

12

EUROPEAN PATENT APPLICATION

21 Application number: **85304587.0**

61 Int. Cl.⁴: **B 01 J 27/22**

22 Date of filing: **27.06.85**

30 Priority: **29.06.84 US 626068**

43 Date of publication of application:
05.02.86 Bulletin 86/6

64 Designated Contracting States:
DE GB NL

71 Applicant: **Exxon Research and Engineering Company**
P.O.Box 390 180 Park Avenue
Florham Park New Jersey 07932(US)

72 Inventor: **Chersich, Claudio Cimatti**
467 Palisade Avenue
Englewood Cliffs New Jersey 07632(US)

72 Inventor: **Fiato, Rocco Anthony**
275 Country Club Lane
Scotch Plains New Jersey 07076(US)

72 Inventor: **Wachs, Israel Ephraim**
340 Rolling Knolls Way
Bridgewater New Jersey 08807(US)

74 Representative: **Field, Roger Norton et al,**
ESSO Engineering (Europe) Ltd. Patents & Licences Apex
Tower High Street
New Malden Surrey KT3 4DJ(GB)

54 **Iron carbide on titania surface modified with group VA oxides as Fischer-Tropsch catalysts.**

57 Catalysts comprising iron carbide on a surface modified titania support wherein said support comprises a surface modifying oxide of tantalum, niobium, vanadium or a mixture thereof, supported on said titania, wherein at least a portion of said surface modifying oxide is in a non-crystalline form. These catalysts are useful for Fischer-Tropsch hydro-carbon synthesis reactions. Preferably, at least about 25 wt.% of said surface modifying oxide will be in a non-crystalline form.

EP 0 170 408 A1

1

2

3 This invention relates to catalyst composi-
4 tions of matter comprising iron carbide supported on a
5 surface modified titania support. More particularly,
6 this invention relates to Fischer-Tropsch catalyst
7 compositions comprising iron carbide supported on a
8 surface modified titania support, wherein said support
9 comprises a surface modifying oxide of tantalum, vana-
10 dium, niobium or mixture thereof supported on the sur-
11 face of said titania and wherein at least a portion of
12 said surface modifying oxide is in a non-crystalline
13 form.

14

15 The use of iron-titania mixtures as Fischer-
16 Tropsch catalysts for converting mixtures of CO and H₂
17 to hydrocarbons is well-known to those skilled in the
18 art. For example, U.S. Patent 2,543,327 discloses
19 titania promoted iron oxide for Fischer-Tropsch syn-
20 thesis wherein the iron oxide is in the form of natur-
21 ally occurring magnetite and preferably as Alan Wood
22 ore. In this disclosure a typical catalyst is shown as
23 prepared by mixing about 13,600 grams of Alan Wood ore
24 with 98 grams of titania and 216 grams of potassium
25 carbonate used as a promoter. The ratio of hydrogen to
26 carbon monoxide disclosed as being preferably at least

1 2/1 and the results show that the catalyst has relative-
2 ly poor activity with a large selectivity towards the
3 production of methane and very little selectivity
4 towards the production of C₂+ hydrocarbons. That is,
5 the Fischer-Tropsch product was primarily methane.
6 Similarly, British patent 1,512,743 also discloses a
7 titania promoted, massive iron type of Fischer-Tropsch
8 catalyst wherein iron oxide is mixed with titanium
9 oxide, zinc oxide and potassium carbonate with the
10 resulting mixture being sintered and then reduced for
11 many hours at 500°C. Although this catalyst has rela-
12 tively reasonable activity with regard to conversion of
13 the CO and H₂ mixture, the product was primarily (i.e.,
14 about 73%) olefinic, unsaturated C₂/C₄ hydrocarbons and
15 with only about 10% of C₂/C₄ saturated hydrocarbons or
16 alkanes being produced. U.S. Patent 4,192,777 and
17 4,154,751 while directed towards the use of potassium
18 promoted Group VA metal cluster catalysts in Fischer-
19 Tropsch synthesis reactions, suggest that iron sup-
20 ported on titania would be useful Fischer-Tropsch
21 catalysts but do not disclose the preparation of same.
22 In their examples, they disclose iron on various sup-
23 ports other than titania with the amount of iron on the
24 support generally being less than about 5 percent. U.S.
25 Patent 4,261,865 discloses an iron titanate-alkali
26 metal hydroxide catalyst for preparing alpha-olefins
27 for mixtures of CO and H₂. That is, the catalyst is
28 not iron supported on titania along with an alkali
29 metal hydroxide but rather an iron titanate compound.

30 Another example of a titania-promoted mas-
31 sive iron catalyst for Fischer-Tropsch synthesis may be
32 found in the Volume 17, No. 3-4 React. Kinet. Catal.
33 Lett., pages 373-378, (1971) titled "Hydrocondensation
34 of CO₂ (CO) Over Supported Iron Catalysts". This

1 article discloses an iron oxide, titania, alumina,
2 copper oxide catalyst promoted with potassium. Simi-
3 larly, in European patent application EP 0 071770 A2
4 Fischer-Tropsch catalysts are disclosed which include
5 iron-titania catalysts wherein the iron to titania
6 ratio can be greater than 1/10. The actual iron-titan-
7 ia catalyst is not an iron supported on titania cata-
8 lyst but an iron/titania catalyst produced by a copre-
9 cipitation technique wherein the active iron catalytic
10 component is distributed throughout a titanium oxide
11 matrix. Thus, the resulting catalyst was not iron
12 supported on titania but rather a bulk phase iron/-
13 titania mixture which, when used for Fischer-Tropsch
14 synthesis, produced predominantly olefins. The amount
15 of olefins produced was generally greater than about
16 80% of the total hydrocarbon product.

17 With regard to iron/titania catalysts for
18 Fischer-Tropsch wherein the iron is supported on ti-
19 tania, a 1982 article by Vannice, Titania-Supported
20 Metals as CO Hydrogenation Catalysts, J. Catalysis, v.
21 74, p.199-202 (1982), discloses the use of an iron/-
22 titania catalyst for Fischer-Tropsch synthesis wherein
23 the amount of iron, calculated as metallic iron, is 5
24 percent of the iron/titania composite and the catalyst
25 shows extremely little activity for Fischer-Tropsch
26 synthesis. An article by Reymond et al, Influence of
27 The Support or of an Additive on The Catalytic Activity
28 in The Hydrocondensation of Carbon Monoxide by Iron
29 Catalysts in "Metal-Support and Metal-Additive Effects
30 in Catalysis", B. Imelik et al (Eds), Elsevier, Nether-
31 lands, p.337-348 (1982), also discloses the use of
32 iron/titania Fischer-Tropsch catalysts wherein the iron
33 is supported on the titania.

1 U.S. 4,149,998 to Tauster et al relates to
2 heterogeneous catalysts consisting of Group VIII
3 metals, including iron, dispersed on oxide carriers
4 selected Ti, V, Nb, Ta and
5 mixtures thereof and zirconium titanate and BaTiO₃.
6 However, there is no suggestion in this patent that the
7 catalytic metal be dispersed on a surface modified
8 titania.

9
10 It has now been discovered that catalysts
11 comprising iron carbide supported on a surface modi-
12 fied titania support wherein said support comprises a
13 surface modifying Group VA oxide of tantalum, niobium,
14 vanadium and mixture thereof supported on the surface
15 of said titania and wherein at least a portion of said
16 surface modifying oxide is in a non-crystalline form
17 are useful catalysts for Fischer-Tropsch hydrocarbon
18 synthesis. Moreover, Fischer-Tropsch reactions con-
19 ducted with these catalysts have been found to result
20 in increased olefin and decreased methane make compared
21 to Fischer-Tropsch catalysts comprising iron supported
22 on titania wherein the surface of the titania has not
23 been modified with a Group VA modifying oxide. Further,
24 the catalysts of this invention produce a greater
25 amount of heavier products and exhibit superior cata-
26 lyst maintenance than similar catalysts on titania
27 whose surface has not been modified with a Group VA
28 oxide.

29 In a preferred embodiment at least about 25
30 wt. % of the surface modifying oxide of tantalum,
31 niobium, vanadium or mixture thereof present on the
32 titania surface will be in a non-crystalline form. In

1 a particularly preferred embodiment, the catalyst will
2 be pretreated with CO at elevated temperature prior to
3 use.

4

5 The term surface modified titania as used
6 herein refers to titania whose surface has been modi-
7 fied by an oxide of niobium, vanadium, tantalum or
8 mixture thereof in an amount such that the modified
9 support exhibits properties different from titania
10 whose surface has not been modified and also different
11 from bulk niobia, tantalum, vanadia or mixture thereof.
12 Concomitantly, the final catalyst composition will
13 exhibit properties different from iron carbide sup-
14 ported on unmodified titania or on bulk niobia, tanta-
15 la, vanadia or a mixture thereof.

16 Thus, the catalyst support useful for pre-
17 paring the catalysts of this invention comprise titania
18 whose surface has been modified with an oxide of a
19 Group VA metal (vanadium, niobium, tantalum or a mixture
20 thereof). That is, the surface of the titania has been
21 modified by an oxide of vanadium, niobium, tantalum or a
22 mixture thereof in an amount such that the catalyst
23 exhibits properties different from titania whose sur-
24 face has not been modified and different from bulk
25 oxides of vanadium, niobium, tantalum or a mixture
26 thereof. Those skilled in the art know that the oxides
27 of niobium, tantalum, vanadium and mixtures thereof are
28 crystalline in their bulk form. Thus, at least a
29 portion of and preferably at least about 25 wt.% of the
30 Group VA metal oxide will be in a non-crystalline form.

1 This will be accomplished if the metal oxide loading on
2 the titania broadly ranges between about 0.5 to 25 wt. %
3 of the total catalyst weight.

4 In the catalyts of this invention the iron
5 carbide is supported on the surface modified titania.
6 Consequently, the catalyts of this invention are pre-
7 pared by a two-step sequential process wherein the
8 surface modified titania support is prepared first,
9 followed by depositing the iron carbide or iron carbide
10 precursor on the support. Thus, in the first step an
11 oxide or precursor thereof of a metal selected from the
12 group consisting of niobium, tantalum, vanadium and
13 mixture thereof is deposited on the titania to form
14 either the surface modified support or, in the case of
15 one or more precursors, a support precursor. The sup-
16 port precursor will then be calcined to oxidize the
17 oxide precursor and form a support comprising titania
18 whose surface has been modified by an oxide of a metal
19 selected from the group consisting of niobium, tanta-
20 lum, vanadium and mixture thereof wherein at least a
21 portion of said surface modifying oxide is in a non-
22 crystalline form.

23 The catalyst support precursors of this
24 invention may be prepared by techniques well-known in
25 the art, such as incipient wetness, impregnation, etc.,
26 the choice being left to the practitioner. When using
27 the impregnation technique, the impregnating solution
28 is contacted with the titania for a time sufficient
29 to deposit the oxide precursor material onto the ti-
30 tania either by selective adsorption or alternatively,
31 the excess solvent may be evaporated during drying
32 leaving behind the precursor salt. If an impregnation
33 or incipient wetness technique is used to prepare a
34 support precursor of this invention, the transition

1 metal oxide salt solution used may be aqueous or
2 organic, the only requirement being that an adequate
3 amount of precursor compound for the selected Group VA
4 transition metal oxide or oxides be soluble in the
5 solvent used in preparing this solution.

6 The support precursor composite will then
7 normally be dried at temperatures ranging from about
8 50°-300°C to remove the excess solvent and, if neces-
9 sary, decompose the salt if it is an organic salt to
10 form a catalyst precursor. The support precursor
11 composite is then converted into the surface modified
12 titania support by calcining at temperatures of from
13 about 150° to 800°C and preferably 300°-700°C in a
14 suitable oxidizing atmosphere such as air, oxygen, etc.
15 The time required to calcine the composite will, of
16 course, depend on the temperature and in general will
17 range from about 0.5-7 hours. Reducing atmospheres may
18 also be used to decompose the transition metal oxide
19 precursors, but the resulting composite will then re-
20 quire subsequent calcination to convert the reduced
21 metal component to the oxide form.

22 The supports of this invention will general-
23 ly have metal oxide loadings of from about 0.5 to 25
24 wt.% metal oxide on the titania based on the total
25 support composition, preferably from about 1 to 15
26 wt.%, more preferably from about 2-10 wt.% based on
27 the total support composition.

28 It is important to this invention that the
29 iron carbide is supported on and not merely mixed with
30 the surface modified titania support.

1 The catalyst will be prepared by depositing
2 a suitable iron precursor component onto the surface
3 modified titania support from a precursor solution
4 using any of the well-known techniques such as in-
5 cipient wetness, multiple impregnation, pore-filling
6 etc., the choice being left to the convenience of the
7 practitioner. As has heretofore been stated, it is
8 important for the iron precursor to be deposited onto
9 the support as opposed to other methods for catalyst
10 preparation such as co-precipitation or physical mix-
11 tures. After impregnation, the impregnate is dried to
12 remove excess solvent and/ or water therefrom. The dry
13 impregnate can then be converted to a catalyst of this
14 invention employing a number of different methods. In
15 one method, the impregnate will be converted directly
16 to a catalyst of this invention by contacting same with
17 a CO containing reducing gas, preferably a reducing gas
18 containing a mixture of CO and H₂. Thus, it will be
19 appreciated to those skilled in the art that the cata-
20 lyst of this invention can be formed from the impreg-
21 nate in-situ in a Fischer-Tropsch hydrocarbon synthesis
22 reactor. However, it is preferred to employ a sequen-
23 tial treatment of first contacting the dry impregnate
24 with an H₂ containing reducing gas that does not con-
25 tain CO to reduce the impregnate, followed by contact-
26 ing the reduced impregnate with CO or a CO containing
27 gas such as a mixture of CO and H₂ to form the catalyst
28 of this invention. As a practical matter, it may be
29 commercially advantageous to form the catalyst of this
30 invention by subjecting the impregnate to calcining to
31 convert the supported iron precursor component to iron
32 oxide, followed by subsequent reduction and formation
33 of the catalyst of this invention.

1 Promoter metals such as potassium or other
2 alkali metals may be added via impregnation, etc. be-
3 fore the composite is contacted with a reducing at-
4 mosphere and/or CO containing gas to form the catalyst
5 of this invention. In general, the amount of promoter
6 metal present will range from about 0.5 to 5 wt.% based
7 on the amount of iron (calculated as Fe_2O_3) supported
8 on the titania.

9 If one desires to obtain a catalyst of this
10 invention via a supported iron oxide route, then the
11 dry impregnate will be calcined in air or other suit-
12 able oxidizing atmosphere at a temperature of from
13 about 120 to 300°C for a time sufficient to convert the
14 supported iron precursor component to iron oxide. After
15 the iron/surface modified titania impregnate has been
16 calcined to convert the supported iron precursor com-
17 pound to iron oxide, the iron oxide/titania composite,
18 with or without one or more promoter metals, is re-
19 duced in a hydrogen-containing, net-reducing atmos-
20 phere at a temperature broadly ranging from about
21 300-500°C for a time sufficient to convert the iron
22 oxide to metallic iron. It has been found that if one
23 tries to reduce the iron oxide/titania composite at a
24 temperature below about 300°C, (i.e., 250°C), the cata-
25 lyst of this invention will not subsequently be
26 formed.

27 Irrespective of the route one employs to
28 form a catalyst of this invention, whether by reduction
29 followed by contacting with CO, direct formation of the
30 catalyst or through the supported iron oxide route, it
31 is important not to contact the composite with a re-
32 ducing gas at temperatures above about 500°C.

1 Reduction temperatures exceeding about 500°C
2 will produce a catalyst which exhibits relatively low
3 CO hydrogenation activity with less than 50% of the C₂+
4 hydrocarbons being alkanes. Further, even at a 500°C
5 reduction temperature a less effective catalyst will be
6 produced if the reduction occurs for too long a time,
7 i.e., about ten hours or more. Thus it will be appre-
8 ciated that the temperature range for reducing the
9 composite to form a catalyst cannot be critically
10 quantified with any degree of precision inasmuch as
11 there exists a time-temperature continuum for proper
12 reduction.

13 In a preferred embodiment of this invention,
14 the catalyst composite will first be reduced, followed
15 by contacting with CO at temperatures ranging from
16 about 200 to 500°C and preferably 200 to 400°C for a
17 time sufficient to form a catalyst comprising iron
18 carbide supported on the surface modified titania. It
19 has been found that a CO treatment following hydrogen
20 reduction dramatically improves the activity of the
21 catalyst for CO conversion with only slight changes in
22 product selectivity. Iron carbide on the surface
23 modified titania support will also be achieved by
24 treating the calcined iron/support composite with a
25 mixture of CO and H₂, but it is preferred to use the
26 sequential treatment comprising hydrogen reduction
27 followed by CO treatment. Further, when using this
28 sequential treatment to produce a catalyst of this
29 invention, it is preferred that the temperature used
30 for the CO treatment be lower than that used for the
31 hydrogen reduction. Thus, in general the CO treatment
32 will occur at a temperature of about 100 to 200°C lower
33 than the temperature used for the hydrogen reduction.

1 It has also been discovered that, if a cata-
2 lyst of this invention has been prepared by hydrogen
3 reduction and then contacted in-situ, in a reactor,
4 with a feedstream comprising a mixture of CO and H₂ to
5 form a catalyst of this invention, the activity of the
6 so formed catalyst will be substantially increased by
7 reducing or eliminating the hydrogen content of the
8 feedstream, raising the temperature in the reactor an
9 additional 50 to 150°C for a short period of time
10 (i.e., 3-5 hours), followed by reestablishing the
11 original reaction conditions.

12 Predominantly C₂+ alkane hydrocarbons are
13 produced from mixtures of CO and H₂ by contacting said
14 mixtures with the catalyst of this invention at temper-
15 atures ranging from about 200 to 350°C and preferably
16 from about 250-320°C. The reaction pressure will gen-
17 erally range from about 100-500 psig and more prefer-
18 ably from about 150-300 psig, although pressures out-
19 side this range may be used if desired. However, if one
20 goes too low in pressure (i.e., <50 psig), catalyst
21 activity will be greatly reduced and methane production
22 will predominate. Upper pressure limits will generally
23 be dictated by economic considerations. The H₂/CO mole
24 ratio in the reaction zone will generally range from
25 about 1/2 to 3/1, preferably from about 1/2 to 2/1 and
26 still more preferably from about 1/2 to 1/1.

27 The invention will be more readily under-
28 stood by reference to the following examples.

1 Catalyst Support Preparation

2 Degussa P-25, a mixture of anatase and
3 rutile titania, was used as the titania support. Both
4 of the catalyst supports were prepared in a glove box
5 in a nitrogen atmosphere to prevent decomposition of
6 the transition metal oxide precursors. In all cases 10
7 grams of the P-25 titania powder were slurried in 100
8 cc of ethanol to which was added the transition metal
9 oxide precursor, with the resulting mixture stirred
10 overnight, under flowing nitrogen, to evaporate the
11 ethanol. Each dry mixture was then taken out of the
12 glove box and 3 cc of water added. The resulting
13 mixture was stirred overnight in air, then the dry
14 powder placed in a quartz boat and slowly heated in a
15 1/1 flowing mixture of O₂ in He up to 400°C. At 400°C
16 the He flow was cut off and the powdered, catalyst
17 support precursor then heated from 400 to 575°C in
18 100% O₂. Each sample of catalyst precursor was held
19 at 575°C in the O₂ for two hours to calcine the pre-
20 cursor into a surface modified titania support of this
21 invention.

22 The transition metal oxide precursors were
23 obtained from Alfa, Inc. and were Nb(C₂H₅O)₅ and
24 VO(C₂H₅O)₃. The amounts of niobia and vanadia pre-
25 cursors added to each slurry of 10 g P-25 in 100 cc of
26 ethanol were 2.5 and 0.46 grams, respectively. The
27 resulting catalysts contained 10 wt.% niobia on ti-
28 tania and 2 wt.% vanadia on titania. The niobia and
29 vanadia contents of the catalysts were expressed as
30 niobium pentoxide and vanadium pentoxide.

1 EXAMPLE 1

2 A 5-8 cc sample of catalyst, containing 4
3 wt.% Fe as elemental iron on the support, was loaded
4 into a 3/8 inch O.D. 316 stainless steel tubular reac-
5 tor. The system was then flushed with nitrogen at
6 atmospheric pressure and then flushed with 90% H₂/10%
7 N₂ at atmospheric pressure. The reactor was then
8 heated to 500°C in flowing 90% H₂/10% N₂ (100 cc/min)
9 and maintained at these conditions for 5 hrs. After
10 this, the reactor was cooled to the desired reaction
11 temperature, 290-315°C, and the pressure increased to
12 300 psig. The reducing gas was then replaced with 1/1
13 H₂/CO at a flow rate (standard hourly space velocity)
14 of 500 V/V/hr. The exit gas from the reactor was fed
15 into a gas chromatograph for on-line analysis of C₁-C₁₅
16 hydrocarbons, CO, CO₂ and N₂.

17

18 The results of experiments A-D are presented
19 in Table 1. The runs can be compared either at condi-
20 tions for nearly equal conversion, run A vs. Run C and
21 Run B vs. Run D, or at identical conditions, Run A vs.
22 Run D. In all cases the vanadium containing system is
23 found to generate lower levels of methane than the
24 standard catalyst. Comparison of these catalysts at
25 identical conditions, Run A vs. Run D at 350°C, also
26 indicates that the vanadium containing system is more
27 active. The modified TiO₂ catalyst of the present
28 invention is clearly superior to the unmodified analogue
29 for production of desired α -olefin products while mini-
30 mizing the formation of unwanted methane.

1

Table 1

2 3 4 5	4 wt.% Iron on Titania	4 wt.% Iron on Titania Surface Modified With An Oxide of Vanadium			
6	Run	A	B	C	D
7	Temp. °C	305	315	290	305
8	% CO Conversion	47	60	49	70
9	Wt.% Selectivity (CO ₂ Free)				
10	CH ₄	21.0	24.4	16.1	17.8
11	C ₂ ⁼	0.4	0.6	2.7	2.8
12	C ₂ ^o	16.1	16.2	20.2	16.8
13	C ₃ ⁼	11.7	9.7	16.6	18.6
14	C ₃ ^o	13.7	12.7	14.4	16.5
15	C ₄ ⁼	2.5	3.0	1.9	2.0
16	C ₄ ^o	7.1	7.4	8.1	10.9
17	C ₅ ⁺	27.5	26.0	20.0	14.6

18 Conditions: 1:1 H₂:CO, 500 v/v/hr, 300 psig, pre-
 19 treatment with H₂ at 500°C for 5 hr. C₅⁺
 20 determined by nitrogen internal standard
 21 method.

1 The activity and carbon number distributions
2 for the unmodified Fe/TiO₂ and the V and Nb surface
3 modified Fe/TiO₂ catalysts during Fischer-Tropsch
4 synthesis are presented in Table 2. The addition of V
5 and Nb affected the activity and selectivity of the
6 Fe/TiO₂ catalysts. The incorporation of V and Nb to
7 the TiO₂ surface increased and decreased the conversion
8 of CO, respectively. The stability of the modified
9 catalysts was superior to that of the unmodified
10 Fe/TiO₂ catalyst (less coking). The V and Nb modified
11 Fe/TiO₂ catalysts substantially decreased the CH₄ yield
12 and increased the C₅⁺ yield. Whereas Fe/TiO₂ yields
13 substantial amounts of paraffins (70-90% paraffins in
14 hydrocarbon) the V and Nb modified Fe/TiO₂ catalysts
15 produced substantial amounts of olefins and low amounts
16 of paraffins. In addition, XRD analysis of the spent V
17 and Nb modified Fe/TiO₂ catalysts did not show the
18 presence of FeTiO₃ in the catalysts. Thus, the addi-
19 tion of V and Nb to the surface of the TiO₂ altered the
20 Fe-TiO₂ interaction and the nature of the products
21 obtained from such a catalyst during Fischer-Tropsch
22 synthesis.

1 .

Table 2

2		4%	4% Fe(TiO ₂	4% Fe(TiO ₂
3		<u>Fe/TiO₂</u>	<u>+ V oxide)</u>	<u>+ Nb oxide)</u>
4	% CO Conversion	27.0	34.3	20.1
5	C ₁	21.0	13.0	14.6
6	C ₂	17.0	21.5	15.0
7	C ₃	29.0	12.0	11.9
8	C ₄	9.0	8.0	6.0
9	C ₅ ⁺	24.0	45.5	52.5

10 CONDITIONS: 270°C, 300 psia, 500-600 V/V/M, H₂:CO=1

CLAIMS:

1. A catalyst comprising iron carbide supported on a surface modified titania support wherein said support comprises an oxide of a metal selected from niobium, vanadium, tantalum and mixtures thereof, supported on said titania wherein at least a portion of said supported
5 oxide of niobium, vanadium, tantalum or a mixture thereof is in a non-crystalline form.
2. A catalyst according to claim 1 containing one or more alkali metal promoters.
3. A catalyst according to either of claims 1 and 2 wherein
10 the amount of said iron carbide, calculated as iron, ranges from about 2 to 20 wt.% of the total catalyst composition.
4. A catalyst according to claim 3 wherein the amount of supported iron carbide, calculated as iron, ranges from about 4 to 10 wt.% of the total catalyst composition.
- 15 5. A catalyst according to any one of the preceding claims wherein at least about 25 wt.% of said supported oxide is non-crystalline.
6. A process for producing a catalyst comprising iron carbide supported on a surface modified titania support wherein said support
20 comprises an oxide of a metal selected from niobium, vanadium, tantalum and mixtures thereof, supported on titania wherein at least a portion of said supported oxide is in a non-crystalline form, said process comprising the steps of:

1 (a) depositing iron on the surface modified
2 titania support from a solution of iron precursor
3 compound in an amount such that the final catalyst will
4 contain supported iron in an amount of at least about 2
5 milligrams of iron, calculated as Fe_2O_3 , per square
6 meter of titania support surface;

7 (b) calcining the iron precursor supported
8 on titania produced in step (a) at a temperature of
9 from about 120 to 500°C for a time sufficient to
10 decompose said iron precursor material and convert at
11 least a portion of said supported iron to Fe_2O_3 ; and

12 (c) contacting said calcined composite
13 formed in step (b) with hydrogen at a temperature of
14 from between about $300\text{--}500^\circ\text{C}$ for a time sufficient to
15 convert at least a portion of said supported iron to a
16 reduced composite; and

17 (d) contacting said reduced composite
18 formed in (c) with CO at an elevated temperature of at
19 least about 200°C for a time sufficient to form said
20 catalyst.

21 7. A process according to claim 6 wherein said
22 reduced composite is contacted with CO at a temperature
23 broadly ranging between about 200 to 500°C prior to
24 use.

25 8. A process for producing hydrocarbons,
26 including alkane hydrocarbons, from gaseous feed mix-
27 tures of CO and H_2 comprising contacting said feed, at
28 a temperature ranging from about 200 to 350°C and for a
29 time sufficient to convert at least a portion of said
30 feed to alkane hydrocarbons, with a catalyst according to
31 any one of claims 1 to 5.

32



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl 4)
X	US-A-4 436 834 (WRIGHT) * Claims 1,4,8-10; column 5, lines 52-61; column 4, lines 58-63; column 7, lines 18-22; example 5 *	1-4,6-8	B 01 J 27/22

D,A	US-A-4 149 998 (TAUSTER)		

A	DE-B- 973 187 (REINPREUSEN)		

A	GB-A- 678 941 (STANDARD OIL)		

A	US-A-2 690 449 (CLAUDE W. WATSON)		

The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23-10-1985	Examiner THION M.A.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			