



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US92/03601 <b>(22) International Filing Date:</b> 1 May 1992 (01.05.92) <b>(30) Priority data:</b> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%;">694,200</td> <td style="width: 40%;">1 May 1991 (01.05.91)</td> <td style="width: 30%;">US</td> </tr> <tr> <td>724,994</td> <td>1 July 1991 (01.07.91)</td> <td>US</td> </tr> <tr> <td>751,198</td> <td>29 August 1991 (29.08.91)</td> <td>US</td> </tr> <tr> <td>791,737</td> <td>8 November 1991 (08.11.91)</td> <td>US</td> </tr> </table> <b>(71) Applicant (for all designated States except US):</b> CATALYTICA, INC. [US/US]; 430 Ferguson Drive, Building 3, Mountain View, CA 94043 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> LOFFLER, Daniel, G. [AR/US]; 3809 Ross Road, Palo Alto, CA 94303 (US). SCHUBERT, Paul, F. [US/US]; 959 Jonathan Court, Campbell, CA 95008 (US). GUTH, Françoise [FR/US]; 160 Cowper Street, Palo Alto, CA 94301 (US). DALLA BETTA, Ralph, A. [US/US]; 865 Doverton Square, Mountain View, CA 94040 (US).		694,200	1 May 1991 (01.05.91)	US	724,994	1 July 1991 (01.07.91)	US	751,198	29 August 1991 (29.08.91)	US	791,737	8 November 1991 (08.11.91)	US	<b>(74) Agents:</b> WHEELLOCK, E., Thomas et al.; Morrison & Forster, 545 Middlefield Road, Suite 200, Menlo Park, CA 94025 (US).  <b>(81) Designated States:</b> AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE, DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC (European patent), MG, ML (OAPI patent), MN, MR (OAPI patent), MW, NL, NL (European patent), NO, PL, RO, RU, SD, SE, SE (European patent), SN (OAPI patent), TD (OAPI patent), TG (OAPI patent), US.  <b>Published</b> <i>With international search report.  Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
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<b>(54) Title:</b> COMPOSITE CATALYST COMPOSITION AND FISCHER-TROPSCH PROCESS USING THAT COMPOSITION														
<b>(57) Abstract</b>  This invention is a composite catalyst comprising a water-gas shift catalyst coated by a thin film zeolitic material which, in turn has a Fischer-Tropsch catalyst deposited on its outer surface. The zeolite has the function of allowing short chain hydrocarbons and steam to the water-gas shift catalyst and to allow the return of the carbon monoxide and hydrogen products back to the Fischer-Tropsch catalyst at its outer surface. The process utilizing this catalyst composite makes use of the complementary properties of the various catalyst portions. A stream of short chain hydrocarbons (e.g., C <sub>1</sub> -C <sub>4</sub> alkanes or alkenes) and steam is passed to the catalyst composite where it diffuses past the Fischer-Tropsch catalyst through the zeolitic layer to the water-gas shift catalyst. At that surface, the short chain hydrocarbon reacts with water to produce carbon monoxide and hydrogen. These products then diffuse back to the surface where they react on the Fischer-Tropsch catalyst to produce hydrocarbon oligomers.														

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5           COMPOSITE CATALYST COMPOSITION AND FISCHER-TROPSCH  
                  PROCESS USING THAT COMPOSITION

Related Applications

                  This application is a continuation of U.S.  
10   Serial No. 07/791,737 (filed November 8, 1991) which in  
turn is a continuation of U.S. Serial No. 07/751,198  
(filed August 29, 1991) which in turn is a continuation  
of U.S. Serial No. 07/724,994 (filed July 1, 1991) which  
is a continuation of U.S. Serial No. 07/694,200 (filed  
15   May 1, 1991).

FIELD OF THE INVENTION

                  This invention is a composite catalyst  
comprising a water-gas shift catalyst coated by a thin  
20   film zeolitic material which, in turn, has a Fischer-  
Tropsch catalyst deposited on its outer surface. The  
zeolite has the gatekeeper function of allowing short  
chain hydrocarbons and steam into the water-gas shift  
catalyst and allowing the return of the carbon monoxide  
25   and hydrogen products back to the Fischer-Tropsch  
catalyst at its outer surface.

                  The process utilizing this catalyst composite  
makes use of the complementary properties of the various  
catalyst portions. A stream of short chain hydrocarbons  
30   (e.g., C<sub>1</sub>-C<sub>4</sub> alkanes or alkenes) and steam is passed to  
the catalyst composite where it diffuses past the  
Fischer-Tropsch catalyst through the zeolitic layer to  
the water-gas shift catalyst. At that surface, the short  
chain hydrocarbon reacts with water to produce carbon  
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monoxide and hydrogen. These products then diffuse back to the surface where they react on the Fischer-Tropsch catalyst to produce hydrocarbon oligomers.

5 BACKGROUND OF THE INVENTION

The hydrogenation of carbon monoxide by the Fischer-Tropsch process permits the synthesis of hydrocarbons ranging from methane to high melting point paraffins, depending on the catalyst and process  
10 conditions. Cobalt based catalysts for Fischer-Tropsch synthesis have been extensively used during the first half century until the end of World War II. Precipitated Co-ThO<sub>2</sub>-MgO catalysts were the standard used in Germany's fixed bed reactors during the war. Although those  
15 catalysts gave the highest yields and longest life, they present some drawbacks. Cobalt is a relatively expensive metal, the methane fraction in the reaction products is rather high, and the metal cannot process carbon  
20 monoxide-rich synthesis gas because its water-gas shift activity is low. Recent developments in coal gasifiers and in slurry reactor technology have prompted the development of new forms of cobalt catalysts with improved product distribution and water-gas shift activity.

25 The mechanism of Fischer-Tropsch synthesis has not yet been completely elucidated. Identification of the important steps in the reduction of carbon monoxide is still controversial. In the past, global kinetics and bulk catalyst phases, such as carbide formation and  
30 adsorption stoichiometry, have been used to infer the reaction mechanism. Current research emphasizes the identification of surface species and uses transient studies and isotopic techniques to differentiate among proposed mechanistic pathways. There appears to be  
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reasonable agreement that the reaction is initiated by adsorption and dissociation of  $H_2$  and carbon monoxide, the latter species forming active surface carbide that may or may not be bonded to hydrogen. Subsequent  
5 dehydrogenation produces surface methylene or methyl groups first, then methane.

The kinetics of the synthesis reaction have also received significant attention recently. The rate-controlling step is variously identified as the  
10 dissociation of carbon monoxide or the addition of hydrogen to the surface carbon  $CH_x$  species. The latter interpretation is more widely supported. The impact of a better understanding of the mechanism on the ability to achieve more selective catalysts is unclear, however,  
15 although such an understanding could lead to more active and thus more cost effective catalysts.

The Fischer-Tropsch synthesis proceeds via a polymerization reaction in which the hydrocarbon product grows through the addition of single hydrocarbon monomer  
20 units. This growth mechanism implies that the product distribution can be described by the Anderson-Schulz-Flory (ASF) equation for the most probable distribution. Thus the entire product distribution can be defined using this equation. Hydrocarbon product distributions from  
25 carbon monoxide- $H_2$  synthesis, including commercial data from the South African Coal, Oil, and Gas Corporation (SASOL) plant, are consistent with ASF polymerization kinetics. Very recent data obtained using sophisticated analytical techniques further support the applicability  
30 of ASF polymerization kinetics.

There are a number of important implications of hydrocarbon growth via a polymerization process. These include production of  $C_1$  products only in 100% selectivity; well-defined maximum allowable selectivities  
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for all  $C_n$  products, where  $n > 1$ ; and product distributions that are generally very broad.

There have been attempts to produce hydrocarbon fuels and petrochemical feedstocks in high selectivity by finding a mechanism that bypasses polymerization or limits it from proceeding beyond a certain stage. Three such approaches are:

○ Synthesis that begins with a  $C_1$  hydrocarbon intermediate (for example, methanol, which can be produced from carbon monoxide and  $H_2$  in 100% selectivity) and that then permits the use of very selective routes to higher hydrocarbons. A typical example of this approach is the synthesis of methanol and its subsequent reaction over ZSM-5 type zeolites, as practiced by Mobil Oil Company, to produce lower olefins or aromatics at very high selectivities.

○ Shape selective catalysts that both limit the molecular size of the product molecules and minimize catalyst deactivation due to coke formation.

○ Synthesis through an entirely different mechanism than the chain growth process described by ASF kinetics.

Fischer-Tropsch technology is practiced on a commercial scale by SASOL. This operation uses two types of technology: an older fixed-bed (ARGE) reactor and a newer fluidized-bed (Synthol) unit. These units are differentiated by their catalysts, product distributions, productivity, and required downstream processing. The products of both of these reactors, however, are consistent with the ASF polymerization process.

An analysis of both the SASOL data and the older Fischer-Tropsch literature suggests that a variety of parameters are important in controlling product distribution. These include catalyst composition as a

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function of active metal promoters, support, surface area, and porosity; temperature; pressure; feed H<sub>2</sub> to carbon monoxide ratio; reactor design; and conversion. By careful selection of operating conditions and catalyst, the Fischer-Tropsch reaction can be operated at any desired degree of polymerization to achieve the product distribution specified by the ASF polymerization model.

It is likely that the next generation of Fischer-Tropsch plants will be based on slurry phase reactors. While the technology of hydrocarbon synthesis from synthesis gas in liquid phase (slurry) reactors is relatively old, pre-World War II, the use of slurry reactors for Fischer-Tropsch chemistry is undergoing a renaissance. This is because of certain potential economic advantages, such as integration of the liquid phase Fischer-Tropsch process with the new generation of more efficient coal gasifiers.

The chief incentives for using slurry reactors appear to be good temperature control and the ability to use hydrogen-lean synthesis gas. These two effects are probably not totally independent.

Hydrocarbon synthesis in the slurry reactor is complex from an engineering standpoint due to the existence of mass-transport resistances. In general, the access of reactant gases to the catalyst may be seen as a function of the solubility of the gases in the liquid medium and the rate of diffusion of the gases, once in the liquid, to the catalyst surface. However, possibly more important than the effect of transport limitations on reaction rate is the influence of those limitations on H<sub>2</sub> to carbon monoxide ratio at the catalyst. Models of the three phase system show that under a variety of operating conditions the liquid phase H<sub>2</sub> to carbon

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monoxide ratio can be substantially higher than the gas phase or feed  $H_2$  to carbon monoxide ratio. For a typical slurry phase system with a feed  $H_2:CO = 1.0$ , a liquid phase  $H_2:CO = 2.3$  can be predicted. This results from the combined solubility and diffusivity differences for  $H_2$  and carbon monoxide, leading to a mass transfer coefficient for  $H_2$  that can be 37 times that for carbon monoxide.

In addition to the influence of mass-transfer effects, the proper choice of  $H_2$  to carbon monoxide feed and usage ratios can increase the effective  $H_2$  to carbon monoxide ratio at the catalyst surface. It is clear that this ability of the slurry phase reactor to provide an effective high  $H_2$  to carbon monoxide ratio at the catalyst surface is of paramount importance permitting this system to operate with low  $H_2$  to carbon monoxide ratio feeds.

In addition to the hydrodynamics of the slurry system, the presence of the liquid phase may have other beneficial effects. These include temperature control, avoidance of hot spots, and minimization of the Boudouard reaction; solvent washing effects to remove heavy hydrocarbons and/or free carbon; and enhancement of the water-gas shift reaction. These effects may also contribute to the ability of slurry phase reactors to tolerate low  $H_2$  to carbon monoxide ratio synthesis gas.

The objective of our cobalt based catalysts is improved activity (to minimize metal usage) and selectivity towards high boiling point linear paraffins (wax). Any wax produced should be suitable for cracking into diesel fuel. A water-gas shift function should be incorporated to the catalyst in order to process carbon monoxide rich synthesis gas. Conventional cobalt catalysts prepared from metal salts and cobalt carbonyls

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deposited on supports such as silica, alumina, and titania have been studied in slurry phase reactors. Promoters such as thoria and zirconia are usually employed along with additives like Re or Ru. Efforts made to incorporate a water-gas shift function on those catalysts have not been successful. This prompted us to consider exploring other types of catalysts, such as molecular sieve based preparations.

The use of molecular sieves as bifunctional catalysts for Fischer-Tropsch has been studied since the introduction of ZSM-5 by Mobil over a decade ago. Many of those early efforts were concerned with overcoming selectivity limitations imposed by the ASF kinetics by generating secondary reactions or new polymerization schemes using dual component catalysts that associate the carbon monoxide function with the acidic/molecular shape selective behavior of the molecular sieve. It has been shown that the gasoline fraction is considerably increased by mixing a classical Fischer-Tropsch catalyst with an excess volume of ZSM-5 (Caesar, 1979; Chang, 1979). More recently, Shell has patented a Ru-faujasite-type catalyst modified with a borane solution resulting in high selectivities to paraffinic products in the range  $C_{27}-C_{30}$  (U.S. Patent No. 4,415,676).

A zeolite Fischer-Tropsch catalyst has three potential advantages. In principle, the Fischer-Tropsch function can be highly dispersed in the fresh catalyst, reducing the metal loading needed to attain a specific activity. Also, the zeolite can selectively modify (by acid catalyzed shape selective reactions) the primary Fischer-Tropsch product. Finally, a water-gas shift function could be introduced into a molecular sieve based catalyst. For example, CoAPO-34 could be modified by Zn

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and Cu components as to introduce the water gas shift activity.

Our approach is to introduce a water-gas shift function in the catalyst and yet zeolite composite materials with high surface area. These novel materials comprise a conventional porous support lined with a thin layer of zeolite crystallites providing a useful high surface area. The zeolitic layer can support the cobalt metal providing the Fischer-Tropsch function, while serving as a "gatekeeper" for a water-gas shift function located at a catalytic surface beneath it. The molecules participating in the water-gas shift reaction may diffuse through the zeolite layer to catalytic sites on the porous support. The larger hydrocarbon molecules, unable to enter the zeolite pore structure, will react only on the Fischer-Tropsch active sites located on the zeolite surface.

#### DESCRIPTION OF THE INVENTION

As noted above, this invention is a composite catalyst having an inner water-gas shift catalyst, a thin film of a zeolite coating the water-gas shift catalyst, and a Fischer-Tropsch catalyst dispersed throughout the outer surface of the zeolitic layer. Additionally, the intention involves a process of using the composite upon a hydrocarbon steam stream to produce higher molecular weight hydrocarbons through complementary water-gas and Fischer-Tropsch reactions in the catalyst composite.

#### Preparation of Zeolites

Conventional zeolite materials are prepared by crystallization from solution. High surface area zeolite coated metals have been prepared by nucleating zeolite crystallites in solution and letting them settle

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gravitationally onto copper foils (Davis et al, 1990). We prepare high surface area zeolite materials by controlled *in situ* zeolite crystallization on porous supports such as silica, alumina, zirconia, thoria, or mixtures. These are novel materials because of their structure. The surface of the support is substantially or completely lined by a thin layer of zeolite crystallites providing a useful high zeolite surface area. Such a geometric surface, in addition to the usual zeolite microporosity, advantageously offers an increased number of active sites on the external zeolite surface and short diffusion paths to internal active sites.

The key to preparing high surface area zeolites is to obtain small crystallites with a narrow size distribution. Reducing the crystallite size increases the surface to volume ratio. For cube shaped crystals, a tenfold decrease in particle size results in a 100 fold increase in external surface to volume ratio. The zeolite crystallites can be envisaged either as collections of very small crystals essentially covering the surface of the support, or a thin, continuous layer of zeolite on the support surface. Significant perturbation of the zeolite structure and its electronic field may occur at the zeolite/matrix interface, especially if the small crystallites or film are grown *in situ* on the support. This binds the crystallites to the matrix surface and produces a continuum between matrix and zeolite structure. The optimum layer thickness or crystallite size is between 2 to 10 nm. This provides a useful level of zeolite on the support, produces a high zeolitic surface and, maximizes matrix effects by minimizing the zeolite layer thickness.

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Analytical techniques suitable for determining whether a thin zeolite layer has been produced are known. We have found that a combination of an x-ray diffractometer (XRG) and a thermogravimetric analysis-differential scanning calorimeter (TGA-DSC) will give a qualitative indication of the presence of the thin film. That is to say, if the XRG does not detect the crystalline material (because of the small amount of zeolite present) but the TGA-DSC shows a substantial weight loss at an elevated temperature (e.g., 300-650°C), there likely is an amount of zeolite present. The weight loss is due to the oxidation of the organic template which may be used to produce the zeolite coating.

#### 15 The Role of Promoters, Additives and Support Materials

The major constituents of cobalt Fischer-Tropsch catalysts are cobalt, a second metal (generally Re or Ru, although Pt and Pd may also be used) oxide promoters ( $\text{ThO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{MnO}$ ) and the support. It is likely that the function of the second metal is to lower the reduction temperature of cobalt, presumably by providing a source of spill over hydrogen atoms that facilitates the reduction of the cobalt and prevents the formation of coke. The oxide promoters probably improve the selectivity and lower the deactivation rate of the catalyst.

Our materials are molecular sieve based cobalt catalysts. These are basically dual function catalysts where the cobalt metal provides the Fischer-Tropsch function while the molecular sieve modifies the product and protects the water-gas shift function from deactivation. The acidity of the support has to be carefully controlled to obtain the desired product (long chain paraffins) and low methane selectivity. This can

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be achieved adding alkali and alkaline earth promoters (i.e Li, Na, K, Ca, Mg or mixtures).

### Metal Deposition

5                   Several approaches may be used in preparing molecular sieves containing reduced and highly dispersed metal particles useful as Fischer-Tropsch catalysts. These metal containing catalysts possess unusual selectivity resulting from the synergy between the  
10 activity of the metal function and the zeolite acidity or shape selective properties. Specifically, the molecular sieves may be USY, Si-rich mordenite, offretite, zeolite omega, ZSM-5, silicalite, X, Y and CoAPO-34.

                  The Fischer-Tropsch reaction produces water,  
15 hence the catalyst must be stable in the presence of steam. For zeolites, steam dealumination and structural collapse could occur unless they have a sufficiently high Si/Al ratio. Other suitable Si-rich zeolites include dealuminated materials like USY, Si-rich mordenite, Si-rich offretite, zeolite omega, and ZSM-5.  
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                  Suitable techniques for metal deposition are listed below.

Ion Exchange and Reduction by Cd Vapor. As part of a research program in which alkali and alkaline-  
25 earth metal vapors were used to reduce ionic metal species in zeolites, Fraenkel (1980) reduced Co(II)-exchanged A and Y zeolite with Cd(0) vapor. Metallic cobalt clusters that could act as active species in carbon monoxide hydrogenation were formed. One concern  
30 is that the resulting Cd<sup>2+</sup> species, which are left in the zeolite, can affect its chemical (stability, acidity) and physical (pore and cage effective size, tortuosity, and molecular circulation) properties. Although this method can be applied to any zeolite, in theory, treatment of  
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small pore sieves (4.5 Å such as zeolite A) is hardly relevant to hydrocarbon synthesis. Also, caution should be exercised when using zeolite materials with low (<5) Si/Al ratios since other cations, such as  $Ba^{2+}$ , can react to form insoluble aluminates that can clog the pores.

Vaporization of Metal Atoms. Vaporizing cobalt under low pressure in an organic solvent such as toluene or cyclooctadiene has been used as the first step in the production of small metal clusters in zeolites (Nazar, 1983; Ozin, 1984). The resulting zero valent metal solvent complex is used to impregnate the zeolite. The solvent is then removed at low temperature leaving metal clusters primarily in the zeolite pores. These metal aggregates have been characterized by Mössbauer spectroscopy and magnetic measurements. Bulk impregnation using this approach is restricted to rather large pore materials that can accommodate the intermediate metal complex.

Microwave Discharge. Microwave discharge decomposition has been used to prepare nearly zero valent highly dispersed clusters of cobalt in X and Y zeolites (Zerger, 1986). Cluster formation occurred following adsorption of the carbonyl precursors from the gas phase. Chemisorption and ferromagnetic resonance data suggest that the cobalt atom aggregates were in the metallic state. Metal dispersions determined by chemisorption measurements and X-ray line broadening results are consistent with the formation of particles smaller than 0.9 nm; that is, small enough to fit in the super cages of these zeolites.

Sorption of Organometallic Complexes. Zeolite catalysts containing a highly dispersed active metal can also be prepared by fixing metal complexes in their void volume. For example, Co-ZSM-5 catalysts have been

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prepared by impregnation with  $C_5H_5Co(CO)_2$  (Shamasi, 1984). Even though a partial ion exchange of Co(II) species for acidic protons occurs, the resulting materials possess higher catalytic activity than the corresponding physically admixed catalysts, probably as a result of their higher cobalt dispersion.

Vapor Phase Deposition from Carbonyls. Cobalt based Fischer-Tropsch catalysts have also been prepared by contacting zeolite NaY with  $Co(CO)_3NO$  and decomposing the encapsulated carbonyl at low temperature in a hydrogen atmosphere (90°C; 1 atm; Ungar, 1986).

Cobalt Fischer-Tropsch Catalysts with Low Methane Selectivity. Methane is readily produced on cobalt catalysts under Fischer-Tropsch synthesis conditions. In fact, the methane fraction obtained on those catalysts is typically larger than predicted by the ASF product distribution curve. There seems to be a correlation between production of methane and catalyst life. Iron based preparations produce less methane but have shorter life than their cobalt based counterparts. In order to reduce methane formation, the hydrogen transfer activity of the catalyst should be depressed. This may result in increased coke formation and shorter catalyst life. The optimum catalyst should balance methane production and coke formation. To reduce the hydrogen transfer activity the acidity of the zeolite should be moderated through the addition of alkali and alkaline-earth promoters. It is also likely that molecular sieve based catalysts may present a distinct advantage in reducing coke formation through shape selective processes. Thus, it may be possible to reduce the hydrogen transfer activity without severely compromising catalyst life.

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Cobalt Fischer-Tropsch Catalysts with Water-Gas Shift Activity. It is well known that cobalt Fischer-Tropsch catalysts possess reduced water-gas shift activity. Attempts to improve this function by incorporating additives to conventional preparations have not been successful (Withers et al, 1990). We incorporate Fe, Cu and/or Zn into molecular sieve based catalysts prepared as described above. In the conventional low surface area molecular sieves we expect that the different chemical environment of the Fischer-Tropsch function and the water-gas shift additives provides our catalyst with the dual function characteristics needed for simultaneously carrying out the Fischer-Tropsch synthesis and water-gas shift reactions.

Our concept is to incorporate a water-gas shift function into cobalt Fischer-Tropsch catalysts by the use of high surface area zeolites. Preparation of these catalysts may require three steps. First, a water-gas shift catalyst such as Fe, Cu or Zn is deposited on a porous support (e.g silica or silica/alumina). A thin layer of zeolite (e.g. silicalite, ZSM-5, faujasite, X or Y) is deposited to cover the surface of the water-gas shift catalyst/support. Finally, cobalt is deposited on the zeolite surface. A sketch of the resulting multilayered structure is presented in Figure 1. This structure allows transformation of carbon monoxide into hydrocarbons on the external active sites (cobalt clusters) while the water-gas shift reaction takes place on the subsurface active sites. The zeolite layer effectively prevents bulky hydrocarbons from reacting on the water-gas shift sites but at the same time permits the diffusion of the smaller molecules (CO, CO<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub>) to those sites. This mechanism requires the zeolite

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structure to remain diffusionally transparent to small molecules, i.e. no coking reactions should take place on the zeolite layer that clog the pores. Careful control of the zeolite acidity is critical to the operation of these composite catalysts.

Cobalt Fischer-Tropsch Catalysts with Water-Gas Shift Activity and Low Methane Selectivity. A composite high surface area zeolite on a porous support catalyst including a water-gas shift function may be produced as described above. The hydrogen transfer activity on the zeolite layer is adjusted as described above so to minimize the production of methane.

Catalyst Pretreatment. The initial pretreatment will be hydrogen activation at reaction temperature.

#### Catalyst Synthesis

The catalyst synthesis scheme described below is to a particularly desirable catalyst. The scheme produced a cobalt supported on a thin film of silicalite protecting the water-gas shift catalyst which are, in turn, on catalyst microspheres. This is a desirable catalyst form for fluid bed or slurry phase reactors.

Spray Drying. Commercially available spray dried microspheres may be suitable starting materials for catalyst supports. Modification of this support (including addition of the water-gas shift function) would then be provided by impregnation. However, by spray drying the supports, we incorporate the support modifiers or water-gas shift function into the support matrix, producing not only novel supports, but materials which can be readily modified to achieve the desired combinations of composition, porosity, and strength.

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Impregnation. Incorporation of the cobalt and possibly the water-gas shift function or support modifiers is accomplished through impregnation of the catalyst support.

5           Materials can be predeposited in the catalyst support matrix to alter the distribution of the promoters as a function of distance from the particle center. Egress of the impregnating solution (aqueous or non-aqueous) from the catalyst particle may change the  
10           distributions, and is highly affected by the drying/calcining conditions. For this catalyst system the water-gas shift function may be distributed throughout the support matrix or at the support-zeolite interface. However, the cobalt should be deposited or  
15           selectively moved to the zeolite surface.

Crystallization. Three methods have been used to control the thickness of the zeolite layer grown on the support. In these methods, the porous support supplies some or all of the nutrients needed to form the  
20           zeolite structure. The additional nutrients are supplied by solution addition to the support. In the first method, the support (e.g., silica) is impregnated to incipient wetness with a solution containing sodium silicate, sodium hydroxide, and optionally sodium  
25           aluminate and tetrapropylammonium bromide. The impregnated support may be dried to limit the water remaining in the pores. The impregnated support is then placed in a vessel, and transferred to a controlled temperature and humidity chamber. Under these  
30           hydrothermal conditions zeolite crystallization is initiated. After the desired zeolite level is achieved, the crystallization is terminated.

          In the second method, the zeolite is immersed in the nutrient containing solution, and zeolite  
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crystallization is initiated in the slurry. After a brief time, the slurry is filtered, and the support particles with zeolite nuclei may be further dried to limit the water remaining in the pores. This material is placed in an open vessel, and transferred to a controlled temperature and humidity chamber. Under these hydrothermal conditions zeolite crystallization is resumed. After the desired zeolite level is achieved, the crystallization may be terminated.

10 In the third method, a solution is prepared which has the correct levels of sodium silicate, sodium hydroxide, and optionally sodium aluminate and tetrapropylammonium bromide to initiate zeolite crystallization in the absence of the support.

15 Crystallization is started under hydrothermal conditions and proceeds until zeolite nuclei are present in the solution. The support is then impregnated with this zeolite seeding solution. The impregnated support is then placed in a vessel, and transferred to a controlled temperature and humidity chamber. Under these hydrothermal conditions zeolite crystallization is resumed. After the desired zeolite level is achieved, the crystallization may be terminated.

25 Standard methods for *in situ* zeolite growth require heated, stirred crystallization reactors which are known equipment. Key crystallization parameters are those which are typically encountered for zeolite synthesis, and include time, temperature, nutrient concentrations, template selection, etc.

30 Drying and Calcining. Drying and calcining are standard procedures in the processing of the catalyst. Various moving bed or moving belt driers and calciners may also be used for production of the catalyst.

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Catalyst Reduction. The cobalt must be reduced for use in the reactor. This can be carried out by several methods. It may be performed in the catalyst preparation facility, and then the catalyst transported  
5 to the reactor. At the reactor, the transporting container may be attached to reactor in a manner minimizing the exposure to air. The reduced catalyst is then added to the reactor. Reduction of the catalyst at the reactor site probably more desirable because it would  
10 greatly reduce the possibility that a portion of the cobalt was oxidized during storage or transport. This would be accomplished by having a pretreatment chamber connected to the reactor. The catalyst is added to the pretreatment chamber, reduced, and then dropped directly  
15 into the reactor without exposure to air. Key elements for the reduction include time, temperature, flow rate, and the concentration of reducing gases.

Process. The composite produced as specified above is used in a stream containing water and short  
20 chain hydrocarbons at a temperature, pressure, catalyst to feed ratio (and the like) as suitable to produce higher molecular hydrocarbons than those fed to the catalyst composite.

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ExamplesExample 1(Comparative)

Vapor phase synthesis of a pentasil zeolite was  
30 conducted in a heated stainless steel PARR autoclave lined with TEFLON. The TEFLON liner was partially filled with water. This water partially vaporized upon heating the autoclave. A 5 gram sample of silica pellets (PQ Corp. CS 1010E, surface area  $111 \text{ m}^2/\text{g}$ , pore volume 0.87  
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cc/g, average pore size 157 angstroms) was impregnated to incipient wetness with a solution of 4 parts NaOH, 2 parts tetrapropylammonium bromide powder (TPABr>98%, from Fluka), and 690 parts water. The impregnated pellets were placed in a 22 cc TEFLON tube which was then placed into the autoclave (Figure 1). The autoclave was placed in an oven at 185°C for 15 hours. The synthesis was stopped by removing the autoclave from the oven and cooling in cold water. The solid sample was then placed on a Buchner funnel and any liquid present removed by filtration. The solids were washed with distilled water until the pH of the wash water reached about 7 to 8. The solids were dried overnight on the filter at 130°C in an oven. The X-ray diffraction pattern of the dried sample was obtained and showed an intense peak at  $2\theta=23^\circ$ , which is characteristic of silicalite. Since a strong X-ray diffraction peak was observed, a thin film was not obtained.

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#### Example 2

A series of 33 experiments were conducted to determine whether "X-ray-amorphous" thin films of zeolites could be prepared using vapor phase synthetic techniques similar to those used in Example 1. For each experiment, two grams of silica were used and were impregnated with 2 cc of a solution consisting of one part tetrapropylammonium bromide (TPAB) powder (TPABr>98%, from Fluka), and 690 parts water, and an amount of NaOH which was varied from 0.5 to 9.5 parts to obtain the OH- to silica ratio shown in Table 1 for each experiment. After impregnation, the samples were placed in a glass beaker and dried for the time shown in Table 1. The vapor pressure depression was obtained by placing appropriate NaCl solutions (1.5 to 5.0 M) in the

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TEFLON autoclave liner instead of the distilled water of Example 1. After synthesis, the samples were washed by stirring the pellets in 300 ml of distilled water, and then filtering them as in Example 1. The samples were  
5 analyzed using X-ray and using thermogravimetric analysis-differential scanning calorimetry (TGA-DSC). TGA-DSC gives simultaneously the weight changes and the magnitude of the corresponding thermal effect as a function of temperature applied to the sample. The  
10 oxidative decomposition of the organic template (TPAB) occluded in the zeolite structure was observed and the weight loss used to calculate the amount of zeolite in the sample. Weight loss between 400° and 600°C is characteristic of TPAB loss. The crystallinities  
15 obtained from X-ray diffraction and TGA-DSC are shown in Table 1. Samples which are X-ray amorphous (crystallinity by XRD is 0%) but which have crystallinity by TGA-DSC are materials of this invention.

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Silicalite designed experiments results

X<sub>1</sub>: Synthesis temperature (deg. C)      X<sub>4</sub>: OH/SiO<sub>2</sub> ratio (10<sup>-3</sup>)  
 X<sub>2</sub>: Drying time at 130°C (minutes)      X<sub>5</sub>: Synthesis time (hours)  
 X<sub>3</sub>: Relative water vapor pressure (P/P<sub>0</sub>)

X <sub>1</sub>	SYNTHESIS PARAMETERS					CRYSTALLINITY	
	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	X <sub>5</sub>	XRD peak area	TG wt%	
160	50	0.90	9.5	13	10696.9	13.1	
160	0	0.90	0.5	13	0	2.7	
160	25	1	9.5	13	27500.6	20.9	
160	25	0.80	0.5	13	0		
160	50	1	5.0	13	26540.8	12.8	
160	0	0.80	5.0	13	27743.4	20.1	
210	37.5	0.95	7.25	6	36942.9	20.7	
110	12.5	0.85	2.75	19	0	6.0	
210	37.5	0.95	7.25	19	34862.8	14.7	
110	12.5	0.85	2.75	6	0	6.6	
160	0	1	5.0	13	30497.9	19.0	
160	50	0.80	5.0	13	7722.1	9.2	
160	25	1	0.5	13	0	4.3	
160	25	0.80	9.5	13	12119	12.6	

Table 1 (continued)

X <sub>1</sub>	SYNTHESIS PARAMETERS					CRYSTALLINITY		
	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	X <sub>5</sub>	XRD peak area	TG wt%		
210	12.5	0.95	2.75	6	16008.2	10.2		
110	37.5	0.85	7.25	19	0	11.7		
210	12.5	0.95	2.75	19	30797.7	18.6		
110	37.5	0.85	7.25	6	0	9.1		
160	50	0.90	0.5	13	0	3.5		
160	0	0.90	9.5	13	46671.7	22.6		
210	37.5	0.85	2.75	6	23105.3	12.7		
110	12.5	0.95	7.25	19	5531.2	11.1		
210	37.5	0.85	2.75	19	5250	7.8		
110	12.5	0.95	7.25	6	0	8.5		
210	12.5	0.85	7.25	6	44782.5	24.0		
110	37.5	0.95	2.75	19	0	5.7		
210	12.5	0.85	7.25	19	44664.1	23.9		
110	37.5	0.95	2.75	6	0	4.2		
160	25	0.90	5.0	25	42881.6	24.0		
160	25	0.90	5.0	1	0	10.2		
160	25	0.90	5.0	13		13.7		
160	25	0.90	5.0	13		13.9		
160	25	0.90	5.0	13		21.1		

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WE CLAIM AS OUR INVENTION:

1. A catalyst component comprising a support of silica, alumina, zirconia, thoria, or mixtures thereof at least substantially covered by a layer of zeolite.
2. The component of Claim 1 where the support is silica.
3. The component of Claim 1 where the support is alumina.
4. The component of Claim 1 where the zeolite is selected from US4, Si-rich mordenite, Si-rich affritite, zeolite omega, ZSM-5, silicalite, zeolite X, or zeolite Y.
5. The component of Claim 4 where the thickness of the layer of zeolite is 2 to 10 nm.
6. A catalyst composite comprising a water-gas shift catalyst covered by a thin zeolitic layer and having a Fischer-Tropsch catalyst dispersed on its outer surface.
7. The catalyst composite of Claim 1 additionally comprising a porous substrate.
8. The composite of Claim 6 where the Fischer-Tropsch catalyst comprises cobalt and a promoter.
9. The composite of Claim 8 where the promoter is selected from Re, Ru, Pd, Pt, ThO<sub>2</sub>, ZnO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, and MnO.

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10. The composite of Claim 9 where the promoter is Re or Ru.

5           11. The composite of Claim 8 additionally comprising a support selected from silica, alumina, zirconia, thoria, or mixtures thereof.

10           12. The composite of Claim 11 additionally comprising Li, Na, K, Ca, Mg, or mixtures.

13. The composite of Claim 6 where the water gas shift catalyst comprises Fe, Cu, or Zn.

15           14. A process for producing oligomerized hydrocarbons comprising contacting steam and a lower molecular weight hydrocarbon with the catalyst of Claim 6 to 13.

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INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US91/03601

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC(5) :CO7C 2/02; B01J 29/04  
 US CL :585/533; 502/66  
 According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**  
 Minimum documentation searched (classification system followed by classification symbols)  
 U.S. : 502/60,64; 518/715

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 3,468,815 (COLE ET AL.) 23 September 1969, See column 2, lines 5-31.	1-13
X	US, A, 4,579,830 (COUGHLIN) 01 April 1986, See example 1.	14

Further documents are listed in the continuation of Box C.  See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or prior date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 05 AUGUST 1992	Date of mailing of the international search report <b>15 SEP 1992</b>
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