

ATTACHMENT X

Review of Exxon Patents

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INTRODUCTION

It is quite apparent from searching the patent literature that Exxon has been actively involved in conducting research on conversion of synthesis gas to fuels and chemical products for many years. They have used CO as a chemical reactant for producing olefins and alcohols in addition to preparing liquid fuels. Since the mid 1970s the number of patents that have been assigned to Exxon and the types of examples contained in those patents reflect an increasing interest in converting synthesis gas to hydrocarbons. The earlier patents that were obtained during this period contain numerous examples of synthesis gas conversion at ambient pressures that gave very small CO conversions, typically less than 10%. More recently, the data reflect a more sophisticated evaluation of catalysts and the beginning of a string of patents that relate to improvements in equipment and operation. The latter are a result of the operation of a sizable pilot facility at their Baton Rouge Laboratory. These patents have addressed many of the finer points of reactor design.

The search was focused on synthesis gas conversion, i.e. the Fischer-Tropsch reaction, and limited to U. S. patents that were assigned to Exxon that were abstracted by Derwent through mid-1995. There are apparently numerous other patents that were issued to Exxon that relate to CO conversion which are not included, such as those related to conversion of CO to hydrocarbons or alcohols. Exxon's approach to developing a patent portfolio in this technology area is unlike most of their competitors, in that they have obtained an extensive number of composition of matter patents.

Supplementing these patents are a large number of process related patents that apply to either methods for preparing these materials or the use of these compositions in the conversion of synthesis gas. In some of the composition of matter patents that are of interest for synthesis gas conversion, the claimed materials are used for hydrocarbon conversion without mention of their use as catalysts for the FT reaction. Based upon the addresses of the inventors in these various patents, it is clear that significant work on the FT reaction has been going on at Exxon's New Jersey and Baton Rouge laboratories. Although there is overlap in the type of work that was being done in these laboratories, it appears from the timing of the patents that the approaches that were being taken were quite independent. Those differences were apparent from the discussion in the patents regarding various elements of catalyst composition and the claims that are made regarding those compositions.

The Exxon patent portfolio includes a large number of patents on iron and iron-containing catalysts. The majority of these cases relate to compositions that have spinel structures that are isostructural with Fe_3O_4 but contain one or two additional metal atoms, with iron usually being the dominant metal. In these patents, the spinel structures are expressed interchangeably either as $\text{M}_x\text{N}_{3-x}\text{O}_4$ or as $\text{M}_{3-x}\text{N}_x\text{O}_4$, where M is almost exclusively Fe. For consistency, the first format is used exclusively throughout this discussion. Other iron-related catalysts are also covered including catalysts in which the iron, as the oxide, is used as a substrate, and others in which the iron is deposited on other substrates.

There is extensive coverage for catalysts in which titania and titania containing materials are used as metal supports. These include combinations of titania with vanadium, tantalum and niobium oxides (Group Vb) which are used either as intimate

mixtures or as coatings on the surface of titania. All of these supports apparently give rise to unique metal-support interactions that had not hitherto been reported. Other coverage was obtained for titanias that are coated with silica. Some of these patents specify titanias having rutile as the dominant crystalline phase which is favored at high temperatures. One case claims an anatase based catalyst that was stabilized through addition of silicon, zirconium and tantalum. In many of these cases, the catalyst is formed by impregnating the oxides with metals from Group VIII, of which cobalt or ruthenium are the most common. In other cases, addition of rhenium, thorium, cerium, copper, hafnium, zirconium, and uranium is claimed. Although many of the catalysts that are covered in these patents fall into one of the above categories, they have also obtained coverage in several related areas. Catalysts comprising ruthenium or combinations of several Group VIII metals on manganese oxide are covered as are cobalt-manganese spinels. Coverage of catalysts comprising Group VIII metals supported on various oxide supports was obtained which specifically apply to FT type processes.

In almost all of these cases the use of an alkali promoter is also covered, either in the main claim or a dependent claim. Almost without exception, potassium is specified as the alkali metal of choice, although in a few rubidium has been specifically mentioned. Most of the patents specify that the catalysts can be used in either a fixed-bed or a slurry type process, although in some cases they can be applied to both. Generally, powder catalysts are specified for slurry operations while sintered spinel type catalysts apply to fixed-bed type operations. There are, however, cases which claim that the catalysts are useful for either slurry or fixed-bed type operations.

The third area of significant coverage includes various process improvement patents that relate to process equipment or operation, most of which have been obtained in recent years. These include 2-stage processes, modified feeds, modified reactor designs, methods of reactor operation and methods of catalyst pretreatment. Many of these patents contain data that were taken from highly sophisticated pilot plant operations, some of which were quite large in size.

Iron

A number of patents were issued to Exxon related to the use of iron in FT synthesis. Most apply to catalysts in which the iron is in combination with other metals. However, two patents were issued that apply to the use of iron alone. These were catalysts that were prepared using a laser technique in which volatile iron compounds were thermally decomposed to form iron carbides having particle diameters of less than 0.1 μm . Most of the iron containing catalysts that are covered in these patents relate to spinels in which Fe is combined with different metals in the spinel structure, including cobalt, manganese, zinc, and titanium. Various promoters are also added, including cerium, copper and potassium. Two patents covered catalysts in which thallium was deposited on an iron support, while others covered catalysts prepared by depositing Fe salts onto supports. One covers an Fe/TiO₂ catalyst that was prepared by converting an impregnated Fe salt to the carbided form. Another covered catalyst prepared by decomposing Fe and Co carbonyl compounds in the presence of CO which deposited them onto finely divided supports which were then reduced in H₂.

Particulate Iron Catalysts

A patent issued to Rice et al. (X.1) claims compositions comprising finely divided particles of iron and carbon in absence of Si produced in a reaction zone in the presence of laser radiation under such conditions of laser flux density, power adsorption, concentration of iron reactants, and pressure sufficient to give non-pyrophoric particles having diameters from 1-100 nm. The iron reactants are selected from iron carbonyls, iron acetylacetonate and ferrocene. A related patent issued to Rice et al. (X.2) claims the same compositions which are subsequently impregnated with 2% of a promoter selected from a group of salts and oxides of alkali and alkaline earth metals. These patents specify these compositions can be used in either slurry or fixed bed FT reactions. Data were presented in the examples for a fixed-bed catalyst in which the claimed composition was deposited on a refractory MgO support. Laser generated Fe carbide, either with or without K, was found to be considerably more active than Fe carbides generated from either Fe_3O_4 or from mixtures of $\text{Fe}(\text{CO})_5$ and C_2H_4 in the presence of $\text{SiH}_2(\text{CH}_3)_2$ (see Table X.1). The Fe_3O_4 and silane generated carbides have lower CO conversions and higher methane yields while the catalysts of these inventions produce more olefins in the $\text{C}_2\text{-C}_4$ fraction.

A catalyst was illustrated which was prepared by reacting Fe_3O_4 until all of the iron was converted to a carbide phase which was predominantly Fe_5C_2 and Fe_3C . The iron carbide phase was dispersed in a matrix of 40 to 70 wt.% of amorphous carbon. The comparison of the activated Fe_3O_4 catalyst and the laser generated catalyst is for activity for CO conversion on a volume of gas/volume of catalyst basis. The laser generated sample contained 5-15 wt.% of amorphous carbon phase. If we take into account (1) the difference in density of amorphous carbon and iron carbide (factor of 2) and (2) the difference in the amount of amorphous carbon (factor of about 5-8), we

calculate that the material produced by the laser technique will contain 10 to 20 times as much iron as the material prepared from Fe_3O_4 . Thus, while the material prepared using the laser technique is about two times as active as the material derived from Fe_3O_4 when the comparison is based on volume of catalyst, it is estimated by us to be 5 to 10 times less active on the basis of the iron content. Furthermore, it has been shown that, under reaction conditions utilized for slurry phase synthesis, a significant fraction of the iron carbide is gradually converted to Fe_3O_4 (X.3) during synthesis. Thus, the relative advantage of the catalyst generated by the laser technique depends upon how it is compared to the precipitated catalyst.

Spinels Containing Fe

The first patents assigned to Exxon that apply to the use of spinel or spinel-derived compositions for converting synthesis gas appeared in 1985. These materials were generally prepared by one of two methods and they had distinctly different morphological features. In one case, high surface area materials were prepared by coprecipitation of salts coupled with moderate heating. These materials have been used directly as slurry catalysts. The second method of preparation involves sintering of metal/metal oxide mixtures at much higher temperatures to give low-surface-area, fused materials, which after grinding and sizing are used directly in fixed bed applications. Hydrogen reduction of either of these products at temperatures of 400°C leads to alloys, which when treated with CO, give high surface area carbides containing considerable carbon inclusion. The reduced and carbided spinels are then used as catalysts in either slurry or fixed-bed applications.

A number of different combination of metal spinels have been patented in this series, all of which, except one, contain iron. In all the Fe cases, the claims cover

spinel compositions that allow the use of high concentrations of Fe. From an economical standpoint, this is favorable since the cost of co-metals is generally greater than for Fe. The different Fe-containing combinations that are covered, most of which are promoted with potassium, are:

- ! Fe-Co, either with or without added Cu,
- ! Fe-Mn containing Cu,
- ! Fe-Zn containing Ce or Cu,
- ! Fe-Zn-Ti and/or Mn with Ce and
- ! Co-Mn with Cu.

The only non-Fe containing spinel that was covered was a Co-Mn spinel that is promoted with Cu. This catalyst is discussed with the manganese supported catalysts.

Fe-Co Spinels. Both high and low surface area spinels are covered. High surface area spinel compositions and reduced and carbided iron-cobalt alloy compositions derived from the spinels that are isostructural with Fe_3C and $\text{chi-Fe}_5\text{C}_2$ are covered in a patent issued to Soled and Fiato (X.4). Because of their fine particle size, the preferred use of these materials is in a slurry process which is covered in a patent issued to Soled and Fiato (X.5). High surface area copper promoted Fe-Co spinel compositions are covered in a patent issued to Soled and Fiato (X.6) while their use as a catalyst in a slurry process is covered in Soled and Fiato (X.7). Low-surface area Fe-Co spinel compositions are claimed by Fiato et al. (X.8) and their use as catalysts in a fixed-bed process is claimed by Fiato et al. (X.9). The use of the carbided and reduced form of these low-surface area Fe-Co spinels in a slurry phase process is claimed by Fiato and Soled (X.10). No patents were found that contain claims related to low-surface area Cu-promoted Fe-Co spinels.

Fe-Mn Spinels. High surface area K and Cu promoted Fe-Mn spinels are covered in a patent issued to Fiato and Soled (X.11). The use of this spinel as catalyst in a slurry process is covered in Fiato and Soled (X.12) and in a fixed-bed process in Iglesia et al. (X.13). The corresponding low surface area spinels derived from sintering mixed oxides was covered in a prior patent issued to McGrath and Rubin (X.14) and assigned to Kellogg. An alternative method for forming Fe-Mn alloys directly at low temperature without going through the spinel is covered by Soled et al. (X.15).

Fe-Zn Spinels. Two patents comprising compositions of Fe and Zn using different promoters were issued. In one patent compositions comprising sintered combinations of metal oxides of Fe and Zn promoted with Ce and K are covered in Gates and Fiato (X.16). In the other, compositions containing Fe and Zn promoted with Cu and K are covered in Soled et al. (X.17).

Fe-Zn Spinels with Ti and/or Mn. Compositions comprising sintered combinations of metal oxides of Fe, Zn, Ti, and/or Mn promoted with K and Ce are claimed in Fiato et al. (X.18).

Fe-Co Spinels

Seven patents assigned to Exxon relate to Fe-Co spinels, five of which were issued either from applications filed on December 14, 1983, or were continuations-in-part of applications filed on that day. Cross reference was also made to applications which apparently never issued as patents. The series of seven patents that did issue fit into three different groups with at least two patents being in each group. One of the groups relates to Cu promoted Fe-Co spinels while the other two groups relate to Fe-Co spinels that are prepared by two different methods. In one group the spinels are prepared by sintering mixtures of metal-metal oxides while in the other, spinels are

prepared by precipitating metal oxides from the respective metal salt solutions. In each of these three groups, two of the patent specifications are identical differing only in their claims. In the one group that includes a third patent, the specification differs only slightly from the other two. For each of the three groups, one patent is a composition of matter case for a specific Fe-Co containing spinel and the other(s) claims either a fixed-bed or slurry process that employs the claimed catalyst composition.

The empirical formula of the spinels claimed in these cases can be written as $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ where compositions having x-values ≤ 2.4 or 2.7 are claimed. Prior art existed for structures having x values of 2, i.e. Fe_2CoO_4 (X.19). Among the various spinel compositions that were patented, there appears to be a pattern of obtaining coverage for both slurry and fixed-bed type FT processes. In the case of the Fe-Co spinels, specific claims are made to fixed-bed processes using catalysts derived from spinels prepared by sintering metal-metal oxide mixtures. These are classified as having low surface areas (less than $5 \text{ m}^2/\text{g}$). For slurry processes, patents were issued that claim use of catalysts derived from both low surface area spinels as well as those prepared by precipitating metal oxides from the respective metal salt solutions. This latter group is classified as high surface area spinels having surface areas greater than $5 \text{ m}^2/\text{g}$. In these Fe-Co spinel cases, patents were not found that claim the use of high surface area spinels in a fixed-bed process, although such claims were obtained for Fe-Mn spinels, which are discussed below.

High surface area spinel compositions are covered in a patent issued to Soled and Fiato (X.4) that claims Group 1A or IIA promoted high surface area spinels having compositions $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ with x-values ≤ 2.4 and BET surface areas $>5 \text{ m}^2/\text{g}$. A second composition in this same patent, given in claim 20, comprises reduced and carbided

iron-cobalt alloy that is isostructural with Fe_3C and has a BET surface area $>5 \text{ m}^2/\text{g}$. A third independent claim covers compositions that are isostructural with $\chi\text{-Fe}_5\text{C}_2$ having surface areas $>5 \text{ m}^2/\text{g}$ that are produced by carburizing iron-cobalt alloy which is isostructural with $\alpha \text{ Fe}$ and has a BET surface area $>5 \text{ m}^2/\text{g}$, which is produced by reducing the high surface area spinel composition. Therefore, compositions are claimed that include the spinel, the reduced alloy and the resulting carburized alloy. The specification is even broader in that it anticipates the application of the spinel, the alloy and the reduced-carburized spinel in either a fixed-bed or slurry-type process. The corresponding process related patent issued to Soled and Fiato (X.5) claims a slurry process that uses the catalyst that is claimed by Soled and Fiato (X.4). The two specifications are identical except for the claims. Although there is a slight difference in the spinel compositions that are claimed in these two cases, in that Soled and Fiato (X.4) claim spinels having Fe/Co ratios $4/1$ while Soled and Fiato (X.5) claims Fe/Co ratios $7/1$, this would not likely have any real impact on the application of the invention.

Low surface area Fe-Co spinel compositions are covered in a patent issued to Fiato et al. (X.8) that claims hydrocarbon synthesis catalyst compositions comprising an unsupported, Group Ia or IIa metal salt promoted low-surface area iron-cobalt spinel, an initial empirical formula $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$, where x is 2.625 , a powder X-ray diffraction pattern isostructural with Fe_3O_4 and having an initial BET surface area $<5 \text{ m}^2/\text{g}$. Various dependent claims are included such as the use of diluents like silicas, aluminas, titanias, oxides of La, Ce, Cr, and Mn and mixtures including zeolites, glasses, etc. K_2CO_3 is claimed as a promoter and potassium promoted compositions are claimed that are substantially carburized by contact with CO/H_2 at elevated

temperatures. Two process patents were issued that are related to use of low-surface area spinel compositions in synthesis gas conversion reactions. One patent, issued to Fiato et al. (X.9), claims a process for synthesizing hydrocarbons containing C₂-C₆ olefins by contacting a fixed-bed of catalyst, having the initial spinel composition specified in Fiato et al. (X.8), with synthesis gas. The specifications of Fiato et al. (X.8) and Fiato et al. (X.9) are identical, except for different claims. The second process patent issued to Fiato and Soled (X.10) claims a slurry process utilizing the carbided and reduced unsupported spinel of Fiato et al. (X.8), which reflects the need to *ex situ* pretreat the spinel before placing it in the slurry reactor.

Catalyst preparation

The following method was used to illustrate the preparation of several of the high surface area spinels. A solution containing Fe and Co nitrate salts and an ammonium α -hydroxy carboxylic (glycolic) acid was evaporated and the recovered solid was heated at 350°C for 2 hours and then impregnated with K₂CO₃ and dried. The material, prior to impregnation with potassium, had a very small particle size, an x-ray diffraction pattern isostructural with Fe₃O₄, and surface area >100 m²/g. The specification refers to prior art for the preparing of Fe₂CoO₄¹⁹ that involved evaporating aqueous solutions of metal glycolates, lactates, and tartarates to dryness. The prior art apparently limited claims to Fe/Co ratios > 4.

The invention was illustrated for various low-surface area spinels prepared by sintering mixtures of metal oxides and metals in combinations having the stoichiometric composition necessary to provide the correct empirical formula. Sintering is done first in an inert or vacuum atmosphere at temperatures preferably from about 800 to 900°C for about 8 to 24 hours. The material is then exposed to air

and heated an additional 24 hours until the x-ray diffraction pattern of the material is isostructural with Fe_3O_4 . Sintered pellets are crushed, sieved and then impregnated with aqueous potassium carbonate to a 1% K loading providing a material having a surface area of 0.25-0.30 m^2/g .

Reduced and carbided slurry catalysts are prepared starting with both high and low-surface area spinels. The preparation starting with low-surface area spinel is described in Fiato and Soled (X.10) and the preparation from high-surface area spinel is described in Soled and Fiato (X.4). In both cases, the respective spinel powders were reduced at 400°C in H_2 for 4 hours to produce an alloy, which was passivated with dilute oxygen. These materials had surface areas of 3 and 8 m^2/g and x-ray diffraction patterns isostructural with alpha iron. The active catalyst was produced by carbiding the alloys in dilute synthesis gas and passivating with dilute oxygen to give products having x-ray diffraction patterns isostructural with chi Fe_5C_2 and BET nitrogen surface areas of 118 and 173 m^2/g . The resulting catalysts contained 60-70% carbon and had the composition $\text{Fe}_{2.85}\text{Co}_{0.15}\text{O}_4/1$ wt.% K.

The form of the active catalyst generated by these two different preparative methods was not differentiated from each other. Both, after reducing and carbiding, give materials that are isostructural with chi- Fe_5C_2 or Fe_3C , apparently contain sizable amounts of carbon, and have surface areas >100 m^2/g .

Slurry Catalysts. A number of examples were provided in the five cases which illustrate the use of catalysts derived from spinels for converting synthesis gas.

Catalysts to be used in slurry reactors were pretreated in various ways before being placed in the slurry reactor and exposing them to synthesis gas at reaction condition.

The methods of pretreatment included:

- ! Adding the spinel to the slurry reactor and reducing in H₂ before exposure to synthesis gas;
- ! Reducing and carbiding the spinel *ex situ* before introducing into the reactor;
- ! Reducing the spinel in H₂ to form the alloy before introducing into the reactor.

Conversion and product distribution data were provided for each of the respective catalysts and compared with data obtained on a high surface area Fe₃O₄/1%K catalyst that was prepared in the same manner as the high surface area spinel.

There was a big difference in the activities of the *in situ* treated spinel slurry catalysts. The high surface area Fe-Co spinel oxide that was reduced in situ with flowing H₂ (1 atm) for 1 hour at 200°C gave 60% CO conversion, whereas both the high surface area Fe spinel and the low-surface area Fe-Co spinel that were pretreated in the same way were inoperable. They gave CO conversions of only 8 and <4%, respectively (see Table X.2). *Ex situ* treatment had little effect on CO conversion of the high surface area spinel derived catalyst which gave essentially the same CO conversion as the *in situ* treated spinel, namely 64 and 60%, respectively. By contrast, *ex situ* treatment of both the low-surface area Fe-Co spinel and Fe spinel catalysts improved their activity, giving 42 and 65% CO conversion, respectively. Apparently insufficient carbided catalyst was formed in the *in situ* pretreatment of the low-surface area spinel, whereas the *ex situ* treatment was sufficiently severe to convert the low-surface area spinel to the carbided form. In the comparisons that were provided, the Fe-Co spinels produced more C₅+ hydrocarbons and less C₂-C₄ olefins than the Fe

spinel catalysts. Although data with a 2/1 H₂/CO synthesis gas mixture in Table X.2 on *ex situ* treated catalysts indicate a difference between the CO conversion of the reduced-carbided low- and high-surface-area Fe-Co spinel derived catalysts, i.e. 42 and 64% conversion, respectively, other data with a 1/1 H₂/CO synthesis gas mixture showed no difference in activity (see Table X.3). The latter data indicate that the *ex situ* reduced and carbided high- and low-surface-area Fe-Co spinel derived catalysts, as well as the activity of the *ex situ* reduced and carbided high-surface-area Fe spinel catalysts, have essentially the same activity. The activity of the *ex situ* low-surface-area Fe-Co spinel and the lack of activity for the *in situ* treated low-surface-area spinel appears to be one reason why Fiato and Soled (X.10) claim a slurry process utilizing only the carbided and reduced low-surface area spinel.

Alloys active for CO conversion are formed by reducing the high-surface-area Fe-Co spinel *ex situ* with H₂ at 350°C for 12 hrs followed by further reduction with H₂ at 400°C for 24 hrs. CO conversions with either 1/1 and 2/1 H₂/CO synthesis gas mixtures were higher than the correspondingly reduced Fe-only spinel, as shown in Table X.4. Although the correspondingly reduced high surface area Fe-only spinel was not quite as active as the Fe-Co alloy, its selectivity for CO₂ production was much smaller. The hydrocarbon selectivity of the Fe-Co spinel was greater and its methane and C₅+ selectivities were less than for the Fe-only spinel. In this series of patents, no claims were made nor information provided on alloys produced from reduced low-surface area Fe-Co spinels.

Fixed-Bed Catalysts. Only catalysts prepared from low surface area Fe-Co spinels were used as fixed-bed catalysts. Although high-surface area spinel derived

catalysts were anticipated for use in fixed-bed reactors, no claims nor examples were found that relate to such usage. An example was provided in which low-surface area $\text{Fe}_{2.85}\text{Co}_{0.15}\text{O}_4$ spinel was reduced at 500°C with a mixture of 90% H_2 in N_2 at 100 psig for 5-7 hrs before exposing to synthesis gas. It was more active for CO conversion than a comparably prepared and treated $\text{Fe}_3\text{O}_4/1\%\text{K}$ spinel, as shown in Table X.5. At a run temperature that was 35°C lower than the control sample, the Fe-Co conversion of CO was higher than for the Fe-only catalyst at the same space velocity. Both CO_2 , hydrocarbon yields and olefin content in the $\text{C}_2\text{-C}_4$ fraction were higher for the Fe-Co catalyst while the C_5+ and C_6+ products were greater for the control.

In all the Fe-Co spinel patents, there was only one example of a spinel having an Fe-Co concentration that did not fall within the claimed limits. That spinel, having an x value of 2.20, falls below the 2.4 value specified in the claims. The CO conversions and hydrocarbon yields were essentially the same for this catalyst as for those that fell within the claimed limits, i.e. x values either ≥ 2.4 or >2.625 , both of which were used in different patents (see Table X.6). Regardless, all of these catalysts had Fe/Co ratios that were greater than 2 (x value 2.0), which was consistent with the prior art value discussed above.

In almost all of the patents regarding the FT reaction that are assigned to Exxon, only a few discuss the exotherm that is observed in any of the experimental reactors. In one of the patents, assigned to Fiato et al. (X.8) claiming Fe-Co spinel derived materials as catalysts for fixed-bed FT reactors, the exotherms observed in those reactors are discussed. Actual maximum bed temperatures are given for runs in which furnace temperatures were from 225 to 290°C. In these runs made with a cobalt spinel having an x value of 2.625 ($\text{Fe}_{2.625}\text{Co}_{0.375}\text{O}_4/1 \text{ wt.}\% \text{K}$), exotherms of 8 to 44°C were

observed at 240°C and 290°C, respectively (see Table X.7). Over this range the corresponding CO conversion increased from 31% to 97%. The CO conversion follows the same trend as does the difference between the furnace and bed temperatures. At the higher temperature, the hydrocarbon selectivity deteriorated resulting in increased conversion to methane, whereas at the lower temperature the olefin selectivity was higher, i.e. 55.3% versus 37.1%, and the C₆₊ yield was also higher. The effect of furnace temperature at 235 and 270°C for a Fe_{2.85}Co_{0.15}O₄/1 wt.% K spinel, where x = 2.85, is also shown in Table X.7. In this case the actual bed temperatures were not reported but can be assumed to be about the same as for runs made at the same temperature. The CO conversion and CO₂ and hydrocarbon yields for the x = 2.85 spinel were essentially the same as for the x = 2.625 spinel. At high conversion, hydrocarbon selectivity of the x = 2.85 spinel was better giving less methane, more C₆₊, and more C₂-C₅ olefin yields. This provides further evidence that lower cobalt concentration provides better yields.

Copper promoted Fe-Co spinels. Two patents claim Cu promoted Fe-Co spinels as slurry phase catalysts. A patent issued to Soled and Fiato (X.6) claims compositions comprising a reduced-carbided Cu-promoted Fe-Co alloy, produced by contacting a Cu-promoted Fe-Co alloy with a carbiding atmosphere, which was prepared by reduction of a Group Ia or Group IIa metal salt promoted Fe-Co spinel possessing a BET surface area greater than 5 m²/gm. The spinels correspond to high surface area spinels prepared by precipitating the Fe and Co nitrate salts, as presented in Soled and Fiato (X.4). A corresponding patent issued to Soled and Fiato (X.7) which, except for the claims, is identical to Soled and Fiato (X.6) claims a slurry

process using a catalyst comprising an unsupported Cu-promoted Fe-Co spinel having an initial BET surface area $>5 \text{ m}^2/\text{g}$ and a Fe/Co ratio 4/1.

Copper promoted spinels are prepared by impregnating Fe-Co spinel with an aqueous solution of cupric nitrate, drying, and then impregnating with an aqueous solution of K_2CO_3 followed by a final drying to give a composition of $\text{Fe}_{2.85}\text{Co}_{0.15}\text{O}_4$ /(1 wt.% K, 1 wt.% Cu). *Ex situ* carbided catalysts were prepared by reducing the spinel in a 40% H_2 , 20% CO and 40% He containing stream at 400°C for 24 hrs. After cooling to room temperature, the oxygen (1%) passivated sample gave an X-ray diffraction pattern isostructural with Fe_5C_2 , had a BET surface area of $150 \text{ m}^2/\text{g}$, and contained 40-50% carbon. Corresponding Co-free and carbided spinels were also prepared by the same method.

Examples were included which illustrate the use of these spinels as catalysts in a slurry reactor both in *in situ* unreduced as well as *ex situ* carbided forms. CO conversion for the *in situ* reduced catalysts followed the sequence Cu/K-promoted Fe-Co spinel > K-promoted Fe-Co spinel > Cu-free Fe spinel (see Table X.8). However, data were not provided that showed relative selectivities for hydrocarbon versus CO_2 formation. The CO conversion activities of the *ex situ* carbided-reduced Fe and Fe-Co spinels were quite similar as were the methane and $\text{C}_2\text{-C}_4$ olefin selectivities. The olefin concentrations (52-59%) in the C_{10} fractions from these catalysts were quite high.

Iron - Manganese Spinels

A composition of matter and three process related patents assigned to Exxon cover iron-manganese spinels. Two cases that were originally filed on December 20, 1983 were abandoned and refiled in December 1985. Both applications resulted in patents that issued in 1986. Apparently at some time during the application process,

claims for a fixed-bed process were split from the slurry bed process application and refiled as a separate application. The latter fixed-bed application was subsequently abandoned, refiled and again abandoned before being refiled in 1990, which apparently resulted in a patent covering a fixed-bed process. Unlike the Fe-Co spinel cases, only high-surface-area Fe-Mn spinels were covered, since prior art appears to preclude coverage for Fe-Mn spinels prepared by sintering mixtures of iron oxide and manganese oxide.

The first patent in this series, issued to Fiato and Soled (X.11), claims compositions comprising an unsupported Group Ia or Group IIa metal and copper promoted Fe-Mn spinel having a BET surface area $>30 \text{ m}^2/\text{g}$, an Fe/Mn ratio >2 , and an empirical formula of $\text{Fe}_x\text{Mn}_{3-x}\text{O}_4$, where x is >2 . The second patent issued to Fiato and Soled (X.12) is identical to Fiato and Soled (X.11), except for the claims, and claims a slurry FT process using a catalyst comprising the composition of Fiato and Soled (X.11). The third patent issued to Iglesia et al. (X.13) claims a fixed-bed FT process using a catalyst comprising the composition of Fiato and Soled (X.11) in a pelletized form.

In the examples, a high-surface area Cu-K promoted $\text{Fe}_{2.25}\text{Mn}_{0.75}\text{O}_4$ spinel was prepared by combining Fe and Mn nitrate, in a molar ratio of 3/1, with a solution of ammonium glycolate having a pH of 6.5 in a ratio to give a total metal ion to glycolate ion ratio of 1/1. Water was removed at room temperature and the solid was air calcined at 175°C for 2 hours to produce the spinel having a surface area $>50 \text{ m}^2/\text{g}$. Promoter was added by impregnating the spinel with 2 atomic % K and 1 atomic % Cu. Interestingly, a paper that appeared in 1985 by Maiti et al., (X.20) at about the same time that the final application was filed, also reported preparing Fe-Mn spinels by base

precipitation of Fe and Mn nitrate salt solutions. The reduced and carbided form of the resulting solids, none of which contained promoters, was active for FT synthesis gas conversion. Even though the Maiti paper disclosed materials related to the claimed compositions, it apparently did not preclude the issuing of a patent for these compositions.

Under slurry conditions, the high surface area K-Cu dual-promoted Fe-Mn spinel gave higher CO conversions than either the comparable K or Cu promoted spinels, as shown in X.Table 9. At half the catalyst loading, CO conversion for the Cu promoted catalyst was higher at 69% than the 34% and 36% conversion for the K-promoted catalyst. The methane selectivity was also favorable in that it was lower for the dual promoted catalyst. The effect of Fe-Mn ratio is shown in Table X.10. CO conversions for Cu-K promoted spinels having Mn concentrations with x values >2, as claimed in this patent, were higher than for two spinels having x values of 0.25 and 1.5, which were below the Mn concentrations in the compositions claimed in this patent.

Unlike patent coverage for the Fe-Co spinels, which claimed both high and low-surface area compositions, none of the patents assigned to Exxon claimed compositions or processes comprising low-surface area Fe-Mn spinels as catalysts or precursors to catalysts for synthesis gas reactions. Such catalysts are apparently covered by a previous patent issued to McGrath and Rubin (X.14), and assigned to Kellogg, which claims a process for converting synthesis gas using a catalyst comprising elementary Fe with manganese oxide and alkali compound as promoters. Fiato and Soled (X.11) showed that a reduced low-surface area Fe-Mn composition reported by McGrath and Rubin (X.14) was inactive for CO conversion in the slurry process. This composition had an empirical formula of $\text{Fe}_{2.86}\text{Mn}_{0.14}\text{O}_4$ /0.7 atomic % K

and was prepared by sintering a paste of $\text{Mn}(\text{NO}_3)_2$ and Fe_3O_4 containing K_2CO_3 at 1400°C for 6 hrs and reducing with H_2 at 371°C for 48 hrs. For comparison, two low-surface area ($<5 \text{ m}^2/\text{g}$) K and K-Cu promoted Fe-Mn spinels were evaluated. They were prepared by fusing a mixture of Fe_2O_3 , Fe and Mn_3O_4 at $800\text{-}1000^\circ\text{C}$ for 48-72 hours and impregnating with K or with K and Cu to give spinels having a composition of $\text{Fe}_{2.25}\text{Mn}_{0.75}\text{O}_4$ and containing 2 atom % K or 2 atom % K/1 atom % Cu. Both of these materials were inactive for CO conversion in the slurry process (see Table X.9). However, based upon the fact that reduced and carbided low-surface area Fe-Co spinels are quite active for CO conversion in the slurry process (see Table X.3), similarly pretreated Fe-Mn spinels may also be active; however, such information was not provided.

The use of glycolate in the production of the $\text{Fe}_x\text{Mn}_{3-x}\text{O}_4$ spinel is covered in an independent claim that specifies the use of α -hydroxy aliphatic carboxylic acid. The spinel prepared in the examples using glycolate, as the carboxylic acid, was more active than spinel prepared by precipitating a solution of the salts using ammonium hydroxide. The latter spinel was prepared by calcining at 500°C . The CO conversion for the glycolate spinel was 68.9% versus 20.5% for the ammonium hydroxide prepared spinel.

Another related patent issued to Soled et al. (X.15) claims a process for producing powdered metal-based iron alloys which are structurally the same as prepared by reducing $\text{Fe}_{2.25}\text{Mn}_{0.75}\text{O}_4$. This method comprises heating a mixture of powdered mixed metal oxide with a stoichiometric amount of calcium metal in an inert atmosphere at 850°C for 72 hours, leaching out the Ca and calcium products with an

aqueous acid and recovering the metal-based alloy. The other method used by Fiato and Soled (X.11) involves sintering the metal oxides at 1000°C to form the alloy.

The patent issued to Iglesia et al. (X.13) claims a fixed-bed FT process using a catalyst comprising the Cu-K-promoted Fe-Mn spinel composition in a pelletized form. Comparison between a fixed bed and slurry operation for this catalyst indicates the slurry catalyst gives higher conversion, similar CO₂ selectivity, and lower methane and higher C₅+ olefin yields (see Table X.11).

Fe - Zn Spinels

A patent issued to Gates and Fiato (X.16) claims a sintered combination of metal oxides having the following components (preferred metals) from Group VIII (Fe), Group IIB (Zn), Group IA (K), and the Lanthanum Group (Ce). Although there are no limits on the claimed composition, the only catalyst prepared in the examples had an empirical formula of Fe_{2.81}Zn_{0.19}O₄Ce_{0.08}K_{0.08} (atom ratio of 1.0/0.065/0.03/0.03). This corresponds to an Fe₂O₃ concentration of 87 wt.%, which, surprisingly, falls outside the 5-80 wt.% range specified in the independent claim 7. The spinel catalyst was prepared by sintering a mixture of Fe₂O₃, ZnO, and CeO₂ at -1050°C in air for 24 hours. It had a BET surface area <2 m²/g and XRD indicated it was a highly crystalline mixture of mixed spinels and iron oxides in a CeO₂ phase. The composition is very similar to the Fe/Zn/Ti-Mn spinels that are discussed below. The spinels were reduced in H₂ at 500°C for 7 hours, after which they were passivated by exposure to oxygen at 25°C. The reduced form still contained unreduced metal oxides as shown by X-ray diffraction analysis. The passivated reduced catalysts, after preheating in H₂ in a fixed bed reactor at 500°C, gave the same level of CO conversion as a Zn and Ce-free 1% K/Fe₂O₃ that was prepared in the same way. The Zn-Ce containing catalyst gave lower

methane and higher C₇+ liquid selectivity in addition to producing a higher yield of CO₂, as shown in Table X.12.

Another patent issued to Soled et al. (X.17) claims compositions comprising Fe, Zn, and Cu and one member chosen from the group of K, Rb, or Cs wherein the Fe/Zn atomic ratio is ≤ 5 and the alkali metal/Cu atomic ratio is ≤ 2 . The claim specifies spinel compositions having empirical formulas of Fe_xZn_{1-x}O₄ with x values ≤ 2.5 . Although compositions having single phase spinel structures are preferred, the compositions claimed in the patent are not limited to a method of preparation, specific structures or any morphological feature. A corresponding patent, having an identical specification, issued to Soled et al. (X.21) claims a FT process utilizing these catalyst compositions.

Only methods that generate high surface area materials were used in the examples to demonstrate the preparation of three different spinel compositions, i.e. Fe_{2.8}Zn_{0.2}O₄, Fe_{2.45}Zn_{0.55}O₄ and Fe_{2.3}Zn_{0.7}O₄. Only the first catalyst, which was prepared by two different methods, fell within the range specified in the claims. All three catalysts were prepared by mixing a solution of iron nitrate and zinc nitrate with an ammonium glycolate solution having a pH of 6.5, forming a precipitate, and drying and heating in air at 350°C/1 hr. The resulting spinels were impregnated with K₂CO₃ and Cu(NO₃)₂ and dried in a similar fashion. The second Fe_{2.8}Zn_{0.2}O₄ spinel was prepared by adding ammonium hydroxide to a solution of iron nitrate and zinc nitrate to a final pH of 9. The washing, drying and impregnation steps were the same.

Although the catalysts were claimed to be useful in either fixed-bed or slurry FT reactors, the examples included only slurry reactor applications. The effect of promoter on synthesis gas conversion of Cu, K and Cu-K promoted Fe_{2.8}Zn_{0.2}O₄ showed that the K/Cu promoted catalyst gave higher CO conversion and methane selectivity, as shown

in Table X.13. Surprisingly, the highest CO conversion was observed for a spinel having a Fe/Zn ratio less than 5 which falls outside the claimed composition range. It is not clear why this composition was not included in the claimed range of compositions.

Comparative performance tests of the zinc ferrite based catalysts were conducted with 2g samples of catalyst and 72g of octacosane in a 300 cc Parr CSTR. The synthesis gas ($H_2:CO = 2:1$) feed rate was 180 cc/min at 75 psig and 270°C. Activation was accomplished by heating up to and at 270°C in synthesis gas. Nitrogen (20 cc/min) was added as an internal standard. The superficial space-velocity (V/V/hr) based on an initial catalyst density of 1.8 g/cc was approximately 15,000 V/V/hr. CO conversions in excess of 60% were maintained during initial 80 hr test. Methane selectivity of 4.5% (CO_2 free) was obtained. C_{5+} selectivities were >75% on a CO_2 free basis. On this basis, the space velocity (including 20% inert gas) was about 6 NL/hr-g catalyst (Table X.14); this compares favorably with the activity of cobalt catalysts discussed later. The Exxon workers report that the pressure useful in the process will range between 150 and 450 psig and preferably 250 and 400 psig. They state that higher pressures can be used but these can lead to high levels of condensed water which can retard activity. This statement implies that the catalyst either has low water-gas shift activity or is being operated under conditions where the fraction of CO converted to hydrocarbons, and not CO_2 , is very high.

Fe-Zn-Ti and Fe-Zn-Mn Spinels

A patent issued to Fiato et al. (X.18) claims compositions comprising sintered combinations of metal oxides taken from Group VIII (Fe), Group IIb (Zn), Group IVb (Ti) and/or Group VIIb (Mn), Group Ia (K), and the Lanthanum Group (Ce) such that the

sintered combinations comprise a series of spinels of Group VIII (Fe), Group IIb (Zn), Group IVb (Ti) and/or Group VIIb (Mn) and a Group Ia metal oxide in a lanthanum group oxide matrix. The preferred metals are shown in parenthesis. There were specific limits on concentration of the metal oxides in the mixture which are quite similar to the sintered combination in Gates and Fiato (X.16) which included Fe, Zn, Ce and K. In that case, the only limits on concentrations of the metals were in a subordinate claim. The sintered catalysts are red-brown or red-purple, have BET surface areas $\geq 2 \text{ m}^2/\text{g}$ and are highly crystalline. The crystalline phase comprise hematite, magnetite, ilmenite, a series of mixed spinels and CeO_2 . A corresponding identical patent issued to Fiato et al. (X.22) claims a FT process utilizing this catalyst.

The catalysts are prepared, as in Gates and Fiato (X.16) by sintering a mixture of oxides having the correct atomic ratio and reducing in H_2 at 500°C for 6 hrs. The K, Ce, and K/Ce catalysts in a fixed-bed reactor configuration had CO conversion activities that varied with the promoter following the order $\text{K/Ce} > \text{Ce} > \text{K}$, as shown in Table X.15. At a reasonable CO conversion level the $\text{C}_2\text{-C}_3$ olefin selectivity was high and the methane selectivity was lower for the K/Ce spinel. Data were also given at higher reactor temperature, i.e. 305°C , as well as at lower space velocity, which resulted in excess of 80% CO conversion with high olefin concentrations in the $\text{C}_2\text{-C}_4$ fraction plus a sizable yield of C_5+ product.

K, Ce and K/Ce catalysts having compositions in which Ti was replaced with Mn were also included. The atomic ratio of the metallic components in the catalyst containing both K and Ce was 1.0 Fe/1.0 Mn/0.07 Zn/0.05 K/0.04 Ce. On a weight basis, this composition (43.6% Fe_2O_3 /48.2% MnO_2 /3.1% ZnO/1.2% K/3.8% Ce) is excluded from being a covered composition since it fell outside the specified

composition in the main claim. Specifically, the MnO₂ composition of 48.2 wt.% of the total oxides is excluded, unless there is an error in the composition as stated in Example 6, since the claims specify a range for MnO₂ of 10 to 40 wt.% of the combination. The performance of the K, Ce and K/Ce promoted Fe/Mn/Zn spinels in a fixed-bed reactor configuration are shown in Table X.16. The K/Ce dual promoted spinel provides high activity, low methane selectivity and high C₂-C₃ olefin selectivity.

Thallium Impregnated Iron Supports

Two patents were issued regarding thallium and iron catalysts. One is a composition of matter case issued to Wright (X.23) and the second, a process patent issued to Wright et al. (X.24). Both cases involved several filings and abandonments; there is also a difference in the inventors for the two cases. Overall, the texts in these two are very similar, though not identical. The main claims cover all Fe-Tl compositions wherein the thallium compound, being supported or unsupported, is substantially deposited on the surface of the iron compound, with the iron compound in the trivalent state. Included in a dependent claim is incorporation of promoters including Co, Zn, Cr, Mn, Ba and Group I metals.

The main claim appears confusing since it states that the thallium may be both supported and unsupported but is also substantially supported on the surface of the iron. The examples contain numerous examples in which the thallium was impregnated onto the surface of the iron, however one catalyst was prepared by impregnating a melt of ferric nitrate and thallium nitrate onto a magnesium-alumina spinel. This presumably is a supported example. Also, there is nothing in the claims regarding pretreatment of the catalyst to reduce the Tl and Fe to the metallic or

carbided forms, although a number of different methods for preparing the catalysts are included in the examples.

Several techniques for preparing Fe/Tl catalysts were presented in the examples. Several Fe-Tl catalysts were produced having Fe/Tl ratios from 10/1 to 2.5/1 by precipitating solutions of ferric nitrate with ammonium carbonate and impregnating the washed and dried solids (110°C for 12 hrs in air) by an incipient wetness method with solutions of thallium nitrate or thallium chloride. Examples were also given for preparation of other Fe/Tl catalysts supported on alumina, cesium-doped and magnesia-doped aluminas, and commercially available iron oxide. Examples explaining the preparation of several fluoride impregnated catalysts were also provided. Test results were provided on only a limited number of these preparations.

All of the Fe-Tl catalysts that were prepared in the examples were run under FT conditions that gave CO conversions up to 97%. The product contained large concentrations of liquid hydrocarbons in the C₅-C₁₁ range that was rich in olefins and contained a lesser amount of aromatics. Data for a 10 Fe/1 Tl catalyst prepared by precipitating ferric nitrate and impregnating the resulting solid with thallium nitrate and reducing at 270°C/18 hrs are shown in Table X.17. Over a range of temperatures from 270 to 350°C, the maximum C₆+ yield at CO conversions >90% was ~20% with methane yields ranging between 6 and 15%. CO conversion is very dependent on space velocity, however, methane, C₅-C₁₁ liquid, C₁-C₄ gas, alpha-olefin and aromatic selectivities are only weakly dependent on space velocity. It was suggested that the aromatics yield is probably related to conversion of olefins. None of the examples provided any data on CO₂ yields.

The performance of two Fe-Tl catalysts in the FT reaction was compared with an Fe/K and a commercial ammonia synthesis catalyst. Two Fe-Tl catalysts, having Fe/Tl ratios of 10/1 and 5/1, were prepared by precipitating ferric nitrate and impregnating the resulting solid with thallium nitrate. The method for preparing the Fe/K catalyst that contained 4% K is not clear and no further description of the commercial ammonia synthesis catalyst was given. Selected results from runs presented in Example 9 in the patent are shown in Table X.18. In the patent, in several instances, differing sets of results are given for the same run condition without any explanation. For example, included in Table X.18 are two sets of data that were both taken at 350°C and 300 GHSV for the 10 Fe/1 Tl catalyst. Due to the lack of clarity in the presentation of the data, it is difficult to draw any conclusions regarding the CO conversion activities of these various catalysts. However, the product selectivities in these runs are quite similar. The discussion in Example 9 of the patent states that CO conversions were initially in the 80-98% range. Whereas the Fe/0.4K catalyst appeared to lose activity after about 18 hours on stream, conversion for the Fe/Tl catalyst decreased to only 40-60% after several days on stream. The selectivity for the 10 Fe/1 Tl catalyst appears to be maximum at 270°C at a CO conversion of 46.8%.

Iron - Cobalt Impregnated Slurry Catalysts

A patent issued to Fiato et al. (X.25) claims a process for preparing a slurry FT catalyst system in which an Fe-Co catalyst is formed (in situ) in the absence of air. A corresponding identical patent, except for references and claims, issued to Fiato et al. (X.26), claims a FT process utilizing this catalyst system. The catalyst is prepared by adding Fe and Co carbonyl compounds, or Fe and Co compounds which are capable of forming carbonyl complexes, in a CO atmosphere, along with a powdered support,

to a hydrocarbon liquid. The iron and cobalt compounds are present in a ratio of from 35:1 to 1:10. This combination is decomposed in the presence of CO such that the cobalt complex is decomposed to the metal at a lower temperature followed by decomposition of the Fe complex at a higher temperature. The slurry is heated in H₂ to reduce the metals and their decomposition products. Representative complexes are Fe₃(CO)₁₂, bis(dicarbonylcyclopentadienyliron), [CpFe(CO)₂]₂, and Co₂(CO)₈. Potassium carbonate, that promotes olefin formation in the reaction and decreases the formation of methane, may be added to the mixture in the first step.

In the examples in the patent, [CpFe(CO)₂]₂ and Co₂(CO)₈ were added to the reactor either alone or in the presence of a support. In each case shown in Table X.19, the absolute amount of Fe and Co in the reactor was the same except for the run in which Fe₂O₃/1% K was added as the support. In runs with a 1:1 H₂/CO synthesis gas mixture, CO conversions were 20-30% with the C₂-C₄ fraction being predominantly olefinic. After 96 hours on stream, conversion had increased from ~21 to 27%. In a comparative run, an *ex situ* catalyst, Fe_{2.85}Co_{0.15}O₄/1%K, gave <5% CO conversion. For this run, the preparation of the catalyst nor its concentration in the reactor were not given.

TITANIA AND TRANSITION METAL OXIDE SUPPORTS

An extensive number of patents were obtained related to the use of titania containing catalysts in various applications, including the FT reaction. Early patents in this area disclosed the unique features of titania containing supports but did not refer to any FT type of application. However, these cases were fundamental to many of the subsequent patents that were issued for FT application. A patent issued to Tauster et al. (X.27) disclosed compositions comprising Group VIII metals supported on bulk

oxides of titanium, vanadium, niobium, tantalum, zirconium titanate and barium titanate which were reduced in H₂ before use. A corresponding approach of coating a support with titania and adding a Group VIII metal is disclosed in a related patent issued shortly thereafter to Wheelock (X.28). Numerous patents have subsequently been issued using these approaches.

Tauster et al. (X.27) claimed that H₂ reduced Group VIII metals supported on Group IVb and Group Vb oxides are distinctly different from the same metals deposited on common carriers such as alumina, silica, carbon, magnesia, and silica alumina. These metals deposited on common carriers are found to retain their capacity for H₂ chemisorption, whereas the same metals when supported on various Group IVb and Group Vb oxides exhibit a marked suppression of this capacity. This change is attributed to the chemical nature of a strong metal-support interaction (SMSI) that consists essentially of covalent bond formation between metal atoms of the supported phase and metal cations of the oxide support at the surface.

Such an interaction between the supported metal and the support is highly unusual. Typically, the role of the support is simply a geometrical one which exerts the major influence in the preparation of a well dispersed supported-metal catalyst. Thus chemically dissimilar materials, such as alumina and carbon, are able to efficiently disperse supported metals, provided that they are employed in their high surface area form, e.g. >100 m²/g. In these situations no strong chemical interaction between the support and the metallic phase is required to bring about good dispersion. If surface interaction occurred, the results observed for temperature-programmed-desorption of H₂ from Pt/alumina and Pt/silica catalysts, which are very similar, would be expected to be quite different.

The patent argues that although covalently-bonded species are observed in the hexagonal barium titanates and Lewis acid-base intermetallic compounds, which are representative of cation to cation and metal-atom to metal-atom types of bonding, respectively, the metal-atom to cation bonding in the SMSI are unique to the structures of this invention. In a Lewis acid-base intermetallic type of bonding structure, the titanium would be present as zero-valent. By photoelectron spectroscopy, or ESCA (electron spectroscopy for chemical analysis), zero valent titanium was not found in a composition of this invention, i.e. a 2% Rh/TiO₂ catalyst that had been reduced in H₂ at 550°C.

In the broadest sense, the catalyst composition consists of a catalytic metal component selected from the group consisting of Group VIII metals, and mixtures thereof, supported on a transition metal oxide selected from the group Ti, V, Nb, Ta, alkaline earth titanates, and mixtures thereof. These SMSI oxides can be used either in the pure state or, alternatively, in combination with additional oxides such as alumina, silica, magnesia, zirconia, hafnia, thoria, ceria, etc. They may be prepared by coprecipitation from solutions containing precursor salts of the respective oxides or by deposition of the precursor salt of the SMSI oxide on a carrier. The latter compositions, comprising titania deposited on the surface of an inorganic oxide support to which Group VIII metals are added, were disclosed by Wheelock (X.28) who anticipated a stabilizing interaction between Group VIII metals and Group IVb metal oxides.

The key characteristic of the SMSI oxides is that after the critical temperature for reduction is reached, the supported metal is no longer able to absorb H₂ and CO at room temperature. However, the supported metal particles are still in a high state of dispersion and retain their ability to chemisorb oxygen resulting in high ratios of

adsorbed oxygen to metal atoms. Since the SMSI effect is a chemical interaction between the supported metal and the carrier, it is necessary for the metal to be well dispersed in order to provide sufficient interfacial contact between metal and support. Thus large metal crystallites are incapable of significantly affecting the properties of the surface metal atoms in contact with the gas phase. Therefore, the particle size of the supported metal should be preferably 50 D or less. There also is a difference in the temperature of H₂-activation needed to confer SMSI properties on the Group VIII metal, which varies primarily with the particular SMSI support. A SMSI state is achieved when a composition, e.g. Group VIII metal supported on the oxide of Ti, V, Nb, Ta, a mixture thereof, or a Zr or Ba titanate, is subjected, as a final preparative step, to reduction in a reducing atmosphere at a temperature sufficient to cause the composition to exhibit the suppression of H₂ and CO chemisorption.

Properties of Titania Supports. Tauster et al. (X.27) did not address the question of surface area and how it relates to the development of the SMSI state, although they used the argument that chemically dissimilar materials, such as alumina and carbon, are able to efficiently disperse supported metals, provided they are employed in their high surface area form, e.g. >100 m²/g. Based upon data contained in a subsequent patent issued to Arcuri et al. (X.29) the titania supported catalysts prepared by Tauster et al. (X.27) probably had only moderate surface areas. Arcuri et al. (X.29) showed that the rutile to anatase ratio increased with higher air calcination temperatures which caused a corresponding decrease in surface area (see Table X.20). They also found reduction of a calcined sample with H₂ at 450°C did not prevent further decrease in surface area upon further calcination in air at 500°C. These data suggest that the surface areas of the titania used by Tauster et al. (X.27) was initially about 60 m²/g and

because of the thermal transformation of anatase to the rutile form, the final surface areas were probably somewhat less than the starting material and somewhat enriched in the rutile form. In a still later patent issued to Mauldin and Riley (X.30), additional data were reported showing increases in rutile concentration with calcination temperature (see Table X.21).

Vannice and Garten (X.31) described the titania that was probably used in many of these patents as being prepared by flame hydrolysis of TiCl_4 and having a surface area of $\sim 60 \text{ m}^2/\text{g}$ after thermal treatment at temperatures $\approx 500^\circ\text{C}$. A number of the cases referred to a material of this type that was designated as Degussa P-25 and was described as having a BET surface area of $50 \text{ m}^2/\text{g}$ and contained 65% anatase and 35% rutile titania in Wachs and Yang (X.32). Although a number of these patents contained claims that specified limits on the concentrations of the crystalline forms in the titania phase, several actually contained these limits in either the main claim or another independent claim. This, of course, provides an unalterable requirement for the catalyst of the invention and was peculiar to a series of five patents, four of which claim titanias having high rutile contents while the fifth claims a stabilized titania having a high anatase content. Interestingly, the four high rutile cases, that originated from work presumably done at the Baton Rouge laboratories, were filed on the same day, June 29, 1984, and no subsequent patents had such a restriction in their main claim, although several continued to claim such materials in dependent claims. The level of rutile specified in the claims is $>40\%$.

An alternative to using bulk titania is supports in which titania would be coated onto common, inorganic oxides. Such compositions were covered in a patent issued to Wheelock (X.28) which disclosed compositions comprising Group VIII noble metals

and titania deposited onto inorganic oxides. Interestingly, that patent actually specified in its main claim that the titania existed on the surface as clusters. Whether such speculation regarding the morphological form of the catalyst, which was based upon ion scattering experiments, limits the compositions claimed by the invention is not clear. Assuming that it does not, Exxon then has rights to all compositions comprising Group VIII noble metals on titania coated inorganic oxides, of which platinum was specifically mentioned.

Ruthenium on Titania and Transition Metal Oxide Supports

The earliest Ru on titania Exxon patent that was found related to application in NO_x reduction. A composition of matter patent issued to DeLuca et al. (X.33) claimed a composition comprising ruthenium in combination with zirconium titanate or zirconium titanate in admixture with titanium dioxide, but not with TiO₂ alone. Ruthenium on titania compositions had been disclosed in previous patents, one of which was issued to Kobylinski and Taylor (X.34), and assigned to Gulf, which claimed a process for reducing the content of nitrogen oxides in the exhaust gases from internal combustion engines. Such patents probably precluded claiming such compositions.

A problem with Ru/TiO₂ catalysts is the loss of Ru oxide upon treatment at temperatures around 840°C. DeLuca et al. (X.33) claimed decreased volatility of Ru oxide from compositions comprising Ru on zirconium titanate, either with or without additional titania being present. Tauster et al. (X.27) claimed the use of these materials in hydrocarbon conversion reactions but not in a FT type application. Various combinations of these supports, either alone or in combination with supported metals, are claimed in subsequent composition of matter patents or as catalysts in various FT

process application patents. Several patents were issued regarding ruthenium on titania type supports. The claims in all these cases included not only titania but numerous combinations with silica, alumina, carbon, Group Vb metal oxides, and various alkali, alkaline earth and rare earth oxides. Exxon came close to claiming the composition Ru on TiO₂ in a patent issued to Arcuri et al. (X.29) which claimed catalyst compositions comprising ruthenium with rhenium on titania. A companion process patent that utilized this catalyst, which was essentially identical except for the claims, was issued to Arcuri (X.35). The titania support in these compositions were specified as having rutile concentrations >40%. The examples in these patents showed in extended runs with synthesis gas that Ru/TiO₂ that contained rhenium had a longer half-life at a level of 97% CO conversion than rhenium-free catalyst (see Table X.22). The interactive effects of these two metals on catalysts containing 0.5-1.0% Re with ruthenium concentrations from 0.1-1.0% indicate that the highest CO conversions were obtained for catalysts containing 0.5% Re and 1.0% Ru (Table X.23). The effect of the ratio of rutile to anatase in the catalyst is shown in Table X.24 in which the catalyst containing 67% rutile in the titania had the slowest deactivation rate when operating at the 90% CO conversion level. Also, methane selectivities were much lower for the catalysts containing higher levels of rutile.

Several of the ruthenium-titania patents that were issued relate to processes that use Ru on titania. Vannice and Garten (X.31) claimed the use of a reduced Ru on titania, which they prepared by impregnating RuCl₃ onto titania and reducing in H₂ for 1 hr at 450°C. The Ru/TiO₂ catalyst gave higher olefin yields than a related Ru on γ-Al₂O₃ (see Table X.25), albeit at a CO conversion level of 10% or less in both cases. Mauldin (X.36) claims a process for converting methanol in the presence of H₂ using a catalyst

comprising ruthenium composited with titania. At a 4/1 methanol to H₂ ratio, conversion to hydrocarbon product was 76% after 35 hrs on stream (see Table X.26). Either in the absence of H₂ or the presence of added CO, conversions dropped significantly. CO was presumed to adsorb preferentially on the catalyst preventing reaction of the methanol.

Vannice and Tauster (X.37) claimed a FT process using a catalyst comprising Ru deposited on V, Nb and Ta oxides either alone or in combination with silica, alumina, or carbon type supports. Titania was not included in the claims. Preparation of the catalysts was by methods as presented in Tauster et al. (X.27) which was incorporated by reference. Higher olefin yields were obtained with the catalysts of the invention under conditions that the CO conversions were less than 18% (see Table X.27).

Madon (X.38) also claimed a FT process using a catalyst comprising Ru deposited on the same supports claimed by Tauster et al. (X.27), i.e., Ti, V, Nb and Ta oxides. In an improvement over Vannice and Tauster (X.37), this case claimed a process which employed a reduced catalyst which was contacted with a mixture of H₂ and CO for at least 10 hours, after which continued contact with H₂/CO gave a C₅-C₄₀ hydrocarbon product having a paraffin to olefin ratio in the C₅-C₂₀ fraction of \$1.5. With a 0.76% Ru on TiO₂ catalyst, in excess of 80% CO from a 1.39 H₂/CO synthesis gas mixture was converted to liquid products under conditions shown in Table X.28. All of these catalysts were shown to be more active than Ru supported on conventional SiO₂ or Al₂O₃ (see Table X.29).

A patent issued to Wachs and Yang (X.39) claims a catalyst comprising Ru supported on a surface modified titania support wherein the support comprises an

oxide of a metal selected from the group Nb, V, and Ta supported on the titania. In a corresponding patent, Wachs and Yang (X.32) claim a method for preparing this catalyst composition by depositing noncrystalline metal oxides of V, Nb, and/or Ta on a titania support having a 50 m²/g surface area. In a related patent, Wachs and Chersich (X.40) claim a simple Ta₂O₃/TiO₂ composition prepared in this manner. No related patents claiming V and Nb oxide modified titania surface compositions were found. In Wachs and Yang (X.39) the modified support was impregnated with a solution of the Ru precursor which was reduced to the metal form. In the examples, all of the catalysts contained 1% Ru loadings. The activity of the catalysts containing various concentrations of the oxide promoters were compared with an impregnated physical mixture of TiO₂ and Ta₂O₅ in a fixed bed reactor (see Table X.30). Although the patent states that the data clearly show the difference between the catalysts of this invention and prior art Ru/TiO₂ catalysts, it is a challenge to recognize any differences.

A patent issued to Fiato and Miseo (X.41) claims slurry catalyst compositions consisting of titania, the decomposition product of Ru₃(CO)₁₂ formed in the presence of H₂, and an inert alkane hydrocarbon. Fiato and Miseo (X.42) claim a process for preparing the *in situ* Ru/TiO₂ slurry catalyst. Preparation includes adding TiO₂, a Ru carbonyl complex, and an inert alkane hydrocarbon to a slurry reactor and increasing the temperature of the reactor to 230-270°C and pressure from 4 to 20 atm for 2-6 hr while adding a gas mixture of N₂:H₂ to cause the decomposition of the Ru carbonyl complex to form a slurry catalyst composition. In the example, a TiO₂ that had been pretreated with H₂ for several hours was added to the reactor with the Ru carbonyl complex and then subjected to the carbonyl decomposition step. The catalyst was highly active and selective for production of liquid hydrocarbons giving 40 to 60% CO

conversion at 240°C with an alpha of 0.80. When TiO₂ was not present in the reactor, the Ru carbonyl complex was incompletely reduced and gave only 15% CO conversion (see Table X.31). The performance of the slurry catalyst was compared with a particulate Ru/TiO₂ and a Ru supported on ceria and alumina. The Ru - TiO₂ slurry catalyst had the highest CO conversion (55%) with a selectivity very similar to the particulate Ru/TiO₂ catalyst.

A patent issued to Mauldin (X.43) claims a process wherein the Ru on titania catalyst is pretreated with steam or steam and H₂ at 200 to 550°C to mildly agglomerate the ruthenium. By this procedure, Ru particles are generated having the same size as obtained after start-up with synthesis gas. The same effect occurs upon treating in air at 500°C where the crystallite size of the Ru grows from 12 to 30 D. In the examples, a Ru/TiO₂ was prepared by impregnating a titania having a rutile content of 73% with ruthenium nitrate in acetone solution. One portion of this material was calcined in air at 500°C for 4 hours. Another was contacted with mixtures of steam with H₂ or N₂ at elevated temperature, as shown in Table X.32. The oxygen chemisorption decreased while the Ru crystallite size increased. The performance of the Ru/TiO₂ that had been treated in air at 500°C for 3 hrs was compared with an untreated sample. Results after several times on stream, as shown in Table X.33, indicate that the selectivity to methane was higher and to C₂+ hydrocarbons was generally lower than for the untreated catalyst. The catalyst treatments that were presented in the patent, including air or steam with H₂ or a carrier gas, provide an advantage over a non-treated catalyst, as determined by Ru crystallite size, oxygen chemisorption or synthesis gas conversion and selectivity.

A patent issued to Pruett and Bradley (X.44) claims compositions comprising bimetallic cluster compounds containing Ru with Tl, In or Ga. A cluster having the formula $[(C_2H_5)_4N][(Ru_6C(CO)_{16})_2Tl]$ deposited onto an alumina surface was reduced in H_2 at $200^\circ C$ and used for conversion of 1.5/1 H_2/CO mixture at 7 MPa and $275^\circ C$. The product contained a mixture of linear hydrocarbons and alcohols.

Rhodium on Titania

A patent issued to Vannice and Garten (X.45) claims a process in which synthesis gas is passed over a catalyst comprising Rh on a titanium-containing oxide support. The activity of this catalyst, reduced at $450^\circ C$ and 100 kPa, though quite low, was higher than for a Rh on alumina catalyst (Table X.34). The product was largely methane.

Cobalt on Titania and Transition Metal Oxide Supports

There has been a considerable amount of activity by Exxon regarding cobalt on titania catalysts with a number of patents being issued that parallel the ruthenium cases discussed above. Included in the series were three filed on June 29, 1984 from the Baton Rouge laboratory that relate to titanias having rutile concentrations $\geq 40\%$. Very broad coverage was obtained in a patent issued to Payne and Mauldin (X.46) which claims catalyst compositions comprising cobalt on high-rutile titania which are useful for both synthesis gas and methanol conversion. A subsequent patent issued to Behrmann et al. (X.47) claims catalyst compositions comprising cobalt dispersed and impregnated upon the surface of titania to an average depth of 0.02 to 0.20 mm with a cobalt loading, on a total bulk basis, from 0.04 to 0.15 g/cc, which is $\sim 4-17$ wt.%, depending on the packing density of the titania. A related patent issued to Iglesia et al. (X.48) claims a method for preparing supported cobalt catalyst on which the Co is

deposited to a depth of less than about 200 μm on the rim of the catalyst particles. Other patents issued to Payne and Mauldin (X.49) and Behrmann et al. (X.50) claim processes that utilize these catalysts for conversion of synthesis gas. The addition of rhenium as a promoter to this family of catalysts, i.e. rhenium with cobalt on titania, was also covered. Catalysts in which the Co and Re were concentrated at the surface of the spherical particle was claimed by Behrmann et al. (X.47). Rhenium is claimed to improve activity for CO conversion for cobalt as it does for ruthenium. Bulk Co/TiO₂ catalysts, either with or without thoria, were claimed in a patent issued to Mauldin (X.51) with addition of thoria being claimed to be especially beneficial for conversion of methanol. Since the main claim in this case specified an inorganic oxide support, with titania being mentioned in a dependent claim, compositions that were covered were actually broader than titania itself, although titania supports were the only ones used in the examples.

Of the nine examples on Co/TiO₂ in the Payne and Mauldin (X.46) case, the first six relate to conversion of methanol and the last three to conversion of synthesis gas. The latter examples with synthesis gas are repeated in Payne and Mauldin (X.49) while the first six, which are related to methanol conversion, were probably included in Application Number 626,026, which was filed on the same day, as noted in Payne and Mauldin (X.49), but apparently never resulted in an issued patent. A process patent issued to Mauldin (X.52) used the Mauldin (X.51) catalyst comprising rhenium and cobalt on titania.

The examples of bulk titania catalysts in Payne and Mauldin (X.46) were prepared from calcined Degussa TiO₂, which was impregnated with Co nitrate and/or perrhenic acid. The addition of perrhenic acid to the substrate is a puzzle, since none

of the catalysts contain Re, nor do any of the claims refer to catalysts containing Re. At any rate, the impregnated materials were then calcined in air at 250 or 500°C and reduced in H₂ at 450°C. Thoria containing catalysts were prepared by impregnating the support with a thorium compound or salt in a similar manner to give thorium concentration up to 10%. Actually, the specific thorium compounds or salts that were used to impregnate the substrate were not mentioned anywhere in the specification. Another set of cobalt-titania catalysts were also prepared having both high and low rutile concentrations. The low rutile concentration catalyst was prepared by impregnating cobalt carbonyl onto uncalcined Degussa P-25 titania that had a rutile concentration of 28% while the high-rutile catalyst was prepared from Degussa P-25 that had been calcined at 600°C. The impregnated cobalt carbonyl was decomposed either by heating at 257°C in vacuo for 1 hr, or by calcining at elevated temperatures. Catalysts were tested in a fixed bed reactor either with synthesis gas or with methanol after reducing in H₂.

A subsequent patent issued to Behrmann et al. (X.47) claims catalyst compositions comprising cobalt dispersed and impregnated upon the surface of spherical titania with an average thickness of 0.02 to 0.20 mm. A corresponding patent issued to Behrmann et al. (X.50) claims use of these compositions in a FT process. The cobalt loading in these catalysts, on a total bulk basis, was from 0.04 to 0.15 g/cc, which is -4-17 wt.%, depending on the packing density of the titania. Special techniques for depositing the cobalt along with Re as a promoter were used wherein the metals were concentrated at the surface of the spherical titania particles having diameters of approximately 1 mm. The activity of rhenium promoted Co/TiO₂ catalysts, in which the metals are deposited on the surface of spherical titania

substrate, is related to the thickness of the metal layer. With these catalysts that were prepared from spherical titania, the methane concentrations in the hydrocarbon product, relative to the converted CO, was lower than for Co-Re/TiO₂ in which the metals were uniformly distributed onto powdered substrate (see Figure X.1). The metals were deposited onto the surface of the spheres by either spraying a metal-containing solution onto the titania spheres and quickly removing the solvent or treating spheres that had been saturated with one solvent with a metal-containing immiscible solvent which would not penetrate into the particle.

Another method to prepare rim-type supported cobalt catalysts is covered in a patent issued to Iglesia et al. (X.48) who claim that contacting a support particle with a molten cobalt salt results in deposit of the cobalt to a depth of less than about 200 μm on the rim of the support. After reduction in H₂, these catalysts are more active than incipient wetness impregnated catalysts where the Co is evenly distributed throughout the particle, as shown in Table X.35, where a lower GHSV is necessary to achieve the same level of CO conversion. Each of the rim-impregnated silica based catalysts have a higher volume of CO conversion per volume of catalyst per hour. Crushing the 2.2 mm spheres provided a slight increase in CO conversion which denotes some additional diffusional effect in the rim catalysts even though the Co is located primarily at the surface of the particle. There is also an advantage of having higher Co concentrations on higher surface area supports, as shown in Table X.35.

The advantage of incorporating a binder into titania was covered in patents issued to Mauldin and Riley (X.30) which claim support compositions comprising titania in which up to 20% alumina or zirconia is incorporated. A corresponding essentially identical patent issued to Mauldin and Riley (X.53) claims a FT process

utilizing these catalysts. Their data show that incorporating a small amount of alumina increases the volume of CO converted per gram of cobalt/hr, as shown in Figure X.2. This increased activity is attributed to an increase in cobalt dispersion due to the increase in pore volume of the binder. Hydrocarbon synthesis activity suffers at higher alumina concentrations, however, because the Co oxide is only partially reduced on the alumina, as compared to titania where complete reduction occurs. This is reflected in the higher turnover numbers for the titania and the steady decline as incorporation of alumina increases (see Figure X.3). Thus, incorporation of small amounts of alumina results in an increase in activity. Higher dilutions, however, result in a decline in activity. An example is also presented that shows that catalysts prepared by spraying Co salts onto titania substrate containing 3.5% alumina binder using the method of Behrmann et al. (X.47) were more active than spherical titania without the binder.

A method for impregnating cobalt onto supports was covered in a patent issued to Mauldin and Riley (X.54) which claims a process for preparing a FT catalyst in which a catalytically effective amount of Co is impregnated and dispersed as a film or layer on the peripheral outer surface of a particulate porous inorganic oxide support, wherein the catalysts are prepared by spraying a bed of the fluidized particulate support particles with a liquid containing a dispersed or dissolved Co metal compound. The operation is performed at specified operating conditions of 0.6 g liquid/ft³ fluidizing gas. Titania was one of the supports specified in a dependent claim. In the examples, solutions of cobalt nitrate and perrhenic acid were sprayed onto particulate material and reduced at 450°C for 1 hr. Conversion of a 2/1 H₂/CO feed at 200°C, 280 psig and 1000 GHSV after 20 hrs on stream was 79% with product selectivities for CH₄ of 6.0%, CO₂ of 6.0% and C₂+ of 93.6%.

Synthesis Gas Reactions. Co/TiO₂ catalyst has a higher activity toward synthesis gas conversion, as shown in Table X.36, than conventional cobalt on silica or alumina or Co-Mg-thoria on kieselguhr, which was prepared following a published procedure (X.55). The 0.91 Schulz-Flory alpha value for the titania catalyst was higher than for conventional catalysts and was reflected in a C₁₀₊ hydrocarbon yield that was ,75%. Higher CO conversions in these Co/TiO₂ catalyst appear related to higher rutile concentrations and higher O₂ chemisorption values of the starting catalysts as shown in Table X.37. The pseudo first-order CO conversion rate constants calculated by Equation 1 correlate directly with the oxygen chemisorption values for these four catalysts, as shown in Figure X.4.

$$k' \frac{GHSV}{P} \ln \frac{1}{(1+x)} \quad (1)$$

where:

x = fraction CO conversion,

P = reactor pressure in atm, and

GHSV = space velocity at ambient temperature and pressure in hr⁻¹.

Similar results were obtained with catalysts prepared by impregnating cobalt carbonyl onto 28% and 100% rutile titanias where the carbonyl was decomposed by heating in vacuum. Synthesis gas conversion over these catalysts shows that the high rutile catalyst gave much higher CO conversion (see Table X.38). Cobalt catalysts prepared either from the nitrate or the carbonyl gave essentially the same results.

Incorporation of 0.5 to 3% Re in the Co/TiO₂ catalyst further improved both oxygen chemisorption and CO conversion, as shown in Table X.37. The improvement resulting from addition of Re is probably through improving the reduction of the Co in

the pretreatment step (X.56). Results from a 200 hr extended run, presented in (Figure X. show that CO conversion dropped from about -98% to -80%. Comparison with a Ru/TiO₂ catalyst with the Co-Re catalyst under the same conditions (Figure X.6) indicate the Co-Re catalyst was significantly more active than the Ru catalyst while both had similar selectivities for methane and CO₂ (Figure X.7).

Methanol Reaction. Examples of methanol conversions were given for a number of cobalt catalysts including Co/TiO₂, Co-Re/TiO₂, Co/ThO₂/TiO₂, and Co-Re/ThO₂/TiO₂. The effect of rutile concentration on methanol conversion was observed for catalysts containing 12% cobalt on titania. The 100% rutile catalyst completely converted the methanol while the 55% rutile titania support gave only 66% conversion (see Table X.39). The selectivities were also quite different with the catalyst having the lower rutile content being more selective for producing C₂+ hydrocarbon product and less CO₂.

Experimental data showing the effect of adding thoria on the conversion of methanol is provided in Payne and Mauldin (X.46). In these cases the rutile contents of the catalysts were not specified (see Table X.40). Assuming that the titania components in these catalysts had the same rutile concentration, the data show that addition of thoria to the catalyst increases methanol conversion, decreases methane yield, and gives nearly the same Schulz-Flory alpha values. Comparisons with other state-of-the-art catalysts showed that conventional FT 100 Co/5 ThO₂/8 MgO/200 Kieselguhr catalyst gave higher methanol conversion but poorer C₂+ hydrocarbon selectivity under the run conditions. Compared to Co on silica or alumina, both Co-titania catalysts, with or without thoria, gave better C₂+ selectivity at comparable or higher methanol conversion levels. The liquid product was highly paraffinic as

reflected in the 78.2% straight chain paraffinic content of the C₈ fraction from the thoria containing catalyst. Even over the Co/alumina catalyst, where methanol conversion was 64%, the yield of dimethyl ether was only 2.4%, indicating the non-acidic nature of the alumina support. At the low methanol conversion levels, dimethyl ether formation was quite small.

The presence of rhenium with cobalt in 56% rutile titania catalysts, either with and without added thoria, increased MeOH conversion (see Table X.41). Addition of 0.5 wt.% Re to Co/ThO₂/TiO₂ increased methanol conversion quite sharply from 49% to 100%. Conversion to CO₂ increased sharply while C₂+ yields decreased from 74% to 56%. The effect of Re/TiO₂ on methanol conversion was not provided.

Hydrogen partial pressure has a strong effect on methanol conversion and product selectivity. Payne and Mauldin (X.46) showed that increasing the H₂ partial pressure at constant methanol space velocity increased conversion from 38% to 83% (see Table X.42), decreased the yields of CO+CO₂, and sharply increased methane selectivity. The C₂+ yield appears to go through a maximum at a H₂ partial pressure of 17 psi. At low methanol pressures over a 12% Co/2% ThO₂/TiO₂ catalyst, the products are almost exclusively CO and H₂, except for a very small amount of methane.

A patent issued to Mauldin et al. (X.57) claims cobalt-titania catalyst to which is added small amounts of hafnium, zirconium, cerium or uranium to maintain the cobalt in a high state of dispersion and stabilize the catalyst during high temperature air treatment. The concentration of promoter to cobalt was specified as a weight ratio greater than 0.01 to 1 and typically between 0.04-0.25 to 1. Although there were no limits placed on the catalyst composition, the catalysts presented in the examples were prepared by impregnating high rutile titania either sequentially with Zr, Hf, Ce or U

compounds followed by Co nitrate or simultaneously with the promoter metals and cobalt nitrate. In the preparation of these catalysts when the metals were added sequentially, the catalysts were calcined between metal additions. The final catalysts were then calcined at 400, 500 or 600°C to simulate catalyst regeneration and tested for synthesis gas reactions. CO conversions for the promoted catalysts were higher than for the non-promoted catalysts at all air treat temperatures >150°C, as shown in Figure X.8. The 500°C catalyst regeneration data plotted in Figure X.9 show that addition of approximately 0.5 wt.% promoter provides optimal thermal stabilization giving CO conversions of 70-80%. The examples also showed that addition of 0.06 wt.% Hf and 0.3 wt.% Zr, both of which fell within the limits of the claimed compositions, was not adequate to stabilize the Co/titania, although higher concentrations did stabilize the catalysts.

Synthesis gas conversion data were provided for a 2/1 H₂/CO mixture that was passed over a Co-Hf-TiO₂ catalyst at 1000 GHSV and 204°C at 280 psig to give 89% CO conversion with a 91% C₅+ hydrocarbon product selectivity. No other synthesis gas data were provided. Comparative runs with methanol, however, are reported for each of the metal promoters (see Table X.43). All of the promoted catalysts gave higher MeOH conversion than the unpromoted catalysts with about the same selectivities for higher hydrocarbon product.

Silica Promoted Co/TiO₂

A patent issued to Iglesia et al. (X.58) claims compositions of cobalt on an inorganic refractory support comprised of a major portion of titania to which up to 15 wt.% silica has been added. This catalyst is utilized in another process related patent issued to Iglesia et al. (X.59). These two cases are identical except for the claims. The

patent specifies that the Co may be incorporated onto the inorganic refractory titania support either before or after adding the silica or silica precursor. Incorporation of rhenium in the catalyst is covered in a subordinate claim. Although the main claim does not specify Re in the catalyst, the examples include only Re-containing catalysts.

In the examples, a series of catalysts, as described in Table X.44 were prepared starting with a CoRe/TiO₂ (Catalyst A) that was prepared by depositing Co and Re components from an acetone solution onto a 97% rutile titania and calcining at 250°C for 3 hrs. Two silica containing catalysts (Catalysts B and C) were prepared by impregnating Catalyst A with tetraethoxysilane (TEOS), treating with a stream of H₂O (40 Torr) in He while heating at 400°C for 13 hrs after which it was reduced at 250-400°C for 2-14 hrs. A catalyst that was free of silica but exposed to the same H₂O treatment (Catalyst D) was prepared by treating Catalyst A with H₂O (40 Torr)/He while heating at 400°C/13 hrs, after which it was reduced at 250-400°C for 2 to 14 hrs. The activities of the catalysts were determined at run times up to almost 200 hrs under conditions to give ~60% CO conversion. There was little difference in hydrocarbon selectivity observed by incorporating silica into the samples. Although the CO₂ yield was in every case quite small, it dropped to an almost imperceptible level with silica. The increased stability of the silica containing catalysts was observed in reduced carbon buildup at low temperatures on the surface of the catalyst in the presence of CO. The "effect of SiO₂ during carburization suggests that it may prevent short term deactivation during the first few hours in H₂/CO environments; the effect is to increase the apparent site activity by maintaining surface cobalt atoms available during hydrocarbon synthesis."

Anatase Titania Supported Cobalt Catalysts

A patent issued to Soled et al. (X.60) claims both a composition of matter and a method for preparing a catalyst containing anatase titania. What appears to be the omnibus claim is claim 13 which claims a catalyst composition comprising Co composited with a ternary metal oxide support of titania having the general formula $\text{Co/Ti}_{1-x}\text{M}_x\text{O}_2$ where x is 0.01-0.14 and M is selected from the group consisting of silicon, zirconium, and tantalum and wherein the titania is an anatase polymorph stable under oxidative regeneration at temperatures of 400-750 °C. Claim 1, on the other hand, claims a method for preparing this catalyst which comprises contacting a titanium alkoxide or titanium chloride, such as TiCl_4 , with a metal alkoxide or metal chloride, respectively, to form a solution; adding water to the mixture of alkoxides or an aqueous base to the mixture of chlorides to form a co-precipitate; separating the co-precipitate; calcining the dried co-precipitate to form a ternary metal oxide; depositing a cobalt metal compound solution onto the surface of the ternary metal oxide to form a composite; and activating the composite to form a catalyst. Activating the composite includes drying and calcining followed by reduction of the Co. Depending on the precedence of claims 1 and 13, the coverage may be broad as defined in claim 13 or it may be very narrow being confined to the composition prepared by the method disclosed in claim #1.

Neither the claims nor the specification in this case discuss the coexistence of mixtures of rutile and anatase forms in the titania. Likewise, the concentration of the anatase phase in the titania prepared by the method of this invention was also not revealed. If the composition of the claimed catalyst is limited to the material prepared according to the method in claim 1, then the question of anatase concentration is mute. However, if the patent covers all $\text{Co/Ti}_{1-x}\text{M}_x\text{O}_2$ compositions per claim 13 where

M is silicon, zirconium, and tantalum and where titania is in an anatase form, the limits on anatase concentration covers only titania compositions that contain, at most, very small amounts of rutile. Regardless, this case is likely an improvement over Iglesia et al. (X.58) which claims cobalt on silica-modified titania wherein no limitation on the form of the titania is made. It also must be an improvement over Mauldin et al. (X.57) which claims catalysts comprising zirconium added to titania to maintain the cobalt in a high state of dispersion and stabilize the catalyst during high temperature air treatments. In the main claim, there are no limitations on the form of the titania. These three cases, however, provide Exxon with coverage for cobalt impregnated anatase to complement their many cases on rutile-rich titanias.

Apparently the reason why the anatase phase is stabilized at high temperatures is related to substitution of Si, Ta, and Zr cations into the anatase structure of the catalyst which apparently retards the formation of CoTiO_3 preventing the entrapment of the cobalt and preserving its specific surface area. Once cobalt titanates form, a higher temperature is required to reduce them to the metal. Through addition of Si, Ta, and Zr, the amount of the CoTiO_3 is decreased. For a Si incorporated polymorph, the concentration of the CoTiO_3 is decreased, as determined by XRD, and its concentration is a function of calcination temperature, as shown in Figure X.10. Silica incorporation has no affect on the thermal properties of the catalyst but increases by approximately 100 centigrade degrees the temperature for onset of carburization in a synthesis gas stream, as shown in Figure X.11.

Catalysts incorporating each of the promoters were prepared and their stability to calcination was reported in the examples. Anatase titania was prepared by first hydrolyzing $\text{Ti}(\text{t-buO})_4$ and calcining at 430°C . Co as Co nitrate was then impregnated

onto the substrate and calcined at 430-700°C. Calcining at 430°C gives anatase having a surface area of 120 m²/g while calcining at 700°C transforms the anatase to rutile having a surface area of 2 m²/g. Silicon promoted titanate was prepared by adding the silicon alkoxide, tetramethylorthosilicate (TMOS), to Ti(t-BuO)₄ following the above procedure. Surface areas containing various levels of silicon substitution were obtained upon calcination at 700°C:

<u>Si, %</u>	<u>m²/g</u>
1%	52
3%	76
5%	119
14%	133

Zirconium promoted titanate was prepared by adding zirconium n-propoxide to Ti(t-BuO)₄ following the above procedure. A catalyst containing 3% Zr had a surface area of 36 m²/g while a 14% Zr catalyst had a surface area of 56 m²/g, both of which stabilized the anatase. A tantalum promoted titanate was prepared by adding tantalum ethoxide to Ti(t-BuO)₄ following the above procedure. A catalyst containing 14% tantalum had a surface area of 71 m²/g. No FT data were provided in the patent.

Cobalt-Ruthenium on Titania

A patent issued to Iglesia et al. (X.61) claims a catalyst prepared by a process comprising impregnating titania with solutions of cobalt and ruthenium salts, drying, reducing the cobalt and ruthenium, treating the metals with an oxygen containing stream to form the oxides and reducing the oxides. A corresponding patent issued to Iglesia et al. (X.62) claims a process that utilizes this catalyst. The intimate contact of the Co and Ru in the catalyst lowers the temperature at which the cobalt is reduced to the metallic form. This results in a decrease in the amount of carbon deposited upon

heating in synthesis gas at temperatures up to 500°C. Intimate contact is obtained by reducing the metals on the surface, calcining in air to reform the oxides and then reducing to the metal form. Unlike many of the other composition of matter patents, a corresponding process patent was not found.

TGA and DTA data provided in the patent showed that the carbon deposited more slowly on calcined Co-Ru/TiO₂ when subjected to a 1:1 H₂/CO synthesis gas mixture than on either Co/TiO₂ or uncalcined Co-Ru/TiO₂. The patent states that the advantage of the Co-Ru combination relative to other catalysts is that "a combination of increased cobalt oxide reducibility and inhibited catalyst poisoning by carbon are believed to account for the increased number of active sites observed on calcined CoRu/TiO₂ catalysts."

Energy dispersive X-ray (EDX) analysis of uncalcined versus calcined CoRu/TiO₂ catalysts that had been aged in process runs for 700 hrs showed that both aged catalysts were identical. Apparently Ru in fresh uncalcined CoRu/TiO₂ catalyst cannot be detected since its concentration over the surface is below detection limits. However, in calcined CoRu/TiO₂ catalyst that has been reduced, Ru can be detected in the cobalt particles where it concentrates sufficiently to be detected by EDX. Apparently, Ru also concentrates in aged uncalcined CoRu/TiO₂ catalysts since the EDX analysis was the same as the calcined sample.

In the examples, three titania catalysts were prepared starting with a sample containing 70% rutile. The first catalyst, Co/TiO₂, was impregnated with cobalt, calcined at 400°C for 4 hrs in air and reduced in H₂ at 400°C for 16 hrs (Catalyst A). Ruthenium was then impregnated onto this catalyst and reduced to give reduced-Co-Ru/TiO₂ (Catalyst B). A portion of this material was calcined in air at 300°C/4 hrs and

reduced in H₂ to give the calcined-reduced Co-Ru/TiO₂ composition of this invention (Catalyst C). A Co/SiO₂ catalyst was prepared for comparison by impregnating silica with a cobalt salt (Catalyst D). In synthesis gas runs in which the space velocity was adjusted to attain comparable conversion levels (see Table X.45), the cobalt time yields of the calcined-reduced Co/Ru/TiO₂ catalyst was higher than for the other three catalysts. This appears to be similar to Gulf patents where reduced-oxidized-reduced catalysts had a higher activity than the reduced catalyst (X.63). The methane and C₅+ selectivities of reduced-Co/Ru/TiO₂ and the oxidized-reduced Co/Ru/TiO₂ were very nearly the same, but slightly better than Co/TiO₂ or Co/SiO₂ catalysts.

Data were provided that showed that hydrogen regeneration of oxidized-reduced Co/Ru/TiO₂ catalysts that had been aged from 10-30 days, was more complete than for the untreated Co/Ru/TiO₂ catalyst (see Table X.46). CO conversions and methane and C₅+ selectivities were higher for both the fresh and regenerated oxidized-reduced Co/Ru/TiO₂ catalyst than for the untreated reduced Co/Ru/TiO₂ catalyst and the ruthenium free Co/TiO₂ catalyst.

Iron on Titania

A series of three patents were issued to Fiato and Kugler which are identical except for the claims. Fiato and Kugler (X.64) claim a composition consisting of a mixture of iron carbide and ilmenite, either with or without an alkali metal promoter, having an Fe₂O₃ concentration of 2-25 mg/cm², wherein the catalyst is formed by depositing an iron salt onto titania, calcining, treating with H₂ free of CO at 300-500°C until the composite is reduced and then contacting with CO at a temperature that is 100-200°C lower than the H₂ reduction temperature. In this preparation, the iron precursor deposited on the titania is calcined to form the iron oxide which is reduced in

H₂ to form Fe metal which then reacts with CO to form carbide. X-ray diffraction showed that the calcined material contained anatase and rutile forms of TiO₂, FeTiO₃ (ilmenite), and metallic Fe. X-ray diffraction of the sample after CO treatment showed that the TiO₂ and ilmenite were unchanged, metallic Fe disappeared, and Fe₅C₂ was formed.

In one of the other cases, Fiato and Kugler (X.65) claim a process for producing hydrocarbons from synthesis gas using this catalyst composition. In the other, Fiato and Kugler (X.66) claim a process for improving the activity of this catalyst in a FT reaction by cycling the temperature in the reaction zone, by increasing the temperature by 50-150°C above the FT reaction temperature in the absence of H₂ for from 1-6 hours and then returning to reaction temperature and reestablishing the H₂ content of the feed stream. None of the examples actually illustrated the effectiveness of this procedure.

The activity of a series of catalysts indicated that the Fe concentration in these catalysts must be ≥ 2 mg Fe₂O₃/m² of titania (see Figure X.12). The activity of an Fe supported titania catalyst of this invention that had been both reduced and subsequently carbided, with an Fe concentration of 0.002 g Fe/m² TiO₂, was higher than a corresponding material that had not been carbided, i.e. 27 versus 60% CO conversion, respectively. The hydrocarbon selectivities for the carbided catalyst was lower for methane and higher for C₅+.

A patent issued to Wachs et al. (X.67) claims catalysts comprising an iron carbide on a modified titania support comprising at least 25% of an oxide of Nb, V, and Ta in a noncrystalline form and containing at least 2 mg Fe, as Fe₂O₃, per m² support surface. A corresponding process patent, which was essentially identical, issued to

Wachs et al. (X.68) claims a process for producing hydrocarbons using this catalyst. These cases relate to an application by Wachs and Chersich (X.40), that was filed on the same day, that claims compositions of tantalum oxide on titania support that were used as catalyst supports. The background on this case was that the Fe/Group Vb oxide/TiO₂ combination was anticipated in the specification by Tauster et al. (X.27) but not actually claimed as compositions of that invention. The Wachs et al. patent (X.67) differs in that the titania surface was modified by addition of limited amounts of Nb, V, and Ta to modify the TiO₂.

The catalysts used in the example were prepared by slurring Degussa P-25 titania with an ethanol solution containing either Nb(C₂H₅O)₅ or VO(C₂H₅O)₃. The solvent was removed, the V or Nb ethoxides were oxidized, and the resulting powders calcined in pure O₂ at 575°C for 2 hours. The resulting supports contained 10% Nb₂O₅ or V₂O₅ on TiO₂. The Fe precursor was impregnated onto the support, reduced in H₂ at 500°C for 5 hrs, and carbided by exposure to synthesis gas. Results from runs with synthesis gas (see Table X.47) show that at similar CO conversions levels, i.e. 47-49% or 60-70%, the vanadia and niobia catalysts gave lower methane and higher olefin selectivities than a Fe/TiO₂ catalyst. At the same run temperature, i.e. 270°C, the methane yields were lower for the catalysts of the invention.

Nickel on Titania

Two patents related to nickel-titania catalysts were issued; in one, Ni as a promoter of titania based catalysts was claimed while in the second, titania promoted bulk Ni catalysts were claimed. The first patent issued to Vannice and Garten (X.69) claims a FT process that uses a catalyst comprising nickel on a titanium-containing oxide support with a Ni concentration up to 75% by weight. The second patent issued to Kugler and Garten (X.70) claims a FT process using a catalyst comprising bulk nickel promoted with up to 10% titania. These two patents pretty well cover the use of all possible combinations of Ni and titania catalysts in the FT reaction.

In the first patent, Vannice and Garten (X.69) claim that nickel on titania exhibits higher activity, improved selectivity to higher hydrocarbons, improved life and tolerance to sulfur, and resistance to Ni carbonyl formation. The catalysts were prepared by impregnating nickel salts onto the titania support and reducing in H₂ at temperatures >400°C. Synthesis gas conversion at 1 atm over these Ni/TiO₂ catalysts was higher than with bulk nickel or Ni on silica, alumina, and graphite. C₂+ paraffin selectivity versus CO conversion is shown in Figure X.13. In these runs, the Ni/TiO₂ catalysts had higher CO conversions per gram Ni, and lower methane and higher C₂+ hydrocarbon selectivities. Still, the methanation reaction was quite high for the Ni/TiO₂ catalyst. An experiment was described in which the volatility of the Ni was shown to be lower over the TiO₂ catalyst than a Ni/SiO₂ catalyst (see Figure X.14).

In the second patent, Kugler and Garten (X.70) claim the addition of titania to bulk nickel shifts hydrocarbon selectivity from methane to C₂-C₆ hydrocarbons, along with trace quantities of C₇ product. The influence of increasing titania concentration up to 8.4%, as shown in Table X.48, was to increase the CO conversion while the

selectivity to higher hydrocarbons increased. Since the relative rates for CO conversion and CH₄ formation both increased, the changed product distribution reflected the much higher increase in the rate of CO conversion versus the smaller increase in methanation rate. The selectivity of the 8.4% TiO₂ on Ni catalyst is very similar to the selectivity of 10% Ni on TiO₂.

A physical mixture of 1/1 Ni powder and TiO₂ behaved very similarly to Ni powder indicating that for such a physical mixture a synergistic interaction did not occur upon activation in H₂. The effect that was observed with the catalysts prepared by addition of solutions of the Ti oxide precursor to bulk Ni indicates a chemical interaction between the titania and the Ni, since a change in activity and selectivity occurs. Evidence for a chemical interaction was observed in ESCA that showed that Ti exists on the catalyst surface before reduction as Ti⁺⁴. After reduction in H₂ at 250°C, some of the Ti is in a lower oxidation state but not reduced to the metallic form. The titanium promoter changes the surface area and chemisorption properties of the bulk nickel. Small quantities of Ti additive increases the surface area while creating an oxide layer, as observed by ESCA. Concomitantly, H₂ chemisorption was reduced due to physical blockage of the sites. The highest CO conversion level was observed at the lowest H₂ chemisorption level for the Ti promoted samples.

MANGANESE OXIDE SUPPORTS

Exxon has been assigned 2 patents which claim compositions, or use thereof, comprising the five Group VIII metal oxides of iron, cobalt, nickel, iridium and ruthenium on manganese oxide supports which are reduced at a temperature sufficient to suppress hydrogen chemisorption. These cases parallel Tauster et al. (X.27) who claim catalyst compositions comprising Group VIII metals on Group IVb and Group Vb

metal oxides that are reduced at a temperature to suppress hydrogen chemisorption. Since manganese falls in Group VIIIb, it falls outside of Tauster et al. (X.27). There are other manganese patents assigned to Exxon which involve the use of manganese in spinels which are discussed elsewhere in this review.

Ruthenium

A patent issued to Kugler et al. (X.71) claims a FT process that provides improved yields of C₂-C₄ olefins that uses a catalyst comprising ruthenium on a manganese containing support which has been reduced at a temperature sufficient to suppress hydrogen chemisorption. Manganese can be used in its pure form or combined with alumina, carbon, silica, or oxides of Groups IVb and Vb. A 1% Ru/MnO catalyst was prepared by impregnating MnO with RuCl₃ and reducing with H₂ at 450°C. Synthesis gas mixtures, having H₂/CO ratios from 1.6 to 3, were passed over the catalyst at 300°C and at 1 atm pressure to give CO conversions less than 10%. Under those conditions Ru/MnO catalyst gave higher yields of C₂-C₃ olefins and lower yields of CH₄ relative to a Ru/Al₂O₃ catalyst.

Iron, Cobalt, Nickel, Iridium

A composition of matter patent issued to Tauster and Fung (X.72) claims compositions comprising iron, nickel, cobalt and iridium supported on a manganese containing oxide support, the improvement comprising contacting said composition with a reducing atmosphere at temperatures $\geq 300^\circ\text{C}$, except for iridium which requires a temperature $\geq 250^\circ\text{C}$, to produce a catalyst composition which exhibits suppressed hydrogen chemisorption. Under these conditions, the reduced materials would, therefore, be in the SMSI state as defined by Tauster et al. (X.27). Two different 2% Ir/MnO catalysts were prepared by impregnating the metal onto two different MnO

substrates. The two MnO substrates prepared by reducing battery grade MnO₂ in H₂ at 540 and 740°C had surface areas of 21.7 and 7.8 m²/g, respectively. Less than 0.01 atoms of hydrogen were adsorbed per atom of Ir for each of these catalysts that had been reduced in H₂ at 500°C versus values of 0.46-1.08 for samples reduced at 200°C. A sample (prepared at 740°C) reduced at 350°C adsorbed less H₂ (0.041 atoms per atom Ir) indicating it was in the SMSI state.

Cobalt - Manganese Spinel

A patent issued to Soled et al. (X.73) claims compositions comprising a copper promoted Co-Mn spinel having a formula Co_{3-x}Mn_xO₄ where x is 0.5-1.2. Subordinate claims specify a Cu concentration from 0.1 to 5 g-atom percent based on the total amount of Co and Mn in the catalyst and a surface area >5 m²/g. A corresponding patent, having an identical specification, which was issued to Soled et al. (X.74), claims a Fischer-Tropsch process using this composition. The spinel was prepared using the alpha-hydroxy aliphatic carboxylic acid method that has been used for all these high surface area spinels. A Co₂MnO₄ spinel, having a surface area of 30-60 m²/g that is isostructural with Fe₃O₄, was prepared from a solution of Co(NO₃)₂ and Mn(NO₃)₂ in the presence of citric acid and ethylene glycol, which was evaporated and calcined in air at 350°C for 30 min. The resulting spinel was impregnated to give a 1 wt.% Cu concentration. The activity of the Cu-promoted spinel in a slurry reactor with synthesis gas was compared with the spinel without added Cu under conditions shown in Table X.49. The catalyst was first reduced in situ with synthesis gas. The Cu-promoted Co₂MnO₄ spinel had higher activity and gave higher olefin selectivity than unpromoted Co₂MnO₄ spinel or a Co₃O₄/1% Cu catalyst.

GROUP VIII METAL SUPPORTED CATALYSTS

Several patents were issued in which inorganic metal oxides were used as supports for Group VIII metals. A patent issued McVicker and Vannice (X.75) claims catalysts prepared by depositing K or Rb Group VIII metal carbonyl cluster complexes on a high surface area support material, drying in the absence of oxygen and reducing at elevated temperatures. A companion case, issued to McVicker and Vannice (X.76), which is identical both in title and text, excluding claims, covers a process application for these catalysts. The catalysts were prepared by depositing bimetallic carbonyl compounds onto high surface area supports from solutions in organic solvents. At least some, if not all, of the materials were highly sensitive to air. A whole laundry list of potential bimetallic carbonyls were presented, of which 6 were actually used in catalyst preparations. Of the Group VIII carbonyls, only Pd and Os were not specifically included in dependent claims. Re, Ru and Ir, which were actually used in preparing catalysts, were specifically covered in dependent claims. Supports that were specifically claimed were alumina, silica, silica-alumina, titania, zirconia, hafnia, tantalum, niobia, vanadia, and magnesia.

Several catalysts were tested by passing a 3/1 H₂/CO synthesis gas mixture over the catalysts at 250 to 284°C and 1 atmosphere. Under these conditions, very low CO conversions were observed. More long chain olefins were formed over the cluster catalysts of this invention than with conventional catalysts prepared by impregnating alumina (eta) with aqueous solutions of Fe nitrate and KNO₃.

Palladium on Alumina

A patent assigned to Vannice and Garten (X.77) claims a process for producing methane by passing synthesis gas over palladium supported on an acidic metal oxide selected from alumina and HY zeolite with the palladium metal particle being

maintained at <100D. CO conversions of 3.5% were obtained when a 3/1 H₂/CO mixture at 1 atm was passed over these catalysts. Methane was essentially the only hydrocarbon product. The methane yield per Pd surface was higher for the catalysts of this invention than for Ni on a 5% Ni/Al₂O₃ catalyst, although the CO conversion over the nickel catalyst was 55% under these conditions.

Platinum on Alumina

A patent issued to Vannice and Garten (X.78) claims a process for producing dimethyl ether by passing CO and H₂ over platinum supported on alumina. Over a 1.16% Pt/Al₂O₃ catalyst at 274°C for a 1/1 H₂/CO gas mixture at 10 atm pressure, 2.5% CO was converted to hydrocarbons with a hydrocarbon selectivity of 70% methane, 8% ethane, and 23% dimethyl ether.

Nickel on Silica or Alumina

A patent issued to Yates and Murrell (X.79) claim Ni catalysts having Ni surface areas of 200-400 m²/g prepared by slurring a Ni metal precursor in a nonaqueous solvent with a high surface area refractory oxide, removing the solvent and reducing with H₂ to form Ni metal. A use for these catalysts is in hydrocarbon synthesis as in the FT reaction. Ethane hydrogenolysis and benzene hydrogenation are included in the examples. However, no examples are provided that cover conversion of synthesis gas. The specification states that several co-metals, of which potassium is one, should be avoided since they act as catalyst poisons.

MOLYBDENUM CATALYSTS

A patent issued to McCandlish and Kugler (X.80) claims a FT process using a catalyst comprised of molybdenum oxycarbonitride. The catalyst, in which the oxygen, carbon and nitrogen are distributed throughout the bulk structure, is prepared by

thermally decomposing an ethylenediammonium molybdate at 650°C in an inert atmosphere. The catalyst was pyrophoric and could be passivated with oxygen for handling in air. The active form was easily regenerated in H₂ at 450°C. CO conversions up to 20% were obtained over this catalyst at 254 to 315°C with a 1/1 H₂/CO synthesis gas mixture at 1 atm and 2400 GHSV. Methane was the dominant product under these conditions.

ALCOHOL SYNTHESIS

A patent issued to Apesteguia et al. (X.81) claims catalyst compositions consisting of a solid solution or coprecipitated mixture of a first oxide and a second oxide, wherein the first oxide is selected from yttria and rare earth oxides and a second oxide is a Group Ia oxide and Group Ib metal. These catalysts are useful for conversion of synthesis gas to alcohols, especially isobutanol and methanol. Several representative catalysts were prepared: Cu impregnated onto cerium oxide; coprecipitated Cu, MgO and ceria; K impregnated onto coprecipitated Cu, MgO and ceria; Cu supported on MgO and yttria. These catalysts provided very large yields of alcohols, primarily methanol along with lesser amounts of isobutanol (see Table X.50). Methane and CO₂ yields were also quite sizable.

PROCESS IMPROVEMENTS

Although the overwhelming number of FT related patents that have been assigned to Exxon are related to catalyst compositions or their use, several patents related to improvements in the design or operation of the FT process have been issued. Many of the more recently issued patents have concentrated on process improvements. The FT-type process improvements that are covered are:

- ! use of 2-stage process configuration to improve hydrocarbon selectivity,

- ! improved product selectivity through olefin addition to the feed,
- ! improved CO conversion and C₅+ selectivity through water addition to the feed,
- ! modified gas inlet system to improve axial distribution of particulate catalyst in a slurry reactor,
- ! use of downcomers to redistribute catalyst in a slurry reactor,
- ! use of pentane as heat transfer fluid,
- ! bundled tubular reactor with shell-side cooling,
- ! fixed-bed start-up protocol to prevent temperature runaway,
- ! method for defining operating conditions for a slurry reactor,
- ! method for activating ex situ reduced cobalt slurry catalyst,
- ! method for rejuvenating and redistributing catalyst in a slurry reactor,
- ! method for removing fines from particulate catalysts.

2-Stage Processes

Two different 2-stage process configurations are covered. In one, a patent issued to Kim and Fiato (X.82) claims a process in which synthesis gas contacts in a reaction zone in a first bed a first catalyst having a high olefin selectivity and contacting the resulting olefins in a second bed with a catalyst having a high selectivity for converting olefins to heavier paraffinic hydrocarbons. The claim specifies that the first bed catalyst is selected from a group consisting of Fe/Zn/Ce/K, Fe/Mn/K and Fe/Co/K and the second bed catalyst is selected from the group consisting of Ru/TiO₂, Ru/SiO₂, and Ru/Al₂O₃. The process operates at 150-220 psig with the temperature of the first catalyst being about 260-280°C and the second catalyst being about 190-210°C. The range of the preferred H₂/CO ratio, as stated in the specification, was 1.5 to 2.5. An example is provided that shows that over a Fe/Zn/Ce/K catalyst at a CO conversion of 59%, the selectivity to CO₂ was 26% with the remaining product being hydrocarbons (see Table X.51). Hydrocarbon formation is split between the 1st and 2nd catalyst beds in a ratio of 45/55. Based upon approximately equal yields from the two beds and equal yields from each of the two catalysts operating alone, a linear combination predicts a decrease in methane selectivity and an increase in C₁₀+ selectivity when operating in this fashion. Experimentally, the observed methane and C₁₀+ selectivities were even better than predicted (see Table X.52).

A second configuration involves an interstage product separation step. A patent issued to Fiato (X.83) claims a two stage hydrocarbon synthesis process comprising reacting synthesis gas at reaction conditions in a first stage in the presence of a supported cobalt or ruthenium catalyst at a pressure \$10 atmospheres, separating liquid from H₂ and CO, and reacting the remaining H₂ and CO at a pressure less than

10-12 atmospheres, but no greater than the first stage, in the presence of cobalt supported on alumina at reaction conditions. This process configuration takes advantage of the apparently higher activity of Co/Al₂O₃ catalysts at lower partial pressures of CO and H₂ relative to catalysts comprising Co or Re on other oxides supports, such as titania. 2-Stage processes having interstage separation of hydrocarbon product, in which the remaining H₂ and CO are recompressed, have the additional advantage of lower energy requirement.

Product Improvement through Feed Modification

Olefin Addition to Feed. Two patents were issued for processes that reduce methane formation in the FT process through injection of olefins. The first patent issued to Kim (X.84) claims a process with a catalyst comprising Group VIII (Fe, Co, Ru) metals supported on an inorganic oxide support wherein olefins are added to the feed to reduce methane formation. The second patent issued to Iglesia (X.85) claims further methane reduction by injecting the olefins at a point below the inlet of the reactor.

Kim (X.84) showed that injection of ethylene in the feed stream increased CO conversion and decreased methane selectivity. A 2/1 H₂/CO synthesis gas mixture gave a CO conversion of 8.4% and a methane selectivity of 6.4% when passed over a Ru/TiO₂ catalyst at 200°C at 70 psig at a flow rate of 55 standard cm³/3 g catalyst/min. When 8.2 mol % ethylene was injected into the feed stream, CO conversion increased slightly to 9.0% and methane selectivity dropped to 3.5%. When 20% ethylene was added, the methane selectivity dropped even further to 2.7%. In another case, when 4% 1-decene was substituted for ethylene, an approximate 20% decrease in methane selectivity occurred. Over a precipitated bulk Fe catalyst the introduction of 9.6%

ethylene into the same synthesis gas mixture at the same temperature and pressure at a flow rate of 100 standard cm³/10 g catalyst/min caused a 30% decrease in methane selectivity.

In the 2nd case, methane was further reduced through adding the ethylene downstream of the inlet of the reactor. A patent issued to Iglesia (X.58) claims that for a FT process using an Fe, Co or Ru catalyst, the methane yields are further reduced when the olefins are added to the reactor bed below a point equivalent to 10% of the distance from the top to the bottom of the reactor bed and above a point in the reactor bed equivalent to 10% of the distance from bottom to the top of the reactor bed. The addition level is stated as the amount sufficient to suppress methane formation. In the examples, for ruthenium and cobalt-ruthenium on titania catalysts, adding ethylene below the top 1/3rd of the catalyst bed decreased the amount of ethane produced relative to the amount of ethylene added to the feed. Likewise, the amount of C₃+ increased accompanied by a small decrease in methane yield, as shown in Table X.53.

Water Addition to Feed. A patent issued to Kim (X.86) claims enhanced CO conversion and C₅+ selectivity for a once-through, fixed or slurry bed FT process comprising contacting the synthesis gas containing 1-70 vol % water in a reaction zone with a catalyst consisting of cobalt, ruthenium and mixtures thereof on titania converting 90% of the CO to liquid hydrocarbons in the substantial absence of CO₂. This case involved numerous filings and abandonments over an eight year period from the time of the first filing on July 13, 1985. The long background discussion of numerous prior patents outlines the extensive number of related cases. Numerous examples were shown for a range of catalysts exhibiting increased CO conversion,

decreased methane selectivity and increased C₁₀+ liquid yield in the presence of added water.

Reactor Design

Modified Gas Inlet System. Two patents were issued related to the design of FT reactors. One patent issued to Chang and Coulaloglou (X.87) claims a method for improving axial distribution and mixing of particulate catalyst in a slurry bubble column by introducing a secondary gas into the column at a location within the lower 20% of the vertical height of the column but above the gas distributor plate. This gas stream can be part of the synthesis gas feed, recycle gas, inert gas, condensed light hydrocarbons or light synthesis hydrocarbons which vaporize under conditions present in the column. A figure is presented of experimental data taken in a 5 ft diameter by 30 foot high slurry bubble column that shows that the solids distribution in the reactor is more uniform when using this gas inlet configuration.

The basis of this design is that since solids distribution along the axis of a column is a function of gas velocity in the column, by increasing gas velocity, solids distribution will decrease in the lower part of the column and increase in the upper part. The key to the method disclosed in this patent is that introducing a disproportionate share of the gases at an inlet point source close to but above the distributor inlet will reduce the concentration of solids in that particular portion of the reactor and result in an increase in solids concentration in other portions of the reactor. The overall result is a more even distribution of solids in an axial direction.

Downcomers. A patent issued to Behrmann et al. (X.88) claims a method for redistributing catalyst in a slurry reactor by use of a downcomer. The downcomer is specified as a vertical conduit which is open at both ends, fully submerged in the slurry

with the bottom near the bottom of the reactor and the top near the top surface of the slurry. The bottom is shielded by a baffle plate to divert gases from rising from the bottom and gas free slurry enters at the top and passes down the conduit and out at the bottom. The preferred cross sectional area of the downcomer should be no more than 2% of the total cross sectional area of the entire reactor. An example is provided using the same equipment described under Pedrick et al. (X.89) in which the bubble column was run both with and without a downcomer in operation. In both cases rejuvenation tubes were operated in an equivalent manner. The results showed that axial distribution of the catalyst was more uniform when the downcomer was in operation, as shown in Figure X.15.

A patent issued to Chang (X.90) claims a slurry bubble column reactor design incorporating a peripheral downcomer. The reactor comprises a double walled vessel wherein the inner vessel serves as the main reactor zone and the peripheral circumferential top rim of the inner vessel wall, having attached to it an inverted channel having an apex and two edges, being attached to the inner wall along the outer edge of the inverted channel. The second edge of the inverted channel extending over the main reaction zone creating a gas space within its inverted contour with a gas vent extending upward from the inverted channel. A liquid by-pass pipe extends from below the top of the liquid level interface through the inverted channel between the attachment of the inverted channel to the inner reactor wall and the apex of the channel providing a means through which slurry flows into the peripheral downcomer section. This design is shown in Figure X.16 wherein the outer edge 8A of the inverted channel is attached to the top of the inner vessel wall. The innermost edge is in contact with the slurry in the main reaction zone. Gas disengaging from the slurry trapped in the

inverted channel exits into the gas disengagement space 5 through line 12 and slurry exits through line 13 onto the top of inverted channel outside the apex 10 through line 13 into the downcomer section 4. The higher density in the downcomer section promotes flow from the top of the vessel to the bottom. A more complete description of this invention can be obtained by referring to the patent specification.

Heat Transfer System. A patent issued to Stark (X.91) claims a method for removing heat from a FT reactor which comprises passing pentane through the tube-side of cooling tubes, vaporizing the pentane to a pressure greater than the pressure in the reaction zone and recovering the vaporized cooling medium. In a preferred embodiment of this invention the vaporized pentane is sent to an expander where the high pressure energy is recovered. The low pressure vapor leaving the expander is fed to a condenser where it is liquified and then pumped up to pressure and fed back to the reactor. The recovered energy can be used to drive compressors for an air separation plant or turbogenerators to generate electricity.

Tube-in-Shell Reactor. A patent issued to Koros (X.92) claims a slurry FT reactor wherein the slurry catalyst is disposed in a plurality of vertically arranged tubes having a length/diameter ratio of at least 10 with each tube surrounded by a common heat transfer medium disposed within the shell of a shell and tube reactor, the heat transfer medium not in fluid communication with the slurry liquid. The description of the operation of a reactor comprising a 5.76 in ID x 50 ft long pipe mounted in a 12 inch pipe cooling jacket was provided. Liquid heights varied between 12 and 32 feet with linear gas velocities up to 7.9 cm/sec. For a 2.1/1 H₂/CO synthesis gas mixture at a superficial velocity of 5 cm/sec, 2200 GHSV, reactor pressure of 285 psig, and steam

jacket pressure of 140 psig, CO conversions in excess of 50% were obtained. The temperature of this run was not given.

Reactor Operation

Reactor Start-up. A patent issued to Arcuri (X.35) claims a procedure for the start-up of a fixed-bed FT reactor that allows a flexible and more effective response to a potential temperature runaway. While elevating the temperature, pressure and feed flow rate to line-out levels, the composition of the H₂ and CO in the feed is maintained at a H₂/CO mole ratio not exceeding 90% of the mole ratio at lineout. After the temperature, pressure and feed flow rate reach normal operating levels, the H₂/CO ratio is gradually increased to the operating lineout mole ratio.

The patent illustrates the advantage of using this operating protocol relative to using temperature as the main control parameter. Comparative exotherms are provided for two different startup procedures used on a 1/2 inch ID, 6 foot long tubular pilot scale FT reactor that was submerged in a sand bath, as shown in Figure X.17. Following a conventional start-up procedure in which temperature is slowly increased to bring the reactor online, a very significant temperature runaway occurred. In this example, the final target operating conditions were 359°F with a 2.08/1 H₂/CO synthesis gas mixture at 1000 GHSV at 280 psig. The steps that were followed and the corresponding exotherms that resulted in each step were as follows:

1. Synthesis gas mixture and flow rate were established at lineout conditions at a pressure of 60 psig and a sand bath temperature of 337°F. The maximum exotherm in the bed during this period was 5°F.
2. Pressure was then increased to lineout pressure of 280 psig and held 3 days. A maximum exotherm of 12°F resulted.

3. Then temperature was increased slowly from 337 to 353°F and held 24 hours. During this period the maximum exotherm was 21°F.
4. Afterwards, the temperature was increased 2°F over a 40 min period to 355°F. The magnitude of the maximum exotherm remained the same at 22°F.
5. However, when the temperature was increased over a 2 hour period to 359°F, which was a 4°F change in temperature, the maximum exotherm increased to 242 F°, indicating a severe temperature runaway.

By contrast, the exotherms were much less when the procedure taught in the patent was followed, namely using a decreased H₂ content in the feed gas. In this example, the target lineout reactor conditions were 380°F with a 2.1/1 H₂/CO synthesis gas mixture flowing at 1000 GHSV at 280 psig. The steps that were followed and the corresponding exotherms that resulted in each step, as shown in Figure X.18, were as follows:

1. The H₂ feed gas (1.8/1 H₂/CO) rate was brought to 910 GHSV at 60 psig and 337°F. The maximum exotherm was 7°F.
2. The pressure was increased to the lineout pressure of 280 psig over 0.5 hours. The maximum exotherm was 9°F.
3. The temperature was increased almost to the lineout temperature of 374°F in 1 hour during which the maximum exotherm was 17°F.
4. H₂ in feed gas was increased to a 2.0/1 H₂/CO ratio in 1 minute as flow rate increased to 970 GHSV. Maximum exotherm was 23°F.
5. The H₂ in feed gas was increased to a 2.1/1 H₂/CO ratio as flow rate increased to the final 1000 GHSV. The maximum exotherm was 25°F.

During this sequence the exotherm remained under control and space time yield data was higher with a higher CO conversion. Another example was also given that illustrates how rapidly an exotherm can occur in a FT synthesis reactor.

Setting Operating Conditions. A patent issued to Herbolzheimer and Iglesia (X.93) claims a method for operating a solid-liquid-gas bubble column having a diameter >15 cm for FT synthesis over a supported cobalt catalyst in which the solids are fluidized by the gas. The invention comprises:

- (a) injecting gas at an average gas velocity >2 cm/sec;
- (b) fluidizing the particulate catalyst having an average diameter >5 μm in an expanded liquid column >3 meters in height and a particle settling velocity U_s and a dispersion coefficient D , such that

$$0.5 (U_s + U_L) \neq \frac{D}{H}, \text{ where } H > 3m$$

where

$$U_s = \frac{1}{18} d_p^2 \frac{\rho_s - \rho_l}{\mu} g f(C_p), \text{ where } d_p > 5 \mu m$$

- (c) operating at plug flow at a gas velocity U_g , expanded liquid height H , and dispersion coefficient D such that

$$U_g \geq 0.2 \frac{D}{H} \text{ where } H > 3 m, U_g > 2 \text{ cm/sec.}$$

In one example using a Co-Re/TiO₂ catalyst having a density of 2.7 g/cm³, a liquid density of 0.7 g/cm³, and a wax viscosity of 0.01 g/cm³/sec, the particle settling velocity is:

$$U_s \text{ (cm/sec)} = 1.1 \times 10^{-4} [d_p(\mu\text{m})^2]$$

For a 60 μm average particle, $U_s = 0.39$ cm/sec. For a liquid velocity of $0.5 U_s$, and a column height of 3 m, a gas velocity of 2 cm/sec provides a Peclet number of 10, which is the minimum gas velocity allowed that would maintain suspension of the solids in the column and maintain a plugflow operation in the column.

Catalyst Pretreatment

Catalyst Activation and Rejuvenation. A patent issued to Mitchell (X.94) claims a method for activating a fresh, reduced cobalt containing FT catalyst by treating the catalyst with H₂ in hydrocarbon liquids for a period sufficient to increase catalyst productivity. A patent having an identical specification issued to Mitchell (X.95) claims a process using the method of catalyst activation that is run under FT conditions. The method applies specifically to treating catalysts that had been previously reduced ex situ and exposed to the atmosphere before introduction into a slurry system. Such catalysts are suspended in a slurry and treated with H₂ at hydrocarbon synthesis temperature and pressure with temperatures no lower than 40°C below hydrocarbon synthesis temperature. Another patent issued to Mitchell (X.96) claims a method for rejuvenating partially deactivated catalysts which is essentially the same procedure described above. An example for activating a 12% Co-1% Re on a 94% TiO₂-5% Al₂O₃ catalyst by reducing the catalyst with H₂ was given. Following reduction, catalyst was

passivated with a CO/H₂ stream. This passivated catalyst was combined with wax in a slurry reactor and treated with H₂. Synthesis gas productivity over the treated catalyst increased to 100% relative to 25-60% productivity for the non-H₂ treated catalyst. The effect of several periods of catalyst rejuvenation during a 50 day run on catalyst productivity following this method is shown in Figure X.19.

A patent issued to Pedrick et al. (X.89) claims a method by which reversibly deactivated particulate hydrocarbon synthesis catalyst in a gas-slurry reactor is rejuvenated and more uniformly distributed in the reactor. A hydrogen rich gas, injected into the bottom of a vertical draft tube which is fully immersed in the slurry, forces the catalyst up the draft tube while concomitantly reactivating the catalyst, which is discharged from the top into the upper portion of the slurry phase. The examples contained results from a series of balances made during a run in a 4 ft diameter by 35 ft high reactor that show both activation and axial redistribution of the catalyst. During the run, various combinations of draft tubes fed with H₂, which were commonly referred to as rejuvenation tubes, and draft tubes fed with tail gas, were employed. The maximum flue-gas fed draft tube plus rejuvenation tube cross-sectional area for any of the run conditions was 2.6% of the cross sectional area of the reactor. A feed gas mixture comprising 56% H₂/26% CO/13% CO₂/5% CH₄, by volume, was fed to the reactor containing a 12% Co-1% Re on a 94% TiO₂-5% Al₂O₃ slurry catalyst at 210-230°C and 20 atm. When operating the reactor with two-2 inch diameter and two-4 inch diameter flue-gas fed draft tubes and one-3 inch diameter rejuvenation tube, the superficial velocities in the respective locations were:

inlet,	12-14 cm/sec;
outlet,	10.5-12.1 cm/sec;

draft tubes,	58-60 cm/sec;
rejuvenation tubes,	40-70 cm/sec.

Under these conditions the axial dispersion of the catalyst in the reactor improved significantly (Figure X.20) and productivity increased from 41 to 69 (vol CO/hr/vol slurry). The overall reactor temperature differentials from the bottom to the top of the reactor for the individual balances using both lift and rejuvenation tubes was only a couple of degrees.

The effect of rejuvenation tubes on catalyst activity is shown in runs where both flue gas fed draft tubes as well as rejuvenation tubes were used. In a run sequence described in Figure X.21, the decline in activity of catalyst was followed for a period of 3 days after which one 3 inch rejuvenation tube was brought on line. Immediately upon addition of H₂ an exotherm was observed followed by an immediate increase in catalyst activity recovering its initial activity in 1-2 days, after which it remained constant. After lineout, adding another rejuvenation tube provided no additional benefit. The exotherm in the rejuvenation tube was also used as a method to determine the degree of aging of the catalyst.

The beneficial effect of heating the rejuvenation tube to a temperature higher than the surrounding slurry was also demonstrated. Although the temperature in the rejuvenation tube is typically a few degrees higher than the surrounding slurry, through insulation of the tube and heating with steam, even higher temperatures can be attained. During one period in which the rejuvenation tube was heated sufficiently to raise the temperature an additional 10°F, CO conversion in the reactor increased from 26 to 36% over a 24 hr period whereas in a prior balance period without external

heating being applied to the rejuvenation tube, CO conversion had dropped from 32 to 26% over a 12 hr period, as shown in Table X.54.

A patent issued to Hsia (X.97) claims a FT process comprising a slurry reactor design coupled with a continuous rejuvenation reactor. Deactivated catalyst is reactivated and rejuvenated using an external rejuvenation reactor vessel to which catalyst from the synthesis reactor is continuously fed via a downcomer from the top of the slurry bed in the synthesis reactor to the bottom of a slurry bed in the external rejuvenation reactor vessel (see Figure X.22). Likewise, rejuvenated catalyst is fed to the synthesis reactor via a downcomer from the top of the slurry bed in the rejuvenation reactor to the bottom of the slurry bed in the synthesis reactor. Slurry flow from synthesis reactor vessel to the rejuvenation vessel and the flow of rejuvenated catalyst back to the synthesis reactor vessel are driven by gravity since both vessels are under the same pressure. A drawing is included but no examples are given.

Removal of Catalyst Fines. A patent issued to Hsu and Robbins (X.98) claims a method for removing $<1 \mu\text{m}$ particles adhering to catalyst particles containing a Group VIII metal supported on an inorganic refractory oxide. The method comprises dispersing the particles to which the $<1 \mu\text{m}$ particles adhere in a liquid comprising a Fischer-Tropsch derived wax, agitating the dispersion and concentrating the $<1 \mu\text{m}$ particles in the supernatant liquid and separating the $<1 \mu\text{m}$ particles by decanting this layer from the larger particle containing phase. Although examples are given in which the liquid used in the particle classification step includes solvents other than Fischer-Tropsch derived wax, the claims only apply to the latter (see Table X.55). Catalysts stirred with FT wax at 130°C gave initially a filtration rate of $5.8 \text{ gal/ft}^2/\text{min}$ which decreased to $0.05 \text{ gal/ft}^2/\text{min}$ after stirring for 44 hours. Using the method of this

invention of extended stirring and separating the decant after 3 cycles, the filtration rate improved to 14.5 gal/ft²/min.

Apparatus for Substantially Plug-Flow, Slurry Phase Synthesis

Koros (X.92) has patented a slurry apparatus that permits a substantially plug-flow slurry-phase operation in an arrangement of multiple tube reactors in a shell. Thus, the concept of the mechanical part of the tube and shell reactor resembles a Sasol Arge reactor; however, numerous additional features are incorporated to permit slurry-phase operation.

In Figure X.23, the syngas is added through 12 and is dispersed through sparger 14 into the liquid slurry medium, held at a level so as to maintain a gas-liquid interface, with the gas held in the space between 15, the slurry-gas interface and 18, a distributor tray.

A series of reactor zones, 20, are arranged within the shell, such as the ones shown by the example in Figure X.24.

The reactor tubes are held in place by lower, 22, and upper, 28, tube sheets. The space between the distributor plate, 18, and the lower tube sheet, 22, may or may not contain catalyst in addition to the slurry liquid. A detail of the distribution zone is provided in Figure X.25. The bubbly liquid from area 9 enters the tube/bubble cap 19A/19B. The bubble cap is aligned vertically with the reaction zone tube 20. The bubble cap is sized to give a pressure drop and injection velocity sufficient to decrease the size of the bubbles and to suspend the catalyst in the reaction zone (injection velocity about 20 to 100 ft/sec.). The gas to liquid transfer rates are at least equal to the conversion rate of the syngas gas.

Preferred slurry materials are stated to be Fischer-Tropsch waxes and C₁₆-C₁₈ hydrocarbons. The concentration of solids are usually about 10-50 wt.%, preferably 30-40 wt.% solids.

Catalyst/slurry addition/withdrawal may be effected through line 32. The region between tube sheets, 28 and 30, allows interconnection between the upper ends of the reaction zones for gas, liquid and catalyst. Tube sheet 30 holds filter cartridges, 31, which may be manufactured from sintered metal mesh, woven metal fibers, glass fibers, cloth or fibrous carbon, which can retain the catalyst particles while allowing the wax to pass. The filter cartridges are aligned vertically above each reaction zone. A gas-liquid disengagement zone lies above the filter cartridge tube sheet, and liquid product, separated from catalyst, can be withdrawn through tube 40 and/or 33. A demister, 41, separates gas from liquid droplets; residual gases are withdrawn through tube 42.

During operation the catalyst, 21, is preferably located in the reaction zone although some catalyst may be found in the liquid zones above or below the upper and lower tube sheets.

The catalyst most preferred is cobalt on titania (primarily in the rutile form) with less than about 70 m²/g. Preferred promoters are stated to be rhenium and hafnium.

It is stated that "...catalyst particle size is not critical..." but is preferably in the 20-150 micron size range.

The example described the operation of a single reactor (6" o.d., 5.76 i.d.) about 50 ft. tall mounted inside a 12" pipe to serve as a cooling jacket. Feed gas to the reactor was preheated.

The catalyst was prepared by impregnation cobalt onto titania extrudates which were crushed and screened to give ca. 30 micron diameter particles (presumably the catalyst contained promoters). The catalyst was reduced in hydrogen in a fluidized bed, and then the slurry wax was introduced. Following a prescribed procedure of start-up, they attained a CO conversion in excess of 50% at GHSV = 2800. Following a brief reactor upset, the unit was restarted at a higher steam jacket pressure (140 psig) and higher reactor pressure (285 psig at the reactor gas outlet). The reactor maintained CO conversion of 60-70% (2800-3600 hr⁻¹) for nearly seven days of synthesis. This material was stated to be a "...very active HCS catalyst." Methane selectivities were in the range of 2.7 to 3.2%. Assuming the steam jacket pressure represents steam/water, this corresponds to 354°F (178°C); presumably the reactor side would not be at a much higher temperature.

This summarizes the patents abstracted through October 19, 1994; Appendix will cover later period.

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Table X.1. Activity of laser generated iron carbide catalysts Reaction Conditions: 270°C, 2/1 H ₂ /CO, 200 sccm, 75 psig, in octacosane				
	Carbide from Fe ₃ O ₄	Laser derived carbide	Laser derived carbide + K	Laser derived carbide + Si
Preparation Method	Fe ₃ O ₄ reduced in H ₂ @450°C/5-7 hrs and treated with H ₂ /CO/350°C	Fe(CO) ₅ /C ₂ H ₄ laser feed	Fe(CO) ₅ /C ₂ H ₄ laser feed/ impregnated with 2% K as K ₂ CO ₃	Fe(CO) ₅ /C ₂ H ₄ / SiH ₂ (CH ₃) ₂ laser feed
V/V cat/hr	2000	4000	4000	500
% CO conversion	71.9	82.5	66.5	5.0
Selectivity, wt% CO ₂ free basis				
CH ₄	16.1	9.5	5.6	15.9
C ₂ -C ₄ Paraffins	17.3	7.8	0.8	27.0
C ₂ -C ₄ Olefins	18.9	27.0	11.5	19.0
% olefins in C ₂ -C ₄	50.7	77.6	93.5	41.0

Table X.2. Activity of high and low surface-area Fe-Co spinels for synthesis gas conversion. <i>In situ</i> catalyst reduced in slurry with H ₂ at 200°C and 1 atm for 1 hr. <i>Ex situ</i> catalyst reduced with H ₂ at 300°C+ and then H ₂ /CO at 350°C+. Run in slurry reactor at 250°C, 1200 v/v/hr, 2/1 H ₂ /CO, 70 psig, 600 rpm in octacosane; time on stream not specified.						
	Starting Spinel					
	Fe _{2.85} Co _{0.15} O ₄ /1 wt.% K high surface area		Fe ₃ O ₄ /1%K high surface area		Fe _{2.85} Co _{0.15} O ₄ /1 wt.% K low surface area	
	in situ	ex situ	in situ ^a	ex situ	in situ	ex situ
Spinel surface area, m ₂ /g	>100	>100	>100	>100	0.29	<0.3
CO Conv, mol %	60	64	8.0	65	<4.0	42
CO ₂	36	36	5.2	39	na	24
Hydrocarbons	24	28	2.8	26	na	18
HC Selectivity wt%						
CH ₄	4.5	8.2	11.4	12.8	na	9.3
C ₂ -C ₄ paraffins	2.5	3.6	8.6	8.0	na	5.5
C ₂ -C ₄ olefins	17.5	27.4	34.3	32.2	na	27.0
C ₅ +	75.5	60.8	31.4	47.0	na	58.2
Taken from Example 3, Table III and Example 5, Table IV U.S. Patent 4518707 (X.4). a. Taken from Table V of U.S. Patent 4518707 (X.4).						

Table X.3. Activity of *ex situ* reduced and carbided high and low surface-area Fe-Co spinels. High and low-surface-area spinels were reduced *ex situ* with H₂ at 300°C+ followed by carbiding with H₂/CO at 350°C+. Reactions run in slurry reactor at 250°C, 1200 v/v/hr, 1/1 H₂/CO, 70 psig, in octacosane.

	Starting Spinel x = 2.85	
	high >100 m ² /g	low < 5 m ² /g
CO conv, mol %	45	44
CO ₂ , mol %	26	29
HC yield, mol %	19	15
HC Selectivity wt%		
C ₁	4.4	5.9
C ₂ -C ₄	19.3	25
C ₂ -C ₄ olefins	90	90
C ₅ +	76.3	69.1

Data taken from Example 2, Table II in U.S. Patent 4544672 and Ex 4, Table III in U.S. Patent 4518707 (X.4).

Table X.4. Activity of alloys in a slurry reactor prepared *ex situ* from high surface-area Fe-Co spinels. Spinels reduced *ex situ* with H₂ at 350°C /12 hrs followed by 400°C/24 hrs, but not carburized. Run in slurry reactor at 270°C, 70 psig, 1200 v/v/hr, 600 rpm in octacosane.

	Fe ₃ O ₄ /1%K high surface area		Fe _{2.85} Co _{0.15} O ₄ /1 wt.% K high surface area	
	1.0	2.0	1.0	2.0
H ₂ /CO	1.0	2.0	1.0	2.0
CO Conv, mol %	44	28	55	54
CO to CO ₂ , mol %	26	15	34	34
CO to HC, mol %	18	13	21	20
HC Selectivity Wt.%				
CH ₄	4.4	2.1	5.8	6.5
C ₂ -C ₄ paraffins	1.9	0.6	3.4	2.7
C ₂ -C ₄ olefins	25.2	10	25.2	27.3
C ₅ +	68.7	87.2	65.0	63.4

Data taken from Example 7, Table VI, U.S. Patent 4518707 (X.4).

Table X.5. Activity of low-surface area spinel derived catalysts in a fixed-bed reactor. Catalysts treated with flowing 90% H₂/N₂ at 500°C at 100 psig for 5-7 hrs. Run in fixed bed reactor with 1/1 H₂/CO at 300 psig.

	Fe ₃ O ₄ /1%K		Fe _{2.85} Co _{0.15} O ₄ /1 wt.% K	
Time on stream, hrs	1	12	1	12
V/V/hr	570	1000	570	1000
Furnace Temp°C ^c	305	305	270	270
CO Conv, mol %	79	67	98	98
CO to CO ₂ , mol %	36	31	42	40
CO to HC, mol %	43	36	56	58
Wt% selectivity				
C ₁	8.5	5.8	9.1	7.4
C ₂ -C ₄ paraffins	5.2	4.7	6.2	6.2
C ₂ -C ₄ Olefins	26.6	30.6 ^b	39.4	50.3 ^b
C ₅ +	59.7	-	45.2	
C ₆ +	-	58.9	-	36.1

Data taken from Example 1 of U. S. Patent 4537867 (X.8). Catalysts prepared by sintering mixtures of metal oxides.
b. Applies to C₂-C₅ olefins.
c. Actual bed temperatures were not reported.

Table X.6. Effect of Co concentration on Fe-Co spinel catalyst performance after 12 hrs on stream. Catalysts treated with flowing 90% H₂/N₂ at 500°C at 100 psig for 5-7 hrs. Catalysts run in fixed bed reactor at furnace temperature of 295°C, 300 psig, 1000 v/v/hr, 1:1 H₂:CO.

x in Fe _x Co _{3-x} O ₄	2.97	2.85	2.625	2.20
Time on stream, hrs	12	12	12	12
CO Conv, mol %	97	98	97	98
CO ₂ , mol %	27	40	41	42
HC, mol %	70	58	56	56
Selectivity				
CH ₄	8.3	7.4	18.0	13.2
C ₂ -C ₆ olefins	46.5	53.1	41.4	53.0
C ₂ -C ₆ paraffins	6.9	7.2	13.3	10.6
C ₇ +	38.3	32.3	27.3	23.2

Data taken from Example 7, Table 7 of U. S. Patent 4537867 (X.8).

Table X.7. Effect of temperature on performance of Fe-Co spinels in fixed bed reactor
Samples for 1-12 hrs on stream at 300 psig, 1000 v/v/hr, 1/1 H₂/CO.

	Starting Spinel						
	Fe _{2.625} Co _{0.375} O ₄ /1 wt.% K					Fe _{2.85} Co _{0.15} O ₄ /1 wt.% K	
	225	240	260	270	290	235	270
Furnace Temperature, °C	225	240	260	270	290	235	270
Bed Temperature, °C	230	248	304	325	340	na	na
CO Conv, mol %	30	31	97	98	98	29.4	98.0
CO ₂ , mol %	4	7	40	33	41	8.0	42.0
HC, mol %	26	24	57	55	57	21.4	56.0
Selectivity							
CH ₄	8.1	8.2	19.1	16.7	19.1	2.6	5.2
C ₂ -C ₅ olefins	42.3	55.3	37.1	31.9	24.8	18.1	33.6
C ₂ -C ₅ paraffins	14.4	22.0	17.7	10.6	14.8	2.7	4.4
C ₆ +	35.2	34.5	26.1	40.8	41.3	76.8	55.9

Taken from Examples 8 and 12 of U.S. Patent 4537867 (X.8).
na = not available

Table X.8. Cu promoted high-surface area Fe-Co spinels as slurry catalysts.
Slurry reactor runs at 270°C, 2000 v/v/hr, 2/1 H₂/CO, 75 psig, 600 rpm in octacosane.

	Fe ₃ O ₄ /2%K		Fe _{2.85} Co _{0.15} O ₄ /2 wt.% K	Fe _{2.85} Co _{0.15} O ₄ /2 wt.% K/1 wt% Cu K	
	In-situ	Ex-situ	In-situ	In-situ	Ex-situ
CO Conv, mol %	67	49	77	86	54
Wt% Selectivity					
CH ₄	2.0	3.8	4.4	4.2	4.5
C ₂ -C ₄ Olefin %	47.5	77	91	87	85
C ₁₀ Distribution					
a-olefins		50	49	59	46
n-paraffins		8	14.9	15	18
n-alcohols		2	1.0	3	1
β-olefins		17	4.1	2	6.0
all else		23	31	21	29

Taken from Tables I and II, U.S. Patent 4607020 (X.6).

Table X.9. Effect of promoters on both high and low surface area $\text{Fe}_{2.25}\text{Mn}_{0.75}\text{O}_4$ spinels. Runs made at 270°C, 75 psi, 120 H₂/60 CO/20 N₂ cc/min flows, 70-80 g octacosane solvent, 20+ hrs on feed, 2 gm cat.

atomic % K	-	2.0	2.0	2.0	2.0	2.0
atomic % Cu	1.0	-	1.0	1.0	-	1.0
Surface area, m ² /g	>50	>50	>50	>50	<5	<5
gm catalyst	2	2	1	2	2	2
% CO conv	34	36	69	83 ^a	nil	nil
wt Selectivity						
CH ₄	8.8	3.5	1.7	2.3		
olefins in C ₂ -C ₄	78	91	94	92		
olefins in C ₁₀ +	?	?	63	65		

Taken from Example 2, Table 2 of U.S. Patent 4618597 (X.11).

a. 30+ hours on feed

Table X.10. Effect of Fe-Mn ratio in $\text{Fe}_x\text{Mn}_{3-x}\text{O}_4$ /2% K/ 1% Cu (>50 m²/g) on synthesis gas conversion. Runs made at 270°C, 75 psi, 120 H₂/60 CO/20 N₂ cc/min flows, 72 g octacosane solvent, 30+ hrs on feed, 2 gm cat.

gm catalyst	2	2	2	8	8
x	0.25	1.5	2.25	2.25	2.85
CO Conv	nil	30	83	87	79
Selectivity					
CH ₄	na	2.6	2.3	4.1	4.2
olefins in C ₂ -C ₄	na	86	93	92	94

Taken from Tables 3-4 of U.S. Patent 4618597 (X.11).

Table X.11. Activity of $\text{Fe}_{2.25}\text{Mn}_{0.75}\text{O}_4/2$ at % K/1 at % Cu as catalysts for FT fixed bed and slurry reactors with 2/1 H_2/CO synthesis gas.			
	Fixed-Bed		Slurry
Temperature, C	263	275	270
Pressure, psig	65	65	75
Cat mesh	40-100	40-100	>140
Fe-SV	2.0	9.0	11.2
CO Conv	50	43	69
Selectivity			
CH_4	8.6	9.5	1.1
$\text{C}_2\text{-C}_4$	26.4	25.0	1.8
C_5+	65	65.5	97
CO_2	35	44.0	38
Olefin % Content			
$\text{C}_2\text{-C}_4$ olefin fraction	82	84	93
$\text{C}_{10}+$ olefin fraction	65	67	63
Taken from Tables 2 and 4 of U.S. Patent 5118715 (X.13).			

Table X.12. Activity of Fe-Zn Spinel. Catalysts pretreated to 500°C in a 9/1 H_2/N_2 mixture at 100 psi and 100 v/v/hr space velocity for 5-8 h. Runs made in 1.7/1 H_2/CO at 300 psi at 550 vol/vol/h, 270°C furnace temperature, 10.5 hrs on stream.		
	1.0 Fe/0.065 Zn/0.030 Ce/0.030 K	Fe/1% K
CO conversion	98	96
wt% selectivity		
CH_4	3.0	9.4
$\text{C}_2\text{-C}_6$	36.0	50.1
C_7+	21.4	14.5
CO_2	39.6	26
Specific olefin/paraffin prodn. ratios were:		
C_2	3.1	2.5
C_3	7.5	8.0
C_4	15.0	8.3
C_5	7.5	3.7
C_6	4.6	2.0

Taken from Example 3, Table V of U.S. Patent 4639431 (X.16).

Table X.13. Activity of Fe-Zn spinels promoted with Cu and K prepared with glycolate. Runs made with 2 g catalysts in at 270°C in 2/1 H₂/CO, 75 psig at 180 cc/min in octacosane for 40-100+ hr periods.

	CO Conv	CH ₄ selectivity	% olefins in C ₄	% Olefins in C ₂ -C ₄	% a-Olefin in C ₁₀ +
Fe _{2.8} Zn _{0.2} O ₄ ·2 at% K	33	2	89		
Fe _{2.8} Zn _{0.2} O ₄ ·1 at%Cu	34	10.1	81		
Fe _{2.8} Zn _{0.2} O ₄ ·2 at%K+1 at%Cu	73	1.9	89		
Fe _{2.8} Zn _{0.2} O ₄ ·2 at% K, 1 at% Cu	80	1.7		93	63
Fe _{2.45} Zn _{0.55} O ₄ ·2 at% K, 1 at% Cu	84	1.7		92	61
Fe _{2.3} Zn _{0.7} O ₄ ·2 at% K, 1 at% Cu	32	2.3		85	nd

Taken from Example 2, 6 and 7 of U.S. Patent 5100856 (X.17). Spinels having Fe concentrations greater than Fe_{2.5}Zn_{0.5}O₄ fall within claimed compositions.

Table X.14

Conversion of Synthesis Gas with Fe_{3-x}Zn_xO₄ in 0.3 L CSTR at 270°C, C₂₈ Solvent, H₂/CO = 2, 75 psig (from U.S. Patent 5118715, (X.13))

Catalyst	Fe _{2.8} Zn _{0.2} O ₄ A	Fe _{2.55} Zn _{0.45} O ₄ B	Fe _{2.3} Zn _{0.7} O ₄ C	Fe _{2.79} Zn _{0.21} O ₄	Fe _{2.79} Zn _{0.21} O ₄	Fe _{2.79} Zn _{0.21} O ₄
% Fe	66.87	60.28	53.70	71.50	71.50	71.50
% g-atom K	---	---	---	2	2	0
% g-atom Cu	---	---	0	1	0	1
CO Conv., %	80	84	32	73	33	34
CH ₄ /% Carbon	1.7	1.7	2.3	1.9	2.0	10.1
Olefin, %						
C ₂ -C ₄	93	92	85			
% a- in C ₁₀	63	61	*			
% a- in C ₄	---	---	---	89	89	81
NL/gFe-hr**	8.97 (7.18)	9.95 (7.96)	11.17 (8.94)	8.89 (7.11)	8.89 (7.11)	8.89 (7.11)
NL/g cat-hr	6.00	6.00	6.00	6.36	6.36	6.36

* Insufficient yield of liquids.

** NL total flow; parentheses, flow based on CO + H₂.

Table X.15. Comparison of Ce,K and K/Ce promoters for 1.0 Fe/0.30 Ti/0.065 Zn/0.03 Ce and/or 0.03 K in fixed-bed reactor. Pretreated at 500°C with 9/1 H₂/N₂ at 800 v/v/hr for 5-6 hrs. Runs made at 270°C, 1/1 H₂/CO at 2.6 MPa at 870 v/v/hr space velocity for time on stream of 30-50 hrs

	K	Ce	K/Ce
CO Conv	2	17	24
wt HC selectivity			
CH ₄	42	24.5	14.8
C ₂ -C ₃ paraffins	6	14.6	12.2
C ₂ -C ₃ olefins	42	14.1	32.5
C ₄ +	10	46.8	40.5

Taken from Example 5, Table VII in U.S. Patent 4657885 (X.18).

Table X.16. Manganese Catalysts with Ce,K and K/Ce in fixed-bed reactor. Pretreated at 500°C with 9/1 H₂/N₂ at 800 v/v/hr for 5-6 hrs. Runs made with 1/1 H₂/CO, 870 v/v/hr, 305°C, 2.0 MPa

	K	Ce	K/Ce
CO Conv	18	62.5	54.9
HC selectivity, wt. %			
CH ₄	10.2	17.5	7.5
C ₂ -C ₃ paraffin	4.1	10.0	2.6
C ₂ -C ₃ olefin	29.2	20.6	24.4
C ₄ +	56.5	51.9	65.5

Taken from Example 6, Table VIII in U.S. Patent 4657885 (X.18).

Table 17. Activity of a 10/1 Fe/Ti catalyst in a fixed bed reactor for synthesis gas conversion. Pretreated with 49 H₂/50 CO/1 N₂ at 270°C at 1 atm and 500 v/v/hr for 18 hrs. Runs made at 270 to 350°C, 1/1 H₂/CO at 120 psia and 150-1200 v/v/hr.

Temp, °C	270	300	325	350
CO Conv, %	90-20	65-40	96-80	97-90
Selectivity				
CH ₄	6-4	6-3	6-10	9-15
C ₅ -C ₁₁	50-54	51-57	50-51	42-51
C ₄ - (Gas)	35-30	34-26	35-39	39-50
Olefins in C ₆ +	21-26	23-26	21-16	14-8
Aromatics	2-3	2-3	4-8	7-14

Taken from Example 5, Tables 1 to 6 in U.S. Patent 4513104 (X.24).

Table X.18. Performance of Fe/Ti Catalysts in a fixed-bed reactor.
 Pretreated with 49 H₂/50 CO/1 N₂ at 270°C at 1 atm and 500 v/v/hr for 18 hrs. Runs made with 1/1 H₂/CO at 300 GHSV and 0.9 MPa (130 psi).

	Fe/0.1 Ti			Fe/0.2 Ti	Fe/.04 K		NH ₃ synthesis catalyst
	350	350	270	350	350	270	
Temp	350	350	270	350	350	270	350
GHSV	300	300	300	300	300	300	300
CO Conv	96.7	63.6	46.8	45.0	55.5	68.9	97.1
Selectivity to HC %	60.9	62.5	69.9	59.6	66.0	wax	69.5
C ₁	10.1	13.0	3.4	16.6	11.1	3.0	3.3
C ₁ -C ₅	38.4	44.7	30.4	46.6	31.8	-	42.2
C ₆ -C ₁₁	45.3	45.4	44.8	39.0	32.5	-	42.3
C ₁₂ -C ₂₃	16.0	9.7	23.8	13.6	24.9	-	14.8
C ₂₃ +	0.3	0.2	1.0	0.8	10.8	-	0.7
Aromatics	12.7	14.02	2.92	10.3	6.57	-	8.65
a-olefins	14.9	9.66	22.31	10.0	16.6 9	-	11.43

Taken from Example 9, Tables 10 and 11 in U.S. Patent 4513104 (X.24).

Table X.19. Activity of *in situ* prepared catalyst in a slurry reactor.
 Runs made at 270°C, 1:1 H₂/CO at 70 psig at 1200 V/V/hr in C16 paraffin solvent, 600 rpm.

Support	wt% support ^a		CO Conv	CO ₂	CH ₄	C ₂ -C ₄ olefins	C ₂ -C ₄ paraffins	C ₅ +
	Fe	Co						
None (Complexes only)	-	-	25	35.4	15.4	17.8	5.3	26.1
Fe ₂ O ₃ /1% K	9.5	3.2	54	50	3.0	7.2	1.1	38.5
Al ₂ O ₃	4.8	1.6	21	25	20.0	18.3	9.0	27.7
Al ₂ O ₃ ^b	"	"	27	9.2	19.8	12.9	6.8	60.5
MgO	4.8	1.6	30	35	18.6	16.1	6.8	23.5
MgO/1% Cu	9.5	3.2	26	50	9.6	14.7	3.8	21.9

Taken from Example 1, Tables I and II, and Example 4, Table V, of U.S. Patent 4532229 (X.25).

a. Same weight of Fe and Co in reactor in all runs, except for Fe₂O₃/1% K run.

b. Product yield after 96 hours on stream.

Table X.20. Effect of air calcination on the crystalline form of titania

	Rutile content, wt%	Surface Area, m ² /g
Degussa P-25	28 ^a -35 ^b	60 m ² /g
500°C in air/16 hrs	55	33-36
500°C in air/16 hrs and H ₂ at 450°C	67	22-26
560°C in air/ 4 hrs ^d	70	30
600°C in air/16 hrs	-100 (>30/1)	10-16
650°C in air/16 hrs ^c	97	14

a. From U.S. Patent 4711871 (X.32).

b. From U.S. Patent 4595703 (X.49).

c. From U.S. Patent 4663305 (X.57).

d. From U.S. Patent 4738948 (X.61).

Table X.21. Effect of calcination on rutile content of titanias

Source	Description	Binder/%	Hg PV ^a , cc/g	Hg PD ^b , D	BET SA, m ² /g	% Rutile in titania	Calcination, °C/hr
Company A	-	none	0.253	140	45	27	-
Company A	-	none	0.162	270	15	92	700/1
Company A	-	none	0.134	250	14	95	700/1
Company A	-	none	0.120	481	5	100	840/1
Company A	Extrudate	none	0.154	389	8	98	650/16
Ti(OC ₃ H ₇) ₄ hydrolysis	-	none	0.160	n.a.	10	94	650/50
Ti(OC ₃ H ₇) ₄ hydrolysis	Extrudate	none	0.299	n.a.	41	n.a.	500/16
Ti(OC ₃ H ₇) ₄ hydrolysis	Extrudate	none	0.180	n.a.	15	n.a.	600/16
Company A	Extrudate	M/3.5	0.387	454	27	82	750/3
Company A	Extrudate	M/3.5	0.326	590	22	96	800/1
Company A	Extrudate	M/3.5	0.354	678	15	98	800/3
Company A	Extrudate	M/3.5	0.301	697	15	100	800/16
Company A	Extrudate	M/3.5	0.276	590	12	100	850/3
Company A	Extrudate	M/3.5	0.254	1151	13	100	850/10
Company A	Extrudate	M/3.5	0.237	1706	10	100	850/72

Taken from Example 1, Table 1 of U.S. Patent 4992406 (X.30).

M binder = 30 TiO₂/70 Al₂O₃

a. PV = pore volume.

b. PD = pore diameter.

Table X.22. Effect of rhenium on stability of Re/TiO ₂ for synthesis gas conversion. Conditions of run: 230°C, 280 psig, 2/1 H ₂ /CO, 1000 GHSV		
	1% Ru and 0.5% Re/TiO ₂	1% Ru/TiO ₂
Half-life, days	231	26
CO Conv	97	97
HC Yield	90	94
Selectivities		
CH ₄	3.7	3.5
CO ₂	7.0	1.5
Taken from Example 1, Table I of U. S. Patent 4558030 (X.29).		

Table X.23. Effect of Re/Ru ratios on Re promoted Ru/TiO ₂ catalyst. Conditions: 280 psig, 2/1 H ₂ /CO, 1000 GHSV				
Wt.% Ru	Wt% Re	CO Conv	C ₁ select	CO ₂ select
0.1	1.0	11	4	20
0.5	0.5	33	7.5	5
0.75	0.5	43	9	6
1.0	0.5	82	5.6	6
Taken from Example 2, Table II of U. S. Patent 4558030 (X.29).				

Table X.24. Effect of rutile content on activity of 1% Ru-0.5% Re on TiO ₂ . Conditions: 230°C, 280 psig, 2/1 H ₂ /CO, 1000 GHSV at 90% CO conversion			
Rutile/Anatase ratio wt	1.2/1	2/1	>30/1
Rutile, wt% in TiO ₂	55	67	-100
C ₁ selectivity	7	4.5	2
Half-life days	4	231	87
Deactivation, ? <i>ln</i> k/day	! 0.18	! 0.003	! 0.008
Pore Vol ml/g	0.4	0.2	0.15
SA m ² /g	35	24	12
Taken from Example 3, Table III of U. S. Patent 4558030 (X.29).			

Table X.25. Selectivity of Ru Catalysts for synthesis gas conversion. Conditions: Catalysts reduced in H ₂ at 450°C for 1 hr before introducing 1/1 H ₂ /Co at 980 kPa (9.5 psig),						
	Temp	%CO Conv	Prod	Total wt%	Olefin, wt%	Paraffin wt%
2% Ru/TiO ₂	267	7	C1	14	-	-
			C ₂ -C ₄	47	32	15
			C ₅ -C ₇	39	23	16
			C8+	-	-	-
5% Ru/?Al ₂ O ₃	274	10	C1	24	-	-
			C ₂ -C ₄	43	19	14
			C ₅ -C ₇	32	6	6
			C8+	12		

Taken from Example 1, Table II of U. S. Patent 4042614 (X.31).

Table X.26. Methanol conversion over Ru/TiO ₂ . Conditions: 230°C, 500 v/v/hr, fixed bed reactor			
Methanol, psi	236	236	236 ^a
H ₂ , psi	0	59	59
CO, psi	0	0	31
Methanol conv at 35 hrs, %	13	76	<3
Reactor effluent composition			
CO	38	1	84
CO ₂	4	12	n.a.
CH ₄	1	24	n.a.
C ₂ +	55	63	n.a.

Taken Example 4, Table IV and Example 6, Table VI of U.S. Patent 4513161 (X.36).
a. GHSV=560.

Table X.27. Activity of Ru on V, Nb and Ta oxides versus prior art.
Conditions: 3/1 H₂/CO, 1 atm, no other data provided.

	Temp C	CO Conv %	Hydrocarbon selectivities		
			CH ₄	C ₂ -C ₅ Olefins	C ₂ +
1% Ru/Nb ₂ O ₅	234	7.8	48	22	52
1% Ru/Ta ₂ O ₅	228	17.7	46	17	54
1% Ru/V ₂ O ₅	243	4.1	45	28	55
1% Ru/SiO ₂	232	4.1	87	2	13
1% Ru/Al ₂ O ₃	244	14.1	71	10	29

Data taken from U. S. Patent 4171320 (X.37).

Table X.28. Reaction of a 0.76% Ru on TiO₂ in a fixed bed reactor.
Conditions: reduced at 400-450°C for 2-4 hrs in H₂. Run in 1.39/1 H₂/CO

Run No	3	5	7	14
Pressure, atm	3.0	3.0	5.0	4.3
°C	206	224	218	213
GHSV	198	301	494	1240
H ₂ Conv	84	84	89	26
CO Conv	84	84	89	30
Selectivity on CO ₂ free basis				
CH ₄	4.8	6.1	5.4	6.9
C ₂ /C ₄	9.15	11.6	7.9	17.8
C ₅ -C ₂₀	76.5	74.4	72.7	64.1
C ₂₀ -C ₄₀	8.3	6.2	11.3	8.3
C ₄₁ +	0.15	0.13	1.5	0.2
Oxygenates	1.13	1.4	1.2	2.7
C ₂ = in C ₂				40
C ₃ = in C ₃				84
C ₄ = in C ₄				82
Total olefin in C ₇ -C ₁₂				39
Total olefin in C ₄ -C ₂₀				31

Taken from U. S. Patent 4477595 (X.38).

Table X.29. Effect of support on activity of Ru catalysts
Fixed bed reactor with supported Ru, reduced at 400-450°C for 2-4 hrs in H₂

	0.76 Ru/ TiO ₂	0.56 Ru/ Nb ₂ O ₃	0.67 Ru/ Ta ₂ O ₃	1.57Ru/ SiO ₂	0.56Ru/ Nb ₂ O ₃	1.1 Ru/ TiO ₂	1.57Ru/ SiO ₂	1.1Ru/ TiO ₂	1.1Ru / Al ₂ O ₃
H ₂ /CO	1.39	1.39	1.39	1.39	2	2	2	2	2
Pressure, atm	5.0	5.0	5.2	21	7	4.6	4.6	2.1	2.1
°C	203	196	200	251	229	209	209	214	214
GHSV	298	300	303	200	1225	300	300	303	303
H ₂ & CO Conv	86	88.3	79	88.7	81	82	5	87	32
Selectivity									
CH ₄	2.9	2.0	5.5	7.5		4.3	10.6	6.7	16.6
C ₂ /C ₄	6.2	2.5	18.5	17.4		12.5	34.0	12.8	19.5
C ₅ -C ₂₀	65.5	62.1	66.5	71.3		81.6	51.1	68.8	59.2
C ₂₁ +	25.4	33.4	9.5	3.8		-	-	9.2	2.1

Taken from U. S. Patent 4477595 (X.38).

Table X.30. Activity of Ru on oxide modified titania surfaces.
Conditions: 230-250°C, 300 v/v/hr, H₂/CO=2, 60 psig, fixed bed reactor

	1% Ru/TiO ₂	1% Ru/TiO ₂ +10%Nb	1% Ru/TiO ₂ +10%Ta	1% Ru/TiO ₂ +1%Ta	1% Ru/TiO ₂ +2%V	Physical Mixture 1% Ru/TiO ₂ +10%Ta
Temp	238	230	235	232	252	240
H ₂ +CO conv	37	43	19.5	31.5	71.3	47.4
CO ₂	3.8	1.9	3.7	3.2	3.5	5
CH ₄	14.5	10.9	10.9	15.3	12.5	8.4
C ₂	8.3	6.6	14.8	4.2	3.3	4.2
C ₃ +C ₄	23.0	17.3	13.8	24.0	10.0	16.9
C ₅ +	50.4	63.3	56.8	53.3	70.7	65.5
HC products						
Alcohols	5.1	0	0	1.4	3.8	3.0
olefins	39.1	67.7	6.3	44.2	15.6	46.4
paraffins	34.	32.3	93.7	54.4	80.6	50.3

Taken from U. S. Patent 4711871 (X.32).

Table X.31. Activity of Ru/TiO ₂ slurry catalyst. Conditions: 1 g catalyst, 50 g octacosane, 6/3/1 H ₂ /CO/N ₂ , 1200 v/v/hr, 6 atm, 1 std L/g catalyst/hr						
Catalyst 1% Ru	°C	% CO Conv	Selectivity			
			CO ₂	CH ₄	C ₂ -C ₄	C ₅ +
Ru/TiO ₂ Particulate, reduced 450°C	250	49	3.2	14.4	8.9	73.5
Ru/TiO ₂ Particulate, not prereduced	260	10	2.0	20.0	30.0	48.0
Carbonyl based						
Ru	260	15	tr	4.7	19.5	75.8
Ru/CeO ₂	240	<5	nil	na	na	na
Ru/Al ₂ O ₃	240	25	3.0	19.3	9.4	68.3
Ru/TiO ₂	240	55	6.7	12.3	17.5	63.5

Taken from U.S. Patent 4752600 (X.41).

Table X.32. Effect of steam treatment of Ru/TiO ₂		
Treatment of Ru/TiO ₂	O/Ru ratio from O ₂ chemisorption	Ru crystallite size D
None	1.46	12
Air at 1 atm, 500°C/3 hrs	not reported	30
9/1 H ₂ O/H ₂ at 280 psig, 300°C/4 hrs	1.08	15
9/1 H ₂ O/H ₂ at 280 psig, 230°C/16 hrs	0.88	18
3% H ₂ O in N ₂ at 1 atm, 500°C/3 hrs	0.98	16

Taken from Table 1, U.S. Patent 4647592 (X.43).

Table X.33. Effect of air treat on activity of Ru/TiO ₂ Run in 2/1 H ₂ /CO, 210°C, 280 psig, and 1000 v/v/hr					
Hrs	CO Conv	Selectivity to HC, %	wt.% selectivity		
			CH ₄	CO ₂	C ₂ +
No air treat					
0.7	84.8	80.3	7.3	5.3	87.4
1.4	94.8	90.8	4.9	4.2	90.9
2.4	94.7	88.2	3.6	6.9	89.5
3.0	98.3	89.6	3.6	8.8	87.6
3.7	97.7	89.5	3.8	8.4	87.8
Air treated sample					
0.7	78.6	72.1	3.0	8.3	88.7
1.3	91.9	85.0	2.3	7.5	90.2
2.2	94.5	88.5	2.3	6.4	91.3
3.0	93.7	88.6	2.5	5.4	92.1
3.7	93.1	88.9	2.5	4.5	93.0
Taken from Table II, U.S. Patent 4647592 (X.43).					

Table X.34. Activity of Rh Catalysts for synthesis gas conversion. Conditions: 1.6/1 H ₂ /CO, 100 kPa (1 atm), Catalyst reduced 450°C 1 hr,				
	Temp	%CO Conv	CH ₄ mol %	C ₂ -C ₅ yield, mol %
2% Rh/TiO ₂	248	1.3	74	26
2% Rh/Al ₂ O ₃	265	3.5	15	85
Taken from U. S. Patent 4116994 (X.45).				

Particle size, mm	2.2	2.2	0.1-0.2	2.2
Co Conc, wt%	13.0	13	13	20.9
Co Distribution	even	rim	rim	rim
Rim thickness, μm	-	80±30	80±30	120±30
Surface area, m ² /g	80	80	80	350
Hrs on stream	193	318	175	315
GHSV	420	650	940	1750
CO Conv, %	64.5	66.0	48.0	64.0
CO Conv, vol/vol/hr	90	150	210	342
Selectivity				
CH ₄	12.0	8.3	4.7	12.7
C ₂ -C ₄	5.1	4.4	4.7	5.3
C ₅ +	82.0	87.0	90.5	81.3
CO ₂	0.9	0.4	0.1	0.7
Taken from Tables 1, 2, and 3 or U.S. Patent 5036032 (X.48).				

Cat		CO Conv	Selectivities			Schulz-Flory
			CO ₂	CH ₄	C ₂ +	
A	12 Co/TiO ₂ ^b (this invention)	88	1.1	8.6	90.3	0.91
B	100 Co/5 ThO ₂ /8 MgO/200 Kieselguhr ^a (known)	43	4.3	10.3	86.4	-
C	12 Co/SiO ₂ (known)	72	1.6	8.7	89.7	0.85
D	25 Co/1.8 Ti/100 SiO ₂ (known)	21	1.9	13.8	84.3	0.74
Taken from Example 7 in U. S. Patent 4542122 (X.46).						
a. Conventional FT catalyst						
b. Rutile/anatase ratio of 3.2. Reduced in H ₂ at 450°C for 1 hr						

Table X.37. Activities of Co and Co-Re on TiO₂ in a fixed-bed reactor. (Data shown in Figure 1 in Patent 4542122) Catalyst impregnated with nitrate/perrhenic acid and calcined in air at 500°C/3 hrs. Catalysts reduced in H₂ at 450°C for 1 hr. Runs made at 200°C, 2.15/1 H₂/CO, 280 psig, GHSV=1000.

Metals, wt% on TiO ₂	Rutile in TiO ₂ , wt%	Air treat°C for 3 hrs	O ₂ chemisorp. μ mol O ₂ / g cat	%CO Conversion	Surface area m ² /g	CH ₄	CO ₂	C ₂ +
12 Co	53	250	213	67	36	9.7	0.2	90.1
12 Co	100	250	265	79	10	11.5	0.7	87.8
12 Co	56	500	178	54	33	9.9	-	90.1
12 Co	100	500	202	67	10	11.7	0.3	88.0
12 Co-0.1 Re	100	500	145	67				
12 Co-0.5 Re	56	500	343	85				
12 Co-0.5 Re	100	500	285	82				
12 Co-3 Re	56	500	399	81				

Table I in U.S Patent 4568663 (X.51).

Table X.38. Effect of Anatase-Rutile Ratio on Co/TiO₂ catalyst. Catalysts impregnated with cobalt carbonyl from pentane solution. Run conditions: 200°C, 280 psig, 1000 GHSV, H₂/CO=2.15/1

Co, wt%	10.1	9.2
Rutile in Titania, wt%	28	-100
Pretreatment Conditions:		
1st Stage	250°C/ air/3 hrs	250°C/ air/3 hrs
2nd Stage	450°C/ H ₂ /1 hr	450°C/ H ₂ /1 hr
CO Conv, mol %	5	97
CH ₄ Yield, mol %	15.1	5.4
O ₂ Chemisorption, umol/g cat	53	205

Example 9 in U.S. Patent 4542122 (X.46) and Example 3 in U.S. Patent 4595703 (X.49).

Table X.39. Effect of rutile content on Co/TiO ₂ . Run at 230°C, 40 MeOH:2 H ₂ :1 CO ₂ :7 Ar, 400 psig, GHSV=500.		
Rutile content, %	55	100
MeOH Conv	66	100
Carbon Product Distribution		
CO	2.6	0.8
CO ₂	15.6	27.8
CH ₄	9.0	17.1
C ₂ +	72.8	54.3
Taken from Example 6 in U.S. Patent 4542122 (X.46).		

Table X.40. Activity and selectivity of Co on titania based catalysts for methanol conversion (rutile not specified). Run conditions: 230°C, 400 psig, GHSV=500, 40 MeOH:2 H ₂ :1 CO ₂ :7 Ar						
	12% Co/TiO ₂	12% Co/2% ThO ₂ /TiO ₂		100 Co/5 ThO ₂ /8 MgO/200 Kieselguhr ^a	12% Co/SiO ₂	12% Co/Al ₂ O ₃
MeOH Conv, 35 hr	52	70 ^b		97	38	64
Carbon Product Distribution						
CO	5.5	3.1	2.9	1.0	4.3	2.8
CO ₂	12.9	17.0	12.6	38.4	22.3	21.8
CH ₃ OCH ₃	0.2	0.3	0.5	-	0.1	2.4
CH ₄	11.2	8.6	7.4	19.5	7.0	9.9
C ₂ +	70.2	71.0	76.6	41.1	66.3	63.1
Schulz-Flory Alpha	0.86	0.88	n.p.	n.p.	n.p.	n.p.
Example 5 of U.S. Patent 4542122 (X.46). a. Conventional FT catalyst b. Two sets of data provided for the same conditions having the same MeOH conversion that was not otherwise specified. n.p. = not provided						

Table X.41. Effect of Re on MeOH conversion over Co/TiO ₂ with or without ThO ₂ . Run conditions: 230°C, 400 psig, GHSV=500, MeOH/Argon=4. Catalysts calcined 500°C			
	12 Co/ 2 ThO ₂ /TiO ₂	12 Co/2 ThO ₂ / 0.5 Re/TiO ₂	12 Co/ 0.5 Re/TiO ₂
Rutile Conc, %	56	56	56
MeOH Conv	49	100	87
Product Distribution			
CO	6	2	2
CO ₂	14	28	22
CH ₄	6	14	9
C ₂ +	74	56	67
Table III in U.S. Patent 4568663 (X.51).			

Table X.42. Effect of H ₂ partial pressure on MeOH conversion. Co/ThO ₂ /TiO ₂ (rutile and catalyst composition not specified) at 230°C, 500 GHSV, 400 psig			
Partial Pressures, psig			
MeOH	332	332	332
Ar	83	66	0
H ₂	0	17	83
MeOH Conv, wt%	38	52	83
Carbon Product Distribution			
CO	8.5	3.9	0.9
CO ₂	11.3	8.9	12.2
CH ₃ OCH ₃	1.0	0.4	0.1
CH ₄	4.6	5.7	15.9
C ₂ +	74.6	81.1	70.9
CH ₄ in hydrocarbon, wt%	5.8	6.6	18.3
Table IV in U. S. Patent 4542122 (X.46).			

Table X.43. Effect of promoter on MeOH Conversion on Co/TiO₂.
Conditions: 230°C, 400 psig, LHSV=0.67, 20 MeOH/1 H₂/4 Argon

Catalyst composition					
Wt% Co	5.0	4.34	4.65	4.55	4.73
Promoter @ 1 wt%	none	Zr ^a	Hf	Ce	U
MeOH Conv	31	37	34	49	46
Rate MeOH Conv, g/hr/g Co	1.6	2.3	1.9	2.8	2.6
Carbon Prod Distribution					
CO	16	13	16	10	9
CO ₂	8	9	7	9	13
CH ₄	8	8	8	7	9
C ₂ +	68	70	69	74	69

Table IV, Example 2 in U.S. Patent 4663305 (X.57).
a. The Zr salt was ZrO(O₂CCH₃)₂.

Table X.44. Effect of silica promotion on CoRe/TiO₂ in a fixed-bed reactor.
Conditions: 200°C, 2.1 MPa, H₂/CO=2, run at space velocity to give ~60% CO conversion.

	(A) CoRe/TiO ₂		(D) CoRe/TiO ₂		(B) CoRe/TiO ₂ +SiO ₂		(C) CoRe/TiO ₂ +SiO ₂	
% SiO ₂	0		0		4		5.2	
Steam treat H ₂ O (40 Torr)/He at 400°C/13 hrs	No		Yes		Yes		Yes	
reduction in H ₂	250°C for 13 hrs		250-400°C for 2-14 hrs		250-400°C for 2-14 hrs		250-400°C for 2-14 hrs	
Hrs on stream	50	139	49	190	47	120	49	119
CO Conv	61.5	64	67	58	69	61	60	55
mol CO conv/g atom Co-hr	5.7	5.5	5.1	4.4	7.5	6.8	8.3	7.5
CH ₄	5.3	5.1	4.6	5.0	5.2	5.6	5.4	5.8
C ₂ (O/P)	0.6 (0.12)	0.6 (0.14)	0.6 (0.17)	0.6 (0.19)	0.7 (0.11)	0.7 (0.13)	0.6 (0.13)	0.6 (0.14)
C ₃ (O/P)	2.1 (1.9)	1.9 (2.1)	2.2 (2.6)	2.1 (2.8)	2.4 (2.0)	2.5 (2.1)	2.3 (2.0)	2.3 (2.1)
C ₄ (O/P)	2.3 (0.70)	2.16 (0.63)	2.0 (1.6)	1.9 (1.6)	2.4 (1.1)	2.6 (1.3)	2.6 (1.2)	2.5 (1.3)
C ₅ +	89.5	89.9	90.3	90.1	89.3	88.5	89.1	89.1
CO ₂	0.2	0.2	0.3	0.3	0.07	0.06	0.05	0.04

Combined Table 1 and Table 2 of U.S. Patent 4794099 (X.58).
(O/P) = olefin/paraffin ratio

Table X.45. Effect of Precalcination on FT activity of Co-Ru/TiO₂ catalyst in fixed-bed reactor. Runs made at 200°C, 60H₂/30CO/7N₂, 75 psia, space velocity adjusted; catalysts 70% rutile titania,

	D	A	B	C
	20% Co/ SiO ₂	11.6% Co/ TiO ₂	Reduced 11.6% Co/ 0.14% Ru/TiO ₂	Calcined-reduced 11.6% Co/ 0.14% Ru/TiO ₂
1st Calcination	none	400°C/16 hrs	400°C/16 hrs ^a	400°C/16 hrs ^b
Reduction/oxidation /reduction step ^c	No	No	No	Yes
CO Conv	65	50	64	68
CH ₄ select	7.4	9.3	6.8	6.5
C ₅ + select	82	80.2	87.3	87.8
Co time yield ^d	1	0.6	2.0	2.9

Taken from Table III in U. S. Patent 4738948 (X.61).

a. Ru impregnated to catalyst A after 1st calcination.

b. Started with catalyst B.

c. Calcined in air at 300°C/4 hrs and then reduced in H₂

d. moles CO converted per hr g-atom Co in catalyst.

Table X.46. H₂ Regeneration of Air-calcined-reduced Co-Ru/TiO₂ Catalysts Aged 10-30 days

	CO Conv, %	Co time yield, hr ⁻¹	CH ₄	C ₅ +
Cat A. Co/TiO ₂	At 560 kPa, 200°C, H ₂ /CO=1			
Initial	20	0.6	8.9	80.1
Aged	20	0.5	9.5	81
H ₂ Treated	20	0.5	9.5	80.5
Cat. B CoRu/TiO ₂	At 2060 kPa, 200°C, H ₂ /CO=1			
Initial	50-60	2.6	7.0	86
Aged	50-60	2.0	8.2	84
H ₂ Treated	50-60	2.6	6.5	87
Cat. C. CoRu/TiO ₂ Calc	At 2060 kPa, 200°C, H ₂ /CO=1			
Initial	50-60	4.5	5.5	91.0
Aged	50-60	3.9	6.4	88.8
H ₂ Treated	50-60	4.8	4.9	91.5

Taken from Example 5, Table IV in U. S. Patent 4738948 (X.61).

Table X.47. Synthesis gas conversion activity of Fe-coated, vanadia and niobia modified titanias in a fixed-bed reactor. Runs made with 1:1 H ₂ /CO, 500 v/v/hr, 300 psig							
	4% Fe/TiO ₂			4% Fe/TiO ₂ +V			4%Fe/TiO ₂ +Nb
Temp	305	315	270	290	305	270	270
CO Conv	47	60	27.0	49	70	34.3	20.1
Selectivity (CO ₂ free)							
CH ₄	21.0	24.4	21.0	16.1	17.8	13.0	14.6
C ₂ -C ₄ olefins	14.6	13.3		42.7	23.4		
C ₂ -C ₄ paraffins	35.9	36.3	55.0	21.2	44.2	41.5	32.9
C ₅ +	27.5	26.0	24.0	20.0	14.6	45.5	52.5
Taken from Tables 1 and 2 in U. S. Patent 4559365 (X.68).							