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(54) Titre : COMPOSITION CATALYTIQUE UTILE DANS LA REACTION DE FISCHER-TROPSCH  
(54) Title: CATALYTIC COMPOSITION USEFUL IN THE FISCHER TROPSCH REACTION

(57) **Abrégé/Abstract:**

Catalytic composition comprising a larger quantity of Cobalt, in metal form or in the form of a derivative, and smaller quantities of Ruthenium and Tantalum, in metal form or in the form of a derivative, the above elements being dispersed on a carrier selected from the oxides of at least one of the elements selected from Si, Ti, Al, Zn, Sn, Mg.



CATALYTIC COMPOSITION USEFUL IN THE FISCHER TROPSCH  
REACTION

Abstract

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tive, and smaller quantities of Ruthenium and Tantalum,  
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CATALYTIC COMPOSITION USEFUL IN THE FISCHER TROPSCH  
REACTION

The present invention relates to a catalytic composition which can be used in effecting the preparation reaction of hydrocarbons by means of the Fischer-Tropsch synthesis; it also relates to the catalytic process for the preparation of hydrocarbons which comprises its use.

In particular, the present invention relates to a new catalytic composition containing cobalt, promoted by ruthenium and tantalum, obtained by reacting derivatives of the above elements in the presence of a suitable carrier consisting of an oxidic material as illustrated hereunder. This composition is effective in the conversion of the synthesis gas to hydrocarbon products, with a high selectivity to liquid and waxy, essentially linear paraffinic products.

The selection of cobalt as main constituent of the active phase is due to the fact that this favours the

formation of saturated linear hydrocarbons with a high  
molecular weight, with respect for example to more  
economical systems based on iron. The use of higher  
temperatures on the one hand favours the conversion of  
5 the synthesis gas but on the other hand hinders the  
formation of higher hydrocarbons to the advantage of  
lighter fractions.

The known art mentions numerous examples of  
catalysts based on cobalt used for the synthesis of  
10 paraffinic products with different distributions.

From the first works of Fischer in 1932 (H.H.  
Storch, N. Golumbic, R.B. Anderson, "The Fischer  
Tropsch and Related Synthesis", John Wiley & Son, Inc.,  
New York, 1951), which describe the development of a  
15 Co/ThO<sub>2</sub>/MgO system supported on kieselguhr, up to the  
present day, patented systems based on cobalt are  
essentially: Co/Mg/ThO<sub>2</sub> supported on kieselguhr (1954,  
Reinpruessen A.G.), Co/MgO supported on bentonite  
(1958, M.W. Kellog), Co/Th/Mg (1959, Rurchemie), Co/Th  
20 supported on Silica-gel (1960, Esso Res. & Eng.),  
Co/Mg/Zr/Kieselguhr (1968, SU-A-660.324, Zelinskii  
INST.), Co/Ru/Kieselguhr (1976, US-A-4.088.671 GULF),  
Co/Zr/SiO<sub>2</sub> (1980, GB-A-2.073.237, Shell), Co/Ru support-  
ed on Titania (1988, US-A-4.738.948 Exxon), Co/Re/REO,K  
25 supported on Alumina (1988, EP-A-313.375, Statoil),

Co/Mo,W/K,Na/SiO<sub>2</sub> (1991, GB-A-2.258.414, IFP),  
Co/Ru/Cu/K,Sr/SiO<sub>2</sub> (1993, EP-A-581.619, IFP).

The effect of the promoters on the system based on cobalt is manifold but can be subdivided however into  
5 various groups in relation to the function of the promoter itself (B. Jager, R. Espinoza in Catalysis Today 23, 1995, 21-22).

For example promoters such as K, Na, Mg, Sr, Cu, Mo, W and metals of group VIII basically increase the  
10 activity. Ru, Zr, rare earth oxides (REO), Ti increase the selectivity to hydrocarbons with a high molecular weight. Ru, REO, Re, Hf, Ce, U and Th favour the regeneration of the catalyst. Among the various promoters ruthenium is certainly the most widely used.

15 The most recent evolution in catalytic systems for the synthesis of hydrocarbons has aimed at increasing both their activity, in terms of conversion of the reaction reagents, and the selectivity to linear hydrocarbons with a high molecular weight. This has  
20 been made possible by the identification of various promoters to be coupled with cobalt, some of which are mentioned in the brief review above.

This evolution has been developed mainly in the last twenty years. In fact, the increase in the price  
25 of crude oil in the 1970s' motivated the exploration of

other ways of producing liquid fuels and chemicals, one possibility being the transformation of hydrocarbon products with a high molecular weight (waxes) obtained by the Fischer-Tropsch synthesis.

5       As far as the Fischer-Tropsch synthesis is concerned, this can refer to the hydrogenation process of carbon monoxide to produce higher hydrocarbons and oxygenated molecules with a prevalently linear chain.

10       The wide range of catalysts and modifications of these indicated in the known art and the wide range of operating conditions for the reduction reaction of the carbon monoxide with hydrogen allows considerable flexibility in the selectivity of the products, products ranging from methane to heavy waxes with oxygenat-

15       ed products as by-products. The distribution of the products can be described by the known growth mechanism deduced from a polymerization kinetics determined by Anderson Shultz and Flory (P. Biloen, W.M.H. Sachtler, Advance in Catalysis, Vol. 30, pages 169-171, Academic

20       Press, New York, 1981; R.B. Anderson, Catalysis, Vol. IV, P.H. Emmett ed., Reinhold, New York, 1956). In accordance with this mechanism, with the assumption of restricting the range of products to maximize for example the C<sub>5</sub>-C<sub>11</sub> fraction (gasoline-range, about 56%)

25       selectivities of methane and the gaseous fraction

(C<sub>2</sub>-C<sub>4</sub>) of more than 42% would be obtained. In addition the range of products obtained would be essentially paraffinic-linear and olefinic with a low octane number. The only possibility therefore of deviating  
5 from the nature imposed by the Fischer-Tropsch polymerization kinetics is to identify catalytic systems which do not obey said kinetics. An example are systems which basically combine the properties of Fischer-Tropsch catalysts with the shape selectivity of zeolites  
10 (US-A-4.157.338).

The possibility of maximizing the selectivity to heavy liquids and waxes (essentially paraffinic and without sulfur) offers on the other hand many advantages. More specifically, by maximizing the paraffinic  
15 liquid-solid fraction it is possible to minimize the selectivity to methane and gas fraction, one of the greatest problems in the case of direct synthesis to gasolines (C<sub>5</sub>-C<sub>11</sub>) and light olefins (C<sub>2</sub>-C<sub>4</sub>). By subsequent treatment (e.g. hydrocracking) of this liquid-  
20 solid fraction, a high quality medium distillate is obtained compared to the middle distillate obtained from petroleum (Ball J., Gas. Matters, April 27, 1989, pages 1-8). Finally catalysts with a reduced water gas shift activity and low reaction temperature, such as  
25 catalysts based on cobalt, have low selectivities to

CO<sub>2</sub>, above all if compared to catalysts based on iron.

Among the factors capable of influencing the distribution of the products, apart from the nature of the catalyst, the reaction conditions should also be taken into consideration. In general, an increase in the temperature causes a lowering of the selectivity to higher hydrocarbons (C<sub>12+</sub>, C<sub>22+</sub>) and a higher conversion of the synthesis gas. Viceversa an increase in the hourly volumetric flow-rate of the synthesis gas (GHSV) determines a decrease in both the conversion of the reagent gas and the probability of propagation of the hydrocarbon chain on the surface of the catalyst, in other words a decrease in the selectivity to higher hydrocarbons. There are therefore limits of selectivity and conversion which impose precise ranges of practicality to the reaction conditions to be adopted.

The present invention therefore relates to an improved catalytic composition based on cobalt with respect to those of the prior art, as it allows conversions of the mixture of CO and H<sub>2</sub> to be obtained (using SiO<sub>2</sub> as carrier) in the presence of or without CO<sub>2</sub>, known as synthesis gas, into linear saturated hydrocarbons containing from 75% to 85% by weight of C<sub>5+</sub>, from 38% to 52.0% by weight of C<sub>14+</sub>, together with selectivities to methane of less than 11.5% and with a produc-

tivity of  $C_2$ , of more than  $310 \text{ gC}_2/\text{Kg}_{\text{cat}} \cdot \text{h}$ .

In accordance with this, the present invention relates to a catalytic composition comprising a greater quantity of Cobalt, in metal form or in the form of a derivative, and smaller quantities of Ruthenium and Tantalum, in metal form or in the form of a derivative, preferably in the form of an oxide, the above elements being dispersed on a carrier selected from the oxides of at least one of the elements selected from Si, Ti, Al, Zn, Zr, Sn, Mg.

The content of the above elements in the final catalyst, expressed as metal form of these and defined as weight percentage with respect to the weight of the catalyst, varies within the following ranges:

Element	Range	Preferred range
COBALT	1-50	5-35
RUTHENIUM	0.05-5	0.1-3
TANTALUM	0.05-5	0.1-3

Thus, the invention as claimed more specifically relates to a catalytic composition comprising:

- from 5 to 50% of cobalt, in metal form or in the form of a derivative;
  - from 0.05 to 5% of ruthenium, in metal form or in the form of a derivative;
- and

- from 0.05 to 5% of tantalum in metal, form or in the form of a derivative;

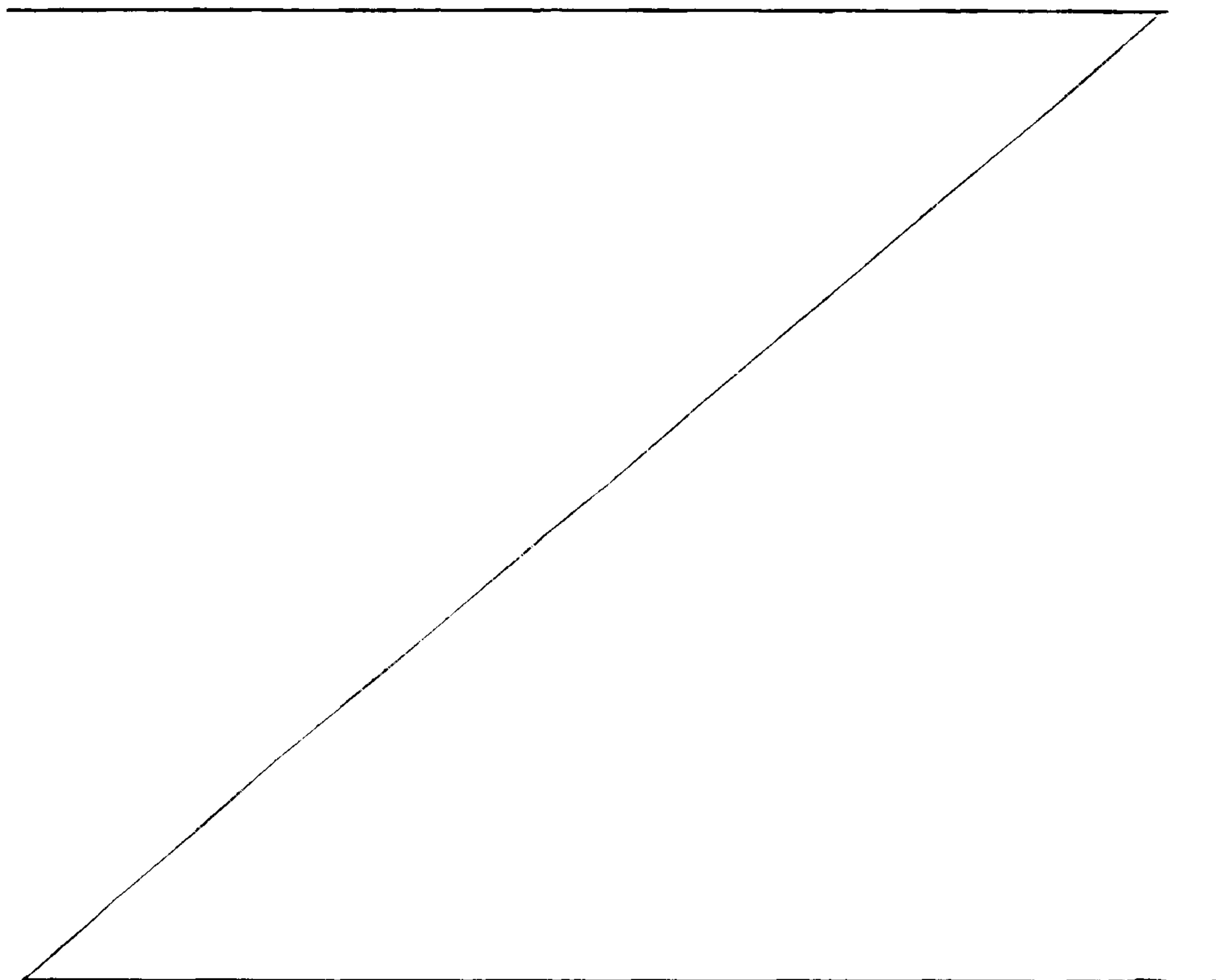
the cobalt being present in a greater amount than ruthenium and in a greater amount than tantalum, the above elements being dispersed on a carrier selected from the oxides of at least one of the elements selected from Si, Ti, Al, Zn, Sn and Mg;

the percentages being expressed by weight of the element in the metal form based on the weight of the catalytic composition.

More preferably, the cobalt used in the catalytic composition of the invention is present in a quantity of from 12 to 50% by weight. Even more preferably, cobalt is used in a quantity of from 12 to 35% by weight.

10

As mentioned above, the inert carrier of the catalytic composition of the present invention is selected from the oxides of at least one of the elements selected from Si, Ti, Al, Zn, Zr, Sn, Mg, and relative mixtures. The inert carrier which can be used



is independent of the crystallographic structure of the above oxides. For example, all types of alumina such as  $\gamma$ ,  $\eta$ ,  $\delta$ ,  $\theta$ ,  $\kappa$ ,  $\alpha$ , and relative mixtures, can be used.

5           When the inert carrier essentially consists of  $\text{TiO}_2$ , the latter can either be in the form of rutile and/or anatase.

In the preferred embodiment, the inert carrier essentially consists of silica.

10           The cobalt, ruthenium and tantalum can be deposited using various methods well-known to experts in the field such as, for example, ion exchange, impregnation, dry impregnation (also called incipient imbibition), precipitation and coprecipitation, gelation and mechanical mixing.

In the preferred embodiment, the cobalt is deposited on the inert carrier using the dry impregnation technique. According to this method the inert carrier is put in contact with a volume of solution, preferably aqueous, of a salt of cobalt practically equal to the pore volume.

25           With respect to the deposition of ruthenium and tantalum, this is preferably carried out with the impregnation technique. According to this method the inert carrier, onto which the cobalt was previously

deposited, is totally covered with a solution, preferably non-aqueous, of salts of ruthenium and/or tantalum.

A further object of the present invention therefore relates to a process for the preparation of the catalytic composition of the present invention which  
5 comprises a first deposition on the inert carrier, preferably via dry impregnation, of a Cobalt salt and subsequently a second and third deposition of a Ruthenium salt and Tantalum salt, preferably via impregna-  
10 tion; the second and third impregnation possibly being carried out inversely or contemporaneously; the above inert carrier preferably being silica.

In the preferred embodiment, the process of the present invention comprises the following steps:

- 15 a) production of a first catalytic precursor (A) containing Cobalt and at least part of the inert carrier, by dry deposition of Cobalt on the inert carrier; subsequent calcination, reduction and passivation of the inert carrier containing Cobalt;
- 20 b) production of a second catalytic carrier (B) containing Cobalt, Ruthenium and at least part of the inert carrier, by deposition of ruthenium on the first catalytic precursor (A) according to the impregnation technique; subsequent calcination, reduction and  
25 passivation of the inert carrier containing Cobalt and

Ruthenium;

c) production of the final catalytic composition by deposition of Tantalum on the catalytic precursor (B) according to the impregnation technique, subsequent  
5 calcination, reduction and passivation of the inert carrier containing Cobalt, Ruthenium and Tantalum; steps (b) and (c) possibly being carried out inversely or contemporaneously.

Some of the operating details will be more evident  
10 on reading the experimental examples provided, whose technicality however, should not be considered as limiting the catalytic compositions of the present invention.

As already specified, the present invention also  
15 relates to a process for the preparation of hydrocarbons from synthesis gas in the presence of the catalytic system described above.

The conditions for using these catalysts are, in turn, those known in the art for the embodiment of the  
20 Fischer-Tropsch synthesis.

The conversion of the synthesis gas into hydrocarbons takes place at a pressure normally of between 1 and 150 bars, preferably from 10 to 100 bars, at a temperature generally within the range of 150 to 350°C,  
25 preferably from 170 to 300°C, even more preferably

from 200°C to 240°C. The hourly volumetric rate is generally from 100 to 20,000, preferably from 400 to 5,000, volumes of synthesis gas per volume of catalyst per hour. The ratio H<sub>2</sub>/CO in the synthesis gas is generally from 1:1.5 to 5:1, preferably from 1.2:1 to 2.5:1.

The catalyst can be used in the form of fine powder (10-700 μm approximately) or in the form of particles having an equivalent diameter of from 0.7 to 10 mm, respectively in the presence of a liquid phase (under the operating conditions) and a gaseous phase, or a gaseous phase. The liquid phase can consist of at least one hydrocarbon having at least 5, preferably at least 15, carbon atoms per molecule. In the preferred embodiment, the liquid phase essentially consists of the same reaction product.

For purely illustrative purposes, it can be mentioned that the catalysts of the present invention can be used in a fixed bed reactor, fed in continuous with a mixture of CO and H<sub>2</sub> and operating under the following conditions:

- reaction temperature: 200-240°C
- reaction pressure: 20 bars
- space velocity (GHSV): 500-1500 h<sup>-1</sup>
- 25 - mixture H<sub>2</sub>/CO: 2/1

The reaction temperature is set so as to obtain a conversion at least 45% higher than the volume of the fed carbon monoxide (conv.CO%).

Following these conditions, the catalysts prepared in examples 1 to 4 were evaluated, whose compositions are summarized in table 1.

The results of the reactivity tests are indicated in tables 2 and 3.

**Example 1 Reference Catalyst A**

(Co/Ru/SiO<sub>2</sub> 15% Co, 0.2% Ru)

A silica carrier (having a surface area of 520 m<sup>2</sup>/g, specific pore volume of 0.8 m<sup>3</sup>/g, average particle diameter of 0.5 mm, specific weight of 0.42 g/ml) is dry impregnated with a nitric solution of Co(NO<sub>3</sub>)<sub>2</sub>\*6H<sub>2</sub>O in such quantities as to obtain a percentage of Co equal to 15% by weight with respect to the total. The silica thus impregnated is dried at 120°C for 16 hours, calcined at 400°C in air for 4 hours, then treated in a stream of H<sub>2</sub> at a space velocity (GHSV) of 1000 h<sup>-1</sup> inside a tubular reactor at 400°C for 16 hours. The sample thus reduced is passivated in a mixture of (1%)O<sub>2</sub>/(99%)N<sub>2</sub> with GHSV of 1000 h<sup>-1</sup> for 2 hours at room temperature.

A 7.5 10<sup>-3</sup> M solution of Ru(NO<sub>3</sub>)<sub>3</sub>\*xH<sub>2</sub>O obtained with the following procedure: precipitation in the form of

hydroxide at pH=7.2 of  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ , subsequent elimination of the chlorides, redissolution in conc.  $\text{HNO}_3$  and dilution in  $\text{CH}_3\text{COCH}_3$  in a ratio 1:250 v/v, is added to the monometallic sample  $\text{Co/SiO}_2$ .

5        The acetone solution of ruthenium is added to the sample in such a quantity as to have 0.2% of Ru by weight with respect to the total. The slurry is left under stirring for 2 hours and then dried under vacuum at 40°C. This is followed by a calcination phase in air  
10 at 350°C for 4 hours and reduction/passivation analogous to that described above.

**Example 2 Catalyst B**

(Co/Ru/Ta/SiO<sub>2</sub> = 15% Co, 0.2% Ru, 0.2% Ta).

For the preparation of the catalyst B, a solution  
15 of  $\text{Ta}(\text{EtO})_5$  0.01 M in ethanol is added to 50 g of catalyst A in such a volume as to obtain a final weight percentage of tantalum equal to 0.2%.

The suspension thus obtained is left under stirring for two hours and then dried under vacuum at 40°C.

20        The sample is calcined at 350°C for 4 hours in air, reduced to 400°C in  $\text{H}_2$  with GHSV equal to 1000  $\text{h}^{-1}$  and passivated in (1%) $\text{O}_2$ /(99%) $\text{N}_2$  with GHSV of 1000  $\text{h}^{-1}$  at room temperature.

**Example 3 Catalyst C**

25 (Co/Ru/Ta/SiO<sub>2</sub> = 15% Co, 0.2% Ru, 0.5% Ta).

The preparation of the catalyst C differs from that described in example 2 in the use of a solution of  $\text{Ta}(\text{EtO})_5$  0.01 M in ethanol in such a volume as to obtain a final weight percentage of tantalum equal to 0.5%.

5 **Example 4 Catalyst D**

(Co/Ru/Ta/SiO<sub>2</sub> = 15% Co, 0.2% Ru, 0.9% Ta).

The preparation of the catalyst D differs from that described in example 2 in the use of a solution of  $\text{Ta}(\text{EtO})_5$  0.01 M in ethanol in such a volume as to obtain  
10 a final weight percentage of tantalum equal to 0.9%.

**CATALYTIC TESTS**

**Example 5. EVALUATION OF THE CATALYTIC ACTIVITY OF REFERENCE CATALYST A.**

Catalyst A, reduced and passivated according to  
15 what is described in example 1, is formed in particles having a diameter of from 0.35 to 0.85 mm and subsequently diluted with an inert solid, silicon carbide, having the same particle size as the catalyst and in a volumetric ratio equal to 1:2 catalyst/inert solid. The  
20 catalyst thus diluted is then charged into a tubular reactor and subjected to an activation process in a stream of hydrogen ( $2000 \text{ Nl/h} \cdot l_{\text{cat}}$ ) and nitrogen ( $1000 \text{ Nl/h} \cdot l_{\text{cat}}$ ), at a temperature of 300°C and pressure of 1 bar for 16 hours. The temperature is then lowered to  
25 180°C, the volumetric flow-rate of hydrogen and nitro-

gen is varied (333-1000  $\text{Nl/h}\cdot\text{l}_{\text{cat}}$ ) and (5000-15000  $\text{Nl/h}\cdot\text{l}_{\text{cat}}$ ) respectively, the system pressurized to 20 bars and the carbon monoxide (116.5-500  $\text{Nl/h}\cdot\text{l}_{\text{cat}}$ ) is then introduced to obtain a volumetric ratio  $\text{H}_2/\text{CO}$  equal to 2.

The flow-rate of nitrogen in the starting-up phase of the reaction is progressively lowered until complete elimination according to the following sequence (the lower flow-rates refer to the tests with  $\text{GHSV} = 500 \text{ h}^{-1}$ , the higher flow-rates to  $\text{GHSV} = 1500 \text{ h}^{-1}$ ):

time (hours)	$\text{H}_2$ flow-rate ( $\text{Nl/h}\cdot\text{l}_{\text{cat}}$ )	$\text{CO}$ flow-rate ( $\text{Nl/h}\cdot\text{l}_{\text{cat}}$ )	$\text{N}_2$ flow-rate ( $\text{Nl/h}\cdot\text{l}_{\text{cat}}$ )
0	333-1000	166.5-500	5000-15000
1	333-1000	166.5-500	3750-11250
15 2	333-1000	166.5-500	2500-7500
3	333-1000	166.5-500	1250-3750
4	333-1000	166.5-500	0

At the end of the starting-up phase, the reaction temperature is regulated so as to obtain a conversion of the carbon monoxide with respect to the volume fed (conv.CO%) of less than 20% for at least 48 hours, then in the following 48 hours the temperature is progressively increased until a minimum CO conversion value of 45% is reached without exceeding however the reaction temperature of  $240^\circ\text{C}$ , in order to minimize the produc-

tion of methane as well as the gaseous fractions (C<sub>2</sub>-C<sub>4</sub>).

As indicated in table 2, on increasing the volumetric flow-rates of the mixture H<sub>2</sub>-CO (GHSV from 5 500 h<sup>-1</sup> to 1500 h<sup>-1</sup>) it is necessary to increase the reaction temperature (from 200°C to 240°C) to reach CO conversions higher than the limit of 45%. This is to the advantage of the selectivity to methane (from 7.8% to 29.7%), expressed as percentage referring to the 10 total carbon present in the products (C%), and disadvantage of the selectivities to higher hydrocarbons (C<sub>14+</sub>: from 44.6% to 25.3%, C<sub>9+</sub>: from 66.9% to 48.8%), expressed as percentage referring to the total weight of the whole hydrocarbon fraction produced (wt%).

15 **Example 6. EVALUATION OF THE CATALYTIC ACTIVITY OF CATALYSTS B, C and D.**

The catalysts of the present invention B, C and D, containing tantalum in varying percentages, are subjected to a catalytic activity test. The activation and 20 starting conditions are completely analogous to what is described in example 5.

As shown in table 3, with a total volumetric flow-rate (GHSV) equal to 1500 h<sup>-1</sup> and reaction temperatures of less than 210°C, CO conversions of more than 67% are 25 obtained together with hourly weight productivities of

hydrocarbons with more than two carbon atoms ( $C_{2+}$ ) of more than  $311 \text{ gC}_{2+}/\text{Kg}_{\text{cat}} \cdot \text{h}$ , selectivities to methane of less than 11.2%, selectivities to  $C_{14+}$  hydrocarbons of from 40.4% to 48.7%,  $C_{9+}$  hydrocarbons of from 70.5% to 5 76.7% and finally selectivities to  $C_{5+}$  of between 79.7% and 81.7%.

The above results clearly show the advantages of the catalysts of the present invention with respect to those of the prior art.

10 **Example 7 - Catalysts supported on  $\text{TiO}_2$**

Following the procedures described above a reference catalyst E is prepared completely similar to catalyst A, but having  $\text{TiO}_2$  as a carrier instead of  $\text{SiO}_2$ . In this case the  $\text{TiO}_2$  had a surface area of 25 15  $\text{m}^2/\text{g}$ , a specific pore volume of  $0.31 \text{ cm}^3/\text{g}$  and a content of rutile equal to 81%..

The catalyst E has the composition, in weight percentage, Co/Ru/ $\text{TiO}_2$ : Co=12%, Ru=0.2%.

The catalyst F is prepared in the same way as 20 described for the preparation of catalyst B, having, again in weight percentage, the composition Co/Ru/Ta/ $\text{TiO}_2$ : Co=12%, Ru=0.2%, Ta=0.2%.

The results of the experiments carried out in the presence of these catalysts are indicated in table 4.

25 Also in this case there is an improvement in the

selectivity to heavier hydrocarbons and a lower selectivity to methane in the case of the catalyst promoted with tantalum ( $C_{22+} = 26.2\%$ ,  $C_{9+} = 85.4\%$ ,  $C_{5+} = 89.5\%$ ,  $CH_4 = 6.7\%$ ) with respect to the catalyst without  
 5 tantalum ( $C_{22+} = 18.1\%$ ,  $C_{9+} = 74.3\%$ ,  $C_{5+} = 85.7\%$ ,  $CH_4 = 8.7\%$ )

The improvement however is lower than that of the catalysts supported on silica.

Table 1

10 =====

Example	Cat.	%Co	%Ru	%Ta	Carrier
1	A	15	0.2	-	SiO <sub>2</sub>
2	B	15	0.2	0.2	SiO <sub>2</sub>
3	C	15	0.2	0.5	SiO <sub>2</sub>
15 4	D	15	0.2	0.9	SiO <sub>2</sub>

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Table 2

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Comparative Example 5

Catalyst A:

5	Reaction Temperature	200	220	240
	GHSV h <sup>-1</sup>	500	1000	1500
	Conv. CO (%)	48.5	51.3	47.1
	Prod. C <sub>2+</sub> (g/Kg h)	81.4	149.0	183.5
	CH <sub>4</sub> (C%)	7.8	18.8	29.7
10	CO <sub>2</sub> (C%)	0.3	1.8	2.2
	C <sub>1</sub> -C <sub>4</sub> (wt%)	13.5	32.7	49.0
	C <sub>22+</sub> (wt%)	14.1	15.4	3.2
	C <sub>14+</sub> (wt%)	44.6	40.0	25.3
	C <sub>9+</sub> (wt%)	66.9	64.1	48.8
15	C <sub>5+</sub> (wt%)	86.5	67.3	51.0

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Table 3

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Example 6				
	Cat.B	Cat.C	Cat.D	
5				
	% Tantalum	0.2	0.5	0.9
	Reaction Temp.	206	209	206
	GHSV h <sup>-1</sup>	1500	1500	1500
	Conv. CO (%)	69.1	67.4	68.2
10	Prod. C <sub>2+</sub> (g/Kg h)	326.2	311.5	311.8
	CH <sub>4</sub> (C%)	11.2	10.5	10.0
	CO <sub>2</sub> (C%)	0.1	0.9	0.1
	C <sub>1</sub> -C <sub>4</sub> (wt%)	19.0	20.3	18.3
	C <sub>22+</sub> (wt%)	11.3	15.1	13.9
15	C <sub>14+</sub> (wt%)	40.4	48.5	48.7
	C <sub>9+</sub> (wt%)	70.5	73.1	76.7
	C <sub>5+</sub> (wt%)	81.0	79.7	81.7

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Table 4

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Example 7

5	Catalyst	E	F
	Composition	Co/Ru/TiO <sub>2</sub>	Co/Ru/Ta/TiO <sub>2</sub>
	Reaction Temp.	224	217
	GHSV h <sup>-1</sup>	1500	1500
	Conv. CO (%)	59.9	60.2
10	Prod. C <sub>2+</sub> (g/Kg h)	157.5	157.5
	CH <sub>4</sub> (C%)	8.7	6.7
	CO <sub>2</sub> (C%)	0.2	0.1
	C <sub>1</sub> -C <sub>4</sub> (wt%)	14.3	10.5
	C <sub>22+</sub> (wt%)	18.1	26.2
15	C <sub>14+</sub> (wt%)	49.8	70.4
	C <sub>9+</sub> (wt%)	74.3	85.4
	C <sub>5+</sub> (wt%)	85.7	89.5

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**CLAIMS**

1. A catalytic composition comprising:
  - from 5 to 50% of cobalt, in metal form or in the form of a derivative;
  - from 0.05 to 5% of ruthenium, in metal form or in the form of a derivative;and
  - from 0.05 to 5% of tantalum, in metal form or in the form of a derivative;the cobalt being present in a greater amount than ruthenium and in a greater amount than tantalum, the above elements being dispersed on a carrier selected from the oxides of at least one of the elements selected from Si, Ti, Al, Zn, Sn and Mg;  
the percentages being expressed by weight of the element in metal form based on the weight of the catalytic composition.
2. The catalytic composition according to claim 1, wherein the ruthenium and tantalum are in the form of oxides.
3. The catalytic composition according to claim 1 or 2, wherein the cobalt is present in a quantity of from 12 to 50% by weight.
4. The catalytic composition according to claim 1 or 2, wherein the cobalt is present in a quantity of from 5 to 35% by weight.
- 20 5. The catalytic composition according to claim 1 or 2, wherein the cobalt is present in a quantity higher than 5 and less or equal to 35% by weight.
6. The catalytic composition according to any one of claims 1 to 4, wherein the cobalt is present in a quantity of from 12 to 35% by weight.
7. The catalytic composition according to any one of claims 1 to 6, wherein the ruthenium and tantalum are each present in a quantity of from 0.1 to 3% by weight.

8. The catalytic composition according to any one of claims 1 to 7, characterized in that the carrier essentially consists of SiO<sub>2</sub>.
9. A process for the preparation of the catalytic composition according to any one of claims 1 to 8, which comprises a first deposition on an inert carrier of cobalt and subsequently a second and third deposition of a ruthenium and tantalum; the second and third depositions being optionally carried out inversely or contemporaneously.
10. The process according to claim 9, wherein the cobalt is deposited on the inert carrier according to a dry impregnation technique.
- 10 11. The process according to claim 9 or 10, wherein the ruthenium and tantalum are deposited according to a impregnation technique.
12. The process according to claim 9, characterized in that it comprises the following steps:
- a) production of a first catalytic precursor (A) containing cobalt and at least part of the inert carrier, by dry deposition of cobalt on the inert carrier; subsequent calcination, reduction and passivation of the inert carrier containing cobalt;
- b) production of a second catalytic precursor (B) containing cobalt, ruthenium and at least part of the inert carrier, by deposition of ruthenium on the  
20 first catalytic precursor (A); subsequent calcination, reduction and passivation of the inert carrier containing cobalt and ruthenium;
- c) production of the catalytic composition by deposition of tantalum on the catalytic precursor (B), subsequent calcination, reduction and passivation of the inert carrier containing cobalt, ruthenium and tantalum;  
steps (b) and (c) being optionally carried out inversely.
13. The process according to claim 12, wherein in step (a) the whole of the inert carrier is used.

14. A process for the synthesis of hydrocarbons starting from a mixture essentially consisting of CO and H<sub>2</sub>, in the presence of or without CO<sub>2</sub>, comprising reacting said mixture in the presence of a catalytic composition according to any one of claims 1 to 8.
15. The process for the synthesis of hydrocarbons according to claim 14, wherein the reaction is carried out at a pressure of from 1 to 150 bars and at a temperature of from 150 to 350°C, the ratio H<sub>2</sub>/CO being from 1:1.5 to 5:1.
16. The process according to claim 15, characterized in that the reaction is carried out at a pressure of from 10 to 100 bars and at a temperature of from  
10 170°C to 300°C, the ratio H<sub>2</sub>/CO being from 1.2:1 to 2.5:1.
17. The process according to claim 15 or 16, characterized in that the reaction is carried out at a temperature of from 200°C to 240°C.