

3. IMPROVEMENTS IN THE USE OF CARBON MONOXIDE/HYDROGEN MIXTURES

3.1 GENERAL PERSPECTIVE

In the last two decades, mixtures of carbon monoxide and hydrogen gas have increasingly become a major source for the production of chemicals and liquid fuels. Although synthesis gas is still primarily produced by the steam reforming of natural gas and naphtha, gasification of coal is becoming increasingly attractive for the production of syngas, as a result of both steadily increasing oil prices and enormous coal reserves.

Some of the major syntheses that are feasible with carbon monoxide/hydrogen mixtures are schematically represented in Figure 3-1. Commercially practiced processes for the production of chemicals from syngas and/or methanol include those for oxo chemicals, acetic acid (Monsanto), acetic anhydride (Halcon, Tennessee Eastman), formaldehyde, chloromethanes, and methyl formate (1,2). Synthesis of several other chemicals (vinyl acetate, formic acid, ethylene glycol, and light olefins), though feasible (1,2), has not yet been commercialized. A detailed discussion of these emerging technologies is available in the referenced literature. The primary emphasis in the use of syngas mixtures produced by coal gasification is on the production of high-quality transportation fuels (indirect coal liquefaction to high-octane gasoline or high-octane diesel), which can be achieved either in a direct or indirect way (Figure 3-1). Indirect production can be achieved either through the synthesis of methanol (for instance, in liquid phase, as is done by Air Products/Chem Systems Inc.) followed by methanol-to-gasoline conversion on shapeselective zeolites (Mobil's MTG process), or through the synthesis of Fischer-Tropsch hydrocarbons (following SASOL or slurry-phase technology). However, Fischer-Tropsch synthesis, which is currently practiced by SASOL in fixed-bed and fluidized-bed reactors (Chapter 4), yields products of poor selectivity, which necessitates further upgrading through a sophisticated refinery scheme (3). There are two alternatives to this extensive refining. One is

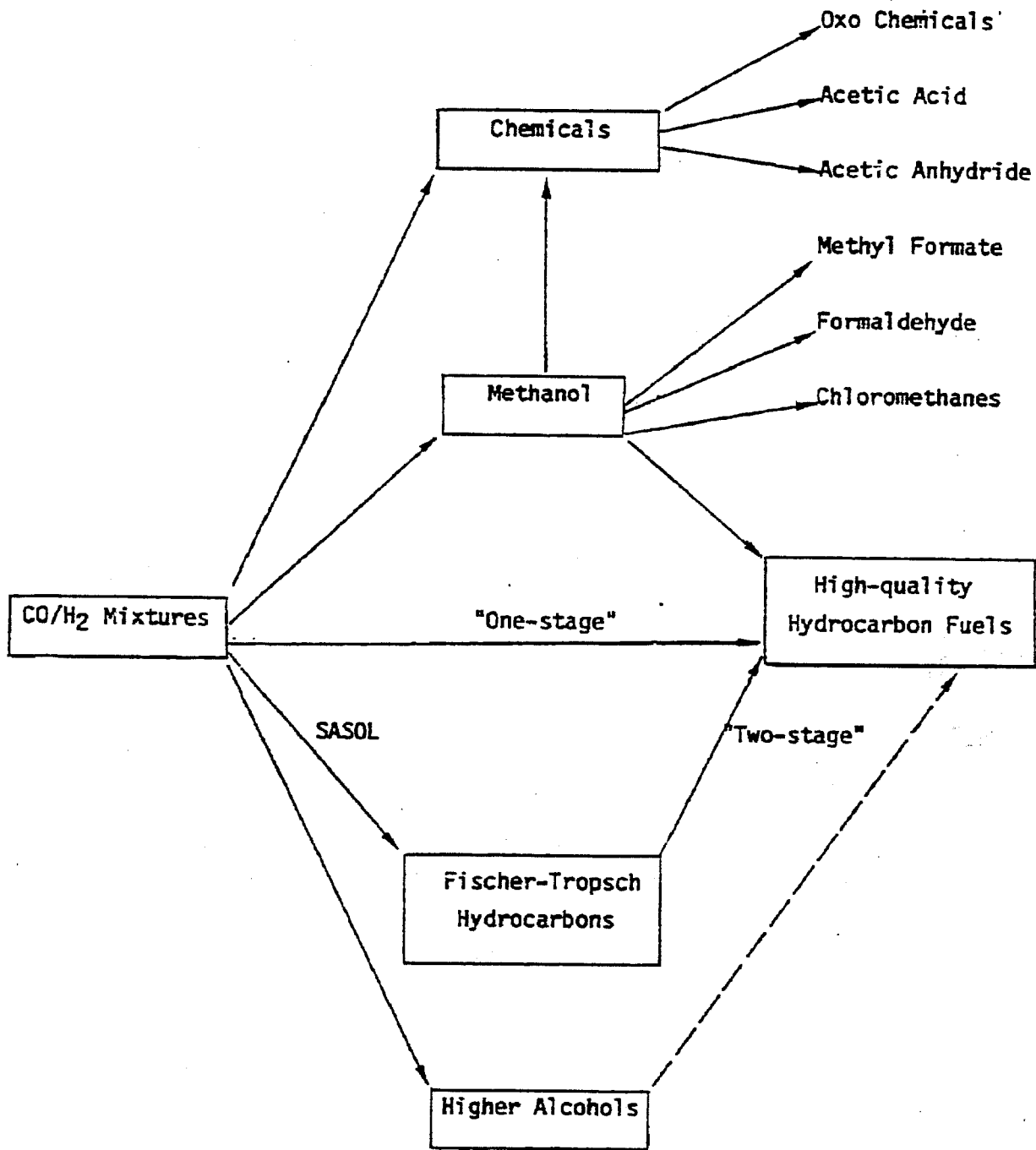


Figure 3-1. Schematic Representation of the Major Uses of CO/H₂ Mixtures

second-stage upgrading on ZSM-5 catalyst (Mobil's "two-stage" process). The second is direct synthesis of high-quality products using modified Fischer-Tropsch or methanol-type catalysts in combination with shape-selective catalysts of high acidity (ZSM-5, silicalites), either as bifunctional catalysts or as physical mixtures (Union Carbide Corporation, Pittsburgh Energy and Technology Center). Two-step approaches have the generic advantages that the operating conditions in each step can be optimized separately for the given catalyst and that the product slate of the first step can be fine-tuned for optimum performance of the catalyst in the second step. Compared to direct, or "one-stage," approaches, they have the disadvantage of higher investment and operating costs.

This chapter reviews some of the recent developments in the indirect and direct synthesis of high-quality fuels. Developments in oxo synthesis are also reviewed because of possible benefits to slurry-phase Fischer-Tropsch technology.

3.2 DEVELOPMENTS IN FUEL SYNTHESIS VIA METHANOL

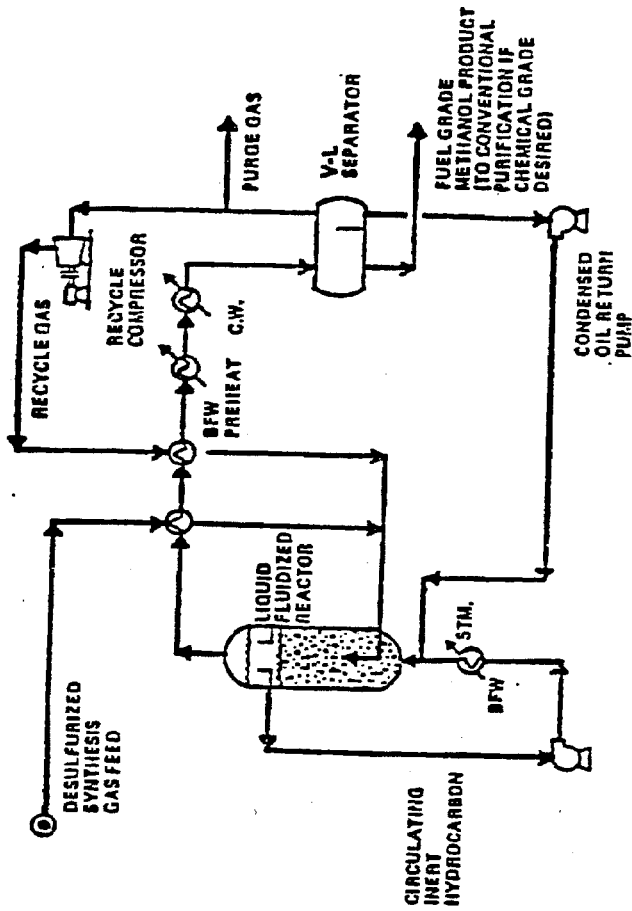
3.2.1 Introduction

For several years, the conversion of methanol to hydrocarbons has been known to occur both on zeolitic (4-9) and nonzeolitic catalysts (10-12). To produce high-quality gasoline, catalysts of the H-ZSM-5 type are preferred, because these catalysts display a high selectivity toward isoparaffins and monocyclic methyl-substituted aromatic hydrocarbons, which constitute the major high-octane components in gasoline. To achieve this selective conversion of methanol into high-octane gasoline, several reactor technologies have been proposed, based on either fixed-bed (13,14) or fluidized-bed (15,16) operation. Mobil's Methanol-to-Gasoline (MTG) process, which makes use of fluidized-bed technology (15), has now reached the pilot-plant stage. A 100-barrel-per-day pilot plant has been in operation one year at the URBK (Union Rheinische Braunkohlen Kraftstoff AG) facility near Koln, West-Germany (17). The plant operates more than satisfactorily at total methanol conversion and yields up to 90 wt% of gasoline of 95-96 RON (research octane number). This project is jointly conducted by

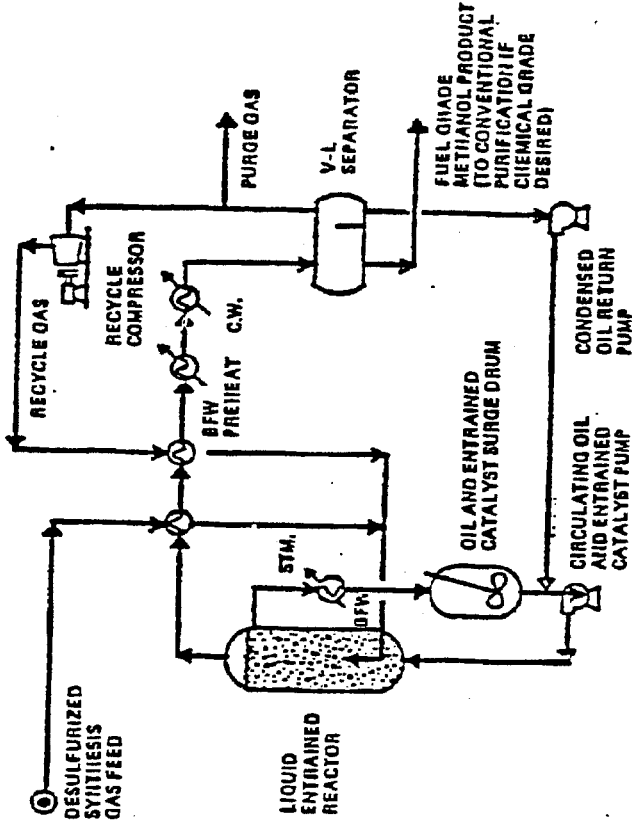
Mobil Research and Development Corporation, Uhde GmbH, and URBK, and is financially supported by the United States Department of Energy and the West German government.

The major problems in this production route to gasoline are associated with the methanol synthesis step. Generic problems of this synthesis, which has now been used commercially for almost 70 years, include low syngas conversions (2-10% CO conversion) per pass (which requires high recycle ratios), poor efficiency in heat removal, and high compression requirements (18). The original high-pressure synthesis was carried out at pressures exceeding 3000 psig, since high pressure is required to at least partially compensate thermodynamically for the temperatures necessary to make the reaction proceed fast enough kinetically to be commercially feasible. A first breakthrough in the field was the use of large centrifugal compressors in one stage rather than several stages of reciprocal compressors. This development actually paralleled the ammonia synthesis development. A second breakthrough was the invention of copper-containing "low-pressure synthesis" catalysts, which permitted the lowering of the operating pressure to about 2000 psig, with some sacrifice in yield per pass but with a decrease in investment cost that more than compensated for potential yield losses. Because methanol synthesis is highly exothermic, one of the major problems has been to remove the heat from the reactor. In fact, thermodynamic equilibrium yields have never been obtained in commercial operation because of heat removal constraints that forced designs to operate at lower than theoretical yields.

To deal successfully with these problems, several reactor designs have been developed, including the multitubed reactor with intermediate cooling developed by Imperial Chemical Industries and the Lurgi heat exchanger reactor. Both of these reactors are used commercially. An emerging technology in this field is synthesis of methanol in the liquid phase, as invented by Chem Systems, Inc. and currently under development at Air Products' LaPorte facility in Texas. Advantages claimed for this liquid-phase operation, which can be carried out either in "liquid-fluidized" (ebullating) or "liquid-entrained" (slurry) mode (Figure 3-2), include high syngas conversions per pass, high efficiency in heat removal, and flexibility toward the composition of the synthesis gas processed



THE LPM6OH PROCESS WITH A
LIQUID-FLUIDIZED CATALYST REACTOR



THE LPM6OH PROCESS WITH A
LIQUID-ENTRAINED CATALYST REACTOR

Figure 3-2. Liquid-fluidized (Ebullating) and Liquid-entrained (Slurry) Operation Modes for Air Products/Chem Systems Liquid-phase Methanol Process Development Unit

Reference: (20)

(20). The last advantage, which is believed to apply generally to all gas/liquid/catalyst systems, is discussed in more detail in Chapter 4. A major problem in ebullating-bed operation is the attrition of present catalysts. Recent developments in methanol synthesis catalysts, especially aimed at improvements in the conversions per pass, are discussed below.

3.2.2 Developments in Catalysts for Methanol Synthesis

Methanol synthesis catalysts, which are currently being tested by Air Products in a gas-phase autoclave reaction prior to use in the liquid-phase process development unit, include experimental combinations of copper with zinc, magnesium, or cerium on several supports such as γ -alumina, chromia, zinc oxide, and silica. Also being considered are combinations of copper with molybdenum, tungsten, and tantalum, and several copper molybdates (CuMoO_4 , Cu_2MoO_5 , $\text{Cu}_2\text{MoO}_5/\text{SiO}_2$) (21,22). Very preliminary results have been discussed in the last two DOE Contractors' Conferences on indirect liquefaction (20,21).

During the last six years, major interest has developed in a new type of catalyst that uses palladium on various supports for the methanol synthesis. This type of catalyst has not yet been used commercially, but it is of great scientific interest because of the pronounced metal-support interactions that have been observed. A general discussion of the SMSI (strong metal-support interaction) phenomenon is given in Chapter 6.

While no clear and convincing evidence is available as to whether the new catalysts or any particular one of them are superior to conventional catalysts, statements have been made that their activity might be greater than that of the present generation of commercial catalysts. This, in itself, would be of commercial interest only if it were possible to operate these catalysts at lower temperatures and pressures than currently used. Since technology of heat removal, not activity, is the limiting factor of present commercial catalysts, the advent of more active catalysts will become of commercial interest only when better modes of heat removal are found. These catalysts may be particularly

applicable to suspensoid operation in liquid media such as proposed by Chemical Systems and, in the liquid system, may have the additional advantages of greater physical strength and less attrition. Some recent findings for this type of catalyst are discussed here.

The phenomenon of metal-support interaction is, by itself, of great importance because it may be applicable to many other areas of metal and metal oxide catalysis. The study that first called attention to the selective formation of methanol from synthesis gas over palladium catalysts, published in 1978, was authored by Poutsma of Union Carbide Corporation (23). This study states that hydrogenation of carbon monoxide over supported palladium catalysts gave methanol in high selectivity at 260°C to 350°C and pressures in the range of 150-16,000 psig. The most significant finding was that methanation (to any appreciable extent) occurred only outside the temperature-pressure regime for which methanol formation is thermodynamically feasible. The behavior of palladium and perhaps of platinum and irridium sharply contrasts with that of the other Group VIII metals for which hydrocarbon formation is a dominating feature. In a comparison with nickel at 314°C and 12.25 atm of synthesis gas (CO/H₂ = 30:70), palladium gave methanol formation, rather than methane, but also showed much less chain-growing activity than nickel. It has been proposed that the inability of palladium and perhaps platinum and irridium to chemisorb carbon monoxide dissociatively at reaction temperatures is responsible for this. This contrasts the dissociative adsorption of CO to that of other Group VIII metals.

Earlier workers, such as Fischer (24) and Yannice (25), have ranked Group VIII metals for hydrocarbon (including methane) synthesis. Palladium catalysts were found to be less active than other Group VIII metals on an alumina support. Support effects were found. Thus, palladium on eta alumina had about 80 times the specific activity of palladium black at 275°C, and even at identical dispersions palladium on eta alumina was 45 times more active than palladium on silica. A high selectivity to methane was observed throughout.

The Union Carbide workers used a tubular reactor with a high-surface-area silica-gel-supported palladium and a gamma-alumina-supported palladium catalyst. Over the range 260-350°C and 150-16,000 psig, methanol was the dominant product. The

only other easily detectable product over palladium on silica catalyst was methyl formate. Other oxygenated products such as ethanol were found in small quantities. In this work, the gamma alumina support was completely comparable in its effectiveness to silica. It thus contrasts sharply with the results reported for methanation.

In another series of experiments, palladium catalysts were used in a Berty-type gradientless reactor. Again, methanol was the major product obtained. This implies that the mechanism of methanol formation on palladium involves addition of an adsorbed H atom to adsorbed CO, and must therefore proceed through partially hydrogenated CH_xO surface complexes. There is an ambiguity in specifying the composition of the metal phase, particularly as small particles are dominated by surface effects that lead to deviation from bulk-phase diagrams.

Earlier workers (26,27) have indicated that, for certain reactions involving hydrogen, an α -Pd-H solid solution and a β -Pd-D-H phase can possess different catalytic activities. The importance of such hydride forms has been confirmed by Fajula, (28). He studied the hydrogenation of carbon monoxide between 260°C and 340°C and 5-50 atm with supported palladium catalysts, using three different silicas and HY and NaY zeolites. He found that the selectivity and activity of the catalysts are strongly dependent on the nature of the support and on the state of the metal on its surface. Methanol is produced on catalysts exhibiting small-size crystallites on which CO is weakly adsorbed, whereas the formation of methane is directly related to density of acidic sites on the surface of the support. Under experimental conditions, the palladium undergoes structural and electronic modifications due to transformation into hydride phases. Preparation of catalysts and their characterization by chemisorption, temperature-programmed desorption, x-ray diffraction, electron microscopy, and photoelectron spectroscopy were studied. A Berty reactor was used for kinetic studies. Methanol was the primary product for the palladium supported on sodium Y and on silica, with only traces of methane and water found. On the other hand, methane was the dominant carbon-containing product obtained on palladium on HY catalysts. In this case, small quantities of methanol were formed. The activity of this catalyst decreased rapidly with contact time.

Palladium on CAB-0-SIL produced a mixture of methane, methanol, and dimethyl ether. The mole ratio of these components changed with the time on stream.

A puzzling finding was that palladium on two different silicas, Davison grade 01 silica and SiO_2 , gave quite different results. The Davison-grade silica produced mostly methane, while the silica produced predominantly methanol. It appears that the silica and CAB-0-SIL are acidic, with similar amounts of reactive acidic groups per gram of catalyst. The Davison-grade silica is neutral. It is assumed that the effect of acidity on the methanation activity is due to the participation of the acidic sites in the methanation reaction path. The study showed large differences in the strength and mode of carbon monoxide adsorption on different individual catalysts. These appear to be related only to the formation of small palladium crystallites, regardless of the support acidity.

The acidity of the support appears to have no influence on methanol synthesis. In the case of the Davison silica 01, the particle size seems to play a dominant role for methanol synthesis, with the efficient catalysts being those containing only small palladium crystallites on which CO is weakly adsorbed. In general, Lunsford (28) concludes that methanol is produced on the catalyst exhibiting small metal crystallites on which carbon monoxide is weakly adsorbed. The methanol yields produced on these catalysts are comparable to those obtained with the industrial copper-zinc oxide catalyst. Formation of methane, on the other hand, is influenced by the acidity of the support. Methanation proceeds most probably via direct CO hydrogenation. Interactions between the partially hydrogenated species and the acidic groups on this support result in an enhancement of the reaction rate. Finally, under reaction conditions, the palladium undergoes structural and electronic modifications due to its transformation into hydride phases. These lead to a disintegration of the metal crystallites and to changes in the reaction rate expressions. For methanation, the transformation of the bulk palladium into its β -hydride phase results in a decrease in the rate constant, whereas for methanol synthesis, only a change in the reaction order versus CO partial pressure is noted.

In an extension of the work by Rabo (23), a group of Japanese scientists has investigated novel palladium catalysts prepared from complexes of the type

M_2PdCl_4 , where M is an alkali metal (29). It was found that with these catalysts, methanol is produced selectively from carbon monoxide and hydrogen, even below atmospheric pressure. Activity for methanol formation depends greatly on all the alkali metal cation, in the following order: lithium > sodium >> potassium > rubidium > than cesium. These new catalysts also increase the activity of methanol and also allow the use of more acidic supports such as alumina and silica alumina, rather than silica. Similar to Lunsford's finding (28), the different behavior for methanol and methane synthesis suggests that different reaction sites operate in each case.

The Japanese scientists (29) refute earlier proposals by Poutsma (23) and Vannice (25) that only methanation proceeds below atmospheric pressure in the flow system. They also point to the work of Ichikawa (30), which, as discussed below, shows that the selectivity of carbon monoxide and hydrogen to products is markedly affected by the nature of the precursor in dispersing the palladium metal particles.

Reaction of carbon monoxide and hydrogen was carried out at 453K to 573K with 5% palladium catalyst supported by silica. The silicas were varied, as were the precursor complexes of the palladium. Palladium/SiO₂ prepared by impregnation with Pd(NH₃)₄Cl₂ resulted mostly in methane, with small amounts of hydrocarbons and CO₂ and no methanol. On the other hand, when (NH₄)₂PdCl₄(Pd/SiO₂-II) or Na₂PdCl₄(Pd-Na/SiO₂) was used, methanol was the main product. The rates of methane formation on these two catalysts were almost the same and the metal surface areas of these two catalysts were comparable, but the rate of methanol formation on Pd-Na/SiO₂ was 36 times as fast as that on Pd/SiO₂-II catalyst. In a study of various alkali-metal cations upon the activity and selectivity of the CO/H₂ reaction at 453K using M₂PdCl₄ complexes, a remarkably high activity for methanol synthesis for the lithium-doped silica palladium catalyst was found, comparable with the sodium-doped catalyst. However, the activities of potassium-, rubidium-, and cesium-doped catalyst decreased drastically (in that order).

When studying the changes in activity and selectivity over palladium catalysts supported on various oxides such as silica, alumina, silica alumina, and zeolite,

the alumina-supported catalysts exhibited quite a high activity (one to two orders of magnitude higher than silica catalysts) and high selectivity for methanol synthesis. The tendency of the activity to increase on acidic supports has also been recognized in the methanation on palladium catalysts.

In an attempt to study the reaction intermediates and surface structure of the active sites for methanol synthesis, the hydrogenation of preadsorbed formaldehyde was studied by raising the temperature to examine the role of the adsorbed formate ion during the reaction of hydrogen with CO. Infrared spectroscopy was used for these studies. After evacuation of ambient formaldehyde vapor and desorption of most of the physically adsorbed formaldehyde, hydrogen was introduced onto the formate ion at 473K. It was demonstrated that the formate ion disappeared; methanol was detected by mass spectrometry. Most of the CO chemisorbed on the catalyst surface remained almost unchanged throughout these experiments. These results suggest that methanol could be formed by hydrogenation of surface formate ion and some surface interconvertible species.

It is apparent that novel catalysts such as lithium-palladium or sodium-palladium are not only very selective but also very active in producing methanol from synthesis gas mixtures under mild conditions, whereas many similar palladium catalysts produce mainly methane. The system is one in which metal catalysts prepared in different ways exhibit remarkably different selectivities in synthesis gas conversion. This could be associated with the nature of the selectivity and the design of the catalysts.

Ichikawa (30) has shown higher selectivities for methanol and ethanol in an atmospheric pressure syngas conversion for metal-supported catalysts prepared from rhodium, platinum, and irridium carbonyl clusters in combination with basic oxides such as magnesia, lanthanum oxide, and zirconia. Infrared spectroscopic, in situ studies revealed the strong interaction between cluster carbonyls and surface OH groups, particularly in the presence of water, to form CO_2^{-2} and CO_3^{-2} anions. The retention of cluster integrity depended on the surface basicity of the supports.

The relative rates of methanol formation depended considerably on the kinds of oxide supports and metal precursors. The platinum carbonyl clusters provided highly active catalysts when the different basic oxides for methanol synthesis, rather than the platinum chloride salt, were used. On the other hand, when the platinum clusters were impregnated on acidic or basic oxides that were too strong, such as silica, WO_3 , and Li_2O , the resultant materials were virtually inactive for methanol production. The striking difference in the activities for methanol synthesis between platinum carbonyl clusters and chloride salt-derived catalysts is related not only to the higher dispersion of metal on the cluster, but to the irreversible inhibition of residual Cl, which blocks the basic sites of CO activation. In contrast to the methanol formation, methanation activity depends marginally on the kinds of supporting materials. This suggests that methanation proceeds over the metal surface and is not as affected by the surface properties of oxides.

Methanol synthesis from syngas over palladium catalysts was also studied by Ryndin and co-workers (31). Catalysts were prepared by adsorption of palladium- $(\text{pi-C}_3\text{H}_5)_2$ on magnesia, zinc oxide, lanthanum oxide, γ -alumina, silica, titania, and zirconia, as well as with silica-supported palladium prepared from palladium chloride and palladium black. Both the activity and selectivity of palladium were strongly affected by the nature of the support and the composition of the palladium precursor. The specific activity for methanol synthesis decreased in the order: $\text{Pd/La}_2\text{O}_3 \gg \text{Pd/SiO}_2$ (derived from palladium chloride) > palladium/zirconia > palladium/zinc oxide, palladium/magnesia > palladium titania > palladium alumina, palladium silica [derived from palladium $\text{pi-C}_3\text{H}_5)_2$] \gg palladium black. The specific activity for hydrocarbon synthesis decreased in the order: palladium/ TiO_2 > palladium/ ZrO_2 > palladium/ La_2O_3 > palladium/ Al_2O_3 , palladium/ SiO_2 [derived from PdCl_2] > Pd/SiO_2 (derived from organo palladium), palladium black > palladium/ MgO > Pd-ZnO . Dimethyl ether production was observed over several of these catalysts.

Methanol and C_1 - C_6 hydrocarbons were observed as the primary products for all catalysts tested, and only occasionally were traces of ethanol detected. For palladium supported on alumina, titania, zirconia, magnesia, dimethyl ether was also observed. It thus appears that dehydration materials give dimethyl ether.

It was found that palladium-zinc oxide catalysts increased in methanol activity over a series of consecutive runs. With the exception of the palladium on silica catalysts, all catalysts exhibit a stable activity for hydrocarbon synthesis. For methanol synthesis, stable activity is achieved after three or four runs during which the activity increases several fold. For palladium on silica and palladium on lanthanum oxide, stable activity is reached within the first ten minutes of the reaction. The exceptionally high methanol synthesis activity of palladium on lanthanum oxide relative to the other catalysts confirms the results of Ichikawa in studies conducted at atmospheric pressure (32). It is concluded that the activity and selectivity of supported palladium catalysts for the hydrogenation of carbon monoxide is strongly influenced by the composition of the support and differs significantly from palladium black. Use of basic metal oxide supports favors the formation of methanol, with the selectivity to this product exceeding 98%. High methanol selectivity (98%) is also observed for palladium supported on silica, a neutral oxide. When an acidic metal oxide, such as alumina, titania, or zirconia, is used as support, the methanol selectivity is suppressed at the expense of forming hydrocarbons. Acidic sites on the support also appear to be responsible for converting some of the methanol formed to dimethyl ether.

A series of papers on synthesis gas reactions on palladium catalyst has been issued. The first of these is by Poels and co-workers (32a). It confirms Ichikawa's finding that the formation of methanol is sensitive to the choice of carrier. This series investigates the question of whether methanol formation is proportional to the palladium metal surface area. Palladium was alloyed with silver, a metal that is not catalytically active for either hydrocarbon or methanol synthesis. It is known that the electronic structure of palladium changes very little upon alloying and that the main effect of the addition of a virtually inactive metal such as silver is to diminish the average size of palladium ensembles. There seems to be no relationship between the surface concentration of palladium in the alloy and palladium in bulk with regard to the activity of the catalyst. This demonstrates that the activation of carbon monoxide for hydrogenation into methanol is a process quite different from that leading to hydrocarbon synthesis on other metals. Carbon monoxide need not be multicoordinated to produce methanol. Multicoordinated carbon monoxide

disappears upon alloying. Single-site CO would be a more likely precursor of methanol formation. However, it is also possible that palladium metal atoms are not the active sites in methanol synthesis. It can be inferred from experimental results that methane is formed at least partially from an oxygen-containing intermediate and that palladium plays a role in the formation in these intermediates.

Ponec (33) prepared palladium catalysts on silica with and without promoters. Magnesium and lanthanum oxides were used as promoters. It was found that the addition of the promoters increased both the selectivity for methanol and the activity of the palladium catalyst. It is hypothesized that promotion of palladium with Mg^{2+} and La^{3+} gives rise to the formation and stabilization of positive centers, Pd^{n+} , which are suggested to be essential for the production of methanol from synthesis gas. Ponec extends this discussion in a later paper (33a). In another paper, Driessen (33b), states that in reactions of synthesis gas over a series of palladium-on-silica catalysts, magnesium and lanthanum compounds used as promoters influence the activity of the catalyst. They increase the selectivity for oxygenates and suppress the selectivity for methane. Interestingly, it is shown that the activity for methanol synthesis is linearly correlated with the amount of palladium extractable from the reduced and used catalyst as palladium acetylacetonate. It is concluded that palladium "ions" are the centers for activation of CO towards methanol, whereas palladium metal supplies hydrogen atoms for hydrogenation.

3.2.3 Conclusions

Work published during the last six years indicates that supported palladium catalysts can be very active and selective for the production of methanol from synthesis gas. It has been clearly established that there is a metal-support interaction, and that different supports and promoters added to other supports can affect both the selectivity and activity of the catalysts. It has also been shown that some of the catalysts are at least as active as the conventional zinc-copper catalysts, and in some cases are more active.

In spite of considerable investigations, the reasons for the specific activity of supported palladium catalysts for methanol are not clearly understood. As they become clearer, it may be possible to further increase activity and selectivity. Such work may also lead to better catalysts for other reactions.

There is also no information regarding the effect of CO₂ and H₂O, which are common impurities in methanol synthesis, nor regarding the catalyst life and activity with prolonged use. It is therefore not clear whether they can be considered competitive with conventional catalysts. There is also no information on the feasibility of regeneration of spent catalysts.

If more active and selective catalysts of good life can be produced, they would be of interest for carrying out the synthesis at lower temperatures and pressures. They would be of particular interest as catalysts in reactors that provide good heat exchange, such as the Lurgi tubular reactor and the Chem Systems liquid-phase reactor.

3.3 DEVELOPMENTS IN FUEL SYNTHESIS VIA FISCHER-TROPSCH CATALYSIS

3.3.1 Introduction

Partly to encompass the problems associated with the methanol route, researchers have primarily focused their efforts on ways to improve the quality of Fischer-Tropsch products, either by upgrading them in a second stage [Mobil's two-stage process (34)] or by developing new catalyst systems capable of directly converting syngas into high-quality fuel (APCI, UCC, and PETC's one-stage approaches). An excellent discussion on the relative challenges and merits of two-stage versus one-stage processes has been given by Poutsma (35). The major challenge in two-stage processes is making the product slate of the first stage (Fischer-Tropsch synthesis) compatible with the fuel requirements for the second-stage ("upgrading") catalyst. The major challenge in one-stage processes is to develop a suitable catalyst. If such development succeeds, one-stage processes would most likely prove to be more economical because of lower

investment and operating costs. This section reviews some of the catalyst developments in this field.

3.3.2 Improvements in Fischer-Tropsch Catalysis

Improvements in Fischer-Tropsch catalysts have been directed toward achieving higher selectivities toward high-quality fuels and toward modifying conventional catalysts by developing novel catalyst systems.

Air Products' approach involves testing novel supported molecular cluster catalysts in liquid phase, aimed primarily at maximizing the yield of diesel products (C₉-C₂₅). Tests on these molecular cluster catalysts (of an as yet unrevealed nature, but probably involving ruthenium or osmium carbonyl chemistry) are currently being conducted in 300 ml and 1000 ml stirred-tank autoclave reactors at temperatures of 220-330°C, pressures of 1.1-3.5 MPa, and gas hourly space velocities up to 1000 h⁻¹ (36). Initial results revealed that the investigated catalysts gave yields of fuel-range hydrocarbons greater than the maxima predicted from a Schulz-Flory distribution of the products (Chapter 8). For example, using synthesis gas with a H₂/CO feed ratio of 0.5, 67.3 wt% of the hydrocarbon product was in the diesel-fuel range (Figure 3-3, curve a), as compared to an expected Schulz-Flory maximum value of 54.1 wt% (1). This deviation from the Schulz-Flory behavior could be due to experimental artifacts such as temperature gradients, unsteady state, or loss of products as a result of unaccounted volatilization or condensation of products, but this is unlikely in view of the scrupulous precautions taken by the APCI workers to avoid these types of artifacts. At this point it is not clear whether this peculiar observation, which may reflect a variation in the chain-growth probability α with the carbon chain length, results from metal particle-size effects on the product distribution (36) as suggested by Mys for uniformly dispersed catalysts (37).

Deviations from the Schulz-Flory distribution were also reported by Union Carbide researchers for a UCC-101 molecular sieve catalyst containing promoted cobalt, in spite of significant methane yield (38). The general approach followed by Union Carbide consists of combining a Fischer-Tropsch metal component (such as promoted

iron or cobalt) with a shape-selective molecular sieve component (such as UCC sieves 101 and 104) to control the hydrocarbon product boiling range quality (39). The Fischer-Tropsch metal component would provide the carbon monoxide hydrogenation function, while the shape-selective and acidity characteristics of the molecular sieve component would control the selectivity of product formation. To this end, several shape-selective component candidates (LZ-105-6, mordenite, Y-62, silicalite, UCC-101, and UCC-104) of various pore sizes, channel geometries, acid concentrations, and acid strengths are currently being tested in Bertly recirculating reactors (5" internal diameter) at conditions of 250-408°C, 25-500 psig, an H₂/CO feed ratio of 2.0, and a gas hourly space velocity of 400 h⁻¹. Promoted iron on UCC-104 molecular sieve produced primarily gasoline-range hydrocarbons, while cobalt on the same sieve, although yielding more methane, produced as much gasoline and more diesel oil (38). As already mentioned, a UCC-101 sieve containing promoted cobalt produced more total fuels than expected from an exact Schulz-Flory distribution of the products. Again, such behavior is not clearly understood. Further investigation seems to be merited.

The approach of combining a zeolite with a transition-metal component was followed by researchers at the Pittsburgh Energy Technology Center (40). They studied the catalytic behavior of ZSM-5 zeolite, either impregnated with Co(NO₃)₂ or C₅H₅Co(CO)₂, or physically admixed to precipitated cobalt oxide. While the physical admixture produced, at 280°C, higher fractional yields of aromatics in the liquid hydrocarbon product than the nitrate-impregnated zeolite, the C₅H₅Co(CO)₂-impregnated ZSM-5 yielded higher syngas conversions and about ten times more gasoline-range hydrocarbons than either of the other catalysts at the same total cobalt load, probably because of its higher metal dispersion. Promotion of cobalt/ZSM-5 with thorium caused a considerable increase in syngas conversion and selectivity toward gasoline-range product, perhaps as a result of the observed reduction in cobalt crystallite size and the increase in the CO/H adsorbate ratio. For example, at 280°C on Co-ThO₂-ZSM-5, nearly 65 wt% of gasoline-range hydrocarbons were produced, containing 26 vol% of aromatics (alkylbenzenes) (40).

Another research area that deserves attention is the development of Mn/Fe catalysts for improved Fischer-Tropsch synthesis (41,42,43). Although generally less active than conventional iron-based catalysts (41), these catalysts are

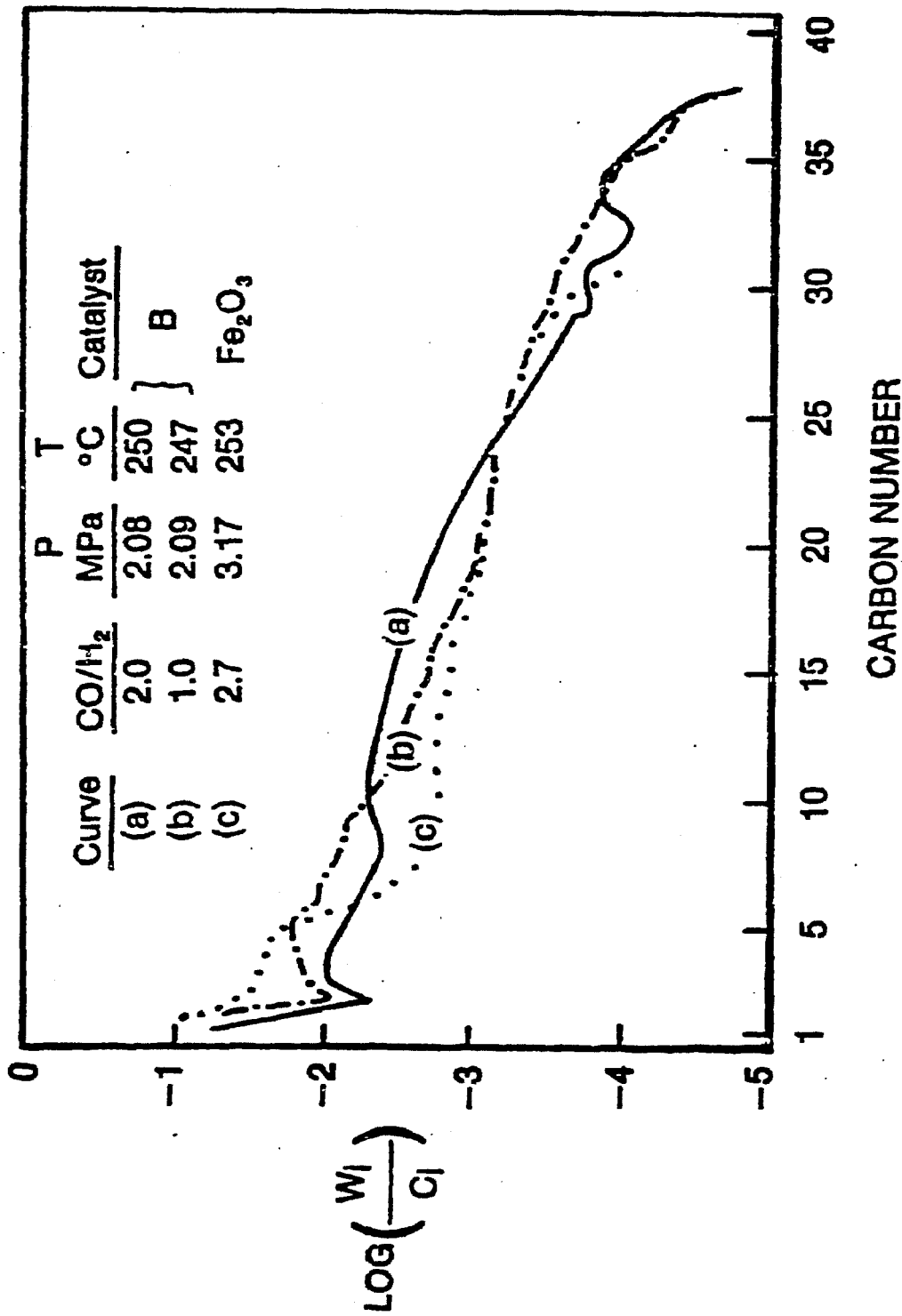


Figure 3-3. Dependency of the Hydrocarbon Weight Fraction on the Hydrocarbon Carbon Number for a Supported Molecular Cluster Catalyst B and a Sintered Baseline Fe₂O₃ Catalyst Promoted with 2% Al₂O₃, 0.5% K₂O, and 0.7% CaO

Reference: (36)

interesting because light olefins (C₂-C₄) can be obtained in relatively high yields: If it is true that the optimum feed for a second-stage (Fischer-Tropsch product upgrading) zeolite catalyst must be highly olefinic and of low average molecular weight (35), synthesis of Fischer-Tropsch hydrocarbons on Fe/Mn catalysts would provide an excellent way to have the feed requirements of the second stage match the product slate of the first stage. Additional advantages of Fe/Mn catalysts are that the temperature range for optimum catalyst performance is 30-70°C higher than the range for traditional Fe-based catalysts (41), making two-stage operation even more attractive, and that the highest yields in low-weight olefins are obtained at H₂/CO feed ratios less than 0.73 (41,42), making syngas mixtures from "second-generation" gasifiers acceptable. Processing a 9.2 wt% Fe/Mn catalyst (Fe/Mn = 1/6) in slurry phase at 303°C, Deckwer (41) indeed observed C₂-C₄ olefin yields up to 60 g/Nm³ converted syngas at H₂/CO feed ratios lower than 0.73 (Figure 3-4), while a drastic increase in methane formation (up to 95 g/Nm³ converted syngas) and a substantial decrease in overall conversion were observed when processing syngas that is richer in hydrogen.

Iron-manganese catalyst systems were also studied by the Pittsburgh Energy Technology Center (43) with the aim of maximizing gasoline-range hydrocarbon product. They tested nine catalysts with a Fe/Mn ratio of 10:90 that were prepared via different precursors in a microreactor. The highest yields (conversion and selectivity) were obtained for catalysts prepared via carbonate or hydroxide (if vacuum-dried) precipitation. The latter catalyst also gave a lower gas make. For screening catalysts of different Fe/Mn ratios (100, 1.33, 0.79, 0.28, 0.11, 0) in a slurry reactor at identical operating conditions, after a standard activation procedure, the highest stability was found for the catalysts with the ratios 20:80 and 10:90, although a general on-stream deactivation was observed for all the catalysts (43).

3.3.3 Conclusions

Improved synthesis selectivity toward motor-fuels is the target of several research groups, and early results indicate the potential of more liquid yields

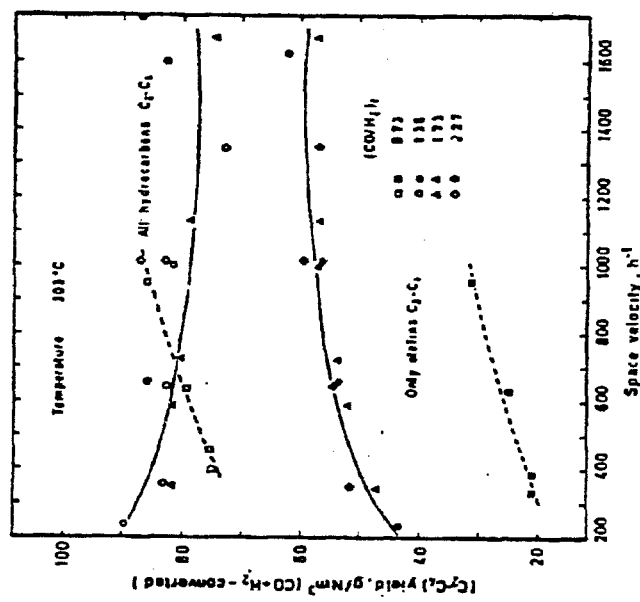
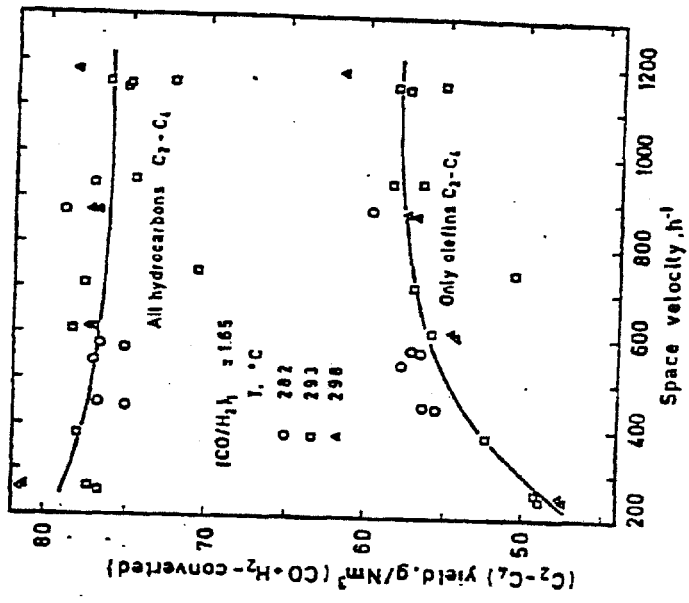


Figure 3-4. Yields of C₂-C₄ Hydrocarbons on Fe/Mn Catalyst (Fe/Mn = 1/6) as a Function of the Space Velocity at Various CO/H₂ Feed Ratios and Temperatures

Reference: (41)

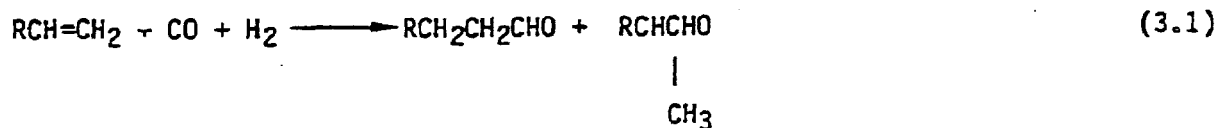
than the maxima predicted from the Schulz-Flory distribution. To be of commercial value, however, the selectivity as well as the activity need to be improved considerably.

3.4 OXO PROCESS IMPLICATIONS FOR FISCHER-TROPSCH TECHNOLOGY

The oxo process and related development activities are reviewed in this section. This is followed by a discussion of the similarities and differences between the oxo process and the Fischer-Tropsch process, and the possible implications of the oxo developments to Fischer-Tropsch technology.

3.4.1 Background

Addition of CO and H₂ to olefins in the presence of catalyst yields aldehydes and ketones. This is the oxo reaction, which is also called hydroformylation. The principal chemistry is



The oxo reaction was discovered by Otto Roelen in 1938 (16) while investigating the Fischer-Tropsch reaction (17). Initially, a cobalt-based heterogeneous catalyst was investigated, but it became clear that the active catalytic species was a homogenous metal carbonyl (18). There are oxo plants worldwide and the United States capacity for oxo chemicals is in excess of 3 billion pounds per year, including n-butanol, isobutanol, propionaldehyde, butylaldehydes, butylnitriles, iso-octyl alcohol, decyl alcohol, and tridecylalcohol.

The most widely used oxo catalyst is cobalt carbonyl with or without a phosphine modifier. The unmodified cobalt catalyst (octacarbonyl) requires a high CO partial pressure and is normally operated at a total pressure of 200-300 atm. Stability is improved with the introduction of an organophosphine ligand to form

a complex, such as $\text{Co}_2(\text{CO})_8[\text{P}(\text{n-C}_4\text{H}_9)_3]_2$. The phosphine-modified catalyst can be operated in pressure ranges of 20-100 atm. However, the modified catalyst is less active than the octacarbonyl and requires somewhat higher reaction temperatures (19). Further reduction in operating severity was made possible with the development of the rhodium carbonyl phosphine complexes. The Rh-based catalyst is highly active and can be operated under mild conditions, for example, 100°C and 15 atm.

Much oxo research has been devoted to increasing the yield of commercially desirable linear isomers over the branched isomers. The Rh-carbonyl without the phosphine tends to favor branched-chain isomers, but the phosphine complexes, such as hydorrhodium carbonyl tris-(triphenylphosphine), are highly selective for the production of linear aldehydes.

The oxo reactions take place in the liquid phase. Selection of the liquid constituents is important because they may have a strong influence on the reaction rate and on the product distribution. Examples of these effects in the hydroformylation of 1-hexene with Rh-carbonyl are given in Table 3-1 (20). Note that in Table 3-1a, the presence of excess triphenylphosphine (PPh_3) per rhodium atom improves the selectivity toward 1-heptanal, the desired product. Benzene is the main solvent in the test. Table 3-1b shows the effect of major solvents and triphenylphosphine on the reaction rate expressed in $t_{1/2}$ (minutes) and on the 1-hexanal selectivity. A polar solvent such as dimethylformamide (DMF) shows a higher rate as well as a higher selectivity over a nonpolar solvent such as benzene. With DMF, the addition of excess PPh_3 markedly increases the rate as well as the selectivity.

Much effort has been made to heterogenize the homogeneous oxo catalysts. The benefits of heterogeneous catalysts are the following:

- Better catalyst-product separation
- Possibility of gas-phase reaction system
- Liquid phase with stable insoluble catalyst in suspension.

Table 3-1

Oxo Yields with Ligand and Solvent

(a) Effect of Excess Ligand

[PPh ₃] ^a excess ^b (M)	Ratio PPh ₃ /Rh	Product distribution (mol%)					Selectivity ^c
		Hexane	Hexene	1-Heptanal	2MH ^d	2EP ^e	
0	0	0.3	3.0	40.6	40.9	15.2	42.0
3.3 × 10 ⁻²	5	—	3.9	64.0	32.1	—	66.7
1.3 × 10 ⁻²	20	—	4.8	72.5	22.7	—	76.2
3.2 × 10 ⁻²	50	Trace	4.6	72.5	22.6	0.3	76.2

^a RhCl(CO)(PPh₃)₃, 6.7 × 10⁻⁴ M; pressure, 500 psi 1/1 H₂/CO; temperature, 100°C; reaction time, 17 hours; solvent, 50 ml benzene; olefin, 25 ml 1-hexene. Table reprinted with permission from *Ind. Eng. Chem., Prod. Res. Dev.* 8, 291 (1969). Copyright by the American Chemical Society.

^b 2-Methylhexanal.

^c 2-Ethylpentanal.

^d Percent of total aldehyde which is 1-heptanal.

(b) Effect of Solvent

Solvent	[Rh] (M)	[PPh ₃] (M)	t _{1/2} (min)	Isomer distribution (mole %)		
				1-Heptanal	2MH ^a	2EP ^b
Benzene	6.7 × 10 ⁻⁴	0	157	41.9	42.3	15.8
DMF	6.7 × 10 ⁻⁴	0	132	70.9	28.8	0.3
DMF	6.7 × 10 ⁻⁴	2.7 × 10 ⁻²	35	74.4	25.6	Trace
Diphenyl ether	6.7 × 10 ⁻⁴	2.7 × 10 ⁻²	212	74.9	25.1	Trace
Benzene	1.3 × 10 ⁻³	4.5 × 10 ⁻²	90	74.0	26.0	—
n-Butyraldehyde	4.5 × 10 ⁻³	4.5 × 10 ⁻²	45	73.0	27.0	—
Diocetyl phthalate	1.3 × 10 ⁻³	0	130	52.1	35.5	12.4
Diocetyl phthalate	1.3 × 10 ⁻³	4.5 × 10 ⁻²	112	72.5	27.1	0.4

^a 2-Methylhexanal. Table reprinted with permission from *Ind. Eng. Chem., Prod. Res. Dev.* 8, 291 (1969). Copyright by the American Chemical Society.

^b 2-Ethylpentanal.

Reference: (20)

One of the techniques tried by researchers is to chemically attach the catalytically active species to the polymer. This is illustrated in Figure 3-5. In this case a silica gel was covered with a polymer formed from styrene and divinylbenzene via either emulsion or solution polymerization. The polymer was then "functionalized" by the reactions shown in Figure 3-5. The beneficial effect of the phosphine linkage was demonstrated by comparison with catalysts formed by direct deposition of $(PPh_3)_2Rh(CO)Cl$ or $RhCl_3$, which exhibited negligible activity.

Another study compared the homogeneous rhodium catalyst with its polymer-bound counterpart in the hydroformylation of 1-pentene (22). The base polymer was prepared from styrene-divinylbenzene. The test results are shown in Table 3-2. It is interesting to note that the 1-hexanal selectivity is significantly higher for the heterogeneous catalyst. The yield is also very good.

Despite many developments some of which are very encouraging, the commercial viability of heterogenization techniques has not been established. Some of the key issues are activity maintenance, metal elution, and regeneration.

3.4.2 Implications for Fischer-Tropsch Development

As noted in the preceding section, the oxo reaction was discovered during investigations of the Fischer-Tropsch reaction. After finding that the active catalytic species was homogeneous, oxo development followed a more-or-less independent path from that of F-T synthesis. Recently, however, the two technologies are coming together again, thanks to the tremendous interest in "C₁ Chemistry" brought on by the oil crisis. Each process could benefit from the advances made by the other in such areas as CO activation, homogeneous F-T catalysis, heterogenization of oxo catalyst, reactor design, and catalyst recovery.

Table 3-3 lists some salient features of the oxo and F-T processes. Both use syngas, but the products and particularly the selectivities differ greatly. The oxo process enjoys very high selectivity, while the F-T process suffers from lack

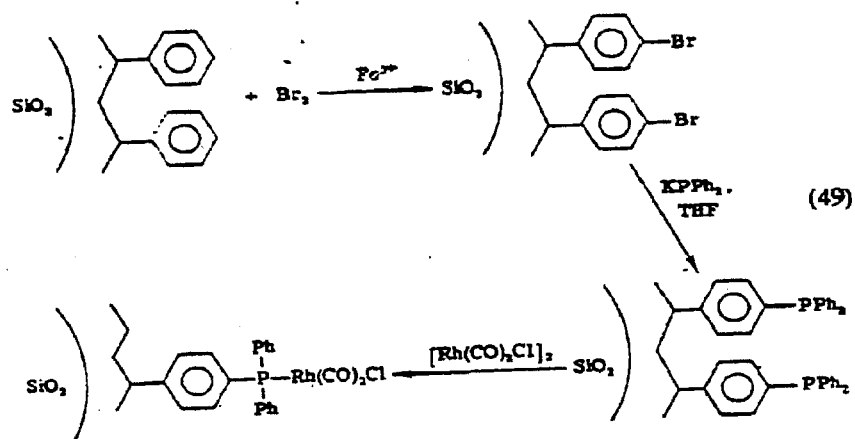


Figure 3-5. Heterogenization of Homogeneous Catalysts

Reference: (21)

Table 3-2

Hydroformylation of 1-Pentene Catalyzed by P-(PPh₂)₃Rh(CO),^a Compared
with Homogeneous HRh(CO)(PPh₃)₃^b

Temp (°C)	Pressure (psi)	Catalyst P ^c		Catalyst H ^c	
		Yield (%)	Selectivity ^d	Yield (%)	Selectivity ^d
50 ^e	400	35	5.1		
60	400	60.5	5.3	99.7	3.1
80	400	96.2	5.5	99.8	2.9
100	400	97.6	6.1	100	2.9
120	400	98.1	6.0	99.8	2.7
140	400	95.9	6.1	96.2	2.4
160	400	90.8	5.7		
100	800	98.6	4.3	99.7	2.8
100	600	98.3	4.6	99.6	2.8
100	400	97.6	6.2	100	2.9
100	200	95.9	8.8	98.3	3.2
100	100	96	12.1	93.7	3.3
60	100	62.7	9.6	99	3.6
80	100	96.1	12.6	98.7	3.8
100	100	92.4	12.1	93.7	3.3
120	100	94.2	16.1	90.5	2.2
140	100	57	10.2	48.6	2.3
140	200	87	8.7		
140	400	95.9	6.1		
140	600	97.5	4.4		
140	800	98.2	4.3		

^a Polymer-bound catalyst.

^b $4.58 \times 10^{-3} M$ Rh; 400:1 olefin: Rh; 19:1 P: Rh.

^c Catalyst P, polymer-bound; catalyst H, homogenous.

^d Selectivity is the ratio of linear to branched aldehydes.

^e Boldface numbers denote variable being changed.

Reference: (22)

Table 3-3

Key Features of the Oxo and Fischer-Tropsch Processes

	<u>Oxo</u>	<u>Fischer-Tropsch</u>
Feed:	Olefin (n carbons), H ₂ , CO	H ₂ , CO
Products:	Aldehyde of n+1 carbons	Hydrocarbon mixture
Reaction Mechanism:	Specific	Random polymerization
H ₂ /CO Mole Ratio:	1	Gas phase: 2 Slurry phase: < 1
Reaction Medium:	Liquid solvent, products plus homogeneous catalyst	Gas phase: solid catalyst, gaseous feed and product Slurry phase: Solid catalyst, solvent, products, gaseous feed
Temperature:	Cobalt catalyst: 140-180°C Rhodium catalyst: 100°C	SASOL (fixed bed): 230°C (~isothermal) SASOL (entrained bed): 160°C (inlet) 350°C (outlet)
Pressure:	Cobalt carbonyl: 3000-5000 psia Cobalt carbonyl with phosphine: 300-1500 psia Rhodium catalyst: < 220 psia	Slurry = 260-270°C . SASOL (fixed-bed): 360 psia (entrained bed): 340 psia Slurry = 150-210 psia
Heat of Reaction:	-30 kcal/g-mol	Gas phase: -39 kcal/g-mol (H ₂ O as by-product) Slurry phase: -49 kcal/g-mol (CO ₂ as by-product)

Table 3-3
(continued)

Key Features of the Oxo and Fischer-Tropsch Processes

Catalyst:	<u>Heterogeneous</u>	<u>Heterogeneous</u>
	Not applicable	SASOL (fixed bed): Fe on silica with K, Cu SASOL (entrained bed): fused iron oxide with promoters ground fluidization Slurry phase: Fe with K or Cu, Ru, Ni, Rh, etc., on supports
	<u>Homogeneous</u>	<u>Homogeneous</u>
	Co or Rh carbonyl with or without organic phosphine modifiers	Fe, W, Ru, Zr, Ir, Rh carbonyls with modifiers.
Product Selectivity:	Linear vs. branched; fairly well controlled	Schulz-Flory limitations; critical economic concern

of selectivity control due to the random polymerization mechanism (23). How to impart specificity to the F-T mechanism has been one of the major themes of the recent research in C₁ chemistry. The various approaches have been covered in Chapters 3, 4, and 8. One approach using homogeneous catalysis has made significant progress, with its success due, in large part, to the well-established scientific base of oxo chemistry. In this regard, those companies that have done extensive research, such as Union Carbide, Ruhrchemie, and Monsanto, should be uniquely qualified to carry out the homogeneous F-T approach.

The need for a H₂/CO ratio of two in the gas-phase F-T reaction is of economic concern (Chapter 5). Attention is currently focused on the slurry-phase counterpart because it appears to operate on syngas of low H₂/CO ratios typical of those produced from advanced coal gasifiers. Inherent to the F-T route of operating on a low-ratio H₂/CO syngas is the high reaction exothermicity, as can be seen in Table 3-1. The slurry-phase process generates 49 kcal/g-mol of heat compared with 39 kcal/g-mol for the gas-phase F-T and 30 kcal/g-mol for the oxo process. The high exothermicity of the slurry-phase F-T would be an added challenge to reactor design. Here again, the know-how of the oxo process, especially regarding heat and mass transfer aspects of the reactor design, should provide a valuable basis for the rather formidable task of scaling up the slurry-phase F-T process. A separate investigation of the oxo process should be made to learn process conditions, reactor dimensions, gas distributor design, etc.

Heterogenization of homogeneous catalysts is an emerging topic in catalysis. As has been mentioned earlier, a few attempts have been made in oxo research, with moderate success. The advantages of such a catalyst are retaining the intrinsic benefits of high activity and selectivity of the homogeneous catalyst and gaining heterogeneity for better product separation. Between the extension of the F-T research toward homogeneous catalysis and the interest in heterogenization for oxo research, there should be a fertile area where both F-T and oxo research can share their knowledge base.