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ROLE OF PROMOTERS IN THE HYDROGENATION OF CARBON MONOXIDE OVER IRON-BASED CATALYSTS (REVIEW)

COUNCIL FOR SCIENTIFIC AND INDUSTRIAL
RESEARCH, PRETORIA (SOUTH AFRICA).
CHEMICAL ENGINEERING RESEARCH GROUP

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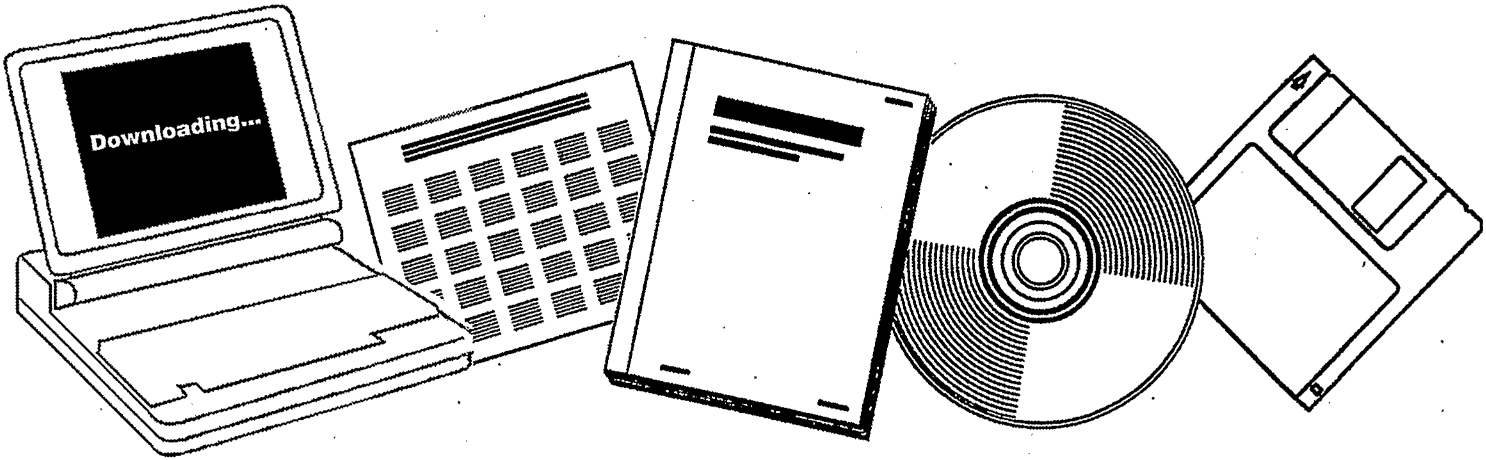

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I R LEITH

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SOUTH AFRICA

SYNOPSIS

The steady-state activity and selectivity of iron-based catalysts in the Fischer-Tropsch synthesis is governed by complex interactions between the reactants and reaction intermediates on the catalyst surface, the bulk carbidic and oxidic phases formed during synthesis, carbonaceous deposits on the surface, and the promoter compounds present as part of the catalyst composition.

Improvements in activity and shifts in selectivity can be obtained by incorporating promoters. However, the understanding of the interplay between promoters and other catalyst constituents is not well-developed. Further research on this is recommended.

KEYWORDS: Hydrocarbon, synthesis, Fischer-Tropsch, hydrogenation, carbon monoxide, iron, promoter, activity, selectivity, review.

File No: 660–50–2

WNNR–VERSLAG CENG 457

DIE ROL VAN PROMOTORS IN DIE HIDROGENERING VAN KOOLSTOFMONOKSIED OOR YSTERHOUDENDE KATALISATORS

Oorsig

I R LEITH

Mei 1983

SINOPSIS

Die selektiwiteit en aktiwiteit van ysterhoudende katalisators in 'n gestadigde Fischer-Tropsch-sintese word bepaal deur die ingewikkelde interaksies tussen die reaktante en die tussenverbindings op die katalisatoroppervlak, deur die metaalkarbiede en -oksiedes wat gedurende die sintese gevorm word, deur koolstofhoudende neerslae op die oppervlak, en deur die promotorstowwe wat deel van die katalisatorsamestelling vorm.

Verbeteringe in aktiwiteit en verskuiwings van die selektiwiteit kan deur toevoeging van promotors verkry word. Die begrip van die interaksie tussen promotors en ander katalisatorkomponente is egter nie goed ontwikkel nie. Verdere navorsing hieroor word aanbeveel.

CONTENTS

1.	**INTRODUCTION**	5
2.	**MECHANISM OF THE FT SYNTHESIS**	6
3.	**CHEMISORPTION OF H_2 AND CO ON IRON**	6
3.1	EFFECT OF ADDITIVES ON H_2 CHEMISORPTION	8
3.2	EFFECT OF ADDITIVES ON CO CHEMISORPTION	8
3.3	COADSORPTION OF H_2 AND CO	9
4.	**IRON–BASED CATALYSTS FOR CO HYDROGENATION**	9
4.1	PRECIPITATED CATALYSTS	9
4.2	FUSED CATALYSTS	10
4.3	PROMOTERS FOR PRECIPITATED AND FUSED CATALYSTS	10
4.3.1	Structural promoters	10
4.3.2	Chemical promoters	10
4.4	MISCELLANEOUS CATALYSTS	11
5.	**STRUCTURE OF IRON CATALYSTS**	13
5.1	PRECIPITATED AND RELATED CATALYSTS	13
5.1.1	Before and after reduction	13
5.1.2	During synthesis	13
5.2	FUSED CATALYSTS	15
5.2.1	Before and after reduction	15
5.2.2	During synthesis	19
6.	**CATALYTIC BEHAVIOUR OF IRON CATALYSTS**	19
6.1	ACTIVITY	19
6.1.1	Time dependent behaviour	19
6.1.2	Role of bulk carbon	19
6.1.3	Role of surface carbon	21
6.1.4	Effect of pretreatment	22
6.2	SELECTIVITY	24
6.2.1	Influence of operating conditions	25
6.2.2	Effect of carbide formation	26
6.2.3	Effect of particle size	27
7.	**PROMOTION OF IRON CATALYSTS**	27
7.1	EFFECT OF PROMOTERS ON ACTIVITY	27
7.2	EFFECT OF PROMOTERS ON SELECTIVITY	28
7.3	MECHANISMS OF PROMOTER ACTION	29
8.	**BASIS FOR FUTURE RESEARCH**	31
9.	**SUMMARY OF FINDINGS**	32
10.	**SUMMARY OF RECOMMENDATIONS FOR FUTURE RESEARCH**	33
11.	**REFERENCES**	34

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1. INTRODUCTION

The gradual depletion of world-wide oil reserves has necessitated a search for alternative routes to liquid transportation fuels and chemical feedstocks.

Coal comprises a substantial fraction of the world's recoverable fossil fuel resources, and it is technically possible to produce a broad range of hydrocarbon fuels and chemicals by the catalytic conversion of coal-derived synthesis gas (CO + H_2).

Two indirect liquefaction routes are currently available. The methanol route(1) involves the conversion of synthesis gas to methanol which is then converted stoichiometrically to water and hydrocarbons over a shape-selective zeolite. A high yield of high octane gasoline is obtained without the need for complex refining of the primary liquefaction product. Alternatively, by varying the operating conditions, high yields of light olefins (C_2 - C_5) may be obtained. The Fischer-Tropsch (FT) route(2) involves the catalytic hydrogenation of carbon monoxide to a complex mixture of hydrocarbons which must be extensively refined into the finished product.

The selectivity of the FT synthesis reaction is determined by a sequence of kinetically controlled reaction steps which are only partially understood. Moderate shifts in the broad product distributions may be obtained within the constraints of the Schulz-Flory distribution law by varying the reaction conditions. However, to obtain high selectivity to a single product or a narrow distribution of products requires the development of improved catalysts.

One approach is to place a physical constraint on the normal chain-growth process, thus limiting the product distribution to lower molecular weight hydrocarbons. This has been achieved by containment of the catalyst in the small pores of a suitable support such as alumina(3) or by the stabilization of small particles of the active metal within the cavities of certain zeolites(4-6) or on inorganic oxide supports(7). Bifunctional catalysts(8) in which the FT active component is intimately associated with shape-selective zeolites of the ZSM–5 type have also yielded narrow product distributions. However, the optimum conditions of operation for each function are often not compatible.

An alternative approach is the chemical modification of conventional iron FT catalysts by the incorporation of promoters and other additives. It is likely to be difficult to achieve a high selectivity to a single product in this way; however, recent studies have indicated(9,10) that certain modifications lead to the formation of low olefins (C_2 - C_4) in high yields. The complex interactions which exist between the various components in promoted catalysts and with the reaction intermediates on the surface are poorly understood.

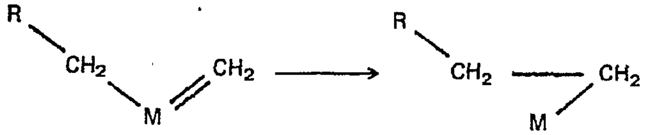
The present report reviews the current state of knowledge about iron-based catalysts for the FT synthesis and identifies areas for further research aimed at improving the basic understanding of the role of promoters and the mechanism whereby they affect catalytic action.

2. MECHANISM OF THE FT SYNTHESIS

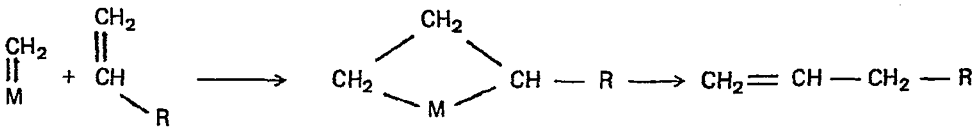
Several very comprehensive discussions on the mechanism of hydrocarbon synthesis from synthesis gas have been published(11-13) so that only a brief summary of the most recent ideas will be given.

Results obtained by several independent research groups indicate the importance of carbon monoxide dissociation in the initiation step of the synthesis reaction. This leads to the build-up of an overlayer of carbidic carbon on the catalyst surface, part of which reacts readily with hydrogen to form adsorbed CH_x species which are thought to be reactive intermediates capable of being incorporated into growing chains or hydrogenated to methane.

Evidence is available which suggests that the $CH_{x,ads}$ is in fact a surface carbene, $CH_{2,ads}$, and by analogy with the well established mechanism of olefin metathesis(14) and also that proposed(15) for the dehydrocyclization of alkanes over transition metals, the chain propagation is thought to occur in a stepwise fashion by cis insertion of a carbene in a metal-alkyl bond.



The incorporation of olefins into the growing chain may be described by a similar mechanism(7) involving a metallo-cyclobutane transition state followed by β-H transfer to form an α-olefin.



Oxygenate formation which is prominent on iron-based catalysts may originate when undissociated CO or an oxymethylene group is inserted in the growing chain, thus blocking further chain growth.

The low space-time yields typically observed in FT synthesis may be explained by the requirement of an ensemble of metal atoms on the catalyst surface for CO dissociation to occur. In the steady state the catalyst is predominantly covered with undissociated CO and only a small fraction of the surface atoms carry growing alkyl groups and carbene.

3. CHEMISORPTION OF H_2 AND CO ON IRON

It is evident from the foregoing discussion on the mechanism of the FT synthesis that the reaction components interact in the adsorbed state. A knowledge of the adsorption behaviour of hydrogen and carbon monoxide on iron, as well as the influence of promoters and additives is therefore important.

Hydrogen – In common with the other FT active metals of Group VIII, hydrogen adsorbs dissociatively on iron[16].

The ease of formation of many transition metal hydrido complexes is evidence of the hydridic character of the metal-hydrogen bond[17]. The transfer of charge from surface metal atoms to hydrogen has been confirmed in some instances by work function measurements[18]. In the case of iron, an increase in work function occurs[19] at low hydrogen coverage and room temperature, attributable to a negatively charged surface hydrogen layer; however, at higher temperatures where less hydrogen is chemisorbed, no change in work function is observed.

Carbon monoxide – Compared with hydrogen, the adsorption of carbon monoxide is rather complex, owing to the fact that molecular and dissociative adsorption of CO are competing processes.

Benziger[20] has analyzed the adsorption of CO thermodynamically for various FT active metals and showed that the state of adsorption depends on the enthalpies for molecular and dissociative adsorption as well as on temperature and pressure. Molecular adsorption is preferred at low temperatures and a transition from molecular to dissociative adsorption occurs with increasing temperature at constant pressure. It is also apparent from his analysis that there is no basis for a correlation between the CO adsorption bond strength on different metals and the propensity for CO dissociation. In fact a stronger molecular binding energy results in the inhibition of dissociation. An estimate of the dissociative behaviour of CO is obtained from a consideration of the adsorption energy of dissociated CO as the thermodynamic driving force. The criterion for observing dissociative adsorption is that the enthalpy for dissociative adsorption is less than or equal to the enthalpy for molecular adsorption.

The metal-carbon bond in chemisorbed CO is made up of two components[21]. The first arises from an overlap of the occupied 5σ orbital of CO with unoccupied metal orbitals, resulting in donation of electrons from the molecule to the metal. The second component is formed by back donation of electrons from occupied metal orbitals to the unoccupied $2\pi^*$ orbitals of CO. The 5σ orbital in gaseous CO is essentially nonbonding with respect to the C – O bond so that the donation of electrons from this orbital does not strongly affect the strength of the C – O bond in chemisorbed CO. On the other hand the $2\pi^*$ orbitals are antibonding with respect to the C – O bond and back donation into these orbitals weakens the bond. The net effect of donation and back donation therefore is the formation of a metal-carbon bond and a concomitant weakening of the C – O bond. Electron donors may be expected to stimulate CO dissociation by donating electron density into the CO-antibonding orbital.

Recent investigations of the adsorption of CO on well-defined iron single crystal surfaces[22,23] and on polycrystalline iron[24] by various spectroscopies have shown that below 200 K adsorption is molecular, but dissociation occurs slowly at 290 K and rapidly at 350 K. Surface defects, such as steps or kinks, can have an important effect on the enthalpy for dissociative adsorption with the result that a shift in the equilibrium from molecular to dissociative adsorption is possible.

3.1 EFFECT OF ADDITIVES ON H_2 CHEMISORPTION

Carbon, oxygen and sulphur – Adlayers of C, O and S on Fe(100) surfaces were all found(25) to reduce the strength of hydrogen adsorption. Sulphur had a much more drastic effect than either oxygen or carbon.

Nitrogen – Amenomiya et al.(26) investigated the influence of chemisorbed nitrogen, probably present as atomic nitrogen, on H_2 adsorption on a promoted iron catalyst. Several types of hydrogen chemisorption were observed, and nitrogen possessed a marked selectivity for blocking strongly adsorbed hydrogen, while the more weakly chemisorbed hydrogen remained unaffected.

Potassium – In contrast to C, O and S which are electronegative species, adlayers of the electropositive potassium were found to enhance(25) the adsorption strength of hydrogen on Fe(100). While bearing in mind possible differences in the chemical nature of the potassium in the two experiments, this result disagrees with that of Dry et al.(27) who found a decrease in the heat of adsorption of hydrogen on a potassium-promoted bulk iron catalyst. It has been suggested(25) that this difference in behaviour may be ascribed to the presence of an oxide layer on the iron surface in the earlier work. Furthermore, work function measurements(19) on pure and alkanized iron films indicated that the presence of potassium has little influence on the strength of hydrogen adsorption.

3.2 EFFECT OF ADDITIVES ON CO CHEMISORPTION

Carbon, oxygen and sulphur – In the presence of sulphur, the strength of the CO adsorption bond on iron is reduced, the rate of adsorption decreased and the dissociation of CO inhibited(24,25,28). Although both oxygen and carbon have a less deleterious effect, adlayers of oxygen and carbon also reduce the strength of CO adsorption and CO dissociation is inhibited.

Nitrogen – Temperature programmed desorption (TPD) studies of CO adsorbed on a promoted iron catalyst indicated(26) that in the presence of chemisorbed nitrogen the amount of strong, and probably dissociative, adsorption of CO is reduced while the weaker molecular adsorption is considerably enhanced. This agrees broadly with the result of Gafner(28), who showed that the presence of a nitrogen overlayer on Fe(110) inhibits the dissociative adsorption of CO.

Potassium – CO adsorption on potassium-promoted Fe(110) surfaces has recently been studied(29) by spectroscopic techniques. Compared with the clean iron surface, the presence of potassium decreases the initial sticking coefficient of CO, enhances the binding energy of molecularly adsorbed CO and increases the amount of CO dissociation. Similar conclusions were also drawn from calorimetric(27) and work function(19) studies on iron.

3.3 COADSORPTION OF H_2 AND CO

While the study of the adsorption behaviour of each gas independently provides valuable insight into the nature of the adsorbed species, the adsorbed state of the H_2/CO mixture on iron is more relevant to the situation pertaining during actual synthesis.

Chemisorption studies at low temperatures(27) showed that when carbon monoxide was preadsorbed on the surface of a reduced iron catalyst, no hydrogen is chemisorbed. This result agrees with the TPD data of Amenomiya et al.(26) who found that preadsorbed CO inhibits all types of hydrogen chemisorption uniformly. When hydrogen is preadsorbed, however, CO adsorption occurs readily.

Subramanyam and Rao(30) showed that carbon monoxide partly displaces adsorbed hydrogen at temperatures less than 325 K, as might be expected from the higher heat of adsorption of CO on iron(31). At higher temperatures, the displacement of hydrogen does not occur. Furthermore, during equilibrium studies it was found that with increasing temperature the amount of hydrogen adsorbed increases but the increase in adsorption of CO is less pronounced.

The total adsorption from H_2/CO mixtures on both unpromoted and potassium-promoted bulk iron catalysts was greater than the sum of the individual components adsorbed separately(30,32). 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. As might be predicted from its influence on the CO adsorption bond strength, addition of potassium to this catalyst decreased the H_2:CO ratio in the adsorbed phase to 0,5 for all mixtures(30).

4. IRON–BASED CATALYSTS FOR CO HYDROGENATION

Two broad categories of iron-based catalysts, precipitated catalysts and fused catalysts, are currently used commercially or have potential industrial application. These have been thoroughly reviewed by Anderson(33) and by Dry(2).

Several novel catalyst systems have been investigated recently with the aim of improving selectivity. The more promising of these are discussed in Section 4.4.

4.1 PRECIPITATED CATALYSTS

The structure and catalytic properties of precipitated catalysts may be influenced by a variety of preparative variables such as starting material, precipitating agent, order and method of addition of these reagents and the pH of precipitation.

Starting with a solution of iron (III) nitrate (in preference to the sulphate or chloride), precipitation is usually accomplished using the carbonates of sodium, potassium or ammonia (in preference to the hydroxides). The final pH of precipitation of 7 to 8 is a critical factor(34) in determining the pore size and distribution.

4.2 FUSED CATALYSTS

Any oxide of iron may be used as starting material for fused iron catalysts since at fusion temperatures in the presence of oxygen they all revert to the stable magnetite. The commercial preparation uses millscale from a steel works, mixed with the desired amounts of promoters and fused in an electric arc furnace.

4.3 PROMOTERS FOR PRECIPITATED AND FUSED CATALYSTS

The function of catalyst promoters in general is not completely understood. As with other catalyst systems, promoters for Fischer-Tropsch catalysts may be classified as structural or chemical according to their mode of action; however, it is not always possible to separate strictly the influence of the two effects on activity and selectivity.

4.3.1 Structural promoters

Difficult to reduce, high melting oxides such as Al_2O_3, ThO_2, MgO, CaO and ZnO, present as minor components relative to the amount of metal, are used as structural promoters for both precipitated and fused iron catalysts. Their principal function is to increase the specific surface area of the reduced catalyst and to improve the temperature stability of the catalytically active phase by inhibition of crystallite growth.

In the case of precipitated catalysts, the promoter oxide is usually precipitated simultaneously with the iron oxide. If the proportion of the structural promoter is increased, the catalyst tends towards a supported catalyst. The precipitated catalyst is often distributed on a support such as kieselguhr, silica or alumina which improves reactant accessibility as well as the mechanical properties of the catalyst. Generally the support is introduced by slurrying it with the iron-containing solution before or during the precipitation stage.

4.3.2 Chemical promoters

The influence of chemical promoters on catalytic activity and selectivity originates from the electronic interactions with the catalytically active metal which modify the adsorption-desorption behaviour of the reactants and products at the catalyst surface. Some chemical promoters also have a considerable influence on the structural properties of the catalyst such as surface area and porosity. In addition, certain chemically reactive structural promoters such as alumina may also behave as chemical promoters.

Alkali – The alkali metal oxides, and in particular potassium oxide, are the most important chemical promoters used in the production of higher hydrocarbons over both precipitated and fused iron catalysts. The potassium oxide is usually added as the carbonate by impregnation of the precipitated iron oxide before reduction or of the magnetite following the fusion process. Alternatively, if silica is included as a support for the precipitated catalyst, the potassium may be added by impregnation with potassium waterglass. The potassium content is controlled by further washing with nitric acid.

The optimum potassium content depends on the composition of the catalyst and on its method of preparation. Unsupported precipitated catalysts should contain less than 1% K_2CO_3 (relative to iron), while for fused catalysts the optimum K_2O content is about 0,5 mass %. When acidic oxides are present as structural promoters or supports, larger amounts of alkali metal are generally required. For instance, the optimum K_2O content for a precipitated catalyst containing 25% SiO_2 is about(35) 5%.

Copper – Co-precipitated iron catalysts for industrial application contain about 5 mass % (relative to iron) of copper. While the presence of copper appears to have little influence on the selectivity of the FT reaction, it does facilitate the reduction of iron oxide(33), resulting in a smaller crystallite size of the reduced iron which in turn permits the formation of an iron carbide phase at lower temperatures. Hence, lower temperatures and shorter catalyst pretreatment times are possible.

Matrix oxides – The co-precipitation of iron oxide with large amounts of the oxides of other 3d metals is claimed to result in catalysts which exhibit a marked selectivity towards lower olefins(9,10). Particular attention has been given to the oxides of Ti, V, Mo and Mn which are difficult to reduce or cannot be reduced completely and which are stable under reaction conditions. Although classified here as a chemical promoter, the precise role of the matrix oxide in modifying the selectivity has not been established. In the case of a Mn/Fe catalyst a partial dissolution of the iron in the matrix oxide evidently occurs, leaving only some available as surface clusters for FT synthesis(36); therefore, the matrix oxide might be better classified as a structural promoter.

Miscellaneous – The FT synthesis reaction involves a complex network of primary and secondary reactions which occur to varying extents depending on the catalyst composition and reaction conditions and results in a range of products. The presence of small quantities of species normally regarded as poisons for metal hydrogenation catalysts, by influencing certain reaction steps, may enhance the formation of desirable products without sacrificing catalytic activity. The promotional effect of small additions of sulphur(37), halide ions(38) and sulphate(39) to iron catalysts may be partly explained in this way.

4.4 MISCELLANEOUS CATALYSTS

Considerable scope exists for influencing the selectivity of the FT synthesis by modifying iron catalysts.

Highly dispersed supported catalysts – In general, the catalytic behaviour of highly dispersed metals is of interest because of the special surface structure and electronic properties of small metal crystals. Highly dispersed iron catalysts are difficult to stabilize because of the ease with which iron sinters. However, the stabilization may be accomplished using special preparative techniques on thermally stable high surface area supports or, alternatively, by using non-conventional supports such as zeolites where metal agglomeration may be inhibited by the pore structure.

Boudart et al.(40) and Topsøe et al.(41) described techniques for producing small metallic iron particles on a magnesium oxide support either by co-precipitation or by ion-exchange of magnesium hydroxycarbonate.

The support itself may play a major role. The metal-support interaction should be optimum so that, on the one hand, mobility of the small particles is such as to ensure maximum thermostability of the catalyst, as appears to be the case for MgO, while on the other hand reduction to the metallic state should occur readily. Molecular hydrogen is unable to reduce the iron ions in Fe(II)- or Fe(III)-exchanged zeolite Y catalysts beyond the ferrous state(42). To overcome this problem, alternative methods of impregnation of zeolite supports have been developed(43), for example, by decomposition of adsorbed iron carbonyls. In addition, this preparative technique enables the shape-selective properties of zeolites such as ZSM–5 to be utilized in influencing selectivity(44).

Olefin-selective catalysts derived from iron carbonyls supported on conventional oxide supports such as Al_2O_3, MgO, SiO_2 or La_2O_3 have been prepared(45). The promotion of such highly dispersed catalysts with alkali metals such as potassium and rubidium may be accomplished using potassium- (or rubidium-) iron carbonyl cluster complexes as precursors(46).

Among other supports which have received attention are carbon(47) and TiO_2(48,49). The strong metal-support interaction (SMSI) exhibited(50) by TiO_2-supported metals can lead to a modification of the electronic properties of the metal particles with consequent effects on adsorptive behaviour as well as on activity and selectivity.

Bimetallic alloy catalysts — Bimetallic alloy catalysts formed by the incorporation of a second inactive metallic component often exhibit modified catalytic behaviour which may be attributed to a combination of electronic and geometric factors. These materials show remarkable specificity in reforming reactions(51) and their use in FT synthesis might also be expected to produce improvements in selectivity. Alloys of iron with ruthenium(52-54), cobalt(44), manganese(10) and platinum(55) have been investigated.

Interstitial compounds — The electronic structure of iron may be altered by the formation of interstitial compounds with the non-metals carbon, nitrogen and boron or combinations of these elements. These compounds may be expected to possess high thermal stability and significantly modified catalytic properties(56).

The unusual selectivity to alcohols of nitrided fused iron catalysts is already well known(57). These catalysts are prepared by treatment of a reduced fused iron catalyst with anhydrous ammonia; during synthesis a carbonitride phase probably exists.

5. STRUCTURE OF IRON CATALYSTS

To understand the synergistic interactions among the various components present in iron catalysts, a knowledge of the surface composition and topography of the catalyst as well as of the oxidation state of the various components both before and during the synthesis reaction is required.

The physical and chemical structure of iron catalysts is strongly dependent on such factors as the method of preparation, the content of additives and promoters and the conditions of pretreatment and reduction. Furthermore, reduced iron catalysts are not stable during FT synthesis but are converted into a variety of oxide and carbide phases depending on the nature of the catalyst.

5.1 PRECIPITATED AND RELATED CATALYSTS

5.1.1 Before and after reduction

The precursor state – The precursor state of conventional precipitated iron catalysts corresponds to that of α-Fe_2O_3. Unsupported α-Fe_2O_3 may also be prepared by the thermal decomposition of hydrated iron (III) nitrate(58), while supported α-Fe_2O_3 is formed by calcination of iron (III) nitrate-impregnated supports such as silica(59,60), alumina(61) or zeolites(62). The calcination of a zeolite support impregnated with the iron carbonyl $Fe_3(CO)_{12}$ resulted in a γ-Fe_2O_3 phase(62).

Reduction – In hydrogen a rapid initial reduction of α-Fe_2O_3 to Fe_3O_4 occurs, followed by a slow further reduction to α-Fe. It is thermodynamically impossible to reduce haematite beyond magnetite if the hydrogen is saturated with water vapour.

The second reduction stage occurs very slowly, particularly when silica is present as a structural promoter. At low iron loadings of 0,1 to 1 mass %, the strong interaction between small iron particles and the support or actual ion-exchange of iron into the support prevents the reduction of the iron beyond Fe(II), even after treatment in hydrogen for extended periods of time. At higher iron loadings when a smaller fraction of iron atoms is in contact with the support and the support interaction becomes less important, reduction to α-Fe is possible to an extent, which depends on the particle size in the precursor(59).

Surface area – The pore geometry and surface area of the usually high area – small pore ferric oxide gel is drastically altered during reduction. The total surface area decreases, the average pore size increases and the pore size distribution shifts towards larger pores. Some representative data by Dry(2) are given in Table 1.

5.1.2 During synthesis

Carbide formation – At least four different iron carbide phases are known to exist. These are summarized in Table 2 together with structural data and values of their Curie temperatures, which provide an aid to the identification of the various phases from thermomagnetic measurements.

TABLE 1 Changes in area and pore structure of silica-promoted precipitated iron catalysts(2)

State	Catalyst	Total pore volume (cm^3g^{-1})	Total area (m^2g^{-1})	Areas in pores > 4,5 nm (%)	Areas in pores > 16 nm (%)
Unreduced	A	0,39	355	5	0
	B	0,67	340	25	19
Partially reduced	A	0,30	195	20	1
	B	0,46	150	45	22

TABLE 2 Principal carbide phases of iron

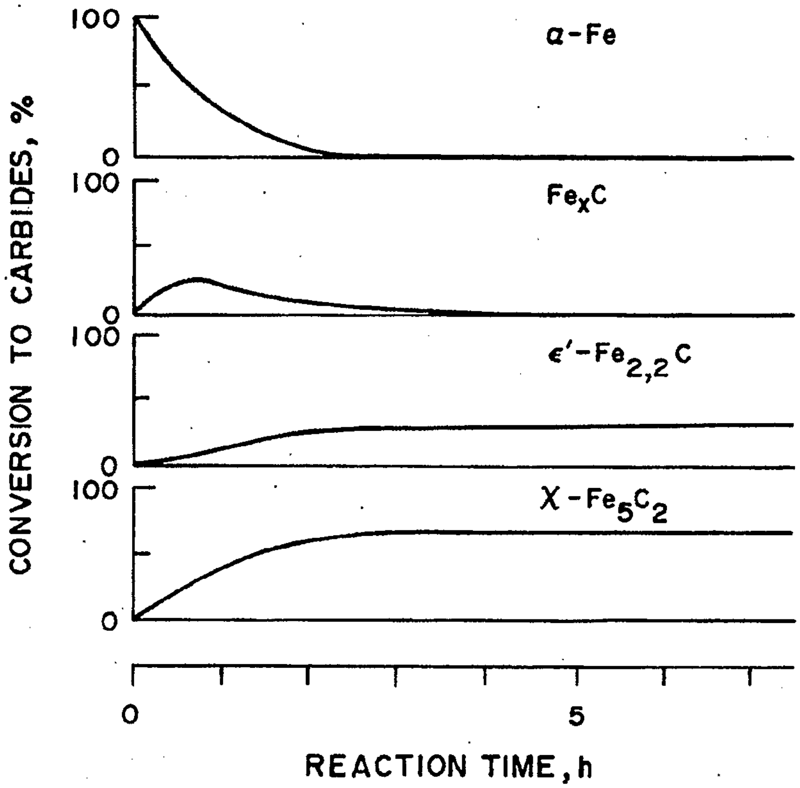
Carbide phase	Structure	Curie temperature T_c (K)
ε'-$Fe_{2,2}C$	Hexagonal close packed (hcp)	~ 720
ε-Fe_2C	Transition from hcp to monoclinic	650
χ-Fe_5C_2 (Hägg)	Monoclinic	525
θ-Fe_3C (cementite)	Orthorhombic	480

The particular combination of carbides formed during FT synthesis is dependent on such factors as the nature of the catalyst (promoted or supported) and the metal particle size, as well as on the duration and temperature of the synthesis reaction.

The conversion of an unpromoted and unsupported precipitated iron catalyst into carbides during FT synthesis has been studied(63) using Mössbauer spectroscopy. The relative contributions of α-Fe and of the various carbides to the overall catalyst composition as a function of the duration of the synthesis reaction at 513 K is reproduced in Figure 1. The principal species present after a short period on stream are ε'-$Fe_{2,2}C$ and χ-Fe_5C_2.

Table 3 summarizes data obtained by various workers on carbide formation in a variety of reduced α-Fe_2O_3 precursor catalysts. Clearly the nature of the catalyst is very important for determining which carbide phases are formed.

FIGURE 1 Conversion of α-Fe to iron carbides(63) during FT synthesis at 513 K



Effect of promoter – Little information exists on the effect of promoters on carbide formation in reduced precipitated catalysts. Early studies(33) indicated the presence of χ-Fe_5C_2 on unpromoted catalysts while hexagonal carbide was also formed in catalysts promoted with potassium or copper. A recent study(65) of a precipitated catalyst promoted with manganese (II) oxide showed that quantities of the carbide phases χ-Fe_5C_2 and ε'-$Fe_{2,2}C$ similar to that found in a pure iron catalyst were formed.

5.2 FUSED CATALYSTS

5.2.1 Before and after reduction

The precursor state – The precursor state of fused iron catalysts corresponds to that of Fe_3O_4. The oxides commonly used as promoters for fused iron catalysts dissolve to some extent in magnetite resulting in a modification of the lattice constants as either the Fe(II) or Fe(III) cations in the inverse spinel structure are replaced by foreign ions(66). The unit cell size is decreased by cations which are smaller than the host cations (eg, Al^{3+}, Li^+, Mg^{2+}) and for larger cations (eg, Ca^{2+}, Mn^{2+}, Ti^{4+}, Na^+) the unit cell size increases progressively. K^+ has no effect on the unit cell size, presumably because it does not go into solid solution. Although SiO_2 does not go into solid solution it does affect the solution of the basic cations Na^+ and Ca^{2+} owing to its ability to combine with them to form silicates which remain as small inclusions throughout the catalyst.

TABLE 3 Carbide phases formed on various catalysts during FT synthesis

Catalyst support	Preparative method	Precursor particle size (nm)	Carbide phases after 6h synthesis at 523 K	Comments	Reference
Unsupported	Precipitation		ε'-$Fe_{2,2}C$ + χ-Fe_5C_2	At 513 K	63
Unsupported	$Fe(NO_3)_3$ decomp.		$Fe_{20}C_9$	Determined by XRD	58
Silica	$Fe(NO_3)_3$ impregnation	10	χ-Fe_5C_2	Interpreted(63) as χ-Fe_5C_2 + ε'-$Fe_{2,2}C$	64
		8	ε-Fe_2C + ε'-$Fe_{2,2}C$		
		< 4	ε'-$Fe_{2,2}C$		
Silica	$Fe(NO_3)_3$ impregnation	16	ε'-$Fe_{2,2}C$		60
Magnesia	Ion-exchange of magnesium hydroxycarbonate	< 4	χ-Fe_5C_2		64
TiO_2/CaO	Precipitation		ε'-$Fe_{2,2}C$ + χ-Fe_5C_2	After 48 h synthesis	63
Alumina	Precipitation		ε-Fe_2C	After 19 h synthesis interpreted(63) as ε'-$Fe_{2,2}C$	61
ZSM–5	$Fe(NO_3)_3$ impregnation	10	χ-Fe_5C_2 + ε'-$Fe_{2,2}C$	At 553 K	
	$Fe_3(CO)_{12}$ impregnation	6	χ-Fe_5C_2		62

Reduction – The rate of reduction of fused iron catalysts is strongly dependent on the type and quantity of promoter present, as well as on the water vapour pressure in the reduction system. Thus the reduction rate is increased by high hydrogen space velocities. Promoters such as Al_2O_3, Cr_2O_3, TiO_2 and MgO retard the rate of reduction but give high surface area catalysts.

When the magnetite is reduced, dissolved alumina or magnesia, for example, is precipitated and collects between the iron particles to augment the structural promoter which may have been present as an intergranular component in the magnetite. The dissolved alumina is apparently present as $FeAl_2O_4$; under severe reduction conditions(67) this is all converted into pure α-Fe particles and alumina, while under less severe conditions, some, if not all, of the $FeAl_2O_4$ is retained and is present as small inclusions within the α-Fe grains.

Results of Anderson et al.(68) also emphasize the inhomogeneity prior to reduction of a typical fused iron catalyst containing magnesium and potassium oxides as promoters. The major portion of the material contains homogeneous magnetite grains; however, a substantial minor component consists of alternate layers of magnetite and another phase consisting of a mixed oxide of iron and magnesium. In general, the inhomogeneous component is more readily reduced than the homogeneous one, probably as a result of the smaller size of the magnetite domains, and yields more highly dispersed iron particles after reduction.

Surface area – Fused iron catalysts have a very low surface area prior to reduction. The porosity, total surface area and the reduced metal surface area progressively increase with the degree of reduction as is illustrated by the data(69) in Table 4.

The presence of particles of promoter between α-Fe crystallites inhibits crystal growth of the α-Fe and results in a high surface area of the reduced catalyst. The extent of this effect is related to the ratio of ionic charge to ionic radius of the promoter cation(70), ie, the lower the value of this ratio the larger the surface area promotional effect. Thus, for example, Al_2O_3 and TiO_2 increase the area while MgO has less effect; MnO, Li_2O and CaO have little influence and K_2O actually decreases the surface area.

TABLE 4 Surface areas and average pore diameters as a function of extent of reduction for a fused iron catalyst(69)

% reduction	Total surface area (m^2g^{-1})	CO adsorption (dm^3kg^{-1})	Average pore diameter (nm)
0	0	0	0
20	2,1	0,16	34,3
40	4,2	0,29	33,3
60	6,3	0,43	33,0
80	8,4	0,57	33,8
100	10,1	1,00	35,2

Surface composition – Using CO chemisorption to measure the surface area of metallic iron, it is found that for most promoters, a large surface area corresponds to a large specific iron surface area; an exception to this is TiO_2, which yields a relatively low metal surface area(70). Although the surface area of alumina-promoted iron is substantially greater than that promoted with magnesia, this difference is not as marked in relation to the iron surface area.

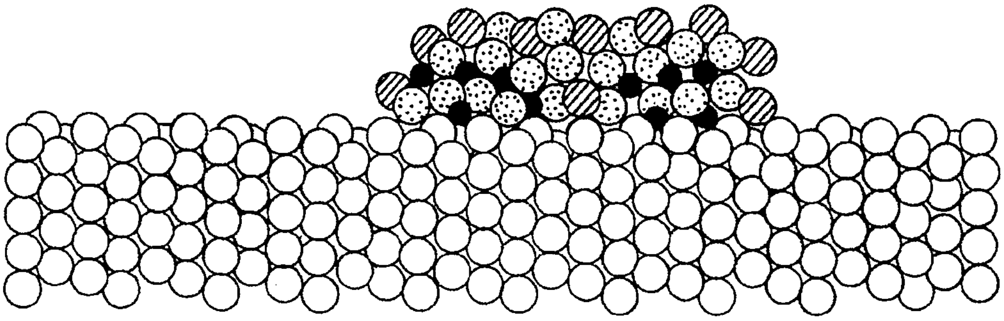
Particles of promoter located between the iron crystallites might be expected to occupy a portion of the iron surface. Selective chemisorption of CO and CO_2 has shown(71) this to be particularly true in the case of potassium oxide; as the proportion of K_2O in the catalyst is increased from 0,09 mass % to 1 – 1,5 mass %, the proportion of the iron surface covered by K_2O increases from 16% to 60 – 70%. On the other hand, with alumina contents in the range 0,4 – 10,2 mass %, the proportion of the iron surface covered by alumina varies in the range 14 – 55%.

This picture of the iron surface has been largely substantiated by a direct study(72) of promoted fused iron catalysts using Auger electron spectroscopy (AES). In the case of a triply promoted catalyst (Fe, K, Al, Ca), about 5 atom % of the surface consists of iron, the balance being promoters.

A model of the surface of a doubly-promoted fused iron catalyst has been proposed(72), based on AES and other data and is illustrated in Figure 2. The surface region is extremely non-uniform with both promoter and iron present in the region. The promoter, in the form of a K_2O–Al_2O_3 complex is believed to be present as surface islands floating on the iron surface rather than buried within the surface region; continuous areas of pure iron exist between these islands. In addition, the iron below the promoter islands is believed to be metallic. The potassium and oxygen ions tend to be above the aluminium ions though some potassium ions probably lie within the island and could be in contact with the iron surface.

FIGURE 2 Model of a doubly-promoted fused iron catalyst surface(72)

○ = Fe; ● = Al; ⊘ = K; ◉ = O



5.2.2 During synthesis

Carbide formation – The carburization studies of Sancier et al.(73) on a fused iron catalyst indicated that during FT synthesis at low temperatures (480 – 573 K) α-Fe is converted to Fe_2C and then to Hägg carbide. The transitory formation of cementite was noted also. At higher temperatures (598 K) the α-Fe is converted directly to Hägg carbide. These results are in general agreement with those of other workers(74,75).

Surface composition – An improved understanding of the surface composition of iron catalysts during FT synthesis has been obtained by the application of surface sensitive techniques(16). In particular the important role of reactive surface carbidic carbon has become apparent (see Section 6.1.3).

A build-up of surface carbon occurs(73,76) following the conversion of the iron to a carbide of approximate composition Fe_2C. XPS studies(54) on iron-rich FeRu alloys indicate that this carbon overlayer growth continues to a depth of 20 – 30 monolayers and causes a strong attenuation of the Fe^+ and Ru^+ SIMS signals. However, the fact that the catalytic activity drops by a factor of only five suggests that the carbon does not cover the surface in uniform layers but that some access to the iron surface remains.

Carbon deposition occurs rapidly during FT synthesis on a potassium-promoted iron powder resulting in a strong diminution of the XPS peaks of iron. However, the potassium signal is not strongly diminished with respect to carbon, suggesting that the potassium diffuses through the carbon layer and maintains a high concentration in the outer surface region(76,77).

6. CATALYTIC BEHAVIOUR OF IRON CATALYSTS

6.1 ACTIVITY

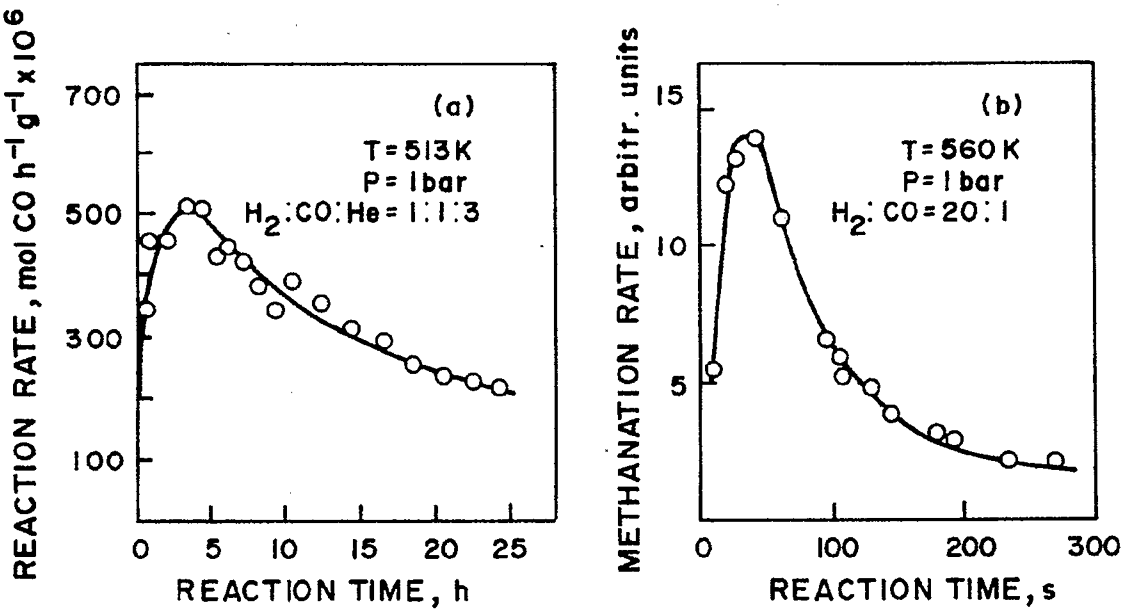
6.1.1 Time dependent behaviour

The activity of freshly reduced iron catalysts in the FT synthesis starts initially from zero and increases slowly to a maximum with time on stream. In this respect iron differs from other FT active metals such as Co, Ni and Ru where the activity is high from the beginning. A rather strong deactivation of the iron catalyst occurs over longer periods on stream. This type of behaviour is illustrated in Figure 3 for both a precipitated catalyst(63) and an iron foil(78). The position of the maximum is a function of the conditions of the synthesis reaction and the nature of the catalyst.

6.1.2 Role of bulk carbon

Several authors(60,63,79) have shown that bulk carbide formation is intimately involved in the development of maximum activity in iron catalysts. However, controversy exists as to whether or not these carbides are directly involved in the synthesis reaction. The situation is further complicated by the existence of several types of carbide.

FIGURE 3 Time dependence of reaction rates during FT synthesis over iron catalysts: (a) reduced α-Fe_2O_3(63); (b) clean Fe foil(78)



Using a silica-supported iron catalyst, Raupp and Delgass(79) found that the reaction rate follows the extent of bulk carbide formation and suggested that the incorporation of carbon into the iron particles controls the concentration of active surface sites. Transient studies by Matsumoto and Bennett(74) indicated that, while the steady-state catalyst bulk corresponds to Hägg carbide, the surface of the active catalyst is covered mostly by a carbon intermediate deposited by the dissociative adsorption of CO, and whose hydrogenation represents the rate controlling step. The initial increase in activity from zero implies that the concentration of this active intermediate increases as the iron is carburized. If the reactivity of the carbon intermediate towards the carburization of iron is high so that its surface concentration is proportional to the extent of carburization, the correlation between FT activity and bulk carbide formation found by Delgass may be explained. The more rapid acceleration of the synthesis rate on a magnesia-supported iron catalyst(79) is consistent with the faster rate of carburization of the smaller iron particles present.

The suggestion that the active intermediate formed during synthesis is the intermediate for both bulk carbide formation and hydrocarbon synthesis is supported by the result(74) that a catalyst possessing a bulk carbide structure but with a clean iron surface exhibits immediate activity in FT synthesis. In this case the active carbon intermediate is immediately available for hydrogenation without competition from bulk carbide formation. This idea is also supported(80) by activity data obtained on low iron content FeRu alloys which do not form bulk carbides during reaction. Furthermore, the carbon formed by the dissociation of CO alone and which carburizes the iron to Hägg carbide is much less reactive with hydrogen than the active carbon formed during synthesis(74), indicating that bulk carbide is not the intermediate.

An extremely rapid increase to maximum activity is observed during FT synthesis over polycrystalline iron foils(78,81) and is associated with the accumulation of a surface carbidic carbon layer. Under the synthesis conditions used, iron foils do not undergo phase transformations to bulk carbide(81).

6.1.3 Role of surface carbon

The decline in activity with time of iron catalysts has been attributed to the formation of a surface multilayer carbon deposit. The rate of removal of active carbon during synthesis is insufficient to prevent this carbon from depositing but at steady state, the removal of carbon by a small very active portion of the surface just compensates for the deposition.

Once the carbon overlayer is generated, its rate of removal in hydrogen is negligible at the normal FT reaction temperature. Regeneration cleans only the active surface, leaving the balance of the carbon deposit unaffected; much higher temperatures are necessary for removal of the carbon layers with hydrogen. It is therefore apparent, in agreement with the transient data of Matsumoto and Bennett(74) that significant amounts of unreactive carbon coexists with the true reaction intermediates.

Nature and reactivity of surface carbon – Kieffer et al.(82) applied the technique of temperature programmed surface reaction (TPSR) to a study of the carbonaceous surface species arising from the dissociation of carbon monoxide on iron. Three types of carbon species with differing reactivities towards hydrogen were distinguished. The first, termed α-carbon, forms during co-adsorption at temperatures up to 515 K and is readily hydrogenated to methane around 470 K. This α-carbon is unstable with respect to temperature, however, being converted to a less reactive form called β-carbon. It was suggested that the α-carbon is present as a thin surface or subsurface layer and the formation of β-carbon during temperature treatment is the result of a further reaction in which the subsurface species diffuse into the bulk. The third species, α'-carbon, formed during the synthesis reaction is very reactive towards hydrogen, producing both methane and higher hydrocarbons. This species probably plays an important role in the synthesis reaction and may be the most abundant surface species that determines the activity of the catalyst.

More detailed information on the chemical state of the carbonaceous layer on iron is provided by the Auger and photoelectron spectroscopic studies on iron crystals by Bonzel et al.(83). Three types of carbon species were identified. The carbonaceous layer formed in the initial phase of CO hydrogenation corresponds to an extensively hydrogenated carbidic carbon designated CH_x or perhaps a polymerized species C_xH_y. This species is unstable with respect to temperature, being transformed into carbidic carbon. A second species present after longer synthesis periods and also identified as a carbidic carbon species with bonded hydrogen, contains less hydrogen than the CH_x species. Both species react readily with hydrogen and have been shown(84) to be intermediates in the synthesis reaction. The presence of similar hydrogenated carbon species on finely dispersed Ni, Co and Ru catalysts have been inferred(85) from isotopic tracer studies and are regarded as major reaction intermediates for FT synthesis over these metals. The third carbon species was ascribed to graphitic carbon which is quite inert towards hydrogen under normal synthesis conditions. The decline in the activity of iron catalysts at longer synthesis times therefore is attributed to a transition from a pure carbidic to a mixed carbidic and graphitic carbon phase.

The transient studies of Reymond et al.(86) lend further support for the participation of partially hydrogenated carbon species, originating from the hydrogenation of surface carbon, in hydrocarbon chain growth. Higher hydrocarbons are immediately formed on exposure of a freshly reduced iron catalyst to an ethylene/hydrogen mixture as a source of C_xH_y fragments. The reaction rate starts at a maximum and no bulk iron carbide is formed.

6.1.4 Effect of pretreatment

The reductive pretreatment which yields the optimum FT activity in iron catalysts depends on the type of catalyst. For precipitated catalysts, a low temperature (490 – 600 K) hydrogen treatment is generally used to minimize the degree of sintering of the metal. Pretreatment in synthesis gas or in carbon monoxide alone may be advantageous as well.

Higher temperatures (670 – 870 K) in hydrogen are required to develop a sufficiently high activity in fused iron catalysts; for a given reduction temperature, the maximum activity is a function of the reduction time(87). A balance must be struck between the degree of reduction of magnetite and sintering of the reduced metal.

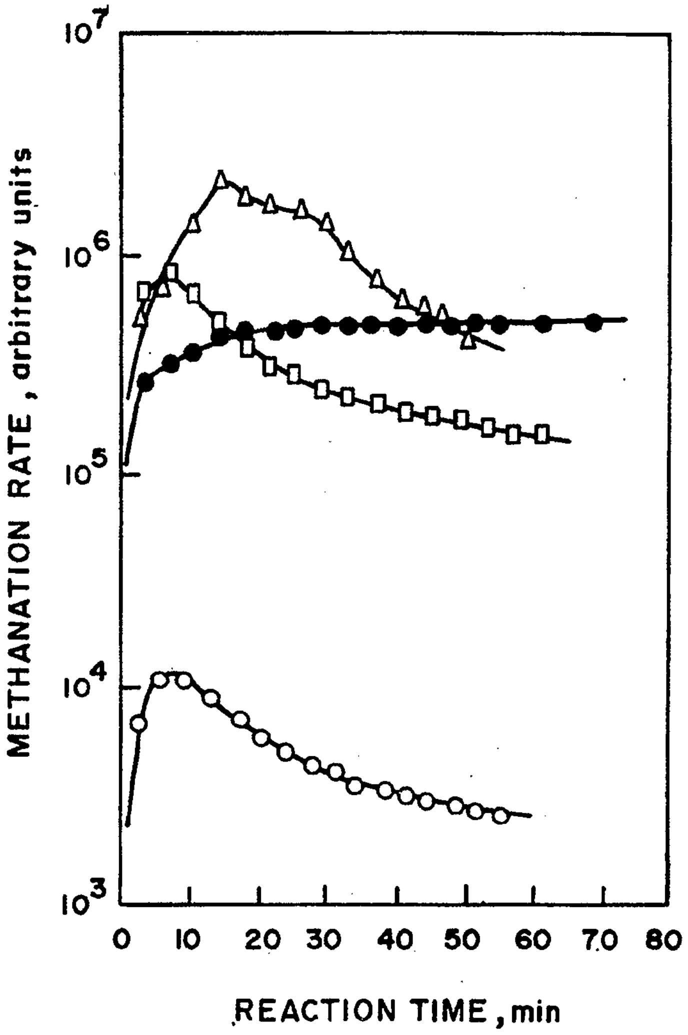
In an attempt to elucidate the possible role in FT synthesis of surface oxides formed by dissociation of carbon monoxide, several authors have investigated the behaviour of either preoxidized or unreduced iron catalysts. Dwyer and Somorjai(81) found a ten-fold increase in the initial rate of methanation over a preoxidized iron foil compared with that of the clean foil. This result cannot be interpreted solely as a promoting effect of oxygen since the oxide surface was shown to be unstable under reaction conditions and was rapidly reduced. The enhanced initial activity was thought to arise from the formation of very active metallic clusters during reaction.

Krebs et al. investigated reduced and unreduced magnetite catalysts(87) as well as oxidized, and oxidized and then reduced iron foils(16) and associated the variations in catalytic activity with variations in surface area resulting from the different pretreatments. Some results for iron foils are illustrated in Figure 4. The oxidized foil, which exhibits surface and catalytic properties similar to those of unreduced magnetite is considerably more active than the clean foil. However, the oxidized and then reduced foils are even more active. The marked deactivation of the reduced samples at longer synthesis times illustrates the greater propensity of metallic iron towards carbon deposition and graphite formation compared with the oxidized material.

The importance of the state of oxidation of the catalyst is further illustrated by a comparison(58,88) of the catalytic and structural properties of reduced and unreduced Fe_2O_3 with a reduced fused iron catalyst during FT synthesis. Figure 5 shows that the unreduced catalyst possesses a higher catalytic activity than either the reduced Fe_2O_3 or the fused catalyst.

FIGURE 4 Effect of pretreatment on the methanation activity of iron foils(16)

○ = clean; ● = oxidized; △ = oxidized and reduced at 570 K;
□ = oxidized and reduced at 670 K



During the early stages of synthesis, the unreduced Fe_2O_3 is converted largely into Fe_3O_4 along with the iron carbide $Fe_{20}C_9$, while the phases present in the reduced catalyst are α-Fe and $Fe_{20}C_9$. The stability displayed by the iron carbonyl-impregnated zeolite prepared by Obermyer et al.(62) was also associated with the presence of substantial amounts of Fe_3O_4 in addition to Hägg carbide.

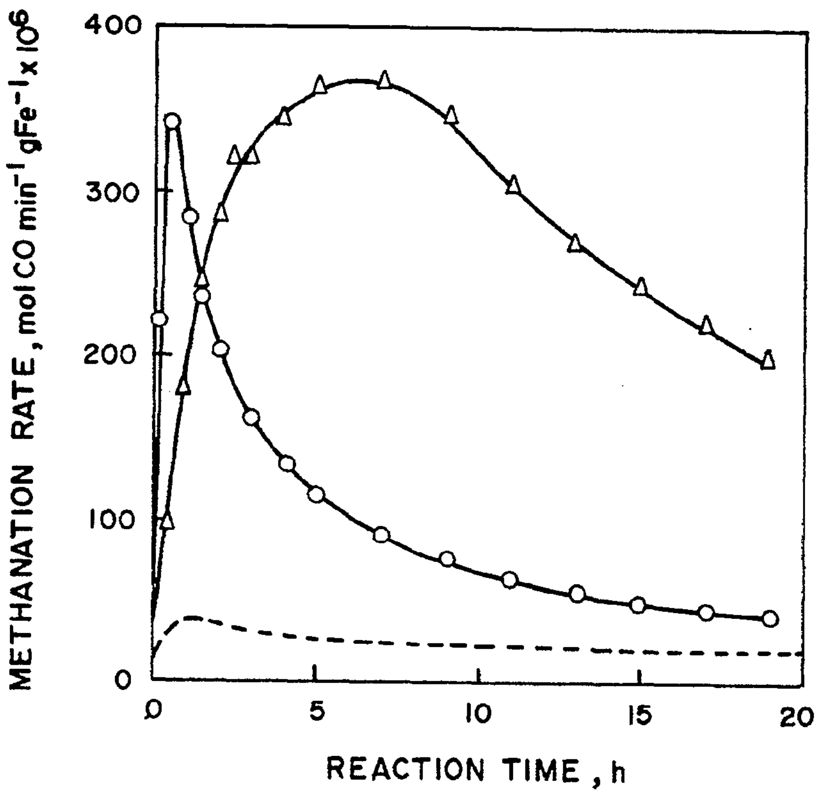
In the case of the unreduced Fe_2O_3, it has been suggested that the active carbon is formed by a thermodynamically feasible redox-type reaction on the Fe_3O_4 phase produced by reduction of Fe_2O_3 during synthesis.

$$2Fe_3O_4 + CO \rightleftarrows 3Fe_2O_3 + C$$

It is possible that more active carbon is formed if the solid partner is Fe_3O_4, rather than α-Fe, and the transformation of active into inactive carbon is also less pronounced on Fe_3O_4 than on α-Fe.

FIGURE 5 Effect of pretreatment(88) on the methanation activity of a fused iron catalyst (– – –) and of α-Fe_2O_3

○ = reduced in H_2 at 523 K for 15 h; △ = pretreated in He at 523 K for 20 min



6.2 SELECTIVITY

The product distribution obtained from iron-based catalysts at medium pressure exhibits similar characteristics to other FT active metals with respect to carbon number, but in general they produce higher amounts of olefins and oxygenated products. Figure 6a shows the molecular mass distribution(89) obtained over iron in both fixed-bed and entrained-bed operation. Methane is present in relatively high molar amounts and a maximum occurs at C_3 - C_5 followed by an exponential decrease to higher carbon numbers. Figure 6b illustrates the variation in olefin content with carbon number.

A further breakdown of the product types obtained in the gasoline and diesel ranges over promoted iron catalysts is given in Table 5.

FIGURE 6 (a) Product distribution; (b) olefin content, obtained over iron synthesis catalysts(89)

o = entrained-bed operation; Δ = fixed-bed operation

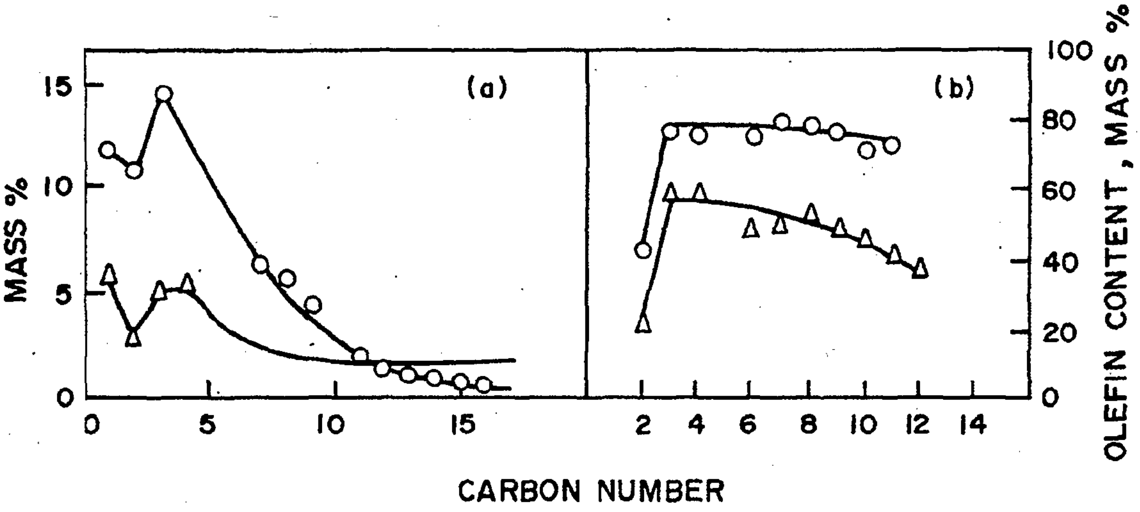


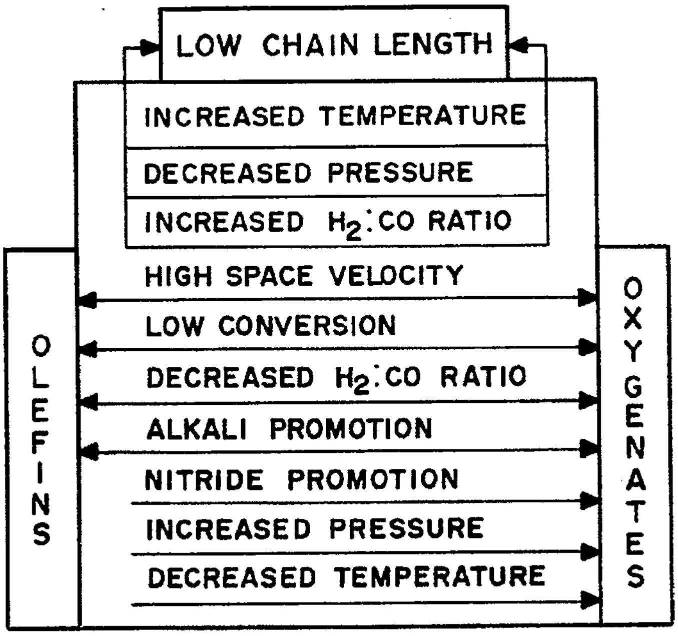
TABLE 5 Hydrocarbons obtained from fixed- and entrained-bed synthesis over iron catalysts(90)

Composition	Fixed-bed		Entrained-bed	
	C_5 - C_{11}	C_{12} - C_{18}	C_5 - C_{11}	C_{12} - C_{18}
Olefins	32	25	65	73
Paraffins (total)	60	65	14	10
n-Paraffins	57	61	8	6
Aromatics	0	0	7	10
Oxygenates (total)	8	7	14	7
Alcchols	7	6	6	4

6.2.1 *Influence of operating conditions*

The carbon number distribution of hydrocarbons obtained over iron catalysts corresponds essentially to the Schulz-Flory distribution law and is thus a function of the probability of chain growth. The value of the probability of chain growth can be varied by using different types of catalyst, by adjusting the promoter content of the catalyst or by altering the synthesis conditions. Gaube et al. demonstrated(91) that, while a precipitated iron catalyst produced a Schulz-Flory product distribution with a single probability of chain growth, two distinct probabilities occur simultaneously when a potassium promoter is added. Figure 7 summarizes the influence of various operating parameters on the hydrocarbon chain length and on the types of compounds present in the synthesis product.

FIGURE 7 Influence of operating parameters on the selectivity of iron FT catalysts



α-olefins are generally accepted as the primary products of the synthesis reaction and are further hydrogenated to paraffins in a secondary reaction. Furthermore, a secondary reaction involving the readsorption(92) of the initial olefinic product and insertion into the growing chain may be an important pathway leading to the formation of higher molecular weight hydrocarbons.

Process parameters such as space velocity and degree of conversion which decrease the residence time of the initially formed olefins can be expected to improve the olefin selectivity. Increased operating temperatures yield a lower molecular mass product; however, the effect on olefin selectivity is not so clearly defined. On increasing pressure, the hydrocarbon selectivity shifts towards higher molecular weight products, the selectivity to oxygenates increases but the olefinicity of the products is not much altered. In general, with iron catalysts, it is found that when the selectivity shifts away from light products, the selectivity to oxygenated products increases and the olefinicity of the hydrocarbons increases.

6.2.2 Effect of carbide formation

A freshly reduced iron catalyst is predominantly a methanation catalyst(60,79,81). Shifts in selectivity occur as the catalyst becomes carbided during synthesis, the most significant changes being in the ratio of saturated to unsaturated hydrocarbons, and in the relative amounts of higher hydrocarbons. Raupp and Delgass(79) showed that for a silica-supported iron catalyst, a relatively greater amount of saturated versus unsaturated hydrocarbons is produced as carbiding proceeds. However, the interpretation of this result is complicated by the increase in activity which accompanies carbiding; the olefin selectivity is particularly sensitive to the conversion level. The selectivity towards higher hydrocarbons also increases as the degree of carbiding increases.

6.2.3 Effect of particle size

There is a growing body of evidence which suggests that chain propagation in FT synthesis is dependent on the metal particle size. Much of this evidence originates from studies of small aggregates of ruthenium(4) and iron(6) stabilized in zeolite supports. However, narrow product distributions have also been observed(10,45) with highly dispersed iron on more conventional oxide supports, and may be attributed to a similar effect.

7. PROMOTION OF IRON CATALYSTS

The need for additives which improve the activity and particularly the selectivity of iron FT catalysts is well established empirically. These additives may be divided into two broad categories – electropositive elements, of which potassium is the most important, and electronegative species. This latter group comprises such elements as O, S and halogens which are normally regarded as catalyst poisons. However, if by inhibiting undesirable side reactions, the catalytic activity or selectivity toward a desired product is enhanced, their function may be regarded as promotional.

7.1 EFFECT OF PROMOTERS ON ACTIVITY

Alkali metal – The influence of potassium on the activity of iron catalysts is not always consistent; it depends on the nature of the catalyst, the content of "acidic" structural promoters and the conditions of operation.

At low alkali levels the activity of precipitated catalysts increases but goes through a peak at higher levels. Anderson et al.(93) found that the addition of 0,5 mass % K_2O to fused iron catalysts increased the activity by six-fold and caused a five-fold improvement in the resistance to sulphur poisoning compared with an unpromoted catalyst. A particle size effect was also observed, the activity and poison resistance both increasing further with decreasing particle size. According to Dry(2), the activity of fused catalysts operating at high temperatures in a fluidized bed, increases sharply with K_2O content and then levels out, while at low temperature in a fixed bed the activity decreases as the K_2O content is increased, possibly owing to the accumulation of heavy hydrocarbons which deactivate the catalyst.

In experimental studies on iron foils(77) it was found that the methanation activity decreases in the presence of potassium, consistent with the enhanced rate of carbon deposition.

Miscellaneous – Reduced iron catalysts which have been nitrided with ammonia exhibit a high and relatively constant activity(57). The stability of the catalyst may arise from the lower selectivity towards high molecular weight hydrocarbons compared with the reduced catalyst and the decreased deposition of elemental carbon.

Kieffer(39) and van Dijk et al.(65) recently reported that the addition of sulphate to iron catalysts results in a stable activity for a diluted synthesis gas at high temperatures. This increased stability compared with the unpromoted catalyst was attributed to a reduced carbon deposition. For the same type of catalyst Snel (this laboratory) did not observe this stability when using undiluted synthesis gas.

7.2 EFFECT OF PROMOTERS ON SELECTIVITY

Alkali metal – Promotion of iron catalysts with alkali has a strong influence on product selectivity. The average molecular weight of the hydrocarbons formed increases as does the olefin and alcohol fraction in the product. α-olefins predominate and the amount of internal olefins decreases with alkali content. The presence of potassium also results in increased CO_2 production. Both promoted and unpromoted regions of the iron surface may exist(91) at low potassium concentrations.

Nitrides – The conversion of reduced iron catalysts to nitrides or carbonitrides produces(57) a marked change in selectivity. A relatively low molecular weight product is formed containing a large fraction of C_1 and C_2 hydrocarbons and alcohols, and insignificant amounts of wax.

Sulphur – While sulphur is generally regarded as a poison for most metal catalysts, the presence of small amounts of sulphur can have a desirable effect(37) on the selectivity of the FT reaction.

The effect of sulphur in reducing the production of high boiling point hydrocarbons and enhancing the olefin content of the hydrocarbons produced was noted as early as 1929. Various authors(94,95) have since supported the claim of enhanced olefin production in the presence of sulphur. In addition, Layng(95) reported that the addition of sulphur causes a reduction in the formation of CO_2, water being the major oxygenated product instead.

The addition of sulphate(39) to a precipitated iron catalyst suppressed methane formation, decreased the production of hydrocarbons higher than C_3 and enhanced the olefin content of the product. It was suggested that following pretreatment of the catalyst or during synthesis, the sulphate ion is reduced to sulphide.

Halogens – The treatment of iron-based catalysts with halogen compounds(96) lowered the methane selectivity and enhanced the production of C_2 - C_4 olefins. Furthermore, the addition of 0,02 to 0,5 mass % sulphur to the halogen-treated catalyst resulted in a further increase in the olefin fraction. As with sulphur the presence of halogen sharply increased the ratio of water to CO_2 formed during synthesis.

Hammer et al.(38) confirmed the effect of halide ions, and chloride in particular, in enhancing the olefin selectivity of a precipitated iron catalyst. The product distribution was also shifted towards lower carbon numbers.

Matrix oxides – Using a co-precipitated Mn/Fe catalyst (Mn:Fe = 9:1) in which the iron is embedded in an MnO matrix, Kölbel and Tillmetz(10) claimed high selectivity towards C_2 - C_4 olefins and only traces of methane. By appropriate choice of conditions and matrix oxide content, Schulz(97) obtained a primary olefin selectivity of about 85% of the hydrocarbon in the C_2 - C_{15} fraction. Vanadium oxide yielded(98) similar results and further improvements could also be obtained by incorporation of ZnO, MgO and alkali.

Miscellaneous – The combination of ruthenium with iron to form unsupported bimetallic alloys produced marked changes in selectivity(54). Owing to iron enrichment, the FeRu alloy surface was largely iron over much of the composition range. A minimum in methane selectivity occurred at about 30 atom % Fe in the bulk of the catalyst and much higher C_2 and C_3 olefin selectivities were observed than with pure iron. A similar enhancement in the C_2 - C_5 olefin selectivity also occurred(52) on silica-supported FeRu bimetallic alloys.

Selectivity changes in iron catalysts may also be brought about by a judicious choice of the support. Rao and Gormley(44) obtained marked variations in the selectivity of iron catalysts (Fe) supported on ZSM–5 or silicalite. The silicalite-based catalyst produced considerable quantities of C_2 - C_4 olefins, which were almost absent from ZSM–5 (Fe). Addition of potassium as a promoter enhanced the C_2 - C_4 olefin fraction from silicalite (Fe) dramatically to a level comparable to that obtained with the Mn/Fe catalyst of Kōlbel. At the same time the C_2 - C_4 paraffin fraction was greatly suppressed with the result that the C_2 - C_4 olefin to paraffin ratio obtained from silicalite (Fe) was vastly superior to the Mn/Fe catalyst.

The liquid-phase product from ZSM–5 (Fe) contained a considerable fraction of aromatics which were almost absent from silicalite (Fe), while oxygenated products formed on silicalite (Fe) were almost absent from ZSM–5 (Fe). Some 92% of the liquid product from ZSM–5 (Fe) was in the gasoline boiling range compared with 77% in the case of silicalite (Fe).

These variations in selectivity, obtained using supports with identical crystal structures, are related to differences in the acidic properties of the support material, causing, *inter alia*, dehydration of oxygenates and aromatization of olefins.

7.3 MECHANISMS OF PROMOTER ACTION

Alkali metal – While the application of modern surface science techniques has led to an improved understanding of the role of potassium in iron-based catalysts, the precise mechanism of potassium promotion remains uncertain.

It is well established(27,29) that the presence of potassium increases the adsorption energy of CO on iron. Following the argument of Dry(27), the increased strength of adsorption of the π-acceptor CO molecule is caused by an increased electron density on the metal owing to electron donation from potassium. The simplified molecular orbital picture of CO adsorption described in Section 3 suggests that the increased charge on the metal should strengthen the iron-carbon bond and at the same time weaken the carbon-oxygen bond thus making it more prone to attack by hydrogen. The stronger metal-carbon bond would increase the surface coverage and residence time of carbon complexes thus promoting chain growth. On the other hand, the reduced hydrogen adsorption resulting from the increased CO coverage would result in a lowering of the hydrogenation activity and a suppression of the secondary hydrogenation of olefins.

The higher probability of CO dissociation on potassium promoted iron has been confirmed(77) experimentally and the decreased methanation activity of potassium-promoted iron foils is attributed to the resultant increase in the rate of graphite precipitation.

The observation of Bonzel et al.(77) that the potassium promoter does not prevent the formation of graphitic carbon on iron nor does it slow down the process of catalyst deactivation, is in disagreement with the results of Somorjai who reported(99) the absence of carbon deposition or catalyst deactivation in the case of potassium promoted oxidized iron foils. It was suggested that potassium catalyzes the removal of surface carbon through a reaction cycle involving the formation of KOH and K_2CO_3 to produce the net reaction

$$C + H_2O \rightarrow CO + H_2.$$

XPS studies suggested(16) that the potassium may be present as potassium hydroxide following the synthesis reaction. The low temperature interaction of water vapour with graphite catalyzed by alkali metal hydroxides or carbonates can result(100) in the hydrogenation or oxidation of the surface carbon to methane or CO and CO_2 respectively.

An explanation of the promoting action of potassium having its origins in electron donation to the metal does not take into account that the potassium is initially present in the promoted catalyst as potassium oxide. The ionization potential of K^+ is very large (3,04 MJ) compared with that of metallic potassium (0,42 MJ) which gives rise to the possibility that electron transfer occurs via O^{2-} rather than K^+. Ozaki et al.(101) has suggested that whatever form the potassium takes, the electron donor properties of the potassium complex as a whole must be considered.

It is possible, however, that K_2O is reduced to metallic potassium during pretreatment or synthesis. A reduction of potassium oxide or hydroxide to elemental potassium by reaction with deposited carbon is one of the steps in a mechanism proposed(16) to account for the segregation of potassium at the surface of the carbon layer formed during synthesis.

Henrici-Olivé and Olivé(102) recently interpreted the role of the potassium promoter in FT synthesis on the basis of well-known reactions in molecular catalysis. Particular emphasis was placed on the fact that the interaction of transition metal carbonyl complexes with electron-acceptor cations such as the alkali metal cations greatly enhances the migratory insertion of the CO ligand into the metal alkyl bond. Thus, if the surface alkyl iron carbonyl species has a suitably positioned neighbouring K^+ ion, the insertion reaction should be greatly accelerated. The enhanced growth rate is then expected to result in an increase in the average molecular weight of the product, assuming that the chain terminating step is not affected. Furthermore, as a result of the more favourable competition between chain initiation and hydrogenation for the metal hydride intermediate, an increased olefin fraction is to be expected.

Several difficulties still remain with this mechanism, however. Firstly, little evidence exists for a chain initiation step involving CO insertion into a metal-hydrogen bond. CO insertion reactions would be expected to favour alcohol formation, which is in fact observed with potassium promoted iron catalysts. Secondly, Li^+ is very reactive(102) in accelerating the homogeneous migratory insertion of CO but it is the least effective(2) of the alkali metals in the promotion of heterogeneous FT catalysts.

Sulphur, oxygen and halogens — No systematic studies have been carried out on the role of S, O and halogens in FT synthesis. In some respects the influence of these electronegative additives on CO and H_2 adsorption is opposite to that of potassium and has been attributed to a suppression of $d\pi$-$p\pi^*$ back-bonding(24).

A low FT synthesis activity and methane selectivity is to be expected in the presence of sulphur on account of the decreased probability of CO dissociation; a more stable catalyst might result from the lower rate of graphite deposition. In addition, a higher olefin selectivity will result, owing to the decreased secondary hydrogenation of the primarily formed olefins.

The effect of sulphur, oxygen and chlorine in restructuring(99) the surface of metal catalysts may also be an important factor in altering their activity and selectivity.

8. BASIS FOR FUTURE RESEARCH

Under steady-state operation, iron-based FT catalysts consist of a variety of carbidic and oxidic phases in addition to reactive and unreactive surface carbonaceous species. The complexity of the system is further compounded by the wide range of additives which may be included in the catalyst composition to improve activity and selectivity. Therefore, considerable research is still required to clarify the complex interactions which exist between the various components present. Initially, attention should be given to gaining an understanding of simple systems containing a minimum of variables, before proceeding to more complicated situations.

The physical and chemical structure of the promoted catalyst is clearly relevant to its catalytic behaviour. Small metal particles stabilized by suitable structural promoters may be expected to exhibit a faster rate of carbiding, a greater number of active surface ensembles exposed to reactants, and modified electronic properties.

Depending on the conversion level, the gaseous environment present during the synthesis reaction changes from reductive to oxidative and, in the presence of promoters, unusual oxidation states for surface atoms may be stabilized which would otherwise be unstable under reaction conditions. Additional oxidic phases may also be formed by reaction between the various catalyst components.

The activity of the catalyst and its stability against deactivation is strongly dependent on the nature and reactivity of the surface carbonaceous deposit formed during synthesis. A detailed study of the influence of promoters on carbon deposition and removal should deal individually with the various types of carbon present. For this purpose the extremely versatile TPSR technique is suitable.

The surface composition under which the reactive CH_x intermediate is most stable will be most favourable for a high activity as well as for a low rate of graphite precipitation and catalyst deactivation. The stabilization of an Fe_3O_4 phase appears to be beneficial in this respect. In the context of hindering or eliminating the formation of graphitic carbon, the potassium-catalyzed reaction of graphite with water vapour is interesting.

The selectivity of iron catalysts in hydrocarbon synthesis is closely coupled to the influence of chemical promoters on the overall electronic properties of the catalyst which, in turn, affect the adsorption-desorption behaviour of reactants and products. While CO dissociation appears to be essential for chain initiation, the carbon complexes formed must not be so strongly adsorbed as to deactivate the surface. For high olefin selectivity, conditions which favour the desorption of the primarily formed olefins are required. With regard to hydrogenation activity, a balance must be struck between the ability to form the partially hydrogenated carbonaceous species necessary for chain growth, and the desirability to minimize the secondary hydrogenation of olefins.

The co-formation of hydrocarbons and oxygenated compounds on iron catalysts has been rationalized by the existence of a parallel mechanism involving the cis insertion of an undissociated CO molecule or of an oxymethylene group in the metal-alkyl bond. This insertion reaction may occur on the same sites as carbene insertion or alternatively, on oxidic patches on the surface. However, not much evidence exists in support of these proposals. A study of the surface species present on nitrided iron catalysts may lead to an understanding of the conditions favouring oxygenate formation and in addition may give some clues to the factors which control the selectivity in other directions.

9. SUMMARY OF FINDINGS

i. The steady-state activity of reduced iron catalysts in FT synthesis develops only after a considerable period on stream.

ii. During the approach to steady-state activity, iron is converted to a variety of bulk carbides and oxides and a surface carbonaceous layer is formed simultaneously.

iii. Surface carbidic carbon species, which are the true reaction intermediates, co-exist with significant amounts of unreactive graphitic carbon which is responsible for catalyst deactivation.

iv. Graphitic carbon precipitates at an appreciable rate when α-Fe is present in the pretreated catalyst; the presence of an Fe_3O_4 phase in the active catalyst results in a more stable catalytic activity.

v. A broad distribution of products, fairly rich in olefins and oxygenates, is obtained during the hydrogenation of CO over iron catalysts.

vi. The product distribution may be shifted to some extent by altering process conditions; the achievement of a narrow product spectrum requires the use of special support materials (which may also introduce bifunctionality), a limitation on the metal particle size, or the incorporation of suitable promoters in the catalyst.

vii. A shift in selectivity towards an olefin-rich product may be obtained by the addition of promoters such as K_2O or MnO; nitride promotion enhances alcohol formation.

viii. The mechanisms by which promoters influence activity and selectivity are poorly understood.

10. SUMMARY OF RECOMMENDATIONS FOR FUTURE RESEARCH

i. Study the influence of promoters on the physical and chemical structure of iron catalysts, on the adsorption-desorption behaviour towards H_2, CO and simple straight-chain α-olefins, on the nature and reactivity of surface carbonaceous deposits and on olefin hydrogenation activity.

ii. Develop further the techniques of temperature programmed reduction (TPR), desorption (TPD) and surface reaction (TPSR) for use in the above studies.

iii. Correlate the information obtained with changes in activity and selectivity in Fischer-Tropsch synthesis.

iv. Study the peculiar properties of nitrided iron catalysts responsible for high oxygenate selectivity with a view to clarifying the factors that influence selectivity; extend this to other interstitial compounds of iron as possible selective catalysts.

v. Attempt to narrow the product distribution, while maintaining a desirable function selectivity, particularly towards olefins, by using supported iron catalysts; proper choice of support materials will require a careful consideration of the factors that influence activity and selectivity.

vi. Consider applying surface sensitive spectroscopies such as XPS and Auger electron spectroscopy in the characterization of the structural and electronic properties of promoted iron catalysts.

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