13X, showed similar catalytic behaviour[270]. A special feature of these catalysts is their high stability (Fig. 26). In contrast to cluster-derived non-zeolite-based iron catalysts which appear to undergo sintering within two days (Fig. 24), the zeolite-supported cluster-derived iron catalysts display a catalytic activity that increases steadily to reach a steady state in ca eight to ten days.

Vanhove *et al.*[271,272] prepared alumina-supported cobalt catalysts by impregnation with solutions of octacarbonyldicobalt in pentane. At loadings of 2 mass %, the product distribution of carbon monoxide hydrogenation at 473 K appeared to be strongly dependent on the pore diameter of the support (Fig. 27) and non-Schulz-Flory statistics are reported. However, at higher loadings (5,3 mass % Co) Schulz-Flory statistics were obeyed. The phenomenon was explained in terms of diffusion effects. It was shown that particle size effects were not responsible for the observed shift in the product spectrum. Neither could the shift be attributed to differences in the acidity of the supports, since acidity determinations showed that the surface acidity and surface hydroxyl concentration were the same for all supports studied.

The effect is an elegant way of limiting the chain growth and could well explain the product spectra observed with Fe/zeolite systems[268-270]. These spectra were obtained under realistic process conditions and deviated from those expected for Schulz-Flory statistics. This carrier effect therefore has great potential for use in light olefin production.

FIGURE 26 Hydrogenation of carbon monoxide over zeolite-supported iron catalysts. (a) H_2 conversion; (b) CO conversion. ☐ = 15,0 % Fe/ZSM-5; O = 16,4 % Fe/mordenite; Δ = 15,0 % Fe/13X (after ref. 270)

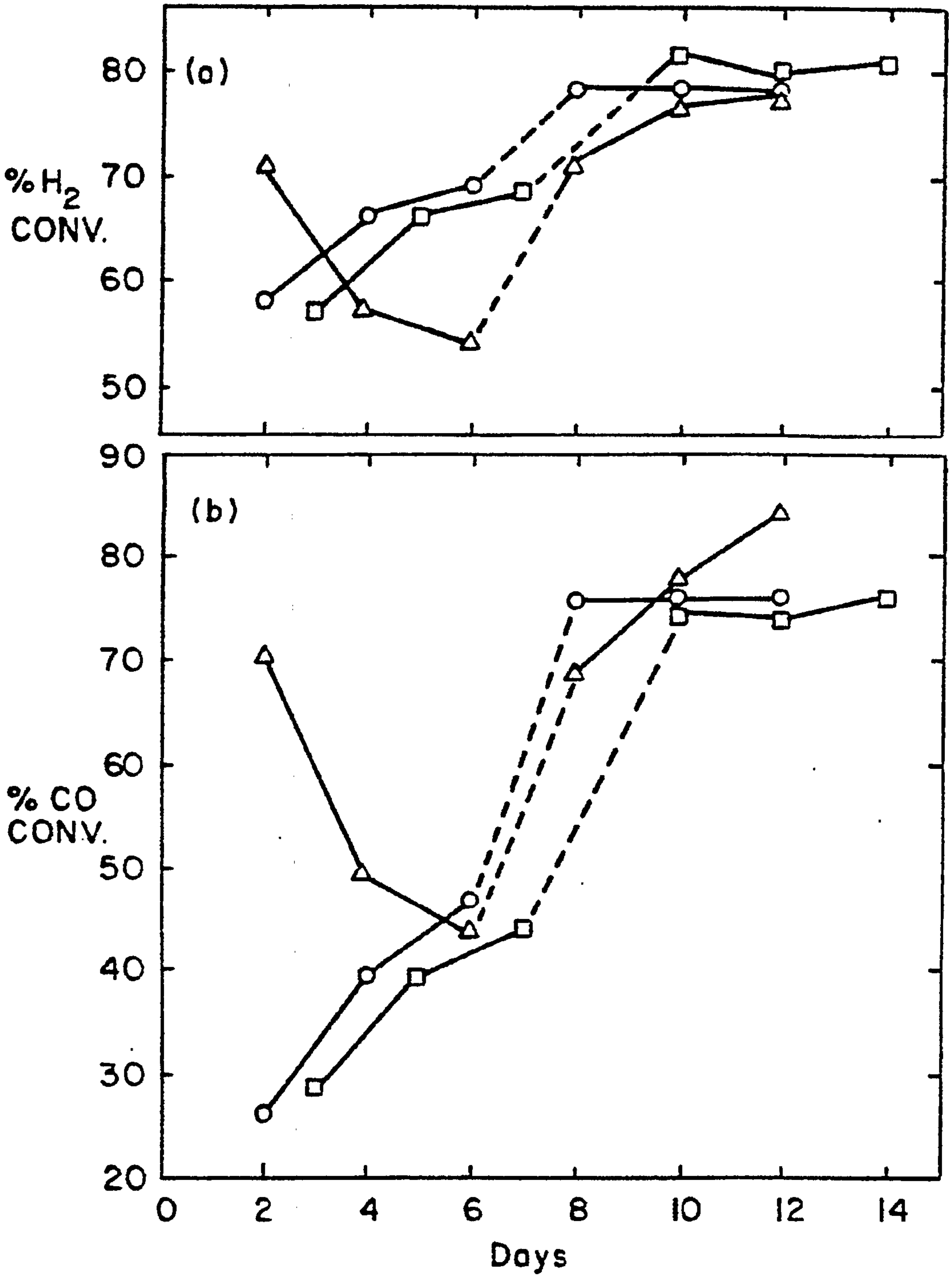
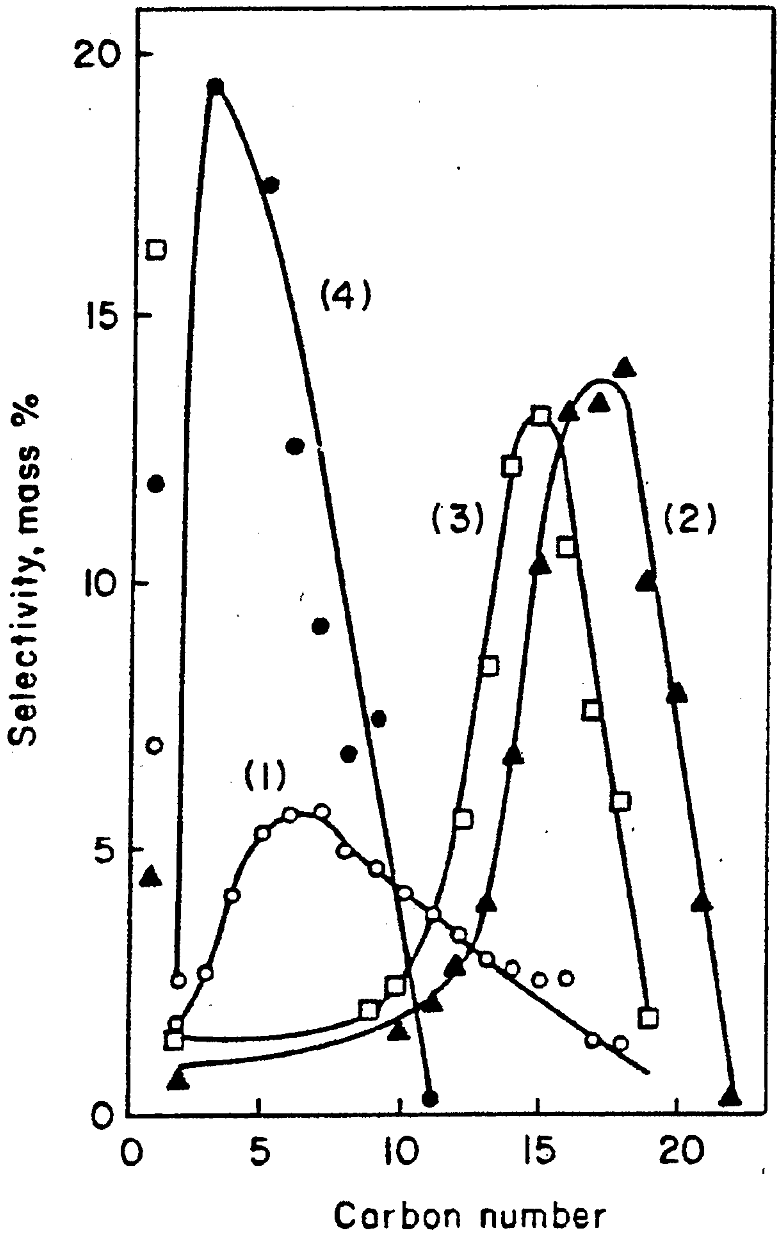


FIGURE 27 Selectivity of C_n hydrocarbons based on CO conversion as a function of the metal loading and the pore size of the support. (1) mean pore radius 300 nm, 5,3 % Co; (2) mean pore radius 300 nm, 1,9 % Co; (3) mean pore radius 30 nm, 2 % Co; and (4) mean pore radius 6,5 nm, 2 % Co (after ref. 271)



The same research group prepared highly dispersed cluster-derived cobalt catalysts for use as Fischer-Tropsch catalysts in the liquid phase[273,274]. The catalysts were synthesized from $Co_2(CO)_8$. Liquid-phase Fischer-Tropsch synthesis yielded up to 75 % olefins, which is highly unusual for cobalt catalysts. A product distribution deviating from Schulz-Flory statistics was observed, in contrast to a cluster-derived *supported* cobalt catalyst which showed a normal Schulz-Flory-type product distribution[275,276]. This suggests that liquid-phase operation can lead to high yields of lower olefins.

Fraenkel and Gates[277] used the "in situ generation of clusters method" for the apparent formation of cobalt carbonyl clusters from zeolite-encaged cobalt atoms during a Fischer-Tropsch experiment. Kinetic measurements showed the zeolite-A-supported catalyst to be highly selective for propene and in one case propene was the only detectable product (426 K, 0,6 MPa).

It could be argued that at these temperatures the catalyst is not a cluster-derived metal but still a cluster. However, another experiment at 569 K and 0,6 MPa also yielded propene as the only product, and at this temperature the catalyst could not have been in the "normal" cluster form. In general, selectivities were highly dependent on the specific zeolite used, but deviations from Schulz-Flory behaviour, ascribed to shape selectivity, are a common feature of these catalysts.

Silica-supported cluster-derived iron-cobalt catalysts are reported to be very olefin selective[278], even at pressures as high as 4 MPa. An interesting feature of these catalysts is the relatively high selectivity for oxygenates, which can be as high as 30 %.

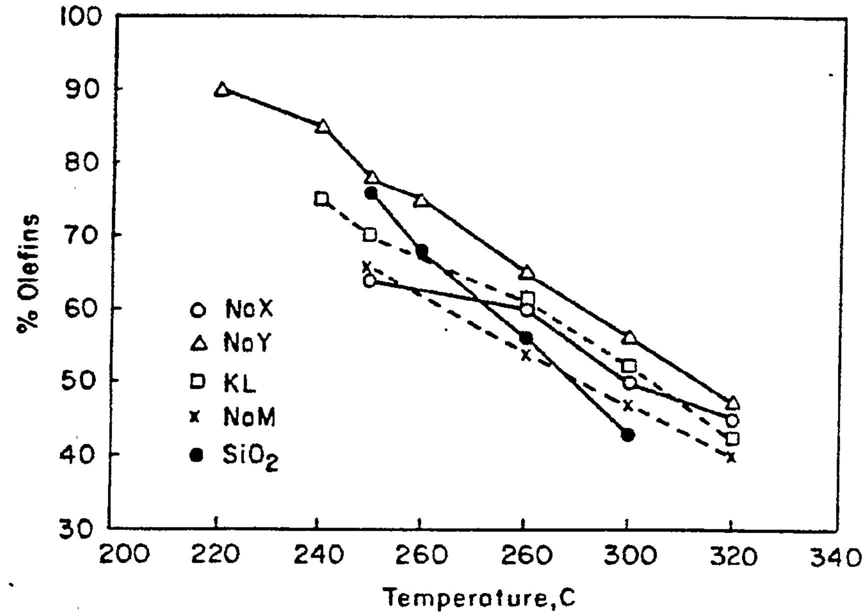
Unusual selectivities are also observed for small complex-derived ruthenium particles[279]. Okuhara *et al.*[280] prepared a highly dispersed Ru/Al_2O_3 catalyst from $Ru_3(CO)_{12}$ which was more active and more selective for C_2 to C_5 olefins than conventionally prepared (incipient wetness impregnation) Ru/Al_2O_3 catalysts. At 530 K selectivities of up to 80 % for light olefins are reported.

NaY-supported Ru catalysts have recently been prepared in three different ways[172,281]: incipient wetness, using a solution of $RuCl_3$, vapour impregnation of $Ru_3(CO)_{12}$, and ion exchange with $Ru(NH_3)_6Cl_3$. The method of preparation has a profound influence on the properties of the catalyst. The particle size was found to be independent of the percentage metal loading in the case of samples prepared by ion exchange or vapour impregnation, but there is an inverse linear relationship between the two parameters in the case of samples prepared by incipient wetness. In addition, the study showed that the chemisorption of syngas is greatly influenced by the preparation method and, in the case of catalysts prepared by vapour impregnation and ion exchange, is similar to the chemisorption behaviour of synthesis gas on the highly dispersed iron surfaces discussed earlier[169]. In the case of vapour impregnation a CO:H ratio of 2,3 was found at ambient temperature. This ratio increased to 4 or 5 for ion-exchanged catalysts (average particle size less than 1,6 nm), but decreased rapidly as the particle size increased. The CO:H ratio for the catalyst prepared by incipient wetness impregnation had a value of ca 1,5 for particles with a size above 5 nm. These modifications to the nature and stoichiometry of CO and H_2 adsorption were ascribed to different site geometries and/or to the interaction of the metal with the zeolite.

The same study showed a general pattern in the catalytic activity of the catalysts. The specific activity for catalysts having similar average particle sizes increases with decreasing CO:H adsorption ratio. This suggests that the availability of activated H_2 determines the catalytic activity during reaction. The selectivity of the catalysts also proved to be highly dependent on the method of preparation and the percentage metal loading. Methane selectivity was highest for the catalyst prepared by incipient wetnesss impregnation, and selectivity for C_2 to C_4 olefins was highest for the vapour-impregnated catalysts [$Ru_3(CO)_{12}$]. In fact, this selectivity was nearly three times greater than that for similarly dispersed catalysts prepared by ion exchange. Therefore, this unusual selectivity cannot be attributed to the type of zeolite (in both cases NaY was used) nor to the dispersion, and has to be related to the use of a carbonyl cluster precursor. Interestingly, although the C_2 to C_4 product fraction obtained with this catalyst was hardly temperature-dependent, the olefin content of this fraction had an inverse relationship with temperature (Fig. 28).

Shamsi *et al.*[282] concluded from a similar study of differently prepared Co/ZSM-5 catalysts that cluster-derived catalysts have a much higher dispersion and activity than similar catalysts prepared by impregnation of the nitrate or by physical admixture of precipitated oxide. In addition, the selectivity was found to be quite different.

FIGURE 28 Temperature-dependence of olefin formation in the C_2 to C_4 fraction of zeolite-supported ruthenium catalysts (after ref. 281)



4.2.3 Degradation of metal complexes

Blanchard and Vanhove[273,274] prepared highly dispersed complex-derived cobalt catalysts for use as Fischer-Tropsch catalysts in the liquid phase. The catalysts were synthesized from $Co(acac)_2$. Liquid-phase Fischer-Tropsch synthesis yielded up to 75 % olefins, which is highly unusual for cobalt catalysts. It is noteworthy that these catalysts did not differ in catalytic behaviour from cluster-derived cobalt catalysts. A product distribution deviating from Schulz-Flory statistics was observed in both cases.

The author prepared several different complex-derived iron catalysts, using iron and mixed-metal citrate complexes[283]. The materials were stable and active catalysts for the selective synthesis of olefins[284] in either unsupported[285], semi-supported[286] or supported form[287].

Variations of the technique have been used successfully for the loading of zeolites with highly dispersed metals. For example, intrazeolite precipitation of insoluble anionic iron cyanide complexes and subsequent reduction of the entrapped iron compound resulted in finely dispersed iron particles distributed throughout the zeolite[288,289]. An FeY catalyst prepared in this way converted synthesis gas to hydrocarbons with unusually high ethene and low methane contents.

It is surprising that this relatively simple and successful technique has not found wider application, in view of the large number and many types of organic complexes available.

Another method for the preparation of small metal crystallites is the reduction of metal salts with potassium in an ethereal or hydrocarbon solvent[290]. Reduction of iron halides with potassium in THF resulted in a catalyst that was highly selective for the formation of lower olefins, butene being preferentially formed[291]. It was suggested that trace amounts of THF coordinated strongly with the iron, thereby modifying the catalytic properties.

4.2.4 Formation of metal whiskers

Metal whiskers are another example of highly dispersed metal particles. Polycrystalline metal whiskers can be prepared by the thermal decomposition of gaseous metal carbonyls in a magnetic field[292-294]. The whiskers are grown by way of dislocations and grain boundaries along the lines of the magnetic field. The dislocation density[293] of these catalysts is of the order of 10^{16} dislocations per m^2. Because of the way they are grown, the catalysts consist of fine metal filaments with a diameter of ca 10 nm.

In the Fischer-Tropsch synthesis iron whiskers are characterized by a product spectrum containing little methane and a higher content of hydrocarbons in the C_1 to C_5 range, and by a slightly higher olefin selectivity relative to normal fused-iron bulk catalysts[295,296]. More than 50 % of the hydrocarbon product has a carbon number higher than 4 (Table 4), which is undesirable if lower olefins are the desired product. As may be inferred from the size of the whiskers (10 nm), the dispersion effect is very small, since this only starts playing a role at a particle size of ca 5 nm.

TABLE 4 Catalytic results of the hydrogenation of carbon monoxide over iron whiskers in a fluidized-bed reactor[295]

Temperature (K)	561	596
Pressure (MPa)	1,1	1,1
VHSV (h^{-1})	320	204
$CO:H_2$ ratio	1,4	1,0
Syngas conversion (%)	58	74
Selectivity as % of hydrocarbon product		
C_1	10	7
C_2 to C_4 olefins	25	32
C_2 to C_4 paraffins	13	5
C_{5+}	52	56

4.2.5 Dispersion by solvated metal atoms

A relatively new technique is the dispersion of metals on the atomic scale in excess solvent (usually organic) at low temperatures[297]. In this way solvated metal atoms are prepared which are used as a source of metal particles for the preparation of highly dispersed catalysts. This technique has been applied successfully to the preparation of both unsupported metal powders and supported metal catalysts. Solvated metal atom dispersed (SMAD) catalysts exhibit very unusual physical and catalytic properties. This is ascribed to the direct proportionality of the reactivity of a metal centre to the strength of its interaction with its coordination sphere ligands (thermodynamic stability), in conjunction with steric restrictions on the approach of reactants to the metal centre (kinetic stability).

This principle has led to the production of SMAD catalysts with high activity and a selectivity directly related to the strength of the metal-solvent interaction. The following effects have been observed for SMAD catalysts:

i) strongly adsorbing solvents influencing the particle size;
ii) competition between solvent adsorption and reactant adsorption; and
iii) an electronic effect of the adsorbed organic species.

SMAD catalysts may have very high dispersions[298–301] and are thought to contain carbonaceous species that may partly encapsulate the small metal aggregates[297], a situation that may lead to unusual selectivities.

Using this method, Nazar *et al.*[302] entrapped very small iron and cobalt aggregates within the supercages of faujasitic zeolites. The metal particles had a narrow size distribution with more than 80 to 90 mass % of the metal present as particles smaller than 1,2 nm. These materials proved to be interesting catalysts for the conversion of $CO:H_2$ mixtures to low-carbon-number olefins with a propensity for forming butenes (Table 5).

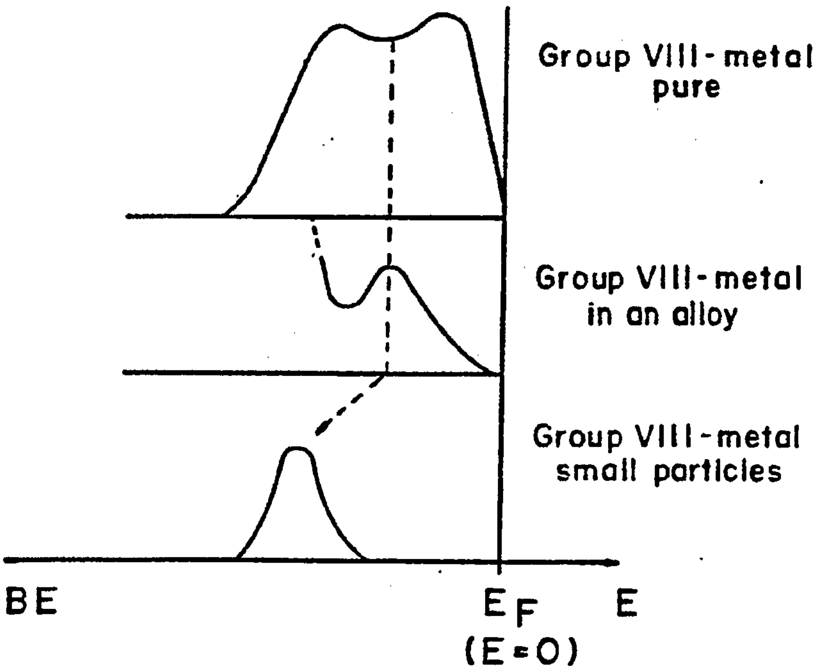
4.2.6 Dispersion by alloys

It is often possible to dissolve a metal in a matrix of another metal. Using this principle, high metal dispersions have been achieved. However, an in-depth review of the subject[303] shows that high dispersions achieved by using small particle sizes cause far greater changes in the electronic structure (demetallization) of the metal than does the making of bulk "solution" alloys (Fig. 29).

TABLE 5 Catalytic activity and hydrocarbon product distribution for 0,5 % Fe/NaY and 2,4 % Co/NaY catalysts in CO hydrogenation[302]

Catalyst	Temperature (°C)	Turnover frequency ($s^{-1} \times 10^3$)	Hydrocarbon distribution (mol %)					
			C_1	C_2	C_3	C_4	C_5	Olefin C_{2+} / Hydrocarbon C_{2+} (%)
Fe_n^o/NaY	250	0,70	19	2	9	47	23	> 90
Fe_n^o/NaY	300	-	50	8	9	15	18	> 90
Fe_n^o/NaY	250	-	85	0	3	10	2	> 90
Co_n^o/NaY	247	0,004	25	0	5	70	0	> 90
Co_n^o/NaY	290	0,013	65	19	9	3	1	> 90

FIGURE 29 Schematic photoemission from a transition metal in the state of a bulk crystal (top) and as a small cluster on a support (bottom). Comparison with photoemission of the same metal when dissolved in a matrix of a Group IB metal (middle) (after ref. 303)



There are many alloy systems with interesting features[303]. One such system, Co-Fe, shows much promise for the selective production of lower olefins. The basicity effect that both metals should have on each other is only partly observed. The addition of cobalt to iron, resulting in a decrease in catalyst basicity, has been reported to increase the selectivity for short-chain hydrocarbons[235,304]. In contrast to the expected decrease in olefin selectivity, an increase has generally been reported[278,305]. In addition, neither a decrease in the heat of adsorption of carbon monoxide nor a uniform increase in catalytic activity has been found[235]. For both parameters a synergistic effect was noted, which is difficult to explain as a catalyst basicity effect but which is more readily accounted for by a catalyst dispersion effect.

In this case one catalytically active component is dispersed in a matrix of another catalytically active component, which explains the increase in both olefin selectivity and catalytic activity. However, many of the available data for the iron-cobalt system are related to operation at total pressures of 100 kPa or less, and at low conversion levels[306].

Arcuri *et al.*[307] and Butt *et al.*[308] studied the catalytic effect of the alloy under more realistic conditions, using a silica-supported iron-cobalt catalyst (Fe/Co = 1) and pure component catalysts. They report an enhanced selectivity for the formation of light olefins at atmospheric pressure, which is not maintained at higher pressures (1,4 MPa). A comparison of the product distributions obtained at low pressures with those obtained at higher pressures indicates that at higher pressures the catalyst yields distributions similar to those found with iron, but, at the same time, exhibits the overall activity of the cobalt catalyst. The Schulz-Flory chain-growth probability increases for both pure component catalysts but decreases for the alloy system when the pressure is increased.

Other experiments showed that the alloy is fairly selective for light olefins and is quite stable under realistic process conditions[309], with no deactivation over a period of 200 h.

Studies by Amelse *et al.*[310] and Unmuth *et al.*[311] indicate that the supported iron-cobalt catalyst takes the form of a bcc alloy with a non-uniform particle size distribution. They tentatively ascribed the anomalous catalytic effect to this non-uniform distribution. The surface composition differs from that of the bulk, showing marked iron enrichment[235,312]. The Fe^{2+}:Fe^{3+} ratio in the mixed-oxide catalyst precursor increased with increasing cobalt content.

4.2.7 Support-induced dispersion

Supports capable of interaction with the metal may have a strong influence on the dispersion. This influence is often seen when supports have a high Lewis acidity. This effect will be discussed in more detail in Section 4.4.

The catalyst dispersion effect can be attributed to both electronic and geometric factors; in addition to an increase in the electron work function, a change in coordination and ensemble effects occurs as the particle diameter is decreased. An ensemble effect necessarily occurs when very large ensembles are required for certain reactions. In addition, the fraction of atoms with low coordination increases with dispersion.

The catalyst dispersion effect meets at least two different requirements: the bond-strength requirement is met by a lowering of the heat of adsorption of both gases without an increase in hydrogenation activity, and the ensemble requirement is satisfied by a decrease in the number of contiguous metal surface atoms. Therefore, the dispersion effect provides an excellent tool for the manipulation of catalytic behaviour. The effect has one potential disadvantage, however, in that high dispersions are often difficult to maintain under synthesis conditions[259].

4.3 Electron withdrawal ligand effect

Barrault and Forquy[145] studied the poisoning of cobalt and iron catalysts by sulphur and observed a typical electron withdrawal ligand effect: a decrease in catalytic activity and a propensity for forming lower olefins. Similar results are reported by Kitzelmann and Vielstich[313] who used a K_2S to achieve a light poisoning (at 0,1 % S) of Fe and Co catalysts. The methane selectivity was reduced by 50 % and the lower olefin selectivity was increased by ca 10 %. In contrast to what has been reported elsewhere, the activity was only slightly lowered by this treatment.

The effect of chlorine on the Fischer-Tropsch synthesis over iron and cobalt catalysts was investigated by Barrault[237] who reported a significant increase in the selectivity for light olefins, a marked drop in methane formation and a dramatic decrease in activity.

Hammer *et al.*[314,315] found that a weak poisoning of iron catalysts by halogen ions suppresses secondary hydrogenation of olefins, resulting in an increased olefin selectivity. A noteworthy feature is the strong influence exerted on the selectivity, while the activity remains essentially constant (Table 6). The higher electron affinity of chlorine clearly results in a stronger effect than is the case for bromine.

TABLE 6 Influence of Cl^- and Br^- ions on the selectivity of K-promoted iron catalysts at constant potassium concentration[314]

Promoter	Mass % in exit gas				CO conversion %
	CH_4	C_2H_4	C_3H_6	C_4H_8	
None	26,2	12,8	24,0	13,2	42,4
K_2CO_3	31,4	17,5	15,1	9,0	64,8
KCl	20,5	23,7	25,6	23,3	65,2
KBr	25,1	21,9	24,9	18,0	64,9

4.4 Support interactions

The type of support used has a profound influence on the catalytic properties of supported catalysts[316]. The three different categories of chemisorption support effects influence the catalytic behaviour of metals in as many ways. The first type was subdivided above into a support basicity effect and a support dispersion effect. The second type was the Schwab effect and the third type involved SMSI. These four effects will now be considered briefly in terms of the selectivity requirements. Again, it is emphasized that the catalytic behaviour is always governed by the combination of all relevant effects. In a recent study of metal-support effects in ruthenium supported on any of nine different oxides, Goodwin *et al.*[317] concluded that the catalytic properties of a metal can be greatly modified by a support. Depending on the support used, the activity of ruthenium could be varied by as much as two orders of magnitude, the olefin selectivity ranged from 0 % to 90 % of the C_2 to C_4 hydrocarbons, and the methane selectivity varied from 21 to 98 mass %. However, they were unable to correlate the catalytic behaviour with any one particular property of the supports and suggested that it is very likely that combinations of properties may be more important in determining the catalytic behaviour than any single property.

4.4.1 Support basicity effect

This effect involves support-induced changes in the electron work function of the catalyst. The catalytic consequences of this effect have been investigated by Leith[197,198] in a study of the role of basic or electron donor sites in the adsorptive and catalytic properties of zeolite-supported ruthenium catalysts for Fischer-Tropsch synthesis. He reports an increased olefin selectivity with higher basicity of the support.

A selectivity-dependence on the support basicity was also demonstrated by Ichikawa[318-322]. He prepared catalysts by the pyrolysis of rhodium carbonyl clusters on various oxide supports. On acidic oxide supports, such as silica and alumina, methanation was the only significant reaction. In contrast, on basic supports, such as ZnO and MgO, methanol was produced with a selectivity exceeding 90 %.

These results could be ascribed to the influence of the electron work function on the chemisorption behaviour of CO and H_2 as discussed before. Basic oxides have higher Fermi levels than other supports and thus greater electron-donating capabilities. These oxides lower the electron work function of rhodium and effect a stronger metal-hydrogen bonding, thus decreasing hydrogenation activity. If a hydrogenation step is assumed to be involved in carbon monoxide dissociation (it has been suggested that a dissociative reduction initiates hydrocarbon synthesis[323]), an increase in the amount of undissociated carbon monoxide on the surface is indicated. This will lead to the formation of more oxygen-containing products. The metal-carbon bond is strong, so that chain growth is suppressed and single-carbon species are the most likely product. Under such conditions the formation of methanol will prevail.

On acidic supports, the opposite is the case and the electron work function of rhodium is increased, resulting in strong hydrogenation activity and a short surface life for carbonaceous entities. The formation of methane is therefore expected to be the main reaction.

Amphoteric supports, such as TiO_2, ZrO_2 and La_2O_3, showed an intermediate picture. Carbon-metal bonding as well as hydrogenation activity were not very strong, so that the formation of single-carbon species was rather limited and only minor amounts of methane and methanol were produced. Apparently only limited chain growth occurred and the hydrogenation activity was too weak for the formation of hydrocarbons, so that ethanol was the major product.

This explanation is to some extent confirmed by the results of Katzer *et al.*[137] who considered the mechanism of carbon monoxide hydrogenation over rhodium supported on basic oxides. They concluded that the lowered electron work function of rhodium causes the amount of undissociated carbon monoxide on the surface to increase. As methanol formation on rhodium occurs by a non-dissociative mechanism[324], its rate of production is enhanced.

Zeolite-supported Co catalysts have received a fair amount of attention. It appears that the catalytic properties of such systems differ, depending on the type of zeolite used. A comparative study of Co catalysts supported on ZSM-5, silicalite and mordenite[325] showed that the activity decreased slightly in the order ZSM-5 > mordenite > silicalite. The chain-growth probability was found to increase in the order ZSM-5 < mordenite < silicalite. The silicalite-supported catalyst showed a markedly suppressed methane formation and a high selectivity for lower alkenes. The metal-support interaction was found to correlate well with the basicity of the zeolite support.

It is clear that the support basicity effect, in line with the catalyst basicity effect, satisfies only one selectivity requirement, that of the bond strength. In consequence, the limitations of the catalyst basicity effect are applicable here.

4.4.2 Support dispersion effect

A support-induced dispersion effect, manifested by a support-dependent suppression of the amount of hydrogen that is chemisorbed, has been demonstrated for supported iron catalysts by McVicker and Vannice[199]. They reported a higher suppression for alumina-supported than for silica-supported small iron particles. This is in line with the higher suppression of hydrogen chemisorption reported for supports with a higher metal dispersion[199], as well as for supports with a stronger Lewis acid character[172,173]. The different particle sizes associated with the dispersion effect may result in rather drastic changes in the catalytic behaviour when the particle size drops below ca 5 nm.

It has been reported[199] that under certain conditions silica-supported iron catalysts exhibit a high methanation rate and a virtual absence of olefins in the product spectrum. In contrast, under identical conditions a much lower methane activity and a more pronounced olefin selectivity were observed for the same catalyst supported on alumina.

Similar results have been reported by Bartholomew *et al.*[326,327] for silica- and alumina-supported nickel catalysts. A hydrogen suppression on alumina-supported cobalt relative to silica-supported cobalt has been reported by Zowtiak *et al.*[328], indicating the same effect for cobalt. The higher dispersion effect of alumina support may perhaps be ascribed to its higher Lewis acidity which causes a stronger interaction between the support and the metal.

The support basicity effect would predict the opposite catalytic effect, based on the differences in Lewis acidities of the two supports. This indicates that, in this case, the dispersion effect dominates.

Further evidence of the dispersion effect may be found in a study reported by Hugues *et al.*[262], who used iron carbonyl-derived catalysts on various supports. They found a drastic support-dependence of the mass selectivity in Fischer-Tropsch experiments. Low loadings of iron on alumina result in non-Schulz-Flory-type product distributions with a maximum at C_2 (Table 7). The same catalyst, supported on silica, shows a much broader product distribution, indicating the operation of a dispersion effect with the alumina-supported catalyst. The silica-supported catalyst had a lower metal loading, which is normally associated with higher dispersions. However, the product distributions obtained indicate that the influence of the support is the more important.

TABLE 7 Activities and selectivities of iron catalysts in the Fischer-Tropsch synthesis as a function of the support[262]

Support	Percentage olefins	Product distribution (mass %) C_1	C_2	C_3	C_4	C_{5+}
Al_2O_3	57	18,8	72,7	7,4	1,1	-
SiO_2	50	22,0	17,5	22,0	19,5	19,0
La_2O_3	53	29,0	20,0	22,0	17,5	11,5
MgO	60	21.0	17,0	24,0	29,0	9,0

Several studies have indicated that graphite as a support promotes the formation of lower olefins[329,330]. However, the support inherently possesses a strong tendency to form graphitic carbon in the form of fibres. A very active iron carbide phase interacting with the carbon support is thought to be responsible for these features.

Iron supported on silica or alumina aerogels is claimed to have unusual catalytic properties[331]. When the iron is initially in the maximum oxidation state, and is not reduced prior to the synthesis reaction, the catalytic activity has been found to be much higher than with prereduced catalysts.

In a study of supported palladium catalysts, Hicks and Bell[332] discovered that certain supports affect the metal morphology, expressed in terms of the distribution of Pd(100) and Pd(111) planes. On silica supports, 90 % of the surface was found to consist of Pd(100) planes and the other 10 % of Pd(111) planes. This distribution did not change with Pd mass % loading.

In contrast, the crystalline morphology of Pd/La_2O_3 catalysts changes with Pd loading. At low mass loadings an almost exclusive exposure of Pd(100) planes is observed, whereas mainly Pd(111) planes are exposed at high mass loadings. Since the coordination of carbon monoxide differs with different planes, coordination-dependent catalytic properties may be expected. Indeed, the rate of methane formation was found to be higher on Pd(111) planes than on Pd(100) planes. A similar conclusion was arrived at by Ichikawa *et al.*[333] from a study of the influence of the dispersion of Pd on the methanation activity of alumina-supported Pd.

An in-depth study of the relation between the metal morphology and catalytic behaviour of supported platinum catalysts[334–337] showed, *inter alia*, that the thermal conditions employed in catalyst preparation affect the structure-sensitive behaviour of alumina-supported catalysts. This was not so for silica-supported systems. This finding again stresses the importance of the influence certain supports can have on the catalyst morphology.

In line with the catalyst dispersion effect, both the bond strength and the ensemble selectivity requirements are met by the support dispersion effect. In addition, the coordination requirement may or may not be met. The potential disadvantage of low stabilities of dispersions, discussed under the catalyst dispersion effect, is perhaps less applicable. Support interactions may stabilize high dispersions.

4.4.3 Schwab effect

Charge-transfer-dependent chemisorption behaviour has some interesting catalytic consequences. An increase in catalyst basicity, as evidenced by excess electron density on the metal crystallites, leads to an unexpectedly strong increase in the hydrogenation activity of platinum L zeolites[201]. A combined decrease in the catalyst basicity and in the dispersion effect, leading to electron deficiency of the metal crystallites, has also been shown to result in a strongly increased hydrogenation activity[202,204].

The Schwab effect could perhaps be considered as a variation of type (i) effects (support basicity and support dispersion), modified by the field of the zeolite. The effect meets the selectivity requirements of bond strength and ensemble and possibly even that of coordination.

4.4.4 Strong metal support interaction (SMSI) effects

Research on the practical use of SMSI in synthesis gas chemistry is gaining momentum since the catalytic activity and olefin selectivity, which are observed to increase with increasing metal support interaction[175,338,339], may reach unusually high values. In order to combine these effects with those observed for cluster-derived catalysts, Santos *et al.*[340] investigated the Fe/TiO_2 system in ammonia synthesis. To separate the SMSI effect from a possible dispersion effect (or apparent metal-support effects as characterized by supported small metal particles which are likely to have a greater portion of their atoms in contact with and influenced by the support than is the case with larger particles of lower dispersion[341]), the dispersion was varied by using different techniques for supporting iron particles, such as aqueous incipient wetness impregnation, non-aqueous impregnation and thermal decomposition of iron pentacarbonyl.

In agreement with other reports, only the last technique produced metallic iron particles smaller than 10 nm. Mössbauer spectroscopic studies of the decomposition of the carbonyl on titania at 380 K showed the formation of Fe_{2+} and Fe^{o}, e.g. subcarbonyl species. In line with normal SMSI effects, these species were reduced to metallic iron on reductive decarbonylation with hydrogen at 700 K. The catalytic properties of this material in ammonia synthesis did not differ from those of iron catalysts on other supports. However, reduction at 800 K resulted in a catalyst with a higher activation energy in ammonia synthesis. In addition, the ammonia partial pressure-dependence of the activity increased.

These results indicate that the SMSI state is only induced at reduction temperatures of 800 K or higher. It is of interest to note that these phenomena were observed for iron particles as large as 20 nm. As the Mössbauer spectra of the iron particles showed only "normal" metallic iron, the metal-support interaction is restricted to the surface of metallic iron particles. A further conclusion from this study is that the SMSI effect and the small particle effect are indeed independent.

The reported loss of sorptive capacity of most metals for hydrogen and carbon monoxide, characteristic of SMSI effects, suggests that these effects would be accompanied by a loss of catalytic activity. Such a loss has indeed been reported for strong hydrogenation-demanding reactions such as the hydrogenolysis of ethane[342] or n-hexane[343,344] and the hydrogenation of benzene[345,346].

A less strong hydrogenation-demanding reaction, such as the Fischer-Tropsch synthesis, may be expected to show a smaller *decrease* in activity. In fact, an *increase* in activity as a result of SMSI is generally reported for many transition metals[175,212,347-350]. The origin of this increase is still unclear, but it has been suggested that the support plays a direct role in the hydrogenation of carbon monoxide[212].

As a result of the reduced hydrogenation activity, the formation of methane and paraffins is largely suppressed. The lower heat of adsorption of carbon monoxide is probably responsible for a shorter surface life of carbonaceous species and a resultant short-chain hydrocarbon product. This type of catalytic behaviour under SMSI conditions is generally reported for transition metals.

Barrault and Renard[351] studied SMSI effects of iron with various supports. They observed SMSI effects at temperatures below the reported minimum of 800 K. Titania, a support that induces olefin selectivity in nickel, was found to have the opposite effect on iron (Table 8). Alumina was a better support for the achievement of high olefin selectivities and manganous oxide was even better. In the case of titania-supported iron, high-temperature reduction decreases the overall activity, increases the propensity for forming shorter-chain hydrocarbons, including methane, and increases the olefin selectivity. Manganous-oxide-supported iron catalysts show the opposite behaviour. High-temperature reduction results in a very substantial increase in overall activity, little change in the mass selectivity and a decrease in the function (olefin) selectivity. Alumina-supported iron catalysts exhibited an intermediate character. The activity of the manganous-oxide-supported iron catalyst was high. After thermal activation at 790 K in hydrogen, it displayed an activity about double that reported for commercial operation with fused-iron catalysts[352].

Nickel has attracted most interest in this respect. Catalytic SMSI effects have been studied with supports such as silica[212,326,327], alumina[326,327], zirconia[175] and titania[212,326,327]. SMSI effects were evident in titania, zirconia and alumina-supported nickel and to a lesser extent in very well-dispersed silica-supported nickel. In all cases the overall activity increased in proportion to the magnitude of the SMSI effect. The specific activity of the titania-supported nickel catalyst was 50 times higher than that of the silica-supported catalyst. Similar support influences were observed for the selective formation of hydrocarbons with a lower molar mass. The formation of methane was suppressed and all supports except titania induced an increase in olefin selectivity.

TABLE 8 Influence of support on the catalytic behaviour of iron in the hydrogenation of carbon monoxide[351]

Support	TiO_2		Al_2O_3		MnO	
Iron loading (mass %)	4,1	4,1	5,0	5,0	4,3	4,3
Reduction treatment in hydrogen	670 K 10 h	790 K 10 h	720 K 10 h	790 K 10 h	720 K 10 h	790 K 10 h
Activity: Mole CO h^{-1} g^{-1}Fe (x 10^3)	6,3	4,4	4,2	3,0	2,8	10,0
Selectivity (%):						
C_1	19,0	25,0	12,0	19,0	3,5	3,8
$C_2^{=}$	1,5	2,9	8,8	5,6	11,5	7,5
C_2^{-}	15,5	17,5	3,6	13,4	-	3,8
$C_3^{=}$	4,1	8,0	7,0	8,0	6,5	6,5
C_3^{-}	8,9	9,0	0,5	1,6	-	0,6
$C_4^{=}$	1,0	0,7	3,5	4,1	4,0	4,6
C_4	7,0	4,0	2,2	1,4	-	2,1
Olefin selectivity	17,0	27,5	77,0	53,0	100	74,0

Burch and Flambard[212] report that titania-supported nickel catalysts, which are thermally activated at 823 K, show an activity in the hydrogenolysis of ethane that is three orders of magnitude higher than that of similar catalysts[342] activated at 773 K. This suggests that the SMSI state for this catalyst system is not initiated at temperatures below 823 K and illustrates again the enormous increase in activity that may result from SMSI.

In contrast, Anderson *et al.*[353] report that inducement of the SMSI state in titania-supported Ni, Pt or Ir catalysts does not result in higher activity in the Fischer-Tropsch synthesis. These catalysts already have a high activity which is also observed after low-temperature reduction. Since the same metals on different supports have a lower activity, the nature of the support rather than the SMSI state itself is thought to be responsible. Similar observations are reported by Yang and Goodwin[354].

Kugler[355] studied the catalytic effects of SMSI on ruthenium supported on titania, alumina and manganese oxide. The formation of methane declined with ruthenium catalysts on supports in the sequence alumina < titania < manganese oxide. The olefin selectivity increased in the same order. The selectivity for the formation of hydrocarbons in the range C_2 to C_4 with ruthenium catalysts on the last two supports is above the maximum predicted by Schulz-Flory statistics.

A similar investigation by Vannice and Garten[356] showed the same effect of alumina and titania on ruthenium. As was to be expected, the support on which SMSI effects are less likely to occur, silica, induced a high methane selectivity and a low olefin selectivity and was only surpassed in this respect by carbon-supported ruthenium. In addition, this investigation showed an effect of pressure. The catalytic activity, methane selectivity and the propensity for producing hydrocarbons and paraffins of a higher molar mass all increased with pressure. This suggests that at higher pressures the availability of active surface hydrogen is enhanced, an observation also reported for iron-cobalt systems[307].

Mériaudeau *et al.*[323,357] studied the SMSI effects of rhodium with titania, alumina, silica and magnesia. The carriers were impregnated with ca 3 % rhodium to yield metal crystallite sizes of 25 to 35 (no units were given) at a dispersion of 0,25 to 0,98. The highest dispersion was observed for silica, and for alumina (which normally induces high dispersions) the value was 0,66. This indicates that dispersion effects are unlikely to occur and SMSI may be studied without masking by other effects. Fischer-Tropsch synthesis at atmospheric pressure and 570 K showed a rapid deactivation (ca 60 % in 4 h) of the titania-supported catalyst. For this reason the different catalysts were compared under steady-state conditions, i.e. after 2 or 3 h on stream. A clear SMSI effect was observed for the titania-supported rhodium catalyst (Table 9).

TABLE 9 Catalytic behaviour of supported rhodium catalysts in the hydrogenation of carbon monoxide[323]

Catalyst	Products					Rate of C_1 formation
	C_1	$C_2^=$	C_2	C_3	C_{4+}	(mmol h^{-1} g^{-1} Rh)
Rh/TiO_2 red. 773 K	20	11	2	25	42	40
Rh/TiO_2 red. 573 K	33	9,5	2,5	25	30	60
Rh/Al_2O_3	53	3	11	21	12	230
Rh/MgO	76	2	8	10,5	3,5	14
Rh/SiO_2	88	1,5	5,5	3	2	115

The catalytic properties follow the same trend as the reduction temperature[323] and it was concluded that the origin of catalytic SMSI effects is associated with the surface mobility of carbidic intermediates. Low surface mobility would result in the rapid formation of methane and high surface mobility would favour CH_x insertion into a metal-carbon bond. The SMSI was thought to be responsible for a lowering of the Rh-C bond strength, resulting in a higher mobility of the carbidic intermediates on the surface.

Wang *et al.*[358] investigated palladium and observed that methane was the only product formed. The activity of this reaction was found to be independent of Pd crystallite size, but showed a 200-fold variation, depending on the support used. The most active catalyst was that supported on titania and the lowest activity was found for silica-supported Pd.

The SMSI effects of platinum were studied by Vannice *et al.*[356,359] and Mériaudeau *et al.*[357]. Again the catalytic behaviour was found to be highly support-dependent. Turnover frequencies on platinum varied more than 100-fold as the support material was changed. The highest activity was found on titania and the lowest on silica, in agreement with the results for supported nickel catalysts reported by Bruce and Mathews[175].

Titania-supported iridium can also be brought into the SMSI state[357] as evidenced by the change in catalytic properties after high-temperature reduction.

In contrast to the reports indicating that high-temperature reduction is needed to initiate the SMSI state, other reports give the impression that in certain cases such treatment is not necessary. However, it is not clear whether an SMSI effect is being encountered in these cases or whether another effect is responsible.

Kuznetsov *et al.*[350] prepared cluster-derived iron catalysts, together with bi-metallic catalysts prepared from mixed iron-manganese clusters. Supported on alumina, silica, magnesia, titania and zirconia, these catalysts showed some interesting features in the Fischer-Tropsch synthesis (Table 10), resulting from a combination of support basicity, dispersion and SMSI effects. The high overall activity of the magnesia-supported catalysts and the low methanation activity of the titania and zirconia-supported mixed-cluster-derived catalysts are particularly noteworthy since these catalysts are prepared from the cluster by pyrolysis in vacuum at a temperature of only 523 K.

Following Santos *et al.*[340], titania-supported cluster-derived iron catalysts are not expected to show any SMSI effect when reduced at temperatures below 800 K. The low methanation activity of the mixed cluster, relative to the methanation activity of $Fe_3(CO)_{12}$ on the various supports, has been ascribed to a basicity effect arising from the presence of manganese. The large differences in activity as a function of the nature of the support are worth noting and illustrate again the major role of this parameter in determining catalytic properties.

In a study of the influence of potassium on supported ruthenium catalysts, Yang and Goodwin[354] found that basicity effects and SMSI effects are complementary. This shows that certain catalytic characteristics of SMSI can even be enhanced by means of the judicious use of promoters.

TABLE 10 Catalytic activity[350] of various catalysts in CO hydrogenation at 523 K

Catalyst	Activity*	Product (mass %)		Percentage olefins in
		C_1	$C_2 + C_3$	$C_2 + C_3$
Fe_2Mn/Al_2O_3	2,3	12	39	96
Fe_2Mn/SiO_2	17,4	10	28	94
Fe_2Mn/MgO	11,4	33	33	93
Fe_2Mn/TiO_2	5,0	5	27	84
Fe_2Mn/ZrO_2	0,6	5	34	98
Fe/Al_2O_3	2,9	27	34	96
Fe/SiO_2	1,1	37	40	72
Fe/MgO	16,2	26	30	83
Fe/TiO_2	0,1	32	34	85
Fe/ZrO_2	2,8	48	25	93

* in mol CO x 10^5 grat. Fe^{-1} s^{-1}. The activity was determined after 20 h on stream.

In agreement with the conclusions drawn for the other types of support interaction, SMSI effects meet the selectivity requirements of both the bond-strength and ensemble type. From the various studies it is clear that the formation of lower olefins and high catalytic activity are favoured by SMSI effects. However, three problem areas may be identified.

The SMSI effect of supports is different for different metals. Production of light olefins over iron catalysts is best achieved by using manganous oxide supports, over nickel catalysts by using zirconia and over ruthenium catalysts by using titania. The reason for these differences is unclear and much more research is needed to understand this support behaviour so that it may be used to best advantage.

Another important aspect is the effect of pressure, i.e. there is a decrease of SMSI effects with increasing pressure. This is similar to the synergistic effect found for the iron-cobalt system, which also disappears at elevated pressures[307]. Chemisorption suppression of carbon monoxide is reported to be maintained at elevated pressures[206]. The position for hydrogen is unclear, but it seems likely that suppression of hydrogen adsorption is not well maintained at higher pressures.

Furthermore, the chemisorption of hydrogen becomes an activated process if the metal surface undergoes demetallization by dispersion. A similar effect as a function of pressure may perhaps result from SMSI demetallization. As very little is known about the nature of SMSI, there may be many reasons for the effect of pressure.

The industrial application of catalysts exhibiting SMSI would involve elevated pressures, and thus there is a need for research into SMSI under industrial conditions.. A further question is the maintenance of activity under such conditions since insufficient data are available on the stability of SMSI effects in catalysts.

A third area of uncertainty is the initiation of the SMSI state. There have been many conflicting reports on the minimum temperature needed for initiation and the catalytic effect of such treatment. Thus far it seems that this varies according to the catalytic metal and support in question and more research in this important area is certainly warranted.

Finally, as discussed in Section 3.2.4, the SMSI state is known to be easily destroyed by oxygen ions[213]. Therefore, the stability of the SMSI state with respect to reaction products such as H_2O and CO_2 is questionable, indicating another important gap in our knowledge.

4.4.5 Effect of matrix supports

Kölbel and Tillmitz[360] were among the first to report a specific catalytic behaviour of iron when it is embedded in a matrix of manganese oxide. They claim that such catalysts (Mn:Fe = 9:1) have a high selectivity for C_2 to C_4 olefins and produce methane in trace amounts only. Schulz *et al.*[361,362] optimized this catalytic system and, by an appropriate choice of Mn:Fe ratio and operating conditions, obtained an olefin selectivity of ca 85 % of the hydrocarbons in the C_2 to C_{15} fraction. Barrault and Renard[363-364] also studied the Fe/MnO system and their results support these observations. Similar results are reported for vanadium oxide as a matrix support[365,366].

Results observed with manganese-oxide-supported cobalt and nickel-cobalt systems[367] show similar trends. In particular the nickel-cobalt systems were stable catalysts, having improved hydrocarbon yields while still retaining good olefin selectivity.

Various reasons have been suggested for the specific behaviour of matrix catalysts, ranging from geometric effects to electronic effects such as basicity, dispersion and SMSI. Studies of the surface structure of iron/manganese oxide catalysts[238,368,369] show that under synthesis conditions the surface consists of various iron oxides (magnetite and haematite), various iron carbides and manganous oxide. Certain phase changes were observed, depending on the reduction temperature employed. Chemisorption of carbon monoxide as well as its dissociation are substantially hindered by the presence of manganous oxide[238,370], and chemisorption of hydrogen is suppressed to an even greater extent[238]. This might indicate that SMSI effects play a role.

It has been reported[355] that Ir/MnO chemisorbs less than one hydrogen atom per 100 surface atoms, suggesting that the strongest metal-support interaction may occur with manganous oxide. Since both Fe/MnO[364] and Co/MnO[367] have been reported to display a very pronounced SMSI effect in both their chemisorption and catalytic behaviours[364], SMSI is likely to be one of the main reasons for the catalytic behaviour of all matrix catalysts.

4.4.6 Geometric support effects

Although the effects discussed above play an important role in support interactions, effects of a different geometric nature may also influence the catalytic behaviour of supported catalysts. One example is the stabilization of dispersions on supports by means of an additive. Since there are many reports of this type of effect in the literature, only one example will be mentioned briefly to illustrate the effect. In the case of silica-supported rhodium catalysts, the addition of ZrO_2 and TiO_2 to the support was reported to prevent aggregation of rhodium metal supported on the ionic surface[320].

4.5 Demetallization of transition metals

It has been demonstrated that manipulation of basicity leads to various changes in catalytic behaviour. However, these changes are not very specific. A certain desired change is always accompanied by many other, often unwanted, changes. For example, if the production of light olefins is to be optimized, an increase in the catalyst basicity will certainly result in increased olefin selectivity. However, the average chain length will also increase. This disadvantageous effect does not occur when an increase in olefin selectivity is effected by demetallization of the catalyst.

In all of the three different types of demetallization considered earlier, i.e. the dispersion effect, electron withdrawal ligand effect and strong metal-support interaction effect, the methane selectivity and the average molar mass of products decreased considerably, but the olefin selectivity increased substantially. Demetallization by the dispersion or electron withdrawal ligand effect results in decreased catalytic activity. This is not the case with the strong metal-support interaction effect, in which the activity increases with demetallization. However, in certain cases this activity may be too high. The exothermic nature of the Fischer-Tropsch synthesis may require that the activity be restricted. A disadvantage of high dispersions is the difficulty of maintaining them under synthesis conditions.

The use of the three different types of demetallization has both advantages and disadvantages. In optimizing the synthesis for light olefins, all requirements are met by demetallization. Catalyst stability and synthesis activity may then be controlled by appropriate combinations of the different types of demetallization. In addition, optional use of the catalyst basicity effect may bring about controlled shifts in the Fermi level of the catalyst to higher or lower values, and thus the average chain length of the products can be controlled.

Reports in the literature indicate that combinations of effects are sought for specific catalytic functions. Solid solutions of Ni or Co in MgO, which may be expected to exhibit a combination of dispersion and support effects, have been used to control selectivity in carbon monoxide hydrogenation[371]. Another example may be found in the $Fe_xSi_yC_z$ materials produced by CO_2 laser pyrolysis for the selective production of lower olefins from syngas[372,373]. However, it has been suggested that these catalysts are much less selective than is claimed, because of the analytical procedures followed[374]. A more successful attempt at combining the influence of the various effects in the design of olefin-selective catalysts has been reported by the author who used complex-derived $Fe_xO_yC_z$ systems[375].

4.6 Geometric effects

As shown in the consideration of the selectivity requirements, geometric effects never occur on their own but are always accompanied by electronic effects. For example, the geometric dispersion effect is associated with electronic demetallization. The associated electronic effect may or may not affect the specific reactions desired. It is, therefore, always difficult to identify a geometric effect. However, some structural promoters have received so much attention that their properties are known to some extent.

Alumina is often included in the catalyst formulation for a variety of reasons. It has been demonstrated to induce high dispersions in the catalyst and it also improves the temperature stability of the catalyst by inhibiting crystallite growth. With regard to its pore structure, it has been suggested that the residence time of the products formed in the pores of alumina may be sufficiently long to allow cracking to take place, thereby reducing the average chain-length of the products[272].

It has long been known in the "art of catalyst formulation" that silica is a 'separator', and for this reason it is often included in the catalyst formulation. Another well-known structural promoter is magnesia. It is often included in the catalyst formulation to give the final catalyst increased mechanical strength.

It has been suggested recently[376] that the nature of K-promotion is more geometric than electronic. The promotion effect is explained in terms of site blocking by the alkali adatoms.

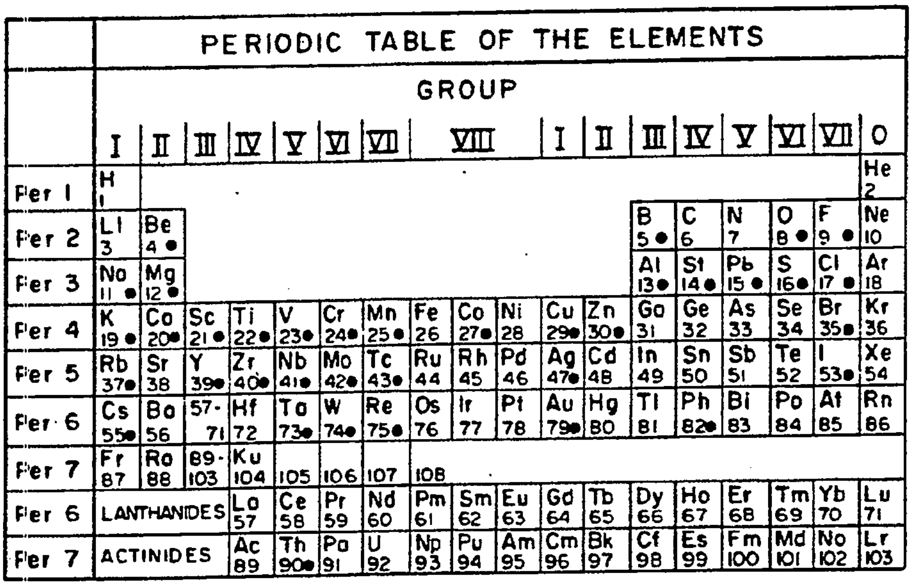
4.7 Promoters claimed to increase olefin selectivity in iron catalysts

Unfortunately, the nature of the promotion is often either not known, or not disclosed for commercial reasons. A survey of the substances that are claimed to increase the olefin selectivity of iron catalysts has been reported by Kieffer[30]. All these substances, as well as those reported after Kieffer's thesis, are grouped in the form of a periodic table in Fig. 30.

The results of this survey will be reported in the order of the periodic table. It should be borne in mind that, for the reasons given above, the nature of the promotion effect is in most cases not disclosed and, therefore, all elements claimed to promote olefin selectivity in iron catalysts will be discussed briefly, regardless of the type of promotion.

Group 1A of the periodic table represents the best-known promoters of the Fischer-Tropsch synthesis. As discussed earlier, their promotion effect has been referred to as the basicity effect for historic reasons. The catalytic

FIGURE 30 Elements that have been reported to increase the olefin selectivity of iron catalysts in the Fischer-Tropsch synthesis



PERIODIC TABLE OF THE ELEMENTS

GROUP

	I	II	III	IV	V	VI	VII	VIII			I	II	III	IV	V	VI	VII	0
Per 1	H 1																	He 2
Per 2	Li 3	Be 4 ●											B 5 ●	C 6	N 7	O 8 ●	F 9 ●	Ne 10
Per 3	Na 11 ●	Mg 12 ●											Al 13 ●	Si 14 ●	Pb 15 ●	S 16 ●	Cl 17 ●	Ar 18
Per 4	K 19 ●	Ca 20 ●	Sc 21 ●	Ti 22 ●	V 23 ●	Cr 24 ●	Mn 25 ●	Fe 26	Co 27 ●	Ni 28	Cu 29 ●	Zn 30 ●	Ga 31	Ge 32	As 33	Se 34	Br 35 ●	Kr 36
Per 5	Rb 37 ●	Sr 38	Y 39 ●	Zr 40 ●	Nb 41 ●	Mo 42 ●	Tc 43 ●	Ru 44	Rh 45	Pd 46	Ag 47 ●	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53 ●	Xe 54
Per 6	Cs 55 ●	Ba 56	57-71	Hf 72	Ta 73 ●	W 74 ●	Re 75 ●	Os 76	Ir 77	Pt 78	Au 79 ●	Hg 80	Tl 81	Pb 82 ●	Bi 83	Po 84	At 85	Rn 86
Per 7	Fr 87	Ra 88	89-103	Ku 104	105	106	107	108										
Per 6	LANTHANIDES			La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
Per 7	ACTINIDES			Ac 89	Th 90 ●	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

results of this effect were realized as early as 1929[377]. The nature of the basicity effect has, to some extent, only recently been understood, although it is still the subject of considerable dispute. The basicity effect, as it is understood at present, involves interactions that are essentially of an electronic nature. However, it is more than likely that a geometric effect is also involved. The effect of potassium has received much attention. Dry investigated this effect extensively[36,38,152,378–382]. However, all Group IA elements display this effect. Schneidt[383] and Rähse[384] report that in the group Na, K, Rb and Cs the promoter effect at equimolar loadings is virtually the same. In contrast, Rieck and Bell[159] found that the methanation activity of Pd/SiO_2 systems was reduced by alkali promotion in the order unpromoted > Li > Na > U > Rb > Cs.

Group IIA promoters have been investigated by Friedrichs[385] and by Hammer and Friedrichs[386] who report that there is an increasing olefin promotion effect in the sequence Ca < Mg < Be. The olefinic product was claimed to be mainly ethene with a lesser amount of propene at ca 10 % of the ethene concentration. The olefin selectivity increases with pressure. Calcium has also been reported to decrease the production of carbon dioxide[166]. The same authors, Yang and Oblad, did not observe any substantial change in the olefin selectivity when iron was promoted with magnesium. The main effect of this promoter seemed to be an improvement of the mechanical strength of iron catalysts[8].

There are no recent reports on the olefin promotion of Group IIIB metals. The only available data[8] are rather old and indicate that scandium and yttrium show some effect.

Group IVB metals have received somewhat more attention. The company Ruhrchemie[387–389] in particular studied these metals and found thorium and titanium quite useful. The uses of titanium were confirmed by Vielstich and Kitzelmann[293].

Of the Group VB metals, vanadium has received the most attention[166,293,365,366,390,391]. Being associated with a basic oxide, its function is probably similar to that of Mn.

All three Group VIB metals have been investigated. Although the use of chromium has been generally reported[123,167,293,314,392], the only relevant information given is that the oxygenate selectivity is somewhat enhanced. This suggests a basicity effect, although the role of this metal in the synthesis reaction is not at all clear. The same could be said about the influence of molybdenum[392,393] and tungsten promoters[21,392–394].

Of the Group VIIB metals, only manganese has received much attention[40,166,167,293,392,395–399]. The effect of manganese has been discussed before at length and does not need to be repeated.

Of the Group VIII metals, cobalt is noted for its synergistic effect with iron. Amelse *et al.*[310] and Vielstich and Kitzelman[293] show that alloying the two metals results in a catalytic activity that is higher than that of the two constituents, but has an olefin selectivity characteristic of iron ore at even higher levels. This synergistic effect exists only at atmospheric pressure and disappears at elevated pressures[307]. A special feature of this alloy is that it does not undergo carburization. Rhodium is occasionally mentioned in the literature[400,401] but its function is not quite clear. The other metals of this Group often have basicity effects, as may be expected from their basicity relative to that of iron.

Group IB metals appear to have little effect on the olefin selectivity. Copper is well known for its enhancement of the catalyst reducibility[8]. Its influence on the hydrocarbon distribution is very slight. The olefin selectivity and the methanation activity both decrease a little and the oxygenate content is somewhat enhanced[166], as may be expected from a metal with a lower basicity.

Silver is seldom reported in this connection. It seems to have an influence similar to that of copper[393]. Hammer *et al.*[315] claim that it decreases the methane selectivity and Halachev and Ruckenstein[402] suggest that copper and silver change mainly the net atomic population (i.e. the localized electrons around each atom) and slightly vary the bond population among nearby atoms. This results in increased electron density on the surfaces. Of course this is nothing but a basicity effect obtained from metals with a lower basicity. The electronic effect of copper on the electron redistribution is suggested to be stronger than that of silver, as may be expected from the values of the electron work functions. Gold is reported to decrease the rate of carbon dioxide formation[295].

Of the Group IIB metals, zinc is a well-known promoter. It is often included in catalyst formulations, but its action is never explained. One of the few suggestions offered is that of Kieffer[30] who claims that zinc retards the effect of poisons such as sulphur.

Of the Group IIIA elements, only boron is occasionally mentioned[393], but again it is not clear why it is used in the synthesis of olefins.

In Group IVA, silicon in particular is a well-known promoter for the olefin synthesis. It is usually added in the oxide form as a support, but it is reported to have a beneficial effect in the elemental form as well[372,373]. Lead is less generally known, but it is claimed to have a beneficial influence[403]. In the case of both elements, however, there are no sound explanations as to the origin of the observed effect.

Of the Group VIA elements, only sulphur has received a great deal of attention[146]. In 1928 a patent was issued to IG Farbenindustrie[377] in which increased olefin selectivity as a result of sulphur promotion was disclosed. In 1932 Fischer reported that sulphur promotes the formation of short-chain hydrocarbons. In their extensive review on the poisoning effect of sulphur, Madon and Shaw[404] point out that in certain cases beneficial promotional effects, rather than simple catalyst deactivation, have been observed. From a study involving modern surface techniques, Wentrcek *et al.*[405] conclude that sulphur initiates the formation of new binding states for carbon monoxide and decreases the affinity of carbon monoxide for iron.

Kishi and Roberts[115] report that sulphur decreases the capacity of the catalyst for dissociating carbon monoxide. Enikew and Krylova[406] suggest that sulphur raises the work function of the surface. This results in a weakening of the iron-carbon bond. If this happens in a controlled manner, the sticking probability, and hence the propagation probability, will be small enough to allow the production of hydrocarbons with the desired short-chain length. This was confirmed by Lehmann *et al.*[407].

A smaller sticking probability usually results in decreased surface coverage by carbon monoxide. This effect was observed by Zein El Deen *et al.*[395], Rewich and Wise[408] and Rhodin and Brucker[140] who, in addition, noted a weakening of the strength of adsorption of carbon monoxide. If the iron-carbon bond is weakened, then the formation of carbonaceous surface deposits must be retarded, as evidenced by observations made by Kieffer[30], Van Dijk[106] and Swift *et al.*[92]. Layng[409] observed that sulphur promotion decreased the production of carbon dioxide. The many reports on sulphur promotion are, of course, readily explained by an electron withdrawal ligand effect.

The influence of Group VIIA elements, the halogens, has been investigated by Hammer *et al.*[314,315] and by Barrault[237], who all report a catalytic behaviour characteristic of an electron withdrawal ligand effect.

5. PROCESSES FOR THE PRODUCTION OF LOWER OLEFINS

5.1 Fischer-Tropsch-based processes

5.1.1 The Synthol process

The Synthol process, as used commercially by SASOL in South Africa, produces a highly olefinic product. Although the process is geared towards the production of transportation fuels, the C_1 to C_4 fraction of the product consists of 55 % olefins, the C_5 to C_{10} fraction contains 70 % olefins and the C_{11} to C_{14} fraction contains 60 % olefins. The total product contains 24 % C_2 to C_4 olefins[410]. It is not unreasonable to expect that this figure would rise considerably if the process were geared towards the production of lower olefins.

5.1.2 Liquid-phase synthesis

Reports on the hydrogenation of carbon monoxide in the liquid phase indicate attractive olefin selectivities and stable catalytic operation. This is generally ascribed to the excellent thermal control of the reaction, owing to the high heat capacity and the thorough mixing of the slurry. As a result of the better temperature control, localized temperature excursions on the catalytic surface are minimized, resulting in a lower methanation rate[411].

A further advantage of liquid-phase Fischer-Tropsch processes lies in their flexibility in permitting a range of operating conditions. Consequently a wide product spectrum is possible. This, in turn, allows changes in market demands to be readily met. Moreover, liquid-phase Fischer-Tropsch processes are claimed to accept synthesis gas with low H_2:CO ratios, thereby giving them a possible economic edge over other processes. Several liquid-phase catalytic systems will be considered briefly.

5.1.2.1 *The Kölbel liquid-phase Fischer-Tropsch process*

Kölbel and Ralek were among the first to report a Fischer-Tropsch process in the liquid phase[24]. The main advantages of this particular process are:

- It is able to accept carbon monoxide-rich synthesis gas without an external shift, allowing the use of more economical second-generation gasifiers.
- High selectivities may be reached. When geared to gasoline production, the process has a rather narrow product distribution in the desired range of liquid hydrocarbons. However, the process may also be geared to olefin production. It is worth noting the extremely low methane yield (ca 3 %) after regeneration of the catalyst.
- There is high single-pass conversion, reducing the need for syngas recycling.
- There is increased thermal efficiency in removing the exothermic heat of reaction.

Van Vuuren[412] acknowledges these advantages, but indicates the existence of serious discrepancies between and gaps in existing knowledge of slurry reactor design. Research in this field is gaining momentum with an increasing number of groups participating in studies of this promising process. Air Products has started an extensive R & D effort to optimize the process in respect of diesel fuels[279,413]. Similar studies are under way at the Massachusetts Institute of Technology[414,415] and at the Laurence Berkeley Laboratories[416,418]. Many more examples of motor fuel synthesis in the liquid phase are available in the literature.

The flexibility of the process, noted by van Vuuren[412], is exemplified by Hubert[419] who geared the process to the production of lower olefins. An increase in the yields of C_2 to C_6 olefins from values of less than 40 g to more than 60 g m^{-3} synthesis gas has been reported. Because of the excellent thermal control, the process is very well suited to the selective production of lower olefins, and improvements on the promising results of Hubert[419] are certainly expected.

5.1.2.2 *Blanchard process*

Blanchard and Vanhove[273,274] applied the dispersion effect in a slurry reactor. Using complex and cluster-derived cobalt catalysts, they formulated a process yielding up to 75 % lower olefins. As may be expected from dispersion effects, the process is characterized by a product distribution that deviates from Schulz-Flory statistics. As cobalt catalysts are generally noted for their production of longer-chain paraffins, Blanchard's discovery may be regarded as a breakthrough. For this reason the results are included in this section, although they have not yet been developed into a process.

Similar results have been reported for a slightly different cobalt-based liquid-phase system[420]. Using bis(2,4-pentadionate)cobalt-lithium aluminium hydride in tetrahydrofuran-tetralin, Mitsudo *et al.*[420] obtained an olefin selectivity of 85 %.

5.1.2.3 *The Texaco process for the production of lower olefins*

Recently a homogeneous process for the production of lower olefins from syngas was presented by Knifton[421]. It consists of two stages, the first entailing the production of aliphatic carboxylic acids. This is accomplished by a homogeneous reaction of syngas through the use of ruthenium catalysts promoted with quaternary phosphonium salts. The second stage involves pyrolysis of the isolated, intermediate ethyl esters. A typical product distribution showed 55 % ethene, 6 % ethane and 34 % propene.

5.1.2.4 *Ethene production through the synthesis and subsequent dehydration of ethanol*

Various two-stage processes involving the production of ethanol from syngas, with homogeneous catalysis as the first stage, have been reported. In the second stage ethanol is dehydrated to ethene. These processes will be discussed in Section 5.3.

5.1.3 Modified Fischer-Tropsch processes for olefin production

There are several possibilities for modifying the classic Fischer-Tropsch process to yield predominantly olefins. A second generation of highly selective catalysts is being developed. Most of these catalysts consist of transition metals which are demetallized to a greater or lesser extent. This class of catalyst has been discussed in detail. Another form of demetallization is that found in interstitial metal compounds. One promising class of compounds is transition metal nitrides. Although they exhibit high selectivities for the production of lower olefins, there are indications that they lack sufficient catalyst stability.

A possible answer to this may be found in the use of other classes of interstitial transition metal compound: borides, silicides and phosphides. Their great inherent mechanical strengths (approaching that of diamond in the case of TiB^2) and high melting points (3 253 K for TiB_2), together with their considerable chemical inertia, has made them of interest in Fischer-Tropsch research.

The structure of these materials is different from that of nitrides and carbides, which do not seem to have any non-metal/non-metal bonding. This type of bonding, however, is prevalent with borides, phosphides and silicides[422], particularly for non-metal contents greater than 1/3.

This third generation of candidate catalysts is included to show possible new routes, although there is little evidence as to their applicability to the synthesis of lower olefins.

5.1.3.1 *Interstitial metal catalysts*

5.1.3.1.1 Transition metal nitride catalysts. To date only studies of iron nitride catalysts have been reported. Initial studies indicate a shift of the product spectrum (relative to that obtained over metallic iron catalysts) to shorter-chain hydrocarbons and a higher content of oxygenates. In addition, better activity maintenance has been reported[423-426]. The catalytic behaviour of iron nitride catalysts has been described as being similar to that of potassium-promoted iron catalysts[427]. Although a description of the various nitride phases and methods for their preparation is available[425], the detailed nitride structures are still not well understood. A partial characterization using X-ray techniques has been reported[428-430] and Mössbauer, as well as magnetization, studies are in progress[430,431].

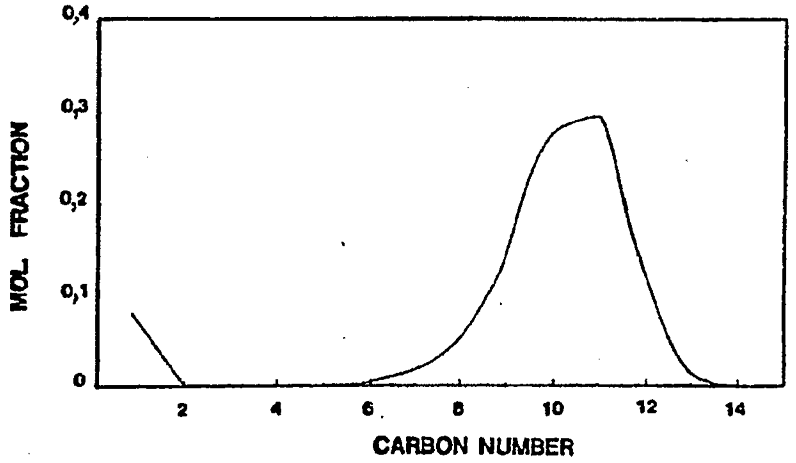
An extensive study of iron nitride catalysts has been undertaken at Purdue University[425,431,432]. Initial results indicate high olefin selectivities for silica-supported iron nitride catalysts. However, the catalytic stability was low. A pure γ-Fe_4N, prepared from highly dispersed iron on Carbolac®, showed considerable retention of the nitride phase, and the improved stability of this catalyst was further reflected in a steady reactivity and selectivity during synthesis.

5.1.3.1.2 Transition metal boride catalysts. Metal borides with a boron content of 33 to 55 (atom) % have a structure in which the boron atoms co-ordinate with six neighbouring metal atoms at the corners of a triagonal prism. The polyhedra are arranged in such a manner that some boron atoms have other boron atoms as their closest neighbours. In this configuration, boron atoms form single or branched chains, adding to the stability of the compound. This is particularly the case for FeB. At higher boron contents (50 to 75 (atom)%), the bonding tendency of boron atoms prevails. Alternate layers of boron and closely packed metal atoms are formed. The boron layers are either planar or puckered. In compounds with a very high boron content (75 to 100 %) the boron atoms are connected in three-dimensional networks.

Nickel borides have long been known for their high activity in hydrogenation reactions[433]. These early data (1952) were not normalized in terms of surface area and should be treated with care. However, later work by Mears and Boudart[434] showed that the specific activity of Ni_2B in the dehydrogenation of isopropanol was similar to that of Raney nickel. In the early 1970's the first reports appeared on the use of borides in the Fischer-Tropsch synthesis[435,436], showing nickel boride to be an active methanation catalyst. The activity of these catalysts was found to be very dependent on the preparation technique used[437-440]. The properties of iron and nickel borides have been investigated more recently using modern techniques[441]; a study of Ni_2B by means of X-ray photoelectron spectroscopy showed a correlation between the hydrogenation activity and the surface states observed[442]. An extensive study by Henbest and Zurqiyah[443] of borides of ruthenium, palladium, rhodium, osmium, iridium, platinum, iron and cobalt in the stereoselective hydrogen transfer of substituted cyclohexanones to 2-propanol revealed that ruthenium borides are particularly effective.

Recently interest in transition metal borides for use in the Fischer-Tropsch synthesis has intensified. Extensive studies of iron and cobalt boride catalysts by the research group of Bartholomew are under way[444-449]. Initial results have shown cobalt boride to be a very active methanation catalyst, with a selectivity and activity in between those of commercial Raney nickel and pure nickel. Reduction of cobalt catalysts at low temperatures resulted in a catalyst with unusual selectivities in carbon monoxide hydrogenation. The product spectrum showed more than 95 % of all products to be hydrocarbons in the range C_5 to C_{16} (Fig. 31). The stability of this catalyst was not very high and deactivation was rapid[445]. The catalytic behaviour of iron boride catalysts was very different. Initial results indicate that these catalysts are very selective for the formation of C_2 to C_4 hydrocarbons, even more so than the highly selective conventional silica-supported iron catalysts[450].

FIGURE 31 Hydrocarbon product distribution for a cobalt boride catalyst during CO hydrogenation (H_2:CO = 2) at 468 K and atmospheric pressure[445]



5.1.3.1.3 **Transition metal phosphide catalysts.** The structure of metal phosphides is similar to that of metal borides. In metal-rich phosphides, phosphorus is nearly always structured in a triagonal prism. The monophosphide structure is different. In its basic form, it consists of a hexagonal stacking of metal atoms with the phosphorus in triagonal prisms. P-P chains are formed (in the case of MnP) or interlinking occurs in the form of P-P pairs (in the case of NiP). Phosphorous-rich metal compounds are again similar in structure to the metal borides.

Comparatively little has been published on the catalytic properties of metal phosphides. Muetterties and Sauer[451] studied the activity of supported ruthenium, rhodium, palladium, nickel and molybdenum phosphides in a variety of reactions such as hydrogenation and isomerization. The most important conclusion drawn from this work was that the phosphides do possess catalytic activity. Although this activity was found to be lower than that of the pure metals, it is difficult to compare the various activities since no results of surface area measurements were given.

5.1.3.1.4 **Transition metal silicide catalysts.** Although silicides also have structures similar to those of the borides, the size of the silicon atom precludes the formation of true interstitial compounds. In fact, the structure is intermediate between that of interstitial and intermetallic compounds. Silicides also have a tendency to form Si-Si networks, particularly at higher silicon contents. However, because of the larger size of silicon, the network is less extensive than that encountered in borides.

Based on their high stability and dispersion, metal silicides may be expected to be interesting catalytic materials in the Fischer-Tropsch synthesis. It is therefore surprising that no reports on catalytic studies involving these materials could be traced to date.

5.1.3.2 *Production of paraffins and subsequent steam cracking to lower olefins*

Dow Chemicals has developed a series of supported and promoted tungsten and molybdenum catalysts which are claimed[400,452-458] to convert syngas to LPG (C_2 to C_5) with selectivities exceeding 70 %. Similar catalysts have been disclosed by Topsøe[459]. Alumina and carbon are used as catalyst carriers and the catalysts are generally promoted with alkali metals. They are designed to work with sulphur-containing feed-gases, and in fact cannot work without sulphur since the active catalyst has to be in the sulphide form.

Because of the low coking rate, high reactor temperatures are possible, allowing high conversion levels. The product stream typically contains 63 % LPG (31 % ethane, 21 % propane, 7 % butane and 4 % pentane). The high ethane and propane contents of this mixture are particularly desirable since these hydrocarbons crack more efficiently to yield the corresponding olefins.

Texaco has developed catalysts for the production of lower paraffins by reducing and chloriding ground magnetite of a specific particle size[460].

5.1.3.3 *Upgrading of Fischer-Tropsch liquids for lower olefins*

Through the use of techniques well known in the petroleum processing industry (e.g. acid catalysis and steam cracking), Fischer-Tropsch liquids may be upgraded to give products with a high content of lower olefins. In addition, Fischer-Tropsch liquids may contain large quantities of oxygenates, such as methanol, ethanol, propanol, higher alcohols and aldehydes. ZSM-5-based technology may be used to convert these oxygenates into hydrocarbons. Through appropriate choice of process conditions and catalyst formulation, a product with a high content of lower olefins may be obtained.

5.2 Catalytic conversion of methanol

Light hydrocarbons may be produced from syngas indirectly through methanol. Through the use of established methanol synthesis technology ($Cu/Zn/Al_2O_3$), methanol is produced at high selectivity, and this is followed by methanol conversion to light hydrocarbons with a high olefin content. Catalysts claimed to produce olefin-rich products include:

- zeolites (Mobil Oil)[461]
- phosphorus-modified H-ZSM-5 (low acidity) (Mobil Oil)[462]
- aluminosilicates containing manganese (Hoechst AG)[463-465]
- medium-pore zeolites (smaller than 0,6 nm) such as chabazite ion-exchanged with a mixture of rare earth chlorides (Texas A & M)[466].

R & D on these processes is continuing. A joint project between Mobil Oil and AECI for the selective production of ethene from methanol was announced in 1976[467]. In the same year an announcement of the construction of a 15 ton/month pilot plant for a similar process was made by BASF[467.468]. Reports in the literature indicate that interest in methanol conversion is increasing. Improvements to the methanol-to-ethene process are regularly published, showing yields of 40 % with distinct possibilities of 50 %. Further research is expected to lead to yields of 60 % and higher[469].

5.3 Indirect ethene production through ethanol

Ethene can be produced by dehydration of ethanol. The latter may be formed either by homologation or directly from syngas.

5.3.1 Through homologation and subsequent dehydration

The discovery in the 1950's that methanol can react with syngas to produce ethanol[470] has sparked off the development of this process. The homologation reaction may be written as

$$CH_3OH + CO + 2H_2 \longrightarrow C_2H_5OH + H_2O \qquad (11)$$

Catalysed by cobalt, the reaction originally yielded only 42 % ethanol. Recent improvements have increased this value to 90 %, albeit at a low reaction rate[471]. The homologation process operates with homogeneous catalysis. Catalysts usually contain cobalt and ruthenium and are promoted with iodine and often phosphorous ligands (Gulf Oil)[472.473]. Other catalysts may be used. British Petroleum[474] developed a cobalt-based catalyst with an iodide, a bromide or a polydentate ligand. A different process is being developed by Union Carbide[475] and is based on a phosphine-iodine-promoted cobalt-ruthenium catalyst. Rhone-Poulenc studies cobalt and ruthenium promoted with alkyl halides[476].

The Gulf process operates at 348 K and 2,6 MPa and converts 30 % of the methanol in one hour at a selectivity of 96 %. Ethanol dehydration is then effected with existing technology (e.g. alumina catalysts).

5.3.2 Through direct ethanol production from syngas and subsequent dehydration

Rhodium-based catalysts can convert syngas to a mixture of linear alcohols in the range C_1 to C_4, acetic acid, acetaldehyde and methane. The major component is ethanol, usually[470,477] at a concentration of 40 to 60 (mol) %. A similar product may be obtained with cobalt-copper-chromium-potassium catalysts[470]. Other catalysts for this process include:

- supported rhodium, developed by Sagami Chemical[478];
- rhodium promoted with uranium and/or thorium[479], or rhodium with molybdenum and/or tungsten[480], or rhodium with manganese[481], all three developed by Union Carbide[482];
- titania-supported rhodium, developed by Exxon;
- gold, silver and rhenium-promoted cobalt catalysts developed by Hoechst, which are claimed[465,483] to have a selectivity for ethanol production of 50 - 65 %; and
- the Phillips catalysts which contain phosphine-promoted cobalt carbonyl and are claimed to produce liquids containing 35 % ethanol, 31 % methanol and 17 % ethylene glycol[484].

5.4 Indirect alkene production through mixed alcohols

Several processes aim at the direct production of mixed alcohols in the C_1 to C_5 range from synthesis gas. Dow Chemicals[485] has developed a process using rugged, selective catalysts, consisting of agglomerated molybdenum sulphides. A similar alcohol blend is produced in a process developed by the Institut Francais du Petrole[486,487]. The catalyst consists of copper, cobalt, rare earth metal, alkali metal, a metal selected from chromium, iron, vanadium or manganese and, optionally, zinc and/or a noble metal.

The alcohol blend can subsequently be dehydrated to lower alkenes using existing technology.

6. CONCLUDING REMARKS

A critical examination of the literature has shown that the selectivity of the Fischer-Tropsch synthesis may be influenced by several effects. These have been classified as a catalyst basicity effect, a catalyst dispersion effect, an electron withdrawal ligand effect and several support interaction effects.

Economic considerations have shown that considerable savings can be made on commercial Fischer-Tropsch operation if the catalyst can accept hydrogen-poor synthesis gas without a resulting loss of activity or selectivity maintenance.

Further savings are possible by keeping the production of methane to a minimum.

A commercially viable process, based on the Lower Olefins Route, would require a minimum of 50 % olefin selectivity in the C_2 to C_5 range, while maximizing the C_2 to C_{12} fraction.

Olefin selectivities above 50 % have been reported but, with the exception of several Fe/zeolite systems in which cracking could well explain the results, all experiments were carried out at either very low conversion levels or at low pressures. Similarly, high olefin selectivities have been noted for moderately acidic carriers (alumina, silica-aluminas) which have been reported to limit the chain length of synthesis products by means of cracking. The product contained a high fraction of light hydrocarbons (the actual value depending on the pore size of the support), higher than that predicted by Schulz-Flory statistics.

Iron-cobalt alloys (50/50) show considerable promise for selective light olefin production.

Methane production may in principle be decreased and the selectivity for light olefins increased by utilizing demetallization effects.

It has been demonstrated that lower olefins may be produced from syngas in many different ways. Economic conditions will dictate which processes will be commercialized. The final choice is difficult to predict since many of the very promising routes are still being developed and the petrochemical industry is faced by many uncertainties of a political, economic or technological nature.

At present the industry is in a depressed state because of over-capacity and low market demand. The establishment of new plant based on novel processes in the near future is therefore unlikely. Because of political pressures and the availability of low-cost coal, this picture may be different in certain countries. The "lower olefins route" may provide a flexible process for the production of automotive fuels and commodity chemicals. On a world-wide scale, the commercialization of second or third-generation syngas-based olefin processes may not be all that distant. It has been suggested[469] that this may happen before 2000.

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