



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

⑬

⑪ Publication number:

**0 169 161**  
**A2**

⑫

## EUROPEAN PATENT APPLICATION

⑰ Application number: 85630113.0

⑥① Int. Cl.4: **C 07 C 1/06**, C 07 F 15/00,  
B 01 J 31/22, C 07 F 13/00

⑱ Date of filing: 12.07.85

③⑩ Priority: 17.07.84 US 631698

⑦① Applicant: **THE GOODYEAR TIRE & RUBBER COMPANY, 1144 East Market Street, Akron, Ohio 44316 (US)**

④③ Date of publication of application: 22.01.86  
Bulletin 86/4

⑦② Inventor: **Hsu, Wen-Liang, 4482 Conestoga Trail, Copley Ohio 44321 (US)**  
Inventor: **Kurr, Richard John, 1222 Vane Avenue, Apt. 3C, Akron Ohio 44310 (US)**  
Inventor: **Maly, Neil Arthur, 953 Maple Street, Tallmadge Ohio 44278 (US)**  
Inventor: **Strozler, Robert William, 173 Elmdale Avenue, Akron Ohio 44313 (US)**  
Inventor: **Parker, Dane Kenton, 945 Norwich Avenue, N.W., Massillon Ohio 44646 (US)**

⑥④ Designated Contracting States: **DE FR GB IT**

⑦④ Representative: **Weyland, Joseph Jean Pierre, Goodyear International Tire Technical Center Patent Department Avenue Gordon Smith, L-7750 Colmar-Berg (LU)**

⑥④ **Polymer bound Fischer-Tropsch catalysts.**

⑥⑦ There is disclosed a resin-metal (complex) catalyst, a method for its preparation, activation and use in carrying out Fischer-Tropsch reactions. The complex is a resin which has attached to it a coordination compound(s) and a metal(s). The complex has utility as a Fischer-Tropsch catalyst. More specifically, the complex is useful for the gaseous conversion of synthesis gas (carbon monoxide and hydrogen) to hydrocarbons.

**EP 0 169 161 A2**

POLYMER BOUND FISCHER-TROPSCH CATALYSTSTechnical Field

This invention relates to polymer supported or polymer  
5 bound metal complexes which exhibit activity as Fischer-  
Tropsch catalysts. Specifically, this invention relates to  
gas phase Fischer-Tropsch reactions wherein a resin metal  
complex catalyst is used in the conversion of synthesis gas  
to hydrocarbons.

10

Background Art

There is a general belief by those skilled in the art  
of polymer supported catalysis that all types of  
polystyrene resins (macroreticular or gel) are inherently  
15 thermally unstable both in the presence or absence of  
oxygen. The upper temperature limit often cited for use of  
these catalyst-resin systems is quoted at approximately  
150°C. See Sherrington "Polymer Supported Reactions in  
Organic Synthesis"; Chap.1 p.27; Wiley: New York, 1980; See  
20 also: International Workshop on Heterophase Attached  
Homogeneous Catalysis, Grenoble, France, 1977 (CNRS and  
NSF) and Chauvin et al, "Polymer Supported Catalysts" Prog.  
Polymer Sci., Vol. 5, p. 100, Pergamon Press, (1977). The  
present innovation is concerned with functionalized  
25 macroreticular polystyrene that has utility as a catalyst  
for vapor phase Fischer-Tropsch reactions at temperatures  
in excess of 200°C.

The use of a catalytic complex containing an  
anthranilic acid ligand for catalytic hydrogenation is  
30 disclosed in U.S. Patent No. 3,755,194 to Avilov et al,  
issued August 28, 1973. The Avilov patent relates to a  
homogeneous catalytic system for the hydrogenation of  
unsaturated compounds at room temperature and one  
atmosphere of hydrogen pressure. In this procedure a  
35 rhenium (I) complex of N-phenylanthranilic acid is  
employed. However, this procedure like other homogeneous  
catalytic systems has the disadvantage that it is difficult

to separate the hydrogenation product from the catalyst itself with the result that the catalyst is a contaminant or an impurity in the final product.

Substituted phosphines have been used to chemically link a catalyst metal to a polymer support. Examples of this are found in Grubbs et al, "Polymer Preprints," American Chemical Society, Division Polymer Chemistry, 1972, Vol. 13, No. 2, pages 828-832 [Chem. Abs. Vol. 81, 6555d (1974)] and also Grubbs et al, "J. Macromol. Sci Chem.," 1973, Vol. 7, No. 5, Pages 1047-1063, [Chem. Abs. Vol. 78, 164622r (1973)].

United States Patent No. 4,230,633 discloses polymer supported metal complexes wherein the ligand is a cycloalkadienyl radical with metals from Group VIII of the Periodic Table. This patent is concerned with the conversion of carbon monoxide and hydrogen to hydrocarbons in a liquid reaction medium.

United States Patent No. 4,292,415 discloses a crosslinked polystyrene with cycloalkadienyl ligands and Group VIII metal carbonyls having utility as a Fischer-Tropsch catalyst in liquid phase reactions. This patent does not suggest the critical relationships that the present invention is concerned with, nor the specific ligands and vapor phase reactions.

Fischer-Tropsch catalysis by polystyrene supported cyclopentadienyldicarbonyl cobalt ( $\text{CpCo}(\text{CO})_2$ ) has been reported by Benner et al, (American Chemical Society Symposium Series 152 (1981) p. 165. The reaction was conducted in a medium pressure glass and stainless steel reactor. Benner et al suspended  $\text{P-CpCo}(\text{CO})_2$  in purified n-octane to swell the resin and allow access to catalyst sites in the interior of the beads; no detectable reaction took place if the solvent was excluded. This is in contrast to the present invention in which the reaction takes place in the vapor phase without the requirement that the polymer be swollen.

United States Patent No. 4,323,698 discloses a weak base anion exchange resin which has been contacted with a solution of a coordination compound having at least two ligands connected to at least one central metal atom, to  
5 chemically bond the resin to the metal atom by replacement of at least one of the ligands of the coordination compound by a functional group of the weak base anion exchange resin. The complex can be used as a catalyst for hydrogenation, carbon monoxide insertion, polymerization,  
10 isomerization, vinyl ester exchange and ethylene oxidation reactions among others.

United States Patent No. 4,144,191 discloses amine resins loaded with bimetallic clusters as novel hydroformylation catalysts. This patent is directed to the  
15 conversion of liquid olefins to alcohols in a one-step hydroformylation process which consists of contacting an olefin, such as 1-hexene in the liquid phase, with a gaseous mixture of carbon monoxide and hydrogen and the presence of a catalyst prepared by loading a bimetallic  
20 cluster onto an amine resin.

United States Patents No. 4,238,358 discloses the use of anthranilic acid as a ligand for rhodium, palladium, platinum and ruthenium complexes. These catalysts are disclosed as reduction catalysts for liquid phase  
25 reactions, i.e. the hydrogenation of olefinic and aromatic hydrocarbons.

The prior art does not disclose or suggest the use of resin metal complex catalysts in vapor phase Fischer-Tropsch reactions. One skilled in this art would readily  
30 realize or assume that resins, particularly polystyrene resins would not hold up at the temperatures at which vapor phase Fischer-Tropsch reactions are conducted. See Catalysis, J.R. Anderson and M. Boudant, Eds. Chapter 4; Springer Verlag (1981). Specifically, the catalyst of the  
35 present invention operates in a temperature range from 175 to 275°C.

Synthesis gas is a mixture of carbon monoxide and hydrogen and can be produced by the gasification of coal with steam and oxygen. A description of conventional methods of coal gasification is provided in McGraw-Hill Encyclopedia of Science & Technology, 1977 Edition, Vol. 3, pages 248-249 (McGraw-Hill Book Company, New York).

Production of methane and higher hydrocarbons from coal by the Fischer-Tropsch reaction typically employs a group VIII catalyst (e.g. Fe, Co and Ni) at temperatures in the range of about 200-350°C and pressures in the range of about 2100-3500 kPa (300-500 psi).

While these processes are successful in making synthetic natural gas or oxygenated hydrocarbons, the operating conditions leave considerable room for improvement. The relatively severe operating conditions require high capital investment and power or energy consumption. In addition, the severe conditions present many operating problems. Accordingly, a catalyst which overcomes these disadvantages of the prior art processes is to be highly commended.

The present invention provides complexes useful as catalysts which enable Fischer-Tropsch synthesis to be achieved at mild operating temperatures and pressures.

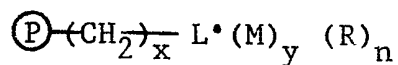
#### Disclosure of the Invention

There are three broad aspects to the present invention:

- (1) novel polymer-metal complexes;
- (2) a process for making the complexes, their activation, and
- (3) the complexes as catalyst for Fischer-Tropsch reactions at relatively mild conditions.

Thus, there is disclosed novel polymer-supported metal complexes of the formula:

35



wherein  $\textcircled{P}$  represents a crosslinked macroreticular polystyrene resin which has a crosslink density of at least 5%;

x is 0 or 1;

5 L represents a ligand selected from the group consisting of bipyridyl, 2-aminopyridine, 2-amino phenol, 2-imino pyridine, sodium anthranilate, potassium anthranilate and anthranilic acid;

y is an integer from 1 through 8;

10 when y equals 1, M represents a Group VIII metal from the Periodic Table and when y is from 2 through 8, M represents one or more metals selected from the group consisting of Group VIII metals from the Periodic Table, hydrogen, manganese, potassium and sodium;

15 R represents a carbonyl or a halogen radical; and  
n represents an integer from 0 through 24.

Further, there is disclosed a heterogeneous catalyst for Fischer-Tropsch reactions conducted in the vapor phase  
20 at a temperature from 175°C to 300°C, said catalyst comprising;

a ligand selected from the group consisting of anthranilic acid, 2-amino phenol, 2-amino pyridine, bipyridyl and sodium or potassium anthranilate, which is  
25 complexed with a metal compound selected from the group consisting of  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ ,  $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ ,  $\text{MnCo}(\text{CO})_9$ ,  $\text{RuCl}_3$ ,  $\text{Co}_4(\text{CO})_{12}$ ,  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ ,  $\text{K}_2\text{Ru}_6(\text{CO})_{16}$ ,  $\text{Ru}_3(\text{CO})_{12}$ , and  $\text{Fe}_3(\text{CO})_{12}$ ;

said ligand being chemically linked to a polymeric  
30 support, said polymeric support comprising from 0 to 20 weight percent chloromethylstyrene, 40 to 70 weight percent styrene and 20 to 40 weight percent divinylbenzene.

Some of the complexes of this invention are compositions based upon divinylbenzene crosslinked  
35 polystyrenes in which the divinylbenzene crosslinking is greater than 4 percent but less than 50 percent. This means that the divinylbenzene crosslinked polystyrenes are

prepared with from 4-50% divinylbenzene based on monomer charge with the remainder being styrene and other monomers (i.e. chloromethylated vinyl benzene). Also, polystyrene may be halogenated and then further reacted. Thus, the  
5 polystyrene resins useful in this invention have pendant halomethyl functionally. The polymer may be a terpolymer in that other comonomers may be present in minor amounts.

The crosslinked chloromethylated polystyrene polymer is preferably macroporous or macroreticular in character  
10 (i.e. pore size of about 100 to 900Å). Those skilled in the art are familiar with the manner of obtaining a macroporous polymer rather than a microporous polymer. See Sherrington supra.

### 15 Experimental

To these macroreticular divinylbenzene crosslinked chloromethylated polystyrene polymers are attached ligands. Conventionally, a ligand is a molecule, ion, or atom that is attached to the central atom of a coordination compound,  
20 a chelate, or other complex. For example, the ammonia molecules in  $[\text{Co}(\text{NH}_3)_6]^{+++}$ , and the chlorine atoms in  $[\text{PtCl}_6]^{--}$  are ligands. Ligands are also called complexing agents, as for example EDTA, ammonia, etc. In the present invention the ligands are molecules that are attached to  
25 the polystyrene polymer and are capable of complexing with metal carbonyls or halides. Ligands such as anthranilic acid or other amines, i.e. 2-aminophenol, are anchored to the halomethylated polymer by known procedures such as  
30 stirring the polymer with excess anthranilic acid or other amines such as dipyridyl in a reaction medium such as ethyl ether, toluene, acetone, or dimethylformamide. As used herein, the term "dipyridyl" refers to the 2,2' isomer, which is also known as "bipyridyl".

The polymer is recovered and then washed with  
35 appropriate solvents such as ethanol. The polymer is then slurried in a reaction medium and there is added thereto the metal or metal cluster carbonyl or halide compound.

Representative of the single metal carbonyls useful in the present invention are  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Fe}_3(\text{CO})_{12}$ , and  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ . Mixed metal carbonyls such as  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ ,  $\text{K}_2\text{Ru}_6(\text{CO})_{16}$ ,  $\text{H}_2\text{FeOs}_3(\text{CO})_{12}$ , and  $\text{MnCo}(\text{CO})_9$  are also contemplated by the present invention. After stirring of this slurry for a suitable length of time, the polymer is recovered, e.g. by filtration, and washed and finally extracted to remove unreacted chemicals.

#### 10 Preparation of Catalyst from Bound Ligand and Metal Carbonyls

Anthranilic acid and 2-aminophenol were previously bound to polystyrene as described above. Both the polymer bound ligand (5 gm) and 0.73 gm of  $\text{Ru}_3(\text{CO})_{12}$  were weighed into a 250 ml 3 neck flask; then 100 ml of toluene was added. The flask was equipped with mechanical stirrer, thermometer, condenser, and nitrogen inlet/exit. The flask was flushed with nitrogen and heated to the 60°C reaction temperature. During the overnight reaction, a nitrogen filled balloon maintained the reaction flask atmosphere. When the reaction was complete, the mixture was cooled and filtered through a polypropylene cloth to isolate the resin. The resin was washed with 500-1000 ml toluene and 200 ml hexane to remove most unreacted metal carbonyl. A 24 hour soxhlet extraction with hexane or 1:1 THF/ $\text{CH}_3\text{OH}$  removed residual extractables. The extracted resin was vacuum dried at 50°C for 3-4 hours. Synthesis of the metal complex was confirmed by elemental analysis, IR, weight gain, and color change.

30 Finally, the metal complex may be subjected to a treatment with a reducing agent, e.g. sodium borohydride, while suspended in a reaction medium. The reducing agent is used to selectively reduce the higher valence state of the metal to the lower catalytic state without affecting or  
35 reducing the anthranilic acid or amine ligand present in the catalytic complex.



Such reducing agents include, for example, sodium borohydride, metallic sodium (in ethanol), sodium hydride, and lithium aluminum hydride.

Polymeric supports in the form of beads, blocks, 5 fibers, spheres, filaments, etc. may be used in the present invention. The use of polymers in the form of beads has been found to be advantageous since the ligand can be incorporated into such beads quite easily merely by stirring a mixture thereof in a suitable organic solvent 10 or, if desired, with heating to a temperature as high as the reflux temperature of the system. The latter expedient may be employed for a better and faster incorporation of the ligand onto the beads. Polymeric beads having a size of about 1 to 10 mm can be suitably employed, although 15 beads having a size as large as 2-5 cm. can also be used with advantage.

Particularly suitable, commercially available polymeric supports for use in the invention are polystyrene polymers (for example, Rohm and Haas XAD-4 Amberlite, or 20 Dow Chemical XFS4022 resin), because of the ease of attaching different chemical groups. Also, chloromethylated polystyrene beads can be advantageously used as a polymeric support.

Other polymers having a reactive group can be provided 25 with pendant functionality wherein, for example, anthranilic acid can be anchored to the polymer by a condensation reaction. Examples of such polymers include chlorinated polystyrene in which chlorine atoms can serve as reactive groups and copolymers of styrene with other 30 copolymerizable monomers. In addition, they may be prepared as described in U.S. Patent No. 2,597,437.

Further, in functional terms, the polymer support may additionally contain reactive functionalities such as sulfonate, methanesulfonate, tosylate, carboxylate, 35 cyanomethyl and the like, which can be readily reacted so as to effect a condensation between the amino group of the ligand and the reactive groups of the polymeric chain.

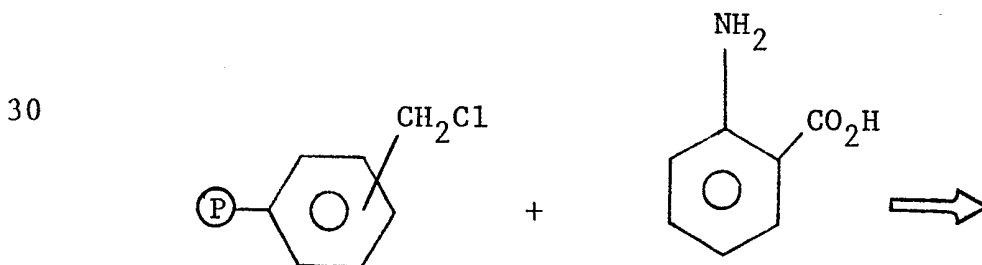
Thus, within this context, it is apparent that a wide variety of polymer supports can be used successfully in connection with the preparation of the heterogeneous catalytic systems of the invention.

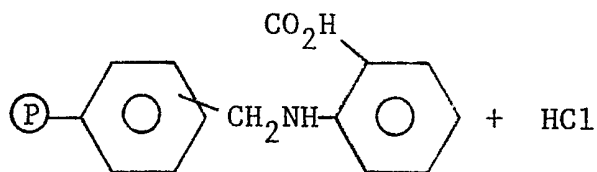
5        Macroreticular resins can be synthesized by the polymerization of styrene, divinylbenzene and chloromethylstyrene using known procedures. The polymer crosslinks during the polymerization. Useful polymers contain 0-15 weight percent chloromethylstyrene, 40-70  
10 weight percent styrene and 20-40 weight percent divinylbenzene.

Isoporous resins can be synthesized by polymerization of styrene and chloromethylstyrene. The polymer is crosslinked after polymerization with a  $\text{SnCl}_4$  reaction.  
15 Chloromethylstyrene content can vary between 10 percent and 90 percent in the uncrosslinked polymer. For more information see, Regas and Papadoyannis, Polymer Bulletin 3, 279-284 (1980) and Peppas, Bussing and Slight, Polymer Bulletin 4, 193-198 (1981).

20        Macroporous and isoporous resins have different pore structures, swelling properties and physical properties because of the different crosslinking procedures. For this reason different catalytic properties might be expected.

In the case of chloromethylated polystyrene beads the  
25 following reaction with the anthranilic acid is believed to occur:

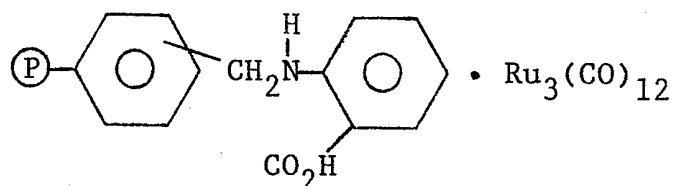




5 In the above reaction scheme the symbol:  $\textcircled{\text{P}}$  represents the polymeric backbone.

When the product of the above-described reaction is then combined with a metal complex, e.g.  $\text{Ru}_3(\text{CO})_{12}$ ; it is believed that the following reaction product is obtained:

10



15

The feedstock advantageously used by the catalysts of this invention is known as syngas or synthesis gas. Synthesis gas can be any of several gaseous mixtures used for synthesizing a wide range of compounds. Such mixtures result from reacting carbon-rich substances (ie. coal) with steam (steam reforming) or steam and oxygen (partial oxidation); they contain chiefly carbon monoxide and hydrogen, plus low percentages of carbon dioxide or nitrogen (less than 2.0%). The organic source materials may be natural gas, methane, naphtha, heavy petroleum oils, or coke (coal). The reactions are nickel-catalyzed steam-cracking (reforming) of methane or natural gas ( $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ ); partial oxidation of methane, naphtha, or heavy oils; and especially in view of the petroleum shortage the water-gas reaction with coke ( $\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$ ).

Synthesis gas with ratios of  $\text{H}_2$  to  $\text{CO}$  of from 1:1 to 2:1 have been found useful in the present invention. Other ratios would be appropriate, however, those skilled in this art will realize that changes in the ratio will affect the reaction in numerous ways.

### Reaction System Used For Tests

Catalysts were utilized in a fixed bed reactor system. The reactor is a 1.4 cm ID x 38.1 cm (0.56 x 15 inch) 316 stainless steel tube. During catalyst tests the reactor  
5 contained about 10 cc of catalyst. Reactors were equipped with axial thermowells and a heating system capable of maintaining temperatures within 5°C along the catalyst bed at 250°C. Each reactor was piped so that any of three gases could be passed through the bed.

10

1. Hydrogen (for catalyst reduction).
2. Helium (for purging).
3. Syngas ( $H_2/CO = 2/1$ ).

15 The Fischer-Tropsch tests were conducted under the following conditions unless specified otherwise:

Synthesis gas molar ratio - 2/1  $H_2/CO$

Pressure - 1034 kPa (150 psig)

20 Temperature - 250°C.

Gas hourly space velocity - 200  $hr^{-1}$

### Catalyst Activation

Activation procedures for polymer bound catalysts are  
25 the sodium borohydride process or vacuum with hydrogen reduction.

The sodium borohydride activation procedure consists of adding unactivated catalyst to absolute ethanol in a reaction flask. After adding a stirring bar, sodium  
30 borohydride was added in small batches. A 30 minute room temperature reaction was enough to complete the reduction. After isolation by filtration, the resin was washed with alcohol, petroleum ether and pentane. The pentane washed resin was charged to the reactor and dried with a helium  
35 stream.

Vacuum and hydrogen reduction activation consists of heating catalysts to a temperature between 225-275°C in a

helium flow. The catalyst was then placed under vacuum for 1 hour. Thereafter, a 2 hour hydrogen flow reduced the evacuated catalyst. After activation the temperature was brought to 250°C and the Fischer-Tropsch reaction was  
5 initiated by adding syngas.

The catalysts may be used without activation, wherein the catalyst is placed in the reactor, the temperature is raised to the reaction temperature and then syngas is introduced into the reactor. It has been unexpectedly  
10 discovered that non-activated catalyst will slowly activate in syngas with time until a steady state is achieved.

#### Test Data

Polymer bound amine ligated metal chloride and metal  
15 carbonyl complexes were tested for Fischer-Tropsch activity. Table I sets out the results of the screening test which utilized different metal complexes, different supporting resins or polymers and different ligands. The reaction conditions and reaction vessel were as previously  
20 described. All catalysts listed were not activated prior to testing unless otherwise noted. These catalysts were initially screened to determine whether or not they would exhibit any Fischer-Tropsch activity. More complete data on activity is presented infra.

25

30

35

TABLE I

## Polymer Bound Fischer-Tropsch Screening

Catalyst #	Metal Cluster or Complex	Ligand	Resin ++	Intended Metal Loading % by wt.	Fischer-Tropsch Activity
1	$H_2FeRu_3(CO)_{13}$	Anthranilic Acid	A	5	Yes
2	$K_2Ru_6(CO)_{16}$	Anthranilic Acid	A	5	Yes
3	$Ru_3(CO)_{12}$	Anthranilic Acid	A	5	Yes
4	$RuCl_3$ *	Potassium Anthranilate	A	5	Yes
5	$Ru_3(CO)_{12}$	2-amino phenol	A	5	Yes
6	$H_2FeOs_3(CO)_{13}$	2-amino pyridine	A	5.5	Yes
7	$Ru_3(CO)_{12}$	2-amino pyridine	A	5	Yes
8	$RuCl_3$ *	2-amino pyridine	A	5	Yes
9	$Ru_3(CO)_{12}$	2-imino pyridine	B	5	Yes
10	$HFeCo_3(CO)_{12}$	Benzyl Iodide	C	3	No
11	$Fe_3(CO)_{12}$	Dipyridyl	B	3	Yes
12	$H_2FeRu_3(CO)_{13}$	Dipyridyl	B	6	Yes
13	$H_4Ru_4(CO)_{12}$	Dipyridyl	B	5	Yes

14	MnCo(CO) <sub>9</sub>	Dipyridyl	B	6	Yes
15	RhCl <sub>3</sub> *	Dipyridyl	B	5	Yes
16	Ru <sub>3</sub> (CO) <sub>12</sub>	Dipyridyl	B	5.2 <sup>a</sup>	Yes
17	RuCl <sub>3</sub> *	Dipyridyl	B	5	Yes
18	IrCl <sub>3</sub>	Double Porphyrin	A	N.A.	No
19	RuCl <sub>3</sub>	Double Porphyrin	A	10	No
20	Co <sub>4</sub> (CO) <sub>12</sub>	Triphenyl Phosphine	B	3	No
21	Fe <sub>3</sub> (CO) <sub>12</sub>	Triphenyl Phosphine	B	3	No
22	Ru <sub>3</sub> (CO) <sub>12</sub>	Triphenyl Phosphine	B	5	No

14

a = actually analyzed

\* = sodium borohydride activated prior to testing

++Resin A is a 70/30 styrene/divinylbenzene macroreticular resin

Resin B is a Dow Chemical XFS4022 20% Divinylbenzene 80% styrene macroreticular resin

Resin C is vinyl benzyl chloride resin obtained from Ionac Inc.

0169161

All the active catalysts in Table I produced broad hydrocarbon product distributions in conjunction with very minor amounts of oxygenates such as methanol, ethanol and others. From Table I it is evident that benzyl iodide, 5 double porphyrins and triphenyl phosphines are unacceptable ligands.

Catalyst Nos. 3, 7 and 9 after screening were subjected to an activation procedure which consisted of one hour under vacuum at 250°C and then one hour under hydrogen 10 at 250°C.

Tables II, III and IV set out CO conversion and light product selectivities for Catalyst Nos. 3, 7 and 9 respectively.

15

20

25

30

35



TABLE II

CO Conversion and Light Product Selectivities for  
 $\text{Ru}_3(\text{CO})_{12}$  • Anthranilic Acid - Catalyst #3

Sample #	Reaction Conditions		CO Conversion (%)		Product Selectivity (%)				
	On-Stream Time (hr)	GHSY ( $\text{hr}^{-1}$ )	Temp. ( $^{\circ}\text{C}$ )	Total	To Hydrocarbon	$\text{C}_1$	$\text{C}_2$	$\text{C}_2=$	$\text{C}_3+$
1	1.0	200	250	22.94	22.94	22.56	2.71	0.00	74.73
2	2.0	200	250	60.02	59.64	24.20	4.56	0.04	71.20
3	2.5	200	250	65.87	65.43	23.41	3.60	0.00	72.99
4	3.0	200	250	71.19	70.63	22.38	3.51	0.00	74.11
5	4.0	200	250	77.66	76.99	21.44	3.18	0.00	75.38
6	4.5	400	250	74.85	74.33	21.70	2.99	0.00	75.31
7	5.0	400	250	69.10	68.69	22.09	2.95	0.00	74.96

OVERNIGHT SHUTDOWN: CATALYST STORED UNDER HELIUM AT ROOM TEMPERATURE

8	1.0	200	250	26.25	26.25	35.09	3.80	0.00	61.11
9	1.5	200	250	39.38	39.27	34.19	5.73	0.00	60.08
10	5.0	200	225	52.07	51.99	20.71	2.31	0.00	76.98
11	5.5	200	225	51.24	51.15	19.12	2.46	0.00	78.42

0169161

TABLE III

CO Conversion and Light Product Selectivities for  
 $\text{Ru}_3(\text{CO})_{12}$  • 2-amino pyridine - Catalyst #7

Sample #	Reaction Conditions		CO Conversion (%)		Product Selectivity (%)			
	On-Stream Time (hr)	GHSV ( $\text{hr}^{-1}$ )	Total	To Hydrocarbon	$\text{C}_1$	$\text{C}_2$	$\text{C}_3^+$	
		Temp. ( $^{\circ}\text{C}$ )						
1	1.5	250	54.27	53.56	30.19	3.98	0.00	65.83
2	3.0	250	63.37	62.31	29.51	3.61	0.00	66.88
3	3.5	250	62.60	61.64	29.96	3.52	0.00	66.52
4	4.0	250	42.27	41.79	34.07	3.80	0.00	62.13

OVERNIGHT SHUTDOWN: CATALYST STORED UNDER HELIUM AT ROOM TEMPERATURE

5	1.0	250	44.55	44.21	48.61	4.65	0.00	46.74
6	1.75	250	45.49	45.16	46.42	4.71	0.00	48.87
7	3.0	225	27.19	27.05	34.14	3.22	0.00	62.64
8	3.33	225	23.38	23.32	30.52	2.77	0.00	66.71
9	5.66	250	40.87	40.58	43.50	4.11	0.00	52.39

0169161

TABLE IV

CO Conversion and Light Product Selectivities for  
Ru<sub>3</sub>(CO)<sub>12</sub> • 2-imino pyridine - Catalyst #9

Sample #	Reaction Conditions		CO Conversion (%)		Product Selectivity (%)				
	On-Stream Time (hr)	GHSY (hr <sup>-1</sup> )	Temp. (°C)	Total Hydrocarbon To	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub> =	C <sub>3</sub> +	
1	1.25	200	250	5.88	5.88	30.07	0.00	0.00	69.93
2	2.33	200	250	5.32	5.32	27.73	0.00	0.00	72.27
3	4.50	200	250	5.40	5.40	24.68	0.00	0.00	75.32
4	6.00	200	275	9.14	9.15	52.28	0.00	0.00	47.72

18

The data contained in Tables II, III, and IV demonstrates that catalysts according to the present invention have acceptable Fischer-Tropsch activity. To further demonstrate the activity of the catalysts of the instant invention 11 active catalysts from Table I were activated and then subjected to extensive testing for Fischer-Tropsch activity. This data is set out in the following Tables V through XVI.

0169161

TABLE V

CO Conversion and Light Product Selectivities for  
 $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  • Anthranilic Acid - Catalyst #1  
 Activated by three hours under vacuum at 250°C and one hour under  $\text{H}_2$  at 250°C

Sample #	Reaction Conditions		CO Conversion (%)		Product Selectivity (%)				
	On-Stream Time (hr)	GHSY ( $\text{hr}^{-1}$ )	Temp. (°C)	Total	To Hydrocarbon	$\text{C}_1$	$\text{C}_2$	$\text{C}_2^=$	$\text{C}_3^+$
1	1.00	200	250	31.54	31.44	22.15	4.05	0.00	73.80
2	17.50	200	250	48.97	58.55	22.12	2.84	0.00	75.04
3	25.00	200	250	53.72	53.20	23.53	3.10	0.00	73.37
4	41.00	200	250	50.47	49.76	25.88	3.39	0.00	70.73
5	47.00	200	250	49.82	49.06	25.67	3.39	0.00	70.94
6	114.75	200	250	44.33	43.25	26.91	3.85	0.00	69.24
7	120.50	200	250	44.49	43.40	26.55	3.69	0.00	69.76

TABLE 2  
 CO Conversion and Light Product Selectivities for  
 K<sub>2</sub>Ru<sub>6</sub>(CO)<sub>16</sub> Anthranilate Acid at - Catalyst #2  
 Activated one hour under vacuum at 250°C and one hour under H<sub>2</sub> at 250°C

Sample #	Reaction Conditions		CO Conversion (%)		Product Selectivity (%)				
	On-Stream Time (hr)	GHSV (hr <sup>-1</sup> )	Temp. (°C)	Total Hydrocarbon To	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub> = C <sub>3</sub> +		
1	2.00	200	250	42.83	41.98	19.22	2.87	0.00	77.91
2	4.50	200	250	45.54	44.71	21.01	2.77	0.00	76.22
3	23.00	200	250	34.63	22.74	22.74	3.26	0.00	74.00
4	24.00	200	250	37.20	37.20	20.84	2.56	0.00	76.60
5	27.00	200	250	35.53	35.53	22.60	2.65	0.00	74.75
6	47.25	200	250	33.33	33.33	22.94	2.63	0.00	74.43
7	53.00	200	275 <sup>a</sup>	51.06	50.73	37.55	4.77	0.00	57.68
8	70.50	200	275 <sup>a</sup>	59.97	59.45	42.01	5.54	0.00	52.45
9	75.00	200	275 <sup>a</sup>	59.68	59.18	42.05	5.53	0.00	52.42

<sup>a</sup> Pressure Rose to 180 psig

TABLE VII

CO Conversion and Light Product Selectivities for  
 RuCl<sub>3</sub> • Potassium Anthranilate- Catalyst #4  
 Activated one hour under vacuum at 250°C and one hour under H<sub>2</sub> at 250°C

Sample #	Reaction Conditions		CO Conversion (%)		Product Selectivity (%)		
	On-Stream Time (hr)	GHSV (hr <sup>-1</sup> )	Total	To Hydrocarbon	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub> = C <sub>3</sub> <sup>+</sup>
1	2.80	150	71.15	69.66	17.59	2.81	0.00 79.60
2	4.08	150	76.90	75.26	16.51	2.59	0.00 80.90
3	23.25	400	42.08	42.01	17.84	2.04	0.00 80.12
4	27.50	400	40.87	40.78	17.94	2.17	0.00 79.89
5	45.50	400	40.08	39.98	17.37	2.17	0.00 80.46
6	116.75	400	40.12	39.98	14.69	2.00	0.00 83.30

TABLE VIII

CO Conversion and Light Product Selectivities for  
 Ru<sub>3</sub>(CO)<sub>12</sub> • 2-amino phenol - Catalyst #5  
 Activated one hour under vacuum at 250°C and one hour under H<sub>2</sub> at 250°C

Sample #	Reaction Conditions		CO Conversion (%)		Product Selectivity (%)		
	On-Stream Time (hr)	GHSV (hr <sup>-1</sup> )	Total	To Hydrocarbon	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub> = C <sub>3</sub> +
1	0.75	200	16.37	16.37	43.37	5.35	0.00
2	2.00	200	47.99	47.99	40.41	4.91	0.00
3	3.00	200	39.05	39.05	41.05	4.66	0.00
4	4.00	200	33.94	33.94	41.73	4.32	0.00
5	5.00	200	37.57	37.47	43.00	4.32	0.00
6	20.72	200	37.97	37.97	47.32	3.88	0.00
7	24.72	200	38.10	38.10	47.15	4.07	0.00
8	27.00	200	56.21	55.92	71.23	6.09	0.00
9	29.00	400	49.07	48.96	75.47	5.76	0.00
10	45.50	400	44.45	44.38	74.75	5.42	0.00
11	46.50	400	44.78	44.70	73.95	5.33	0.00
12	50.00	400	28.67	28.67	45.17	3.89	0.00
13	51.00	400	26.40	26.40	49.62	4.30	0.00

TABLE IX

CO Conversion and Light Product Selectivities for  
 $H_2FeO_3(CO)_{13}$  • 2-amino pyridine - Catalyst #6  
 Activated one hour under vacuum and 1.25 hours under  $H_2$  at 250°C

Sample #	Reaction Conditions		CO Conversion (%)		Product Selectivity (%)			
	On-Stream Time (hr)	GHSY (hr <sup>-1</sup> )	Total	To Hydrocarbon	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub> =	C <sub>3</sub> +
		Temp. (°C)						
1	1.00	200	250	16.82	17.01	6.19	1.41	75.39
2	2.00	200	250	7.88	31.05	10.82	2.68	55.45
3	19.00	200	250	13.42	23.54	6.13	2.13	68.20
4	27.50	200	250	13.22	25.14	5.32	2.97	66.57
5	44.50	200	250	14.66	26.82	5.27	4.19	63.72
6	48.25	200	275	32.18	32.00	7.16	2.92	57.92
7	117.50	200	275	40.15	43.71	10.64	0.69	44.96
8	123.00	200	275	42.27	43.48	10.75	0.71	45.06



TABLE X

CO Conversion and Light Product Selectivities for  
 RuCl<sub>3</sub> • 2-amino pyridine - Catalyst #8  
 Activated one hour under vacuum and one hour under H<sub>2</sub> at 250°C

Sample #	Reaction Conditions		CO Conversion (%)		Product Selectivity (%)				
	On-Stream Time (hr)	GHSV (hr <sup>-1</sup> )	Temp. (°C)	Total	To Hydrocarbon	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub> =	C <sub>3</sub> +
1	0.72	200	250	20.29	20.05	18.79	2.56	0.00	78.65
2	1.67	200	250	28.30	27.82	19.74	2.32	0.00	77.94
3	2.66	200	250	26.54	26.22	20.16	1.99	0.00	77.85
4	19.70	200	250	15.81	15.81	23.07	0.00 <sup>a</sup>	0.00	76.93
5	23.95	200	250	16.48	16.48	21.63	2.54	0.00	75.83
6	43.95	200	250	16.07	16.07	20.44	1.88	0.00	77.68
7	45.45	200	275	30.54	30.41	41.55	3.63	0.00	54.82
8	47.45	200	275	33.40	33.28	41.29	4.52	0.00	54.19
9	48.45	200	275	33.07	32.95	42.63	4.76	0.00	52.61

<sup>a</sup> Trace ethane formed missed by integrator

TABLE XI

CO Conversion and Light Product Selectivities for  
 $\text{H}_2\text{FeRu}_3(\text{CO})_{12}$  • Dipyridyl - Catalyst #12  
 Activated one hour under vacuum and one hour under  $\text{H}_2$  at 250°C

Sample #	Reaction Conditions		CO Conversion (%)		Product Selectivity (%)				
	On-Stream Time (hr)	GHSV ( $\text{hr}^{-1}$ )	Temp. ( $^{\circ}\text{C}$ )	Total Hydrocarbon To	$\text{C}_1$	$\text{C}_2$	$\text{C}_2=$	$\text{C}_3+$	
1	2.25	200	250	18.08	16.67	27.21	4.46	0.00	68.33
2	4.00	200	250	20.93	19.98	26.95	3.96	0.00	69.09
3	5.00	200	250	23.66	22.73	19.83	4.47	0.00	75.70
4	21.17	200	250	20.93	20.59	24.19	2.75	0.00	73.06
5	26.50	200	250	18.54	18.17	28.19	3.40	0.00	68.41
6	45.50	200	250	18.06	17.82	28.81	3.77	0.00	67.42
7	51.00	200	250	18.26	18.01	28.17	3.37	0.00	68.36
8	117.50	200	250	17.82	17.71	29.25	2.94	0.00	67.81
9	122.50	200	275	49.66	48.28	35.78	5.22	0.00	59.00
10	125.00	200	275	51.03	49.57	35.86	4.77	0.00	59.37
11	144.00	200	275	51.92	50.62	33.83	4.60	0.00	61.57
12 <sup>a</sup>	149.00	200	250	18.58	18.31	29.63	4.74	0.00	65.63
13 <sup>a</sup>	165.50	200	250	39.12	38.89	22.41	2.26	0.00	75.33

TABLE XI (cont.)

Sample #	Reaction Conditions		CO Conversion (%)		Product Selectivity (%)			
	On-Stream Time (hr)	GHSV (hr <sup>-1</sup> )	Temp. (°C)	Total Hydrocarbon To	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub> =	C <sub>3</sub> <sup>+</sup>
14 <sup>a</sup>	167.50	200	250	38.70	22.47	2.30	0.00	75.23
15 <sup>b</sup>	171.50	200	250	15.48	26.37	3.12	0.00	70.49
16 <sup>b</sup>	189.50	200	250	16.06	26.15	2.68	0.00	71.17

<sup>a</sup> 350 psig (2413 kPa)

<sup>b</sup> 80 psig (552 kPa)

TABLE XII

CO Conversion and Light Product Selectivities for  
 $H_4Ru_4(CO)_{12}$  • Dipyriddy - Catalyst #13  
 Activated one hour under vacuum and one hour under  $H_2$  at 250°C

Sample #	Reaction Conditions		CO Conversion (%)		Product Selectivity (%)			
	On-Stream Time (hr)	GHSY (hr <sup>-1</sup> )	Total	To Hydrocarbon	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub> = C <sub>3</sub> +	
1	1.50	200	22.19	22.19	52.61	5.59	0.00	41.80
2	3.50	200	22.64	22.64	50.10	5.31	0.00	44.59
3	20.50	200	24.05	25.05	45.41	4.18	0.00	50.41
4	28.00	200	23.58	23.58	45.63	4.39	0.00	49.98
5	45.50	200	22.64	22.64	46.30	4.34	0.00	49.36
6	51.00	200	23.04	23.04	44.81	4.41	0.00	50.78
7	69.50	200	23.43	23.43	43.99	3.92	0.00	52.09
8	73.50	200	32.26	32.26	67.45	5.39	0.00	27.16

TABLE XIII

CO Conversion and Light Product Selectivities for  
 MnCo(CO)<sub>9</sub> • Dipyritydyl - Catalyst #14  
 Activated one hour under vacuum and one hour under H<sub>2</sub> at 250°C

Sample #	Reaction Conditions		CO Conversion (%)		Product Selectivity (%)				
	On-Stream Time (hr)	GHSY (hr <sup>-1</sup> )	Temp. (°C)	Total	To Hydrocarbon	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub> =	C <sub>3</sub> +
1	3.00	200	250	8.82	8.82	10.32	0.00 <sup>a</sup>	0.00 <sup>a</sup>	89.68
2	4.50	200	250	9.91	9.91	10.71	0.00 <sup>a</sup>	0.00 <sup>a</sup>	89.29
3	21.50	200	250	8.89	8.89	7.03	0.98	9.17 <sup>b</sup>	82.81
4	24.50	200	275	26.57	25.53	12.01	3.97	2.54	81.48
5	28.50	200	275	27.65	26.64	11.72	4.09	1.97	82.22
6	46.50	200	275	21.78	21.02	13.09	4.56	1.56	80.79
7	52.50	200	275	20.12	19.52	16.18	4.84	1.33	77.65
8	70.50	200	275	16.68	16.27	17.58	4.05	0.83	77.54

<sup>a</sup> Trace peaks present could not be distinguished from noise by integrator

<sup>b</sup> Overestimated due to noise

TABLE XIV

CO Conversion and Light Product Selectivities for  
 $\text{RuCl}_3 \cdot \text{Dipyridyl}$  - Catalyst #15  
 Activated one hour under vacuum and one hour under  $\text{H}_2$  at  $250^\circ\text{C}$

Sample #	Reaction Conditions		CO Conversion (%)		Product Selectivity (%)				
	On-Stream Time (hr)	$\text{GH}_2\text{S}^{-1}$ (hr $^{-1}$ )	Temp. ( $^\circ\text{C}$ )	Total	To Hydrocarbon	$\text{C}_1$	$\text{C}_2$	$\text{C}_2=$	$\text{C}_3+$
1	1.00	200	250	7.24	7.24	24.67	2.95	0.00	72.38
2	4.00	200	250	5.92	5.92	31.94	0.00	0.00	68.06
3	20.25	200	250	3.42	3.42	26.69	0.00	0.00	73.31
4	22.50	200	275	6.45	6.45	50.24	0.00	0.00	49.76
5	26.50	200	275	6.85	6.85	47.24	6.59	0.00	46.17
6	28.00	200	275	6.72	6.72	46.89	6.37	0.00	46.74
7	93.00	200	275	5.59	5.59	41.96	11.07	0.00	46.97
8 <sup>a</sup>	98.00	200	275	5.30	5.30	41.19	9.22	0.00	49.59
9 <sup>a</sup>	100.00	200	275	6.67	6.67	49.04	7.68	0.00	43.28

<sup>a</sup> Reactor Pressure = 250 psig (1724 kPa)

TABLE XV

CO Conversion and Light Product Selectivities for  
 $\text{Ru}_3(\text{CO})_{12}$  • Dipyrityl - Catalyst #16  
 Activated one hour under vacuum and 1.5 hours under  $\text{H}_2$  at 250°C

Sample #	Reaction Conditions		CO Conversion (%)		Product Selectivity (%)				
	On-Stream Time (hr)	GHSY ( $\text{hr}^{-1}$ )	Temp. (°C)	Total	To Hydrocarbon	$\text{C}_1$	$\text{C}_2$	$\text{C}_2=$	$\text{C}_3+$
1	3.33	200	250	38.95	38.95	42.73	4.97	0.00	52.30
2	6.67	200	250	39.36	39.36	40.09	4.64	0.00	55.27
3	24.50	200	250	38.77	38.77	39.04	4.33	0.00	56.63
4	28.00	200	275	50.10	50.02	56.24	6.25	0.00	37.51
5	30.33	200	275	53.38	53.37	58.75	6.66	0.00	34.57
6	118.91	400	275	56.73	56.67	61.87	6.07	0.00	32.06
7	120.64	400	275	56.90	56.86	61.41	6.03	0.00	32.56
8	124.39	400	250	47.78	47.78	32.78	3.49	0.00	63.73
9	125.74	400	250	50.51	50.51	31.46	3.29	0.00	65.25
10	142.92	400	250	56.53	56.53	28.30	2.96	0.00	68.74
11	149.85	400	250	57.05	57.05	28.00	2.88	0.00	69.12
12	172.93	400	225	43.84	43.84	12.38	0.74	0.00	86.88

TABLE XV (cont.)

Sample #	Reaction Conditions		CO Conversion (%)		Product Selectivity (%)				
	On-Stream Time (hr)	GHSY (hr <sup>-1</sup> )	Temp. (°C)	Total	To Hydrocarbon	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub> =	C <sub>3</sub> +
13	191.13	400	225	50.23	50.23	11.24	0.72	0.00	88.04
14	193.35	400	225	50.29	50.29	11.27	0.69	0.00	88.04
15	196.35	400	175	13.58	13.58	1.32	0.00	0.00	98.68
16	214.93	400	175	11.60	11.60	1.63	0.00	0.00	98.37



TABLE XVI

CO Conversion and Light Product Selectivities for  
 RuCl<sub>3</sub> • Dipyridyl - Catalyst #17  
 No activation other than that noted on Table I

Sample #	Reaction Conditions		CO Conversion (%)		Product Selectivity (%)				
	On-Stream Time (hr)	GHSV (hr <sup>-1</sup> )	Temp. (°C)	Total	To Hydrocarbon	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub> =	C <sub>3</sub> <sup>+</sup>
1	2.75	200	250	6.04	6.04	20.95	0.00	0.00	79.05
2	6.83	200	250	6.11	6.11	20.45	0.00	0.00	79.55
3	27.16	200	250	5.99	5.99	18.35	0.00	0.00	81.65
4	29.33	200	275	12.73	12.73	39.62	5.41	0.00	54.97
5	120.25	200	275	20.11	20.11	39.23	3.96	0.00	56.80
6	144.21	200	275	21.67	21.67	37.14	3.84	0.00	59.02
7	168.23	200	275	22.55	22.55	37.62	4.05	0.00	58.33
HYDROGEN TREATMENT: 250°C, 50 PSIG, 40 SCCM*, ONE HOUR									
8	17.75	200	250	19.69	19.69	18.41	2.12	0.00	79.73
9	20.02	200	250	19.64	19.64	18.22	0.00 <sup>a</sup>	0.00	81.78
10	24.27	200	275	28.98	28.98	42.17	4.64	0.00	53.19
11	41.60	200	275	29.55	29.46	40.93	4.25	0.00	54.82

<sup>a</sup> Trace Ethane formed, missed by integrator  
 \* Standard Cubic Centimeters per Minute

TABLE XVII

CO Conversion and Light Product Selectivities for  
Ru on Al<sub>2</sub>O<sub>3</sub> - Comparative

Sample #	Reaction Conditions		CO Conversion (%)		Product Selectivity (%)				
	On-Stream Time (hr)	GHSV (hr <sup>-1</sup> )	Temp. (°C)	Total Hydrocarbon To	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub> =	C <sub>3</sub> +	
1	0.50	200	250	54.80	47.07	70.94	3.14	0.00	25.92
2	1.00	200	250	58.61	50.71	66.41	3.40	0.00	30.19
3	18.50	200	250	95.39	91.58	7.75	1.71	0.00	90.54
4	21.00	400	250	87.87	85.73	9.22	1.86	0.00	88.92
5	24.50	400	225	70.65	69.85	8.75	1.55	0.15	89.55
6	42.00	400	225	57.97	57.86	8.60	0.86	0.00	90.54
7	45.00	400	225	53.25	53.23	9.70	1.03	0.00	89.27
8	48.25	400	225	53.28	53.27	9.63	0.92	0.00	89.45

For a comparison with a conventional Fisher-Tropsch catalyst, Ru on  $\text{Al}_2\text{O}_3$  was prepared by a conventional literature procedure and tested in the reactor system. From Table XVII it can be seen that the conventional Ru/ $\text{Al}_2\text{O}_3$  catalyst was more active at  $250^\circ\text{C}$  than any polymer bound catalyst. However, at  $225^\circ\text{C}$  (53% conversion), the  $\text{Ru}_3(\text{CO})_{12}$  catalyst #16 was nearly as active ( $\approx 50\%$  conversion). Thus polymer bound catalysts can achieve acceptable Fischer-Tropsch activity at lower temperatures, thus saving energy. Tables XVIII through XXVI set out product selectivities for selected catalysts at different times during a run and at different GHSV, temperatures and pressures. It is evident from the data that Catalyst #14 ( $\text{MnCo}(\text{CO})_9$ -Dipyridyl) and Catalyst #6 ( $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ -2Amino Phenol) produced a substantial amount of olefins.

20

25

30

35

TABLE XVIII

5  $C_1 - C_9+$  Product Selectivities and Olefin Fractions for  
 $Ru_3(CO)_{12}$  • Anthranilic Acid at 250°C, 1034 kPa (150 psig)  
 200 hr<sup>-1</sup> - Catalyst #3

	Carbon Number						
	1	2	3	4	5	6-8	9+
10 Carbon %	24.20	4.56	6.33	6.09	3.84	0.67	54.31
Olefin %	---	0.00	10.18	24.72	12.50	NA	NA

15

TABLE XIX

20  $C_1 - C_9+$  Product Selectivities and Olefin Fractions for  
 $H_2FeRu_3(CO)_{13}$  • Anthranilic Acid at 250°C  
 1034 kPa (150 psig), 200 hr<sup>-1</sup>,  
 After 23 hours on stream - Catalyst #1

	Carbon Number						
	1	2	3	4	5	6-8	9+
25 Carbon %	22.7	3.05	3.08	3.08	2.12	0.59	65.38
Olefin %	---	17.56	36.02	38.48	37.39	NA	NA

30

35

TABLE XX

5  $C_1 - C_9+$  Product Selectivities and Olefin Fractions for  
 $K_2Ru_6(CO)_{16} \cdot$  Anthranilic Acid at 250°C, 1034 kPa (150 psig)  
 200 hr<sup>-1</sup> After 25 hours on stream - Catalyst #2

	Carbon Number						
	1	2	3	4	5	6-8	9+
10 Carbon %	20.84	2.56	1.71	2.04	1.91	0.96	69.98
Olefin %	---	0.00	40.38	43.94	47.61	NA	NA

15

TABLE XXI

20  $C_1 - C_9+$  Product Selectivities and Olefin Fractions for  
 $H_2FeOs_3(CO)_{13} \cdot$  2Aminopyridine  
 at 1034 kPa (150 psig) - Catalyst #6.

	Carbon Number						
	1	2	3	4	5	6-8	9+
25 Carbon %	26.82	9.46	13.54	8.32	3.05	0.42	38.39
Olefin %	---	51.47	63.05	58.85	40.30	NA	NA

30

35

TABLE XXII

C<sub>1</sub>- C<sub>9</sub>+ Product Selectivities and Olefin Fractions for  
 $H_4Ru_4(CO)_{12}$  • Dipyriddy1 at 250°C - Catalyst #13

5

	Carbon Number						
	1	2	3	4	5	6-8	9+
Carbon %	43.99	3.92	4.56	4.08	3.16	2.96	37.33
Olefin %	---	0.00	12.63	24.65	13.53	NA	NA

10

15

TABLE XXIII

C<sub>1</sub>- C<sub>9</sub>+ Product Selectivities and Olefin Fractions for  
 $MnCo(CO)_9$  • Dipyriddy1 at 275°C - Catalyst #14

20

	Carbon Number						
	1	2	3	4	5	6-8	9+
Carbon %	11.72	6.06	7.33	4.87	3.28	1.48	65.26
Olefin %	---	35.12	82.12	78.56	77.17	NA	NA

25

30

35

TABLE XXIV

$C_1$ - $C_9$ + Product Selectivities and Olefin Fractions for  
 $RuCl_3 \cdot$  Dipyriddy at 275°C - Catalyst #15

5

---

	Carbon Number						
	1	2	3	4	5	6-8	9+
Carbon %	37.62	4.05	4.07	3.47	3.11	[52.68] <sup>a</sup>	
Olefin %	---	25.88	47.75	56.31	60.07	NA	

<sup>a</sup>  $C_{6-8}$  and  $C_{9+}$  peaks combined

15

TABLE XXV

$C_1$ - $C_9$ + Product Selectivities and Olefin Fractions for  
 $Ru_3(CO)_{12} \cdot$  Dipyriddy at 250°C - Catalyst #16

20

---

	Carbon Number						
	1	2	3	4	5	6-8	9+
Carbon %	28.00	2.88	5.13	4.91	2.83	2.54	53.71
Olefin %	---	0.00	38.02	44.82	24.02	NA	NA

25

---

30

35

TABLE XXVI

C<sub>1</sub>- C<sub>9</sub>+ Product Selectivities and Olefin Fractions for  
RuCl<sub>3</sub> • Dipyridyl at 225°C (25 hours on stream) Catalyst#17

5

	Carbon Number						
	1	2	3	4	5	6-8	9+
Carbon %	9.63	1.16	9.65	11.08	5.45	1.28	61.75
Olefin %	---	20.07	68.37	63.90	59.20	NA	NA

10

The discovery of the instant invention can be more fully appreciated when one realizes that modification of the polymer bound catalyst can be made to achieve certain desired results from the vapor phase Fisher-Tropsch reaction. Tables XXVII and XXVIII demonstrate that the metal affects selectivity.

20

TABLE XXVII

Methane Selectivity Comparison for  
Three Ru • Dipyridyl Catalysts at 250°C

25

#	Catalyst	On-Stream Time (hr)	Methane Selectivity (%)
30	17 RuCl <sub>3</sub> -	27.16	18.35
	16 Ru <sub>3</sub> (CO) <sub>12</sub> -	24.50	39.04
	13 H <sub>4</sub> Ru <sub>4</sub> (CO) <sub>12</sub> -	28.00	45.63

35



TABLE XXVIII

$C_2-C_5$  Olefin Fraction Comparison for  
Five Dipyridyl Catalysts

5

10 #	Catalyst	On Stream Time (hr)	Temp (oC)	Olefin Percent (%)			
				2	3	4	5
16	$Ru_3(CO)_{12}$	148.00	250	0.00	38.02	44.82	24.02
15	$RuCl_3$	169.45	275	25.88	47.75	56.31	60.07
13	$H_4Ru_4(CO)_{12}$	72.38	250	0.00	12.63	24.65	13.53
12	$H_2FeRu_3(CO)_{13}$	28.32	250	0.00	16.76	26.85	14.39
20	$MnCo(CO)_9$	24.80	275	35.12	82.18	78.56	77.17

25

30

35

Table XXIX sets out data on MnCo catalysts polymer supported vs. conventionally supported. The conventional catalyst data is from the literature.

5

10

15

20

25

30

35

TABLE XXIX  
 Comparison of Polymer Bound and Conventional MnCo Catalysts for  
 Light Olefins Production from Synthesis Gas

-----Catalyst-----		-----Reaction-----			-----Results-----			
#	Components	Total Metal Wt %	Mn/Co Ratio	Temp. (°C)	Press (psig)	Space Velocity (cm <sup>3</sup> /sec/gm cat.)	CO Conv. (%)	C <sub>2</sub> -C <sub>4</sub> Olefin Percent
14	MnCo(CO) <sub>9</sub> - Dipyridyl	6 <sup>a</sup>	1/1 <sup>a</sup>	275	150	7.4	20	65.57
	MnCo-Al <sub>2</sub> O <sub>3</sub>	27	1/2	242	100	0.42	36.0	0
	MnCo-Al <sub>2</sub> O <sub>3</sub> with K <sub>2</sub> O	27	1/2	279	100	0.42	3.0	80.77

<sup>a</sup> Estimated

### Deactivation of Catalyst

The novel catalysts of the invention have demonstrated Fischer-Tropsch activity for extended periods of time (in excess of 200 hours) without significant deactivation.

5 Most significantly, one polymer bound catalyst (Catalyst #6, Table IX) demonstrated increasing activity with time on stream.

Catalyst #16 was submitted for elemental analysis prior and subsequent to the run set out in Table XV. It  
10 was determined that ruthenium was not lost during the Fischer-Tropsch reaction. This is very important since the catalyst still contained all of the valuable ruthenium metal. The metal may be recovered by burning the resin.

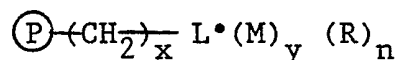
In the past, only conventional catalysts were used for  
15 the vapor phase Fischer-Tropsch reaction. Conventional catalysts generally are supported on either silica or alumina if they are supported at all. They are synthesized by precipitation or fusion techniques and contain no ligand bridges thus making it difficult to obtain small metal  
20 clusters which are desired for the Fischer-Tropsch reaction.

It is clear from these results that the catalytic system of the invention is sensitive and that the exact constitution thereof is critical in obtaining the desired  
25 results. The instant invention provides a significant advance in the Fischer-Tropsch reaction since the reaction conditions are mild and the resultant products are not contaminated with catalyst. This invention being thus described, it will be obvious that the same may be varied  
30 in many ways. Such variations are not to be regarded as a departure from the scope of the invention, and all such modifications are intended to be included within the scope of the following claims.

WHAT WE CLAIM IS:

1) A process for the conversion of synthesis gas to hydrocarbons which comprises contacting said synthesis gas with a catalyst in the vapor phase at a temperature from 175° to 300°C and a pressure of at least 1000 kPa, the improvement characterized by a catalyst represented by the structural formula

10



15

wherein  $\textcircled{\text{P}}$  represents a crosslinked macroreticular polystyrene resin which has a crosslink density of at least 5%;

x is 0 or 1;

20

L represents a ligand selected from the group consisting of dipyridyl, 2-aminopyridine, 2-amino phenol, 2-imino pyridine, sodium anthranilate, potassium anthranilate and anthranilic acid;

y is an integer from 1 through 8;

25

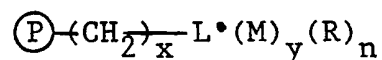
when y equals 1, M represents a Group VIII metal from the Periodic Table and when y is from 2 through 8, M represents one or more metals selected from the group consisting of Group VIII metals from the Periodic Table, hydrogen, manganese, potassium and sodium;

R represents a carbonyl or a halogen radical; and

n represents an integer from 0 through 24.

30

2) Novel polymer-supported metal complexes, characterized by the formula:



35

wherein  $\textcircled{\text{P}}$  represents a crosslinked macroreticular polystyrene resin which has a crosslink density of at least 5%;

x is 0 or 1;

L represents a ligand selected from the group consisting of dipyridyl, 2-aminopyridine, 2-amino phenol, 2-imino pyridine, sodium anthranilate, potassium anthranilate and anthranilic acid;

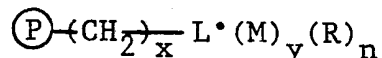
y is an integer from 1 through 8;

when y equals 1, M represents a Group VIII metal from the Periodic Table and when y is from 2 through 8, M represents one or more metals selected from the group consisting of Group VIII metals from the Periodic Table, hydrogen, manganese, potassium and sodium;

R represents a carbonyl or a halogen radical; and

n represents an integer varying from 0 through 24.

3) A heterogeneous catalyst for Fischer-Tropsch reactions conducted in the vapor phase at a temperature from 175°C to 300°C, at a pressure of at least atmospheric, the improvement comprising a catalyst characterized by the formula:



wherein  $\textcircled{\text{P}}$  represents a crosslinked macroreticular polystyrene resin which has a crosslink density of at least 5%;

x is 0 or 1;

L represents a ligand selected from the group consisting of dipyridyl, 2-aminopyridine, 2-amino phenol, 2-imino pyridine, sodium anthranilate, potassium anthranilate and anthranilic acid;

y is an integer from 1 through 8;

when y equals 1, M represents a Group VIII metal from the Periodic Table and when y is from 2 through 8, M represents one or more metals selected from the group consisting of Group VIII metals from the Periodic Table, hydrogen, manganese, potassium and sodium;

R represents a carbonyl or a halogen radical; and

n represents an integer varying from 0 through 24.

4) The heterogeneous catalyst of claim 3 characterized in that the ligand is dipyridyl; the metal compound is  $\text{RuCl}_3$ ; and  $\textcircled{\text{P}}$  is a 10/60/30 chloromethylstyrene/styrene/divinyl- benzene resin.

5) The heterogeneous catalyst of claim 3 characterized in that the ligand is dipyridyl, the metal  $\text{MnCo}(\text{CO})_9$  and  $\textcircled{\text{P}}$  is a 10/60/30 chloromethylstyrene/styrene/divinylbenzene resin.

6) A process according to claim 1 characterized in that L is dipyridyl and M is  $\text{Ru}_3(\text{CO})_{12}$ .

7) A process according to claim 1 characterized in that L is 2-amino phenol, and M is  $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ .

8) A process according to claim 1 characterized in that the temperature is from  $225^\circ$  to  $250^\circ\text{C}$ .

9) A novel polymer supported metal complex according to claim 2 characterized in that L is anthranilic acid and M is  $\text{Ru}_3(\text{CO})_{12}$ .

10) A novel polymer supported metal complex according to claim 2 characterized in that L is dipyridyl and M is  $\text{MnCo}(\text{CO})_9$ .