

PROCESSES FOR PREPARING CATALYSTS

FIELD OF INVENTION

5 **[001]** The present invention relates to processes for the manufacture of supported catalysts and in particular to processes for the manufacture of supported catalysts comprising one or more active metals deposited on a support.

BACKGROUND OF THE INVENTION

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[002] Supported catalysts, in particular supported metal or metal oxide catalysts, are well known in the art. Dispersions of small metal particles on metal oxide substrates are commonly used as catalytic materials. The physical and chemical properties of the final catalyst can depend strongly on the preparation of the substrate prior to
15 deposition of the metal particles, on the methods of deposition used and on any subsequent treatments of the metal/oxide system.

[003] The ability to prepare high loaded metal catalysts that have small particle sizes (high dispersion) and metal particles that are homogeneously distributed on the support surface is an important requirement for effective supported catalysts. In many
20 instances, particularly with base metal catalysts, highly loaded metal catalysts have large metal particles (>10 nm) that are clustered in localized areas on the support. Since catalytic activity of many reactions correlates with the number of available surface metal sites, it is important to be able to produce catalysts with good metal
25 dispersion. Uniformity of the distribution of catalytic metal sites is also an important factor and maximization of the inter-particle distance can help to provide for stable supported catalysts with reduced sintering problems. Supported metal catalysts are often prepared by incipient wetness impregnation of solutions containing metal salts, dried and then calcined to form the oxides. The oxides are then reduced to form the
30 supported metal catalysts.

[004] There have been various attempts in the art to improve the dispersion of active metals deposited on refractory inorganic oxide supports to produce catalysts for use in Fischer-Tropsch processes. In particular there have been various approaches adopted in the art to reduce the amount of rhenium or other group 8 metals required in combination with the catalytic metal.

[005] In WO 98/47618A, multifunctional carboxylic acids having from about 3 to 6 total carbon atoms are co-deposited with sources of catalytically active metal onto a refractory metal oxide followed by calcination to prepare Fischer-Tropsch catalysts. Examples of the multifunctional carboxylic acids include various amino acids.

[006] In WO 98/47620 A, carbohydrate or sugars are either co-deposited with sources of catalytically active metal or are applied after deposition of the source of catalytically active metal onto a refractory metal oxide followed by calcination to prepare Fischer-Tropsch catalysts.

[007] In WO 98/47617 A, polyols are co-deposited with sources of catalytically active metal onto a refractory metal oxide followed by calcination to prepare Fischer-Tropsch catalysts.

[008] In US-A-3761428, platinum and iridium are deposited on a support using an aminoalcohol solution. Activation of the resultant catalyst is for example by heating at 520°C/4 hours (col.4 line 7 and col. 6 lines 53-54).

[009] In US-A-2889287, an aminoacid solution is used to impregnate a catalytic metal onto a support as a chelate. The chelate is then fully decomposed (col.2 lines 36-41).

[010] In JP-A-06182208 (Patent Abstracts of Japan Vol. 018, No. 525 (C-1257), 5 October 1994), there is taught the production of highly dispersed metals on supports using an aminoacid such as glutamic acid as a stabilizing agent. The carrier is

contacted with the impregnating liquid then dried and fired to produce the catalyst. Calcination temperatures of 500-600 C are preferred.

5 **[011]** Journal of Chemical Technology and Biotechnology, Vol. 29, No. 8, 1979, pages 480-486 (Aboul-Gheit Ahmed Kadry) teaches that mono-ethanolamine may be used as an additive to improve distribution of platinum on alumina. The calcinated catalyst is heated in a chemisorption furnace at 773 K (500°C) for 3 hours in hydrogen.

10 **[012]** In US-A-4073750, a nickel precursor such as nickel nitrate is dispersed on a support in a non-aqueous solvent. The solvent is then evaporated and the nickel precursor is reduced with hydrogen to disperse the nickel.

15 **[013]** US-A-4634515 teaches that nickel on alumina catalyst, where the average crystallite size of the nickel is at least 75 Angstrom, may be used as a sulphur trap for a reformer feed.

20 **[014]** US-A-6118037 teaches that a metal-modified silica gel may be used to absorb contaminants from feedstock streams.

[015] There is a continuing need for new methods for the preparation of supported metal catalysts, which enable the dispersion of metal in the final catalyst to be controlled.

25 **[016]** It is therefore an object of the present invention to provide processes for the manufacture of supported metal catalysts, which enables the control of metal dispersion in the catalyst.

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SUMMARY OF THE INVENTION

[017] In the process of the present invention it has been found that by exercising specific control over the reagents and the preparative steps used in the preparation of supported metal catalysts, supported metal catalysts with improved metal dispersion properties may be obtained.

[018] Thus in a first aspect the present invention provides a process for the manufacture of a catalyst comprising a catalytically active metal dispersed on a support, which process comprises:

a) preparing a support having an organic complex of the catalytically active metal deposited thereon by treating a porous support with a compound or salt of the metal and a nitrogen-containing organic compound selected from (i) amino acids and (ii) compounds containing both an amino group and an alcohol group, to form the organic metal complex on the support;

b) partially decomposing the organic metal complex on the support to the extent that the partially decomposed product (I) retains between 10 and 95% by weight of the dry weight attributed to the organic complex prior to partial decomposition, and (II) exhibits one or more infra-red absorption bands between 2100-2200 cm^{-1} that are not present in the organic complex before partial decomposition; and

c) converting the partially decomposed organic metal complex into catalytically active metal.

[019] In a second aspect step (a) of the process comprises;

(a1) treating a support with a compound, or salt, of one or more catalytically active metals to provide a support with one or more catalytic metal precursors deposited thereon, and

(a2) treating the support with one or more catalytic metal precursors deposited thereon with one or more of the specified organic compounds to form one or more organic complexes.

5 **[020]** In a further embodiment of the second aspect prior to treatment of the support with one or more catalytic metal precursors deposited thereon with one or more of the specified organic compounds, the support with one or more catalytic metal precursors deposited thereon may be thermally treated by calcination or pyrolysis. In a further embodiment of this aspect steps (a1) and (a2) may be reversed; the support
10 may be treated in a first step with one or more of the specified organic compounds and the support with one or more of the specified organic compounds deposited thereon may be treated with a compound, or salt, of one or more catalytically active metals to form one or more organic complexes on the support, followed by said partial decomposition of the one or more organic complexes and conversion to
15 catalytically active metal. In all embodiments of the second aspect the conversion to catalytically active metal may be carried out under reducing conditions e.g. in the presence of a source of hydrogen or CO. The organic compounds are the specified nitrogen-containing organic compounds. In the second aspect of the present invention either the treatment with one or more of said organic compounds or the
20 treatment with one or more compounds, or salts, of one or more catalytically active metals may be omitted if either of these compounds is introduced to the support during its preparation or synthesis.

25 **[021]** In the first aspect of the invention the first stage of the process may be achieved by formation of one or more organic complexes during the manufacture or synthesis of the support material. Alternatively the individual components required to form the complex may be incorporated into or within the support during its manufacture or synthesis, with formation of the organic complex occurring during a subsequent process step e.g. such as thermal treatment of such a support
30 incorporating the components.

[022] In a third aspect of the invention the catalyst formed by the process comprises one or more catalytically active metals deposited on one or more support materials wherein the total metal dispersion is 45% or more and the metal dispersion relating to a strongly chemisorbed component of the total metal dispersion is 20% or greater.

[023] In a fourth aspect the invention provides a process for the production of C₅+ liquid hydrocarbons from a hydrogen and carbon monoxide synthesis gas by contact of the said gas at reaction conditions with a catalyst, wherein the catalyst is manufactured according to the first or second aspects of the present invention.

[024] A fifth aspect of the invention provides a method for the removal of sulfur from a mixture comprising one or more organic compounds and one or more sulfur containing compounds, in which method the mixture is contacted with one or more materials comprising active metal dispersed on an inorganic support and prepared using a process according to the first or second aspects of the present invention, under such conditions that sulfur is adsorbed onto the material comprising active metal dispersed on an inorganic support. A preferred embodiment of this aspect is where the conditions selected are the normal conditions for Sulfur Trim treatment in the absence of added hydrogen.

BRIEF DESCRIPTION OF THE DRAWINGS

[025] The present invention will be better understood by reference to the Detailed Description of the Invention when taken together with the attached drawings wherein:

[026] Fig.1 shows a quadrapole mass spectrum of the product of Example 3 heated in air at 4 deg/min,

[027] Fig. 2 shows the transmission infra-red spectra of silica and Examples 3, 8 and 10,

5 [028] Fig. 3 shows an air treatment TGA plot for a supported metal catalyst (0.5 wt% Ru/SiO₂) prepared using impregnation of the metal with triethanolamine and drying at 100° C,

10 [029] Fig. 4 shows an air treatment TGA plot for a supported metal catalyst (0.5 wt% Ru/SiO₂) prepared using impregnation of the metal with triethanolamine and calcination at 300° C,

15 [030] Fig. 5 shows a hydrogen treatment TGA plot for a supported metal catalyst (0.5 wt% Ru/SiO₂) prepared using impregnation of the metal with triethanolamine and calcination at 300° C, and

[031] Fig. 6 shows the air treatment TGA plots for a variety of supported metal organic complexes (1 to 5 wt% metal/support), which have been dried at 100° C after formation of the organic complex.

20 DETAILED DESCRIPTION OF THE INVENTION

[032] The process of the present invention has been found to be effective in producing supported metal catalysts with good levels of metal dispersion and distribution of the catalytically active metal in the final catalyst. An important
25 feature of the process of the present invention is the selection of the components used in the preparation of the supported metal catalysts and the sequence of process steps used in arriving at the final catalyst composition.

30 [033] In all aspects of the present invention the process may utilize a wide variety of inorganic support materials in preparation of the catalysts. These materials may be refractory inorganic oxides and may be selected from a wide variety of porous and

non-porous support materials well known in the art. These include but are not limited to all forms of alumina, especially gamma alumina, all forms of silica, all forms of TiO₂ (both anatase and rutile or mixtures thereof), ZrO₂, activated carbon, silicon carbide, magnesium oxide, zinc oxide and similar metal oxides. The supports may
5 be any combination or mixture of two or more of these materials. The exact nature of the support material used will depend on the proposed use of the catalyst. In all aspects of the present invention the most preferred supports are amorphous supports. Particularly preferred supports are silica supports especially supports comprising amorphous silica. In relation to the fourth aspect of the present invention one
10 preferred support is a titanium oxide support modified with zirconium dioxide. A further class of preferred supports in all aspects of the present invention are porous supports especially supports having mesopores, macropores and mixtures thereof.

[034] For the purposes of the present invention, the terms "macropores" and
15 "mesopores" are used as they are defined in Pure Appl. Chem., 45 (1976), 79, namely as pores whose diameter is above 50 nm (macropores) or whose diameter is from 2 nm to 50 nm (mesopores).

[035] In all aspects of the present invention the support may be a molecular sieve
20 material such as for example a zeolite or zeolite like material. As molecular sieves there may be mentioned silicates, aluminosilicates, aluminophosphates, silicoaluminophosphates, metalloaluminophosphates, metallo-aluminophosphosilicates, or a stannosilicates. The preferred molecular sieve as catalyst support will depend on the chosen application such as for example
25 separations, catalytic applications, and combined reaction and separation applications. These are many known ways to tailor the properties of the molecular sieves, for example, structure type, chemical composition, ion-exchange, and activation procedures. Representative examples are molecular sieves/zeolites of the structure types AFI, AEL, BEA, CHA, EUO, FAU, FER, KFI, LTA, LTL, MAZ,
30 MOR, MEL, MTW, OFF, TON and MFI. Some of these materials while not being

true zeolites are frequently referred to in the literature as such, and this term will be used broadly in the specification below to include such materials.

[036] One class of molecular sieve material that may be used as catalyst supports in all aspects of the present invention are those materials that may be synthesized using amphiphilic compounds as directing agents. Examples of such materials are described in U.S. Patent No. 5 250 282. Examples of amphiphilic compounds are also provided in Winsor, Chemical Reviews, 68(1), 1968. Other suitable molecular sieve materials of this type are also described in "Review of Ordered Mesoporous Materials", U. Ciesla and F. Schuth, Microporous and Mesoporous Materials, 27, (1999), 131-49. Such materials include but are not limited to materials designated as SBA (Santa Barbara) such as SBA-2, SBA-15 and SBA-16, materials designated as FSM (Folding Sheet Mechanism) such as FSM-16 and KSW-2, materials designated as MSU (Michigan State) such as MSU-S and MSU-X, materials designated as TMS or Transition Metal Sieves, materials designated as FMMS or functionalized monolayers on mesoporous supports and materials designated as APM or Acid Prepared Mesostructure. Particularly preferred crystalline molecular sieve materials of this class are the silicate or aluminosilicate mesoporous molecular sieve materials designated as M41S such as MCM-41, MCM-48, and MCM-50. These molecular sieves are described in detail in U.S. Pat. No. 5,098,684 and U.S. Patent No. 5,102,643. A particularly suitable sub-class of this family of materials for use in the present invention are the mesoporous silicas designated as MCM-41 and MCM-48. MCM-41 is particularly preferred and has a hexagonal arrangement of uniformly sized mesopores. MCM-41 molecular sieve materials are described in detail in US 5 098 684. The MCM-41 molecular sieves have a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio when alumina is present that is greater than 100, more preferably greater than 200, and most preferably greater than 300. Other molecular sieves that may be used in all aspects of the present invention include those molecular sieves designated as MCM-1, MCM-2, MCM-3, MCM-4, MCM-5, MCM-9, MCM-10, MCM-14, MCM-22, and MCM-49.

[037] The preferred ordered mesoporous materials for use in all aspects of the present invention are the ordered mesoporous silicas. The most preferred ordered mesoporous silicas are those designated as MCM-41.

5 **[038]** Further examples of mesoporous materials that may be used in the process of the present invention are the mesoporous silicas as described in and prepared according to United States Patent No. 5,951,962. In this reference mesoporous silica is prepared by converting a silica precursor in a water and polymer dispersion containing reaction medium. The preferred polymer dispersion is a cationic polymer.

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[039] High surface area mesoporous alumina solids may be also be used in preparing the catalyst supports for use in the process of the present invention; such high surface area mesoporous alumina solids may be prepared according to the methods described in U.S. Patent No. 6,238,701.

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[040] The support may consist of macroporous materials or materials that are both macroporous and mesoporous, such as those described in U.S. Patent Nos. 5,936,126, 6,248,924 and 6, 284,917.

20 **[041]** One or more of the support materials may be of mixed porosity and may be used in addition to other support materials that have either mesopores or macropores. These materials of mixed porosity may possess mesopores in addition to their macropores. Examples of such material are described in U.S. Patent No. 6, 248,924 and 6, 284, 917.

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[042] In all aspects of the present invention the final catalyst may consist solely of one or more active metals deposited on the surfaces of one or more support materials. The catalyst in these embodiments is free of added inorganic binder. The supports with or without active metal deposited thereon may be shaped into a wide variety of
30 particle sizes. Generally speaking, the particles can be in the form of a powder, a granule, or a molded product, such as an extrudate having particle size sufficient to

pass through a 12.7 μm [2 mesh (Tyler)] screen and be retained on a 40 μm [400 mesh (Tyler)] screen. In cases where the catalyst is molded, such as by extrusion, the catalyst can be extruded before drying or partially dried and then extruded. In these embodiments various extrusion or forming aids may be used in the extrusion or
5 forming process along with one or more solvents.

[043] In all aspects of the present invention the support material with one or more active metals deposited thereon may be formed into composites with inorganic binder or matrix materials that are resistant to the temperatures and other conditions
10 employed in the catalytic processes envisaged for the catalyst. Such materials may also aid in the formation and manufacture of the final catalyst. Such materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays and/or oxides such as alumina, silica or silica-alumina. The latter may be either naturally occurring or in the form of
15 gelatinous precipitates or gels including mixtures of silica and metal oxides. Use of a material in conjunction with the zeolite, i.e., combined therewith or present during its synthesis, which itself is catalytically active may change the conversion and/or selectivity of the catalyst. These materials may be incorporated into naturally occurring clays, e.g., bentonite and kaolin, to improve the crush strength of the
20 catalyst under commercial operating conditions and function as binders or matrices for the catalyst. The support comprising one or more catalytically active metals may be formed into a composition comprising the matrix material in amounts from 99:01 to 05:95 by weight, preferably from 99:01 to 10:90, more preferably from 99:01 to 20:80, and most preferably from 99:01 to 50:50, catalyst support to matrix material.
25 Preferably, if used the additional matrix material is kept to a minimum typically less than 50 wt % of the combined weight of catalyst support and matrix material, ideally less than 40 wt%, preferably less than 30 wt%, more preferably less than 20 wt%, more preferably less than 15 wt%, most preferably less than 10 wt% and in a most preferred embodiment less than 5 wt%. Formation of the composition may be
30 achieved by conventional means including mulling the materials together followed by extrusion and pelletizing into the desired finished catalyst particles. Ideally the

additional matrix material is macroporous or is a material of mixed porosity i.e. both macroporous and mesoporous. The materials of mixed porosity may have a pore distribution in which from about 5 to about 50%, preferably from about 10 to about 45%, more preferably from about 10 to about 30 and in particular from about 15 to about 25%, of the pore volume is formed by macropores having pore diameters in the range from about 50 nm to about 10,000 nm and from about 50 to about 95%, preferably from about 55 to about 90%, more preferably from about 70 to about 90% and in particular from about 75 to about 85%, of the pore volume is formed by mesopores having a pore diameter of from about 2 to about 50 nm where in each case the sum of the pore volumes adds up to 100%.

[044] In all aspects of the present invention the process may be used to manufacture catalysts that are suitable for conducting carbon monoxide hydrogenation reactions especially Fischer-Tropsch reactions. In these embodiments a wide variety of support materials may be utilized such as those described above. Preferred support materials are titanium dioxide (both anatase and rutile), silica, silica-alumina, alumina and mixtures of titanium dioxide and zirconium dioxide. Supports comprising mixtures of titanium dioxide and zirconium dioxide are preferred. In a preferred embodiment the titanium dioxide is first washed to ensure that it is substantially chloride free and is then impregnated with a solution of a zirconium dioxide precursor such as $\text{ZrO}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, optionally dried and calcined to form the $\text{ZrO}_2/\text{TiO}_2$ support. The final support may comprise up to 50 wt % zirconium dioxide, preferably up to 35 wt%, more preferably up to 20 wt %, even more preferably up to 10 wt % and most preferably within the range of 0.1 to 5 wt % of zirconium dioxide based on the total weight of the support. In addition to the support additional components are often used such as promoters or modifiers. Preferred examples of such materials are rhenium, ruthenium, hafnium, zirconium, titanium, chromium, thorium and copper etc. A particularly preferred promoter or modifier is rhenium, which exhibits important properties during calcination of the catalyst after deposition of the one or more catalytically active metals especially and preferably when one of these metals is cobalt. During the calcination stage the rhenium assists in ensuring that the cobalt is

highly dispersed and it also helps to preserve the cobalt oxide formed in a highly dispersed state. A further benefit is that the rhenium lowers the temperature of reduction of the cobalt oxide to its zero valence state, which is its most catalytically active state; in this way rhenium makes it easier to more fully reduce the cobalt. One
5 problem with the use of rhenium in these catalysts is that it is an expensive material. Therefore, there exists a need for means to achieve good cobalt dispersion in these catalysts whilst at the same time reducing or eliminating the amount of rhenium needed to achieve full activity of the catalyst. It has been found that if the process of the present invention according to the first or second aspect is used it is possible to
10 manufacture Fischer-Tropsch catalysts with good cobalt dispersion using reduced amounts of rhenium and/or to achieve higher levels of cobalt dispersion at any given level of rhenium. When the process of the invention is used to manufacture a Fischer-Tropsch catalyst is in accordance with the first aspect of the present invention the organic complex is formed from one or more catalytically active metals
15 and one or more of the nitrogen containing compounds, such as amino acids. Other suitable nitrogen containing compounds are the amines as described below. As an alternative to cobalt or in addition to cobalt other catalytically active metals may be used in preparing the catalyst such as other iron group metals and copper. When the catalysts made by the process of the present invention are for use as a Fischer-
20 Tropsch catalyst, the titania support with or without zirconium dioxide may be used in combination with an inorganic binder such as alumina, silica or mixtures of alumina and silica. In this embodiment it is within the scope of the present invention to form the organic complex on the primary catalyst support i.e. without binder and before mixing with any binder or to form the organic complex on the support in
25 admixture with one or more binder materials.

[045] The process of the present invention may be used to manufacture catalysts that are suitable for the removal of organosulfur contaminants from hydrocarbon streams. The catalysts may be used in the absence of hydrogen to remove sulfur
30 species from a hydrocarbon stream. In such applications the level of metal dispersion in the catalyst is a critical factor in the effectiveness of the catalyst in removing the

sulfur species. It has been found that highly effective sulfur adsorption catalysts may be obtained by using the process according to the first or second aspects of the present invention. By using these processes it has been possible to highly disperse metals with sulfur adsorption activity on suitable supports. In these embodiments of the present invention a wide variety of support materials may be utilized such as those described above. A preferred support material is silica. In addition a wide variety of active metals suitable for sulfur treatment catalysts may be used; the preferred active metal is nickel. A preferred application is the removal sulfur in a process referred to in the art as Sulfur Trim.

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[046] In all aspects of the present invention the process produces a final catalyst that comprises one or more active metals deposited on one or more support materials. A wide variety of active metals may be used in all aspects of the present invention. The choice of active metal is dependent on the intended use of the final catalyst and such correlations between active metal and catalyst use are well known in the art. In all aspects of the present invention examples of active metals that may be used include but are not limited to one or more of the following: Group 1 (Group IA) such as Li, Na or K; Group 2 (Group IIA) such as Mg, Ca and Sr; Group 3 (Group IIIA, IIIB) such as Sc, Y and La; Group 4 (Group IVA, IVB) such as Ti, Zr and Hf; Group 5 (Group VA,VB) such as V, Nb and Ta; Group 6 (Group VIA, VIB) such as Cr, Mo and W; Group 7 (VIIA,VIIB) such as Mn, Tc, and Re; Groups 8, 9 and 10 (Group VIII, VIIIA) such as Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, and Pt; Group 11 (Group IB) such as Cu, Ag, and Au; Group 12 (Group IIB) such as Zn; Group 13 (Group IIIA, IIIB) such as Ga and In; and Group 14 (Group IVA, IVB) such as Ge and Sn. Preference is given to using copper, platinum, rhodium, palladium, cobalt, iron, nickel or ruthenium or a mixture of two or more thereof as active metal. A particular preference is given to using ruthenium, nickel, or cobalt or mixtures of two or more thereof. A particularly preferred active metal is ruthenium.

30 **[047]** The content of the metal component will vary according to its catalytic activity and the proposed use of the catalyst. Thus, the highly active noble metals

may be used in smaller amounts than the less active base metals. For example, about 1 wt. percent or less of ruthenium, palladium or platinum will be effective. The metal component may exceed about 30 percent in a monolayer.

5 **[048]** When the active metal is a highly active noble metal its content in the catalyst in all aspects of the present invention is generally from about 0.01 to about 30% by weight, preferably from about 0.01 to about 20% by weight and in particular from about 0.1 to about 10% by weight, more preferably 1 to 5% by weight in each case based on the total weight of the catalyst used. One preferred catalyst manufactured by
10 the process of the present invention is one that comprises ruthenium alone or in combination with one or more additional active metals at a total content of less than 5% by weight of active metal and preferably at a total content of less than 2% by weight of active metal. Preferably the content of ruthenium is from about 0.01 to 2%, more preferably 0.1 to 1% by weight of the total catalyst.

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[049] When the active metal is not particularly active or given the nature of the proposed application, such as in sulfur removal, high levels are required, in all aspects of the present invention the active metal may be present at levels of 10 wt % or more, preferably 15 wt % or more, more preferably 20 wt % or more and most
20 preferably within the range of 15 to 45 wt % based on the total weight of catalyst used.

[050] According to of the present invention the catalyst is manufactured via a process in which a support is provided with one or more catalytically active metal
25 sites through the use of a specific sequence of process steps. The process has as a first stage the formation of one or more organic complexes. In the first aspect the formation of the organic complex may be achieved through the simultaneous application of the one or more compounds or salts of the catalytically active metals with, preferably in a admixture with, one or more of the specified organic compounds
30 capable of forming a complex with the one or more salts or compounds of the metals. Alternatively the one or more organic complexes may be formed during the

manufacture or synthesis of the support; in this embodiment the support comprises organic complex formed in-situ. In an alternative embodiment the components required to form the organic complex are incorporated into or within the support during its manufacture or synthesis with formation of the organic complex occurring

5 during a subsequent process step such as thermal treatment of the support comprising the components. In the second aspect of the present invention the organic complex is formed in two distinct stages, the first being deposition of a salt or compound of one or more catalytically active metals and the second stage being the application of one or more of the specified organic compounds capable of forming a complex with the

10 one or more metals or salts or compounds of the metals. In the second aspect it is also possible to reverse these two stages with deposition of the specified organic compound preceding deposition of the salts or compounds of the metals, although this stage inversion in relation to the second aspect is not preferred. In the second aspect the stage requiring either the deposition of a salt or compound of one or more

15 catalytically active metals, or the stage requiring the deposition of one or more of the specified organic compounds capable of forming the complex, may be omitted if the compounds of either stage have been introduced into the support used during its manufacture or synthesis.

20 **[051]** In one embodiment of the first aspect a compound, or salt, of one or more catalytically active metals is combined with one or more of the specified organic compounds to form a mixture which is then contacted with a support to deposit the organic complex. In this embodiment the complex may be formed on formation of the mixture or may be formed after contact with the support and after removal of any

25 solvent or solvents used during formation of the mixture. In a further embodiment of these aspects one or more of the specified organic compounds and a compound, or salt, of one or more catalytically active metals are contacted simultaneously with the support to form the organic complex. In yet a further embodiment of this aspect a suitable organic complex of the desired metal may be synthesised and applied to the

30 support via solution of the complex in a suitable solvent for the complex. In yet a further embodiment of the first aspect the organic complex may be formed in-situ

during the manufacture or synthesis of the support material or from components required for formation of the organic complex, that have been incorporated into or within the support during its manufacture or synthesis.

5 **[052]** In the second aspect the support is first contacted with a compound, or salt, of one or more catalytically active metals followed by treatment with one or more of the specified organic compounds to form the organic complex on the support. In an alternative embodiment the support is first contacted with one or more of the specified organic compounds followed by treatment with a compound, or salt, of one
10 or more catalytically active metals to form the organic complex on the support. In either embodiment the compounds may be introduced during manufacture or synthesis of the support.

[053] In the second aspect of the present invention the one or more catalytically
15 active metals may be exchanged onto the support material, impregnated into it or physically admixed with it. The application of the individual components or mixture of components may be achieved by steeping the support in an aqueous metal salt solution, or a solution in a suitable solvent of a compound of the metal. In the first aspect of the present invention a mixture of a compound, or salt, of one or more
20 catalytically active metals with one or more of the specified organic compounds may be brought into contact with the support to form the organic complex. In all aspects one or more of the components or mixtures of components may be brought into contact with the support materials using such methods as dipping, spraying, slurry techniques or any other suitable method. The preferred methods are impregnation of
25 the support using such techniques as incipient wetness or slurry techniques. In all aspect of the present invention suitable metal salts for preparing the metal salt solutions for use in preparing the mixtures are for example nitrates, nitrosyl nitrates, halides, carbonates, carboxylates, acetylacetonates, chloro complexes, nitrito complexes or ammine complexes of the corresponding metals, with preference being
30 given to the nitrates and nitrosyl nitrates and most preferably the nitrosyl nitrates. In all aspects of the present invention the specified organic compounds are present in

addition to the normal counter ion or moiety of the salt or compound of the active metal. However, this may not be the case where the organic complex is prepared in a separate procedure for use in the processes of the present invention; in these circumstances the original counter-ions or moieties for the salt or compound of the metal will have been removed from the purified organic metal complex. The original counter ion may also be absent when the organic complex is prepared in-situ during the manufacture or synthesis of the support or where the components required to form the complex are incorporated into or within the support during its manufacture or synthesis; in these embodiments the counter-ion to the metal may be provided by a charge associated with the support structure or the organic moiety or moieties of the organic complex. When Pt is the active metal it is preferred that it is not complexed with the organic compound as its nitrate salt, preferably it is complexed as a chloride or hydroxide salt.

15 **[054]** In all aspects of the present invention catalysts that have a plurality of active metals applied to the support may have these metals applied simultaneously using the various process of the present invention or the process steps may be repeated to apply the metals in sequence.

20 **[055]** In all aspects of the present invention any the nitrogen-containing organic compounds employed are capable of forming organic complexes with the one or more catalytically active metals. Typically these will be organic compounds that are capable of forming complexes that are stable under the conditions that are normally used for depositing catalytically active metals. Ideally, the organic compounds are selected to provide metal organic complexes that are stable under the conditions normally used for drying catalyst supports after impregnation with one or more catalytically active metals. In all aspects of the present invention the organic compound may be one or more organic compounds used in the manufacture of the support or present during its synthesis, such as for example organic templates used in the manufacture of molecular sieve supports.

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[056] In the process of the present invention the nitrogen-containing organic compounds are compounds that contain one or more amino groups and are (i) amino acids, or (ii) compounds containing both an amino group and an alcohol group within the compound.

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[057] Such above-specified compounds having one or more amino groups may be aliphatic amines, cycloaliphatic amines, aralkyl amines and alkylaryl amines. These may be primary, secondary and tertiary amines. It is preferred that the nitrogen-containing compound is one or more primary, secondary or tertiary amine, preferably one or more aliphatic amines containing one or more alcohol groups such as for example those found in hydroxyalkylamines.

[058] In one embodiment, the nitrogen-containing compound used according to the present invention has the following general formula:



wherein (subject to the compound being selected from compounds containing both an amino group and an alcohol group)

[059] R^1 , R^2 and R^3 independently are one or more of the following groups: $\text{C}_1 - \text{C}_{50}$ -alkyl, $\text{C}_3 - \text{C}_{50}$ -cycloalkyl, aromatic, alkyl substituted aromatic, such as $\text{C}_1 - \text{C}_{50}$ -alkyl substituted aromatic, aromatic substituted aliphatic moieties such as $\text{C}_1 - \text{C}_{50}$ -alkylene moieties substituted with one or more aromatic groups, $\text{C}_1 - \text{C}_{50}$ -hydroxyalkyl, amino- and/or hydroxyl-substituted $\text{C}_1 - \text{C}_{50}$ -alkyl, alkoxyalkyl such as $\text{C}_2 - \text{C}_{50}$ -alkoxyalkyl, dialkylaminoalkyl such as $\text{C}_3 - \text{C}_{50}$ -dialkylaminoalkyl, alkylaminoalkyl such as $\text{C}_2 - \text{C}_{50}$ -alkylaminoalkyl, heterocyclic, aromatic heterocyclic, alkyl substituted heterocyclic and alkyl substituted aromatic heterocyclic, such as $\text{C}_1 - \text{C}_{50}$ -alkyl substituted heterocyclic and aromatic heterocyclic compounds, and heterocyclic substituted aliphatic moieties such as $\text{C}_1 - \text{C}_{50}$ -alkylene moieties substituted with one or more aromatic groups. In addition, R^1 and R^2 may independently be hydrogen. In another embodiment, R^1 and R^2 may form, with the

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nitrogen atom, a nitrogen-containing heterocycle, aromatic heterocycle, alkyl substituted heterocycle or alkyl substituted aromatic heterocycle.

[060] Examples of alkyl groups include; methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, sec-pentyl, neopentyl, 1,2-dimethylpropyl, n-hexyl, isohexyl, sec-hexyl, n-heptyl, isoheptyl, n-octyl, isooctyl, 2-ethylhexyl, n-decyl, 2-n-propyl-n-heptyl, n-tridecyl, 2-n-butyl-n-nonyl and 3-n-butyl-n-nonyl, particularly preferably ethyl, isopropyl, 2-ethylhexyl, n-decyl, 2-n-propyl-n-heptyl, n-tridecyl, 2-n-butyl-n-nonyl and 3-n-butyl-n-nonyl, and C_{40} – C_{200} -alkyl such as polybutyl, polyisobutyl, polypropyl, polyisopropyl and polyethyl. The most preferred aliphatic amines are aliphatic amines having one or more alkyl groups having 1 to 20 carbon atoms and more preferably 2 to 14 carbon atoms.

[061] Examples of cycloalkyl groups include C_3 – C_{12} -cycloalkyl, preferably C_3 – C_8 -cycloalkyl such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl.

[062] Examples of aromatic groups include; phenyl, 1-naphthyl, 2-naphthyl, 1-anthryl, 2-anthryl and 9-anthryl, 1-phenanthryl, 2-phenanthryl, 3-phenanthryl, 4-phenanthryl and 9-phenanthryl.

[063] Examples of alkyl substituted aromatic groups include C_7 – C_{50} alkyl aromatic groups, preferably C_7 – C_{40} -alkylphenyl such as 2-nonylphenyl, 3-nonylphenyl, 4-nonylphenyl, 2-decylphenyl, 3-decylphenyl, 4-decylphenyl, 2,3-dinonylphenyl, 2,4-dinonylphenyl, 2,5-dinonylphenyl, 3,4-dinonylphenyl, 3,5-dinonylphenyl, 2,3-didecylphenyl, 2,4-didecylphenyl, 2,5-didecylphenyl, 3,4-didecylphenyl and 3,5-didecylphenyl, more preferably C_7 – C_{12} alkylphenyl such as 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 2,4-dimethylphenyl, 2,5-dimethylphenyl, 2,6-dimethylphenyl, 3,4-dimethylphenyl, 3,5-dimethylphenyl, 2,3,4-trimethylphenyl, 2,3,5-trimethylphenyl, 2,3,6-trimethylphenyl, 2,4,6-trimethylphenyl, 2-ethylphenyl,

3-ethylphenyl, 4-ethylphenyl, 2-n-propylphenyl, 3-n-propylphenyl and 4-n-propylphenyl.

- [064]** Examples of aromatic substituted aliphatic moieties include C₇-C₅₀ alkylene moieties substituted with one or more aromatic substituents, preferably C₇-C₁₂-phenylalkyl such as benzyl, 1-phenethyl, 2-phenethyl, 1-phenylpropyl, 2-phenylpropyl, 3-phenylpropyl, 1-phenylbutyl, 2-phenylbutyl, 3-phenylbutyl and 4-phenylbutyl, particularly preferably benzyl, 1-phenethyl and 2-phenethyl.
- 10 **[065]** Examples of hydroxyalkyl groups include amines having one or more C₁-C₅₀-hydroxyalkyl groups, preferably C₁-C₈-hydroxyalkyl groups, particularly preferably C₁-C₄-hydroxyalkyl groups such as hydroxymethyl, 1-hydroxyethyl, 2-hydroxyethyl, 1-hydroxy-n-propyl, 2-hydroxy-n-propyl, 3-hydroxy-n-propyl and 1-hydroxy-methyl-ethyl. Particularly preferred hydroxyalkyl group containing nitrogen compounds
- 15 include the mon-, di-, and tri-, substituted aliphatic hydroxyalkylamines such as methanolamine, di-methanolamine, tri-methanolamine, ethanolamine, di-ethanolamine, tri-ethanolamine, butanolamine, di-butanolamine, tri-butanolamine, propanolamine, di-propanolamine, and tri-propanolamine. Also preferred are N,N,-dialkyl-ethanolamines, N-alkyl-diethanolamines, N-alkyl-ethanolamines, N,N,-
- 20 dialkyl-methanolamines, N-alkyl-dimethanolamines, N-alkyl-methanolamines and equivalent propanolamines, butanolamines, hexanolamines and heptanolamines. In these alkanolamines the N-alkyl group may be a hydrocarbon or substituted hydrocarbon group containing from 1 to 50 carbon atoms, preferably 1 to 8 carbon atoms and most preferably 1 to 4 carbon atoms such as methyl, ethyl, n-propyl,
- 25 isopropyl, n-butyl, isobutyl, n-pentyl, isopentyl, n-hexyl, isohexyl etc.
- [066]** Examples of amino- and hydroxyalkyl groups include C₁-C₅₀-alkyl, preferably amino- and/or hydroxyl-substituted C₁-C₈-alkyl, particularly preferably amino and/or hydroxyl-substituted C₁-C₄-alkyl such as N-(hydroxyethyl)aminoethyl
- 30 and N-(aminoethyl)aminoethyl.

- [067]** Examples of alkoxyalkyl groups include C₂-C₅₀-alkoxyalkyl, preferably C₂-C₂₀-alkoxyalkyl, particularly preferably C₂-C₈-alkoxyalkyl such as methoxymethyl, ethoxymethyl, n-propoxymethyl, isopropoxymethyl, n-butoxymethyl, isobutoxymethyl, sec-butoxymethyl, tert-butoxymethyl, 1-methoxyethyl and 2-methoxyethyl, particularly preferably C₂-C₄-alkoxyalkyl such as methoxymethyl, ethoxymethyl, n-propoxymethyl, isopropoxymethyl, n-butoxymethyl, isobutoxymethyl, sec-butoxymethyl, tert-butoxymethyl, 1-methoxyethyl and 2-methoxyethyl.
- [068]** Examples of dialkylamino groups include C₃-C₅₀-dialkylaminoalkyl, preferably C₃-C₂₀-dialkylaminoalkyl, particularly preferably C₃-C₁₀-dialkylaminoalkyl such as dimethylaminomethyl, dimethylaminoethyl, diethylaminoethyl, di-n-propylaminoethyl and diisopropylaminoethyl.
- [069]** Examples of alkylaminoalkyl groups include C₂-C₅₀-alkylaminoalkyl, preferably C₂-C₂₀-alkylaminoalkyl, particularly preferably C₂-C₈-alkylaminoalkyl such as methylaminomethyl, methylaminoethyl, ethylaminomethyl, ethylaminoethyl and iso-propylaminoethyl.
- [070]** Examples of aromatic heterocycles include 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, pyrazinyl, 3-pyrrolyl, 2-imidazolyl, 2-furanyl and 3-furanyl. Examples of alkyl substituted aromatic heterocycles include C₄-C₅₀-mono-hetarylalkyl, such as 2-pyridylmethyl, 2-furanyl-methyl, 3-pyrrolylmethyl and 2-imidazolylmethyl, and C₄-C₅₀-alkylhetaryl such as 2-methyl-3-pyridinyl, 4,5-dimethyl-2-imidazolyl, 3-methyl-2-furanyl and 5-methyl-2-pyrazinyl.
- [071]** Examples of alkylaminoalkyl groups include C₂-C₅₀-alkylaminoalkyl, preferably C₂-C₁₆-alkylaminoalkyl such as methylaminomethyl, methylaminoethyl, ethylaminomethyl, ethylaminoethyl and isopropylaminoethyl.

[072] Examples of dialkylaminoalkyl groups include C₃ -C₅₀ -dialkylaminoalkyl, preferably C₃ -C₁₆ -dialkylaminoalkyl such as dimethylaminomethyl, dimethylaminoethyl, diethylaminoethyl, di-n-propylaminoethyl and diisopropylaminoethyl.

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[073] Examples of heterocyclic compounds, include pyridine, pyrrole, imidazole, oxazole, thiazole, pyrazole, 3-pyrroline, pyrrolidine, pyrimidine, and substituted examples of these heterocyclic compounds. Examples of organonitrile compounds include acrylonitrile, alkyl nitriles such as for example methyl nitrile, and ethyl nitrile.

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[074] Suitable amino acids include natural and synthetic amino acids. The natural amino acids include all isomers of the following: alanine, arginine, asparagines, aspartic acid, cysteine, cystine, 3, 5-dibromotyrosine, 3,5, diiodotyrosine, glutamic acid, glutamine, glycine, histidine, hydroxylysine, hydroxyproline, isoleucine, leucine, lysine, methionine, phenylalanine, proline, serine, threonine, thyroxine, tryptophane, tyrosine and valine. A particularly preferred amino acid is L-arginine.

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[075] In all aspects especially the first and second aspects of the present invention the organic nitrogen containing compounds are preferably amines containing one or more alcohol groups.

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[076] In all aspects of the present invention the specified organic compound may be introduced into the manufacture or synthesis of the support. The organic compound may be an organic template as used in the synthesis of the support when the support is a molecular sieve. Such organic templates are well known in the art. The organic compound may be introduced in addition to any organic template during the manufacture or synthesis of the support. In all aspects when either or all components for the preparation of the organic complex are incorporated into or within the support or the organic complex itself is incorporated into or within the support, the support may be used in the green state.

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[077] The specified organic compound may be used at any suitable level in relation to the amount of salt or compound of the catalytically active metal. The organic compound may be present in excess of that required to form the organic complex. Ideally the compounds are used at an appropriate mole ratio to convert all of the salt or compound of the catalytically active metal to one or more organic complexes. This may be a molar ratio of 1:1 or higher depending on the capacity of the metal to complex with the organic compound, the capacity of the organic compound to complex with the metal and the presence of other complexing ligands such as monodentate ligands. However it is possible to use levels of organic compound which are insufficient to complex with all of the catalytically active metal; in these circumstances not all of the metal is converted to organic complex and the resulting catalyst may contain catalytically active metal sites that have been derived from complexed and non-complexed metal intermediates. Ideally, the mole ratio of organic compound to catalytically active metal is within the molar ratio range of 0.1 : 1 to 40 :1, preferably, 0.1 :1 to 30:1, more preferably 0.2 :1 to 25:1, even more preferably 0.5 :1 to 10:1, most preferably 0.5 : 1 to 5:1. Excess organic compound may be present when the organic compound is incorporated into or within the support during manufacture or synthesis of the support.

[078] When the complex is formed in a mixture before contact with the support the mixture is usually and preferably formed in combination with a solvent, which may be water or an organic solvent or a mixture of water and solvent. The amount of solvent used may vary within wide ranges but is typically sufficient to ensure that the mixture may be effectively contacted with the support so as to wet the support and when the support is porous to allow penetration of the mixture into the porous support. Typically the salt or compound of one or more catalytically active metals and the organic compound(s) are used in amounts which depending on their form allow the required mole ratios indicated above to be achieved in the mixture. The remainder of the mixture comprises one or more solvents which may be present in an amount from 1 to 99 wt % of the weight of the total mixture, preferably 5 to 90 wt % of the weight of the total mixture, more preferably 5 to 80 wt% of the weight of the

total mixture, even more preferably 10 to 70 wt % of the weight of the total mixture and most preferably 10 to 65 wt % of the weight of the total mixture. Additional solvents may also be used in the second aspect of the present invention in order to facilitate application of one or more of the components required to manufacture the catalyst.

[079] In all aspects especially in the first aspect after formation of the organic complex on the support the support may and preferably is dried to remove most of the solvent and/or water present during formation of the complex. Drying may be achieved under ambient conditions such as room temperature or this may be achieved at elevated temperatures. Preferably drying is at a temperature from 100 to 150° C. Preferably, little or no decomposition of the organic complex occurs during the drying phase and drying merely results in the removal of non-complexed volatile materials.

[080] In the second aspect of the present invention the support may be dried after each or all deposition stages. Drying may be achieved under ambient conditions such as room temperature or this may be achieved at elevated temperatures. Preferably drying is at a temperature from 100 to 150° C. Preferably, for the drying stage which follows formation of the complex little or no decomposition of the organic complex occurs during the drying phase and drying merely results in the removal of non-complexed volatile materials.

[081] In the first and second aspects of the present invention once the support comprising one or more organic complexes has been prepared the support is treated so as to partially decompose the organic complex on the support. Although not wishing to be bound by any theory it is believed that this partial decomposition results in the formation in-situ of one or more precursors to the catalytically active metal sites. It is believed that it is, in part, the formation of these precursors and their subsequent conversion that ensures that in these aspects the final catalyst exhibits a high degree of catalytic activity and has high levels of metal dispersion within the

catalyst. An important parameter in the activity of catalytically active metals is the form of the metal on the support and the level of dispersion of the metal on the support. The process of the present invention produces catalysts that comprise catalytically active metal sites that are relatively small and highly dispersed. In addition the level of dispersion is relatively stable.

[082] In all aspects of the present invention when reference is made to relatively small metal particles as active metal sites it is meant metal particles with an average particle size of 10nm or less, preferably 8nm or less, and most preferably 6nm or less.

[083] Chemisorption measurements are commonly used to estimate the size of supported metal catalysts and metal surface area. The general method for measuring metal surface area by chemisorption is described in J. Lemaitre et al.,

"Characterization of Heterogenous Catalysts", edited by Francis Delanney, Marcel

Dekker, New York (1984), pp. 310-324. The total metal surface area is ideally within the range from 0.01 to 30 m²/g, preferably from 0.05 to 25 m²/g, more preferably from 0.05 to 20 m²/g, even more preferably from 0.05 to 15 m²/g, more preferably from 0.05 to 10 m²/g, even more preferably from 0.05 to 5 m²/g and most preferably from 0.05 to 3 m²/g of the catalyst. From chemisorption measurements, the %

dispersion (% of metal atoms that populate the surface of the metal particles) can be estimated since a properly chosen titrant used in the chemisorption measurements adsorbs only on metal atoms populating the surface. Consequently higher dispersion values indicate smaller particles with more of the metal atoms populating the surface.

For many hydrogenation reactions, activity correlates with dispersion. The preferred

method for determining metal dispersion is by using hydrogen as the chemisorption probe molecule under high vacuum static conditions as follows. The sample is held at a temperature of 40°C and an 8-point isotherm (with pressures between 10.6 and 53.3 kPa [80 and 400 torr]) is obtained using H₂ as the chemisorption probe molecule.

The linear portion of this isotherm is extrapolated to zero pressure to obtain the total quantity of hydrogen chemisorbed; this is the combined dispersion. The sample is then evacuated at 40°C to remove any weakly adsorbed hydrogen and the titration

repeated to determine what is referred to as weak adsorption isotherm. The linear portion of this weak adsorption isotherm is extrapolated to zero pressure to obtain the quantity of weakly chemisorbed hydrogen. Subtraction of these two values for combined dispersion and weak dispersion yields the strongly held chemisorbed quantity. Thus this method provides values for the total metal dispersion, the dispersion due to weakly chemisorbed hydrogen and dispersion due to strongly chemisorbed hydrogen. The value for the strongly chemisorbed hydrogen is an accurate indication of metal dispersion. In many prior art references the metal dispersion figures provided are based on the total chemisorbed probe and are not split into strong and weak components. In the present invention it is preferred that the hydrogenation catalysts used have dispersion values relating to the strongly chemisorbed component in excess of 20% more preferably in excess of 25% and most preferably in excess of 30%. In addition total dispersion values in excess of 45% preferably in excess of 50%, more preferably in excess of 55%, and most preferably in excess of 60% are achieved. Preferably 40% or more of the total metal dispersion relates to the strongly chemisorbed component, more preferably 45 % or more and most preferably 50% or more.

[084] In accordance with the present invention the organic complex is at least partially decomposed. In the context of the present invention "partial decomposition" means that the chemical composition of the organic complex is varied; this may be due to a change in the structure of the organic complex or may be due to the chemical destruction of part of or a component of the complex. The method of destruction is selected to ensure that the removal of non-metal chemical species associated with the complex is incomplete. The partial decomposition is due to variations in structure and/or composition that do not normally occur under the drying conditions typically used in catalyst preparation methods. The changes of structure and/or composition under the conditions of the second stage may be detected and monitored using various analytical techniques that are well known in the art such as infra-red spectroscopy, mass spectroscopy, thermogravimetric analysis, gas or liquid chromatography and spectroscopy.

[085] A variety of methods may be used to induce partial destruction of the organic complex. These include chemical methods such as chemically induced hydrolysis or decomposition such as by the treatment with acid or base or ozone or similar chemical active materials. Other methods for inducing partial decomposition include thermal methods such as pyrolysis and/or calcination, both of which are the preferred methods with particular preference being given to calcination. A further method is treatment with steam. In one embodiment the pyrolysis may be carried out in the presence of hydrogen; in this embodiment any subsequent treatment with hydrogen may be omitted. Other methods that may be used are those that would ensure that the organic complex is converted to catalytically active metal such as for example under reducing conditions in the presence of hydrogen and/or CO. In an alternative embodiment in relation to all aspects of the present invention the partial decomposition may be achieved by introducing the support comprising organic complex into the intended catalyzed process itself. In these embodiments the organic complex is decomposed under the process conditions of use if the support comprising organic complex is introduced directly into the catalyzed process or under the conditions used at any point of introduction of catalyst into the process plant such as the conditions in a catalyst regeneration unit or catalyst recycle unit. It is also envisaged that when decomposition is achieved in the process of use then the conversion of the partially decomposed organic complex to catalytically active metal is also achieved in the same process either during the decomposition or subsequent to the decomposition in a separate conversion stage or unit where the conditions may be different from those of the process; such as those present in a catalyst regeneration or recycle unit. The destruction and conversion may be achieved in subsequent catalyst processing steps such as when the catalyst support comprising organic complex is formulated into a final catalyst composition that may comprise one or more binders and/or other formulated components. In these additional steps process conditions may be used that result in decomposition and/or conversion.

[086] When calcination or pyrolysis is used as the method for partial decomposition of the organic complex the exact conditions used will depend on the nature of the

complex and especially its thermal stability and decomposition profile under elevated temperature. By using thermogravimetric methods or mass spectroscopy linked with controlled thermal decomposition of the organic complex it is possible to determine at what temperature either under calcination conditions or pyrolysis conditions the initial decomposition and total decomposition of the organic complex occurs. This indicates the temperature range at which this partial decomposition stage should be undertaken. Alternatively when analysed by infra-red spectroscopy it may be determined at what point in the treatment a certain functional group is either removed from or formed in the organic complex; the temperature at which this occurs if below the total decomposition temperature may be selected as the temperature for the partial decomposition. In the case of the amines containing hydroxyl groups or the amino acids required as the organic compound according to the invention it is the formation of new vibration bands that appear in the infra-red spectra at between 2100-2200 cm^{-1} and tentatively assignable to complex carbon nitrogen species such as nitriles and isonitriles being present in the partially decomposed organic complex. Another method that may be used is where TGA analysis shows total weight loss of the organic complex; temperatures below total weight loss may be selected for partial decomposition.

[087] In all aspects of the present invention when calcination is used to partially decompose the organic complex the calcination temperatures used are typically within the range of 200 to 1000° C, preferably from 250 to 600° C. The exact temperature used will depend on the nature of the organic complex. Factors that may affect the decomposition temperature of the organic metal complex include the nature of the metal and/or organic compound within the complex. Another factor may be the nature of the counter-ion present when the metal is introduced in the form of a salt. The support with the organic complex deposited thereon is calcined at a temperature that is less than the temperature as determined by TGA in air, at which total weight loss of the organic complex occurs. Preferably it is between 200 °C and the temperature at which total weight loss of the organic complex occurs. Under calcination conditions oxygen is present either as a component of an otherwise inert

diluent or as a consequence of calcination being undertaken in air. When pyrolysis is used the pyrolysis may be undertaken in an inert atmosphere free of oxygen or in an atmosphere that also results in conversion to catalytically active metal such as a hydrogen or a CO containing atmosphere that may be and preferably is free of oxygen. When pyrolysis is used the organic complexes may decompose at higher temperatures than those observed under calcination conditions. As with calcination the temperature, under pyrolysis conditions, for partial decomposition may be determined using a variety of methods of which TGA is preferred. For partial decomposition under pyrolysis conditions in an inert atmosphere or under hydrogen, the support with the organic complex deposited thereon is pyrolysed in an inert atmosphere or under hydrogen at a temperature that is less than the temperature as determined by TGA in an inert atmosphere or under hydrogen, at which total weight loss of the organic complex occurs. Preferably it is between 200 °C and the temperature at which total weight loss of the organic complex occurs under pyrolysis conditions in an inert atmosphere or under hydrogen. The support comprising organic complex may be calcined or pyrolysed at the partial decomposition temperature for a period of time that is sufficient to ensure the partial decomposition of the organic complex occurs. Typically this will be for a period of at least 20 minutes, preferably at least 30, more preferably at least 45 minutes and most preferably for 1 hour or more. Typically the period of time is 48 hours or less, preferably 24 hours or less and most preferably 12 hours or less.

[088] The support comprising the decomposition product of the organic complex (ie the product of step (b) of the process of the invention) is a catalyst precursor comprising at least one support material and at least one source of one or more catalytically active metals deposited on the support material, wherein the source of one or more catalytically active metals is the partially decomposed product of one or more metal containing organic complexes. It is preferred that the catalyst precursor exhibits dispersion values, when using hydrogen as the titrant, relating to the strongly chemisorbed component that are less than 1%, more preferably less than 0.75%, yet more preferably less than 0.5%, even more preferably less than 0.25% and most

preferably 0%. According to the invention the precursors exhibit unique absorption bands in their infra-red spectra; thus they comprise one or more infra-red absorption bands within the range $2100\text{-}2200\text{ cm}^{-1}$ not present in the pre-decomposed organic complex. The precursor also retains a significant proportion of the weight of the original organic complex; thus the precursor retains between 10 and 95% by weight of the weight attributed to the organic complex after drying the support with complex formed thereon. The precursor preferably retains between 20 and 75% by weight of the weight of the original complex, more preferably it retains up to 60%, even more preferably up to 50%, and most preferably up to 40%. It is also a property of the precursor when the organic complex is partially decomposed that its reduction temperature to form the catalytically active metal is in excess of the normal reduction temperature required to reduce the fully oxidized metal complex to catalytically active metal, preferably it is at least 5% in excess, more preferably 10% in excess, even more preferably 15% in excess and most preferably 20% in excess of the normal reduction temperature.

[089] In accordance with all aspects of the present invention after partial decomposition of the complex the partially decomposed complex is converted to catalytically active metal. Preferably, the conversion is achieved via treatment of the partially decomposed complex under conditions to reduce the partially decomposed complex; in the presence of a reductant source. In preferred embodiments the reductant source is a source of hydrogen and/or carbon monoxide. In further embodiment in relation to all aspects the conversion may be achieved by introduction of the support comprising one or more partially decomposed organic complexes into a process designed to use the final catalyst; in this embodiment the conversion occurs under the process conditions or the conditions present in a catalyst regeneration or recycle unit associated with the process. In a preferred embodiment this treatment is undertaken using conditions and methods normally used for the activation of catalysts. These conditions and methods are selected to ensure that the catalyst precursor is converted to catalytically active metal. In one embodiment the treatment with reductant e.g. source of hydrogen and/or CO is carried out by contacting the

support comprising partially decomposed complex with a gas stream comprising reductant e.g. a source of hydrogen and/or CO at from 30 to 600° C, preferably from 100 to 550° C, even more preferably from 200 to 500° C, and most preferably from 200 to 450° C. When the reductant stream comprises free hydrogen it preferably
5 consists of from 50 to 100% by volume of H₂ and from 0 to 50% by volume of N₂. The treatment may be carried out under a continuous flow of reductant e.g. source of hydrogen and/or CO under atmospheric pressure or under static conditions at elevated pressures up to 100 bar, preferably 1 to 90 bar, more preferably 1 to 20 bar. The activation may be undertaken for a period of up to 48 hours, preferably no more
10 than 36 hours, more preferably less than 24 hours, and most preferably from 30 mins to 12 hours. In the first and second aspects preferably the support comprising partially decomposed complex is exposed to reductant e.g. source of hydrogen and/or CO at atmospheric pressure and the temperature raised at a rate of 2° C min⁻¹ to the treatment temperature where reductant treatment is continued for a further 1 to 10
15 hours, preferably 2 to 8 hours and most preferably 3 to 6 hours. In the first and second aspects the exact temperature and time are selected to ensure that under the reductant treatment any residual partially decomposed organic complex is removed; therefore the reductant treatment temperature is generally higher than the decomposition temperature of the organic complex and especially the partially
20 decomposed organic complex.

[090] If a plurality of active metals are to be applied to the support and the application is carried out in succession, the various process stages of the present invention may be repeated in order to deposit each metal in sequence.

[091] The total metal surface area is ideally within the range from 0.01 to 30 m²/g, preferably from 0.05 to 25 m²/g, more preferably from 0.05 to 20 m²/g, even more preferably from 0.05 to 15 m²/g, more preferably from 0.05 to 10 m²/g, even more preferably from 0.05 to 5 m²/g and most preferably from 0.05 to 3 m²/g of the
30 catalyst. The metal surface area may be measured by the chemisorption method as herein described.

[092] The catalysts obtained from the processes of the present invention may be used in a wide variety of processes for the conversion of organic compounds where a chemical reaction occurs and is catalyzed. In addition the materials obtained from the first and second aspects of the present invention may be used in a wide variety of processes for the treatment of organic compounds or mixtures of organic compounds in order to convert or remove relatively small amounts of impurities; in this application the materials obtained from the processes of the present invention may be acting as adsorbents.

10 [093] Of particular interest in the present invention is the production of C₅+ liquid hydrocarbons from a hydrogen and carbon monoxide synthesis gas by contact of the said gas at reaction conditions with a catalyst obtained from the processes according to the first and second aspects of the present invention.

15 [094] Of particular interest in the present invention is the treatment of organic compounds especially hydrocarbons in admixture with quantities of sulfur containing compounds especially organosulfur compounds, with materials obtained from the processes of the first and second aspects of the present invention, in order to remove some or all of the sulfur from the organic compounds. Preferably this treatment is under the normal conditions for Sulfur Trim treatment and in the absence of
20 hydrogen.

[095] The process of the present invention is further illustrated by means of the following examples.

25 EXAMPLES

Example 1. Hydrogen treatment and Measurement of H chemisorption values for supported Ru catalysts of Examples 2 to 10

30 [096] (A) Activation. Approximately 0.3 to 0.5 gram catalyst was loaded in the chemisorption cell, reduced in flowing hydrogen at 101 kPa (one atmosphere) total

pressure at the temperature indicated in Tables 1 to 5. The samples were heated to the final reduction temperature at 2°C/min and held at this temperature for three hours. After this treatment the catalyst was activated and ready for use as a catalyst.

- 5 [097] (B) The chemisorption measurements were obtained under static high vacuum conditions. After the hydrogen treatment under (A) hydrogen was then pumped off under dynamic vacuum for 15-30 minutes at the reduction temperature indicated in Tables 1 to 5. The temperature was lowered to 40°C and an 8-point isotherm (with pressures between 10.6 and 53.3 kPa (80 and 400 torr) was obtained using H₂ as the
- 10 chemisorption probe molecule. The linear portion of this isotherm was extrapolated to zero pressure to obtain the total quantity of hydrogen chemisorbed. This is shown in Tables 1 to 5 in the column labeled % dispersion (combined). The sample was evacuated at 40°C to remove any weakly adsorbed hydrogen and the titration repeated to determine the weak adsorption isotherm. The linear portion of this isotherm was
- 15 extrapolated to zero pressure to obtain the quantity of weakly chemisorbed hydrogen. This is shown in Tables 1 to 5 as the column labeled % dispersion (weak). Subtraction of these two values yields the strongly held chemisorbed quantity and is shown in accompanying tables below in the column labeled % dispersion (strong). All values are based on a H/Ru_{surface} ratio of 1.

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Example 2. Preparation of organic complex comprising 0.5% Ru on SiO₂ using aminoalcohol in impregnation solution

- 25 [098] 15.00g of silica support (S.A= 85m²/g, P.D.=50nm) was impregnated with solution prepared by mixing 5.01g of ruthenium nitrosyl nitrate (1.5%Ru), 2.23g triethanolamine and 1.77g water and dried at 100°C for four hours.

Example 3. Calcination of catalyst of Example 2 to 300°C

[099] A portion of sample from Example 2 was calcined in flowing air as the temperature was ramped 1°C/minute to 300°C and held for one hour at that temperature. This treatment resulted in the partial decomposition of the organic complex. A chemisorption measurement was made on this sample after hydrogen treatment.

Example 4. [Comparison]. Calcination of catalyst of Example 2 to 400°C

[0100] A portion of sample from Example 2 was further calcined in air at a heating rate of 1 °C/min to 400°C and held at that temperature for 3 hours. This resulted in the complete decomposition of the organic complex. A chemisorption measurement was made on this sample after hydrogen treatment.

[0101] Table 1 compares the dispersion measurements by H chemisorption of the catalysts of Examples 3 and 4. This comparison shows that the highest dispersions are obtained when the Ru-TEA on silica catalyst is calcined at 300°C, which partially decomposes the complex. After 400°C calcination the organic complex is totally destroyed before hydrogen treatment and it can be seen that the chemisorption values are substantially lower and are unstable as they decrease as the reduction temperature is increased above 250°C. The higher values in Example 3 catalyst remain stable during reduction at 400°C.

Example 5. Preparation of 0.5% Ru on SiO₂ using aminoalcohol in impregnation solution

[0102] 25.00g of silica support (S.A= 250m²/g, P.D.=15nm) was impregnated with solution prepared by mixing 8.37g of ruthenium nitrosyl nitrate (1.5%Ru), 3.71g triethanolamine and 18.00g water and dried at 100°C for four hours.

Example 6. Calcination of catalyst of Example 5 to 275°C

[0103] A portion of sample from Example 5 was calcined in flowing air as the temperature was ramped 1°C/minute to 275°C and held at that temperature for one hour. This treatment resulted in the partial decomposition of the organic complex. A chemisorption measurement was made on this sample after hydrogen treatment.

Example 7. Pyrolyzing catalyst of Example 5 in oxygen-free environment

[0104] A portion of the sample from Example 5 was heated in flowing nitrogen as the temperature was ramped 2°C/minute to 400°C and held at that temperature for one hour. A chemisorption measurement was made on this sample after hydrogen treatment.

[0105] Table 2 compares the dispersion measurements by H chemisorption of the catalysts of Examples 6 and 7. Both treatments generate a remnant of the starting Ru-triethanolamine complex. This comparison shows that the partial decomposition may be achieved at higher temperatures when under inert pyrolysis conditions (absence of oxygen) to form the Ru- organic precursor that gives high dispersion as well as when produced via oxidation.

Example 8. [Comparison]. Sample of 0.5%Ru on Silica with no organic additive

[0106] 15.00g of silica support (S.A= 85m²/g, P.D.=50nm) was impregnated with solution prepared by mixing 5.00g of ruthenium nitrosyl nitrate (1.5%Ru) and 4.00g water and dried at 100°C for four hours. A chemisorption measurement was made on this sample after hydrogen treatment.

Example 9. [Comparison]. Sample of 0.5%Ru on Silica with no organic additive and calcination

[0107] 15.00g of silica support (S.A= 85m²/g, P.D.=50nm) was impregnated with solution prepared by mixing 5.00g of ruthenium nitrosyl nitrate (1.5%Ru) and 4.00g water and dried at 100°C for four hours. The sample was then calcined in air as the temperature was ramped 1°C/minute to 300°C and held at that temperature for one hour. A chemisorption measurement was made on this sample after hydrogen treatment.

[0108] Table 3 compares the dispersion measurements by H chemisorption of the catalysts of Examples 3, 8 and 9. Only the catalyst prepared according to Example 3 in the Table is an object of this invention and has the remnant of the starting Ru-triethanolamine complex. This comparison shows that a high initial dispersion can be obtained on a catalyst that is simply impregnated with an aqueous solution of the ruthenium salt and then dried at low temperature if it is reduced at temperatures as low as 150° C. On reduction at higher temperatures the dispersion numbers decrease dramatically, most probably as a result of sintering. This does not happen with the catalyst of Example 3, which remains stable at 400° C reduction temperatures. If the aqueous salt solution of Ru is calcined first to 300° C the dispersion numbers are very low (Example 9).

Example 10. Preparation of 0.5% Ru on SiO₂ using aminoacid in impregnation solution

[0109] 10.00g of silica support (S.A= 85m²/g, P.D.=50nm) was impregnated with solution prepared by mixing 3.34g of ruthenium nitrosyl nitrate (1.5%Ru), 0.70g L-arginine, and enough water to form a total 10cc solution volume. The sample was dried at 100°C for four hours and the temperature was then ramped 1°C/minute to 250°C and held at that temperature for one hour. A chemisorption measurement was made on this sample after hydrogen treatment.

[0110] Table 4 compares the dispersion measurements by H chemisorption of the catalysts of Examples 3 and 10. Both calcined samples leave a remnant of the starting Ru-amino complexes. This comparison shows that high dispersions are obtained when using either aminoalcohols or aminoacids in the impregnation solution.

5

[0111] The data in Table 5 show the chemisorption data for Examples 5 and 6. This comparison shows that the dried catalyst with the amino complex (Example 5) gives a good dispersion value if directly reduced in hydrogen that is superior to the sample where the complex is completely oxidized to remove the complex (Example 4 see Table 1). However, the dispersion is not as good as that obtained if the organic complex is either partially oxidized or pyrolyzed.

10

Example 11. Measurement of Decomposition Products of Catalyst Precursor formed by partial oxidation of Ru-Triethanolamine complex.

15

[0112] A portion of the catalyst from Example 3 was heated in air at 4 deg/min and the product gas was analyzed by a quadrupole mass spectrometer. The data are shown in Figure 1. Figure 1 shows that a water peak is released slightly below 200°C and then there is formation of CO₂, NO₂ and H₂O as the organic complex is completely oxidized near to 350°C. This shows that the complex contained C, N and H. There may also be O present but this could not be determined using this experiment as the conditions used were oxidizing conditions.

20

Example 12. Infra-Red spectroscopy

25

[0113] The samples containing partially decomposed organic complex derived from Ru-triethanolamine and Ru-arginine were also analyzed using infrared spectroscopy. Approximately 25mg of the materials of Example 3, (TEA, calc 300°C), Example 8 (no organic, dry 100°C) and Example 10 (L-arginine, calc 250°C) were separately formed into 13mm pellets and loaded into an IR spectrometer operating in transmission mode. The samples were heated in vacuum to 150°C before the spectra were obtained.

30

[0114] The data are shown in Fig. 2. The data show the plot of transmittance vs. wave number of the IR radiation. The transmittance decreases where the catalyst absorbs infrared radiation due to a characteristic stretching of a molecular species.

- 5 The peaks between 1500 and 2000 cm^{-1} are primarily silica stretching bands. The presence of absorption features around 2100-2200 cm^{-1} , present on samples from Examples 3 and 10 are reported to be features of complexed carbon nitrogen species such as nitriles and isonitriles (see: Infrared and Raman Spectra of Inorganic and Coordination Compounds, by K. Nakamoto, John Wiley publishers, 3rd edition,
- 10 1978; ISBN: 0-471-62979-0, pages 267-269). The peaks are absent on the starting silica as well as on the sample prepared by aqueous impregnation of the ruthenium complex with no amino alcohol or amino acids present. Consequently these peaks are an indication of the remnant of the starting Ru-triethanolamine and Ru-arginine complexes present after partial decomposition of the organic complex.

15

Example 13. Thermogravimetric Analysis (TGA)

- [0115] Figure 3 shows the air treatment TGA plot for a catalyst sample (0.5 wt% Ru on SiO_2), which had been prepared with triethanolamine as the organic compound
- 20 and dried at 100° C prior to analysis. The TGA plot shows weight loss at temperatures below 300° C due to loss of water and partial oxidation of the complex with triethanolamine. In addition there is a further weight loss at approximately 325° C, which is believed to be due to the complete oxidation of the organic complex.

- 25 [0116] Figure 4 shows the air treatment TGA plot for a similar catalyst to that used in Figure 1 (0.5 wt% Ru on SiO_2), which had previously been calcined at 300° C. Clearly there is an insignificant weight loss below 300° C; this is due to the fact that any material on the supported catalyst that would have been removed below this temperature has been removed by the calcination. The majority of the weight loss in
- 30 the sample is due to the partially decomposed organic complex, which is oxidized at approximately 325° C. This results shows that that calcination below the

decomposition temperature is necessary to form the partially decomposed organic complex.

- 5 [0117] Figure 5 shows the hydrogen treatment TGA for the catalyst sample (0.5 wt% Ru on SiO₂), which had previously been calcined at 300° C. This TGA analysis shows that the partially oxidised organic complex is fully decomposed under the hydrogen treatment conditions at a higher temperature (~400° C) than under calcination conditions.

10 **Example 14. Determination of the decomposition temperature for various organic complexes.**

- 15 [0118] A number of supported organic complexes derived from various metals and nitrogen containing compounds and deposited on either silica or alumina were subjected to air treatment TGA and the decomposition profile for each determined. The TGA data are presented in Figure 6 where TEA is triethanolamine, arg is L-arginine, and arg(TPA-Cl₂) is arginine complex with tetramine Pt dichloride as Pt salt.

Table 1				
Sample of 0.5%Ru Supported on SiO ₂	Reduction temperature	% dispersion (combined)	% dispersion (weak)	% dispersion (strong)
Example 3 Ru-TEA/300°C				
	250	0	0	0.0
	325	0	0	0.0
	400	63.1	28.9	34.1
	400	66.4	29.7	36.7
	400	65.8	28.6	37.3
	400	65.8	29.0	36.9
Example 4 Ru-TEA/400°C				
	250	16.18	7	9.2
	325	9.46	3.97	5.5
	400	8.69	1.67	7.0
	400	6.66	0	6.7

Table 2					
Sample of 0.5%Ru Supported on SiO ₂	Reduction temperature	% dispersion (combined)	% dispersion (weak)	% dispersion (strong)	
Example 6	250	0	0	0.0	
Ru/TEA/275°C air	325	0	0	0.0	
	400	57.6	29.9	27.7	
	400	55.3	31.7	23.6	
Example 7	250	0	0	0.0	
Ru/TEA/400°C N ₂	325	0	0	0.0	
	400	52.8	25.9	26.9	
	400	60.8	30.6	30.2	
	400	64.6	31.4	33.2	
	400	64.7	31.5	33.2	

Table 3				
Sample of 0.5%Ru Supported on SiO ₂	Reduction temperature	% dispersion (combined)	% dispersion (weak)	% dispersion (strong)
Example 3	250	0	0	0.0
Ru-TEA/300°C	325	0	0	0.0
	400	63.1	28.9	34.1
	400	66.4	29.7	36.7
	400	65.8	28.6	37.3
	400	65.8	29.0	36.9
Example 8	150	77.77	40.87	36.9
Ru-aq /100°C	200	72.68	38.24	34.4
	250	66.54	36.51	30.0
	325	53.99	32.64	21.4
	400	45.98	27.67	18.3
	400	43.65	27.2	16.5
	400	42.64	25.84	16.8
Example 9	250	1.22	0	1.2
Ru-aq/300°C	325	0.38	0	0.4
	400	0.23	0	0.2

Table 4				
Sample of 0.5%Ru Supported on SiO ₂	Reduction temperature	% dispersion (combined)	% dispersion (weak)	% dispersion (strong)
Example 3	250	0	0	0.0
Ru-TEA/300°C	325	0	0	0.0
	400	63.1	28.9	34.1
	400	66.4	29.7	36.7
	400	65.8	28.6	37.3
	400	65.8	29.0	36.9
Example 10	250	0	0	0.0
Ru- arginine/250°C	325	0	0	0.0
	400	65.09	33.4	31.7
	400	68.91	34.42	34.5

Table 5				
Sample of 0.5%Ru Supported on SiO ₂	Reduction temperature	% dispersion (combined)	% dispersion (weak)	% dispersion (strong)
Example 5	250	0	0	0.0
Ru/TEA/dry 100C air	400	48.87	30.02	18.9
	400	49.79	29.3	20.5
	400	49.86	30.55	19.3
Example 6	250	0	0	0.0
Ru/TEA/275°C air	325	0	0	0.0
	400	57.6	29.9	27.7
	400	55.3	31.7	23.6

CLAIMS

1. A process for the manufacture of a catalyst process for the manufacture of a catalyst comprising a catalytically active metal dispersed on a support, which process
5 comprises:
- a) preparing a support having an organic complex of the catalytically active metal deposited thereon by treating a porous support with a compound or salt of the metal and a nitrogen-containing organic compound selected from (i) amino acids and (ii) compounds containing both an amino group and an alcohol group, to
10 form the organic metal complex on the support;
- b) partially decomposing the organic metal complex on the support to the extent that the partially decomposed product (I) retains between 10 and 95% by weight of the dry weight attributed to the organic complex prior to partial decomposition, and (II) exhibits one or more infra-red absorption bands between
15 2100-2200 cm^{-1} that are not present in the organic complex before partial decomposition; and
- c) converting the partially decomposed organic metal complex into catalytically active metal.
- 20 2. The process as claimed in claim 1 wherein the conversion to catalytically active metal is achieved by treatment of the support comprising the partially decomposed organic metal complex with a reductant.
3. The process as claimed in claim 2 wherein the reductant is a source of
25 hydrogen and/or CO.
4. The process as claimed in claim 2 or 3 wherein the source of reductant is provided in-situ in a catalysed process.
- 30 5. The process as claimed in any one of claims 2 to 4 wherein the source of reductant is provided in a catalyst regeneration process.

6. The process as claimed in any one of claims 2 to 5 wherein the source of reductant is provided in a catalyst regeneration process or catalyst recycle process associated with a catalysed process.
- 5
7. The process as claimed in any one of the preceding claims wherein the nitrogen-containing organic compound has been incorporated into or within the support during its manufacture or synthesis.
- 10 8. The process as claimed in any preceding claim wherein the nitrogen-containing organic compound is an aliphatic amine containing one or more hydroxyl groups.
- 15 9. The process as claimed in claim 8 wherein the amine comprises an hydroxyalkyl group.
10. The process as claimed in claim 9 wherein the hydroxyalkyl group is C₁ - C₅₀ - hydroxyalkyl.
- 20 11. The process as claimed in claim 10 wherein the hydroxyalkyl group is C₁ - C₈ - hydroxyalkyl.
12. The process as claimed in claim 11 wherein the hydroxyalkyl group is C₁ - C₄ - hydroxyalkyl.
- 25 13. The process as claimed in claim 12 wherein the hydroxyalkyl group is selected from: hydroxymethyl, 1-hydroxyethyl, 2-hydroxyethyl, 1-hydroxy-n-propyl, 2-hydroxy-n-propyl, 3-hydroxy-n-propyl and 1-hydroxy-methyl-ethyl.
- 30 14. The process as claimed in claim 13 wherein the nitrogen-containing organic compound comprises a mono-, di-, or tri-, substituted aliphatic

hydroxyalkylamine.

15. The process as claimed in claim 14 wherein the hydroxyalkylamine comprises one or more of: methanolamine, di-methanolamine, tri-methanolamine,
5 ethanolamine, di-ethanolamine, tri-ethanolamine, butanolamine, di-butanolamine, tri-butanolamine, propanolamine, di-propanolamine, dimethylethanolamine, di-isopropylethanolamine, methyldiethanolamine, dimethylamino-2-propanol and tri-propanolamine.
- 10 16. The process according any one of claims 1 to 7 wherein the amino acid is L-arginine.
17. The process as claimed in any one of claims 1 to 7 wherein the amino acid is selected from all isomers of the following: alanine, arginine, asparagines, aspartic
15 acid, cysteine, cystine, 3, 5-dibromotyrosine, 3,5-diiodotyrosine, glutamic acid, glutamine, glycine, histidine, hydroxylysine, hydroxyproline, isoleucine, leucine, lysine, methionine, phenylalanine, proline, serine, threonine, thyroxine, tryptophane, tyrosine and valine.
- 20 18. The process according to any one or the preceding claims wherein the organic metal complex is partially decomposed by calcination or pyrolysis.
19. The process as claimed in claim 18 wherein the calcination temperature is less than the temperature, as determined by TGA in air, at which total weight loss of
25 the organic complex occurs or the pyrolysis temperature is less than the temperature, as determined by TGA in an inert atmosphere of hydrogen, at which total weight loss of the organic complex occurs.
20. The process as claimed in claim 19 wherein the calcination or pyrolysis
30 temperature is between 200 °C and the temperature at which total weight loss of the organic complex occurs.

21. The process as claimed in any one of claims 18 to 20 wherein the partial decomposition is performed by introduction of the support comprising the organic metal complex into a catalysed process, a catalyst regeneration process or a catalyst
5 recycle process.

22. The process as claimed in any preceding claim wherein, in the catalyst formed by the process, the total metal dispersion is 45% or more and the metal dispersion relating to a strongly chemisorbed component of the total metal dispersion is 20% or
10 greater.

23. The process as claimed in any preceding claim wherein the product of step (b) exhibits dispersion values relating to the strong dispersion component of less than
15 1%.

24. The process as claimed in claim 23 wherein the dispersion is less than
0.5%.

25. The process as claimed in any preceding claim wherein step (b) is
20 performed to the extent that the partially decomposed product retains between 20 and 75 % by weight of the dry weight attributed to the organic complex prior to partial decomposition.

26. The process as claimed in any one of the preceding claims wherein the
25 catalyst support comprises silica.

27. The process as claimed in claim 26 wherein the silica is amorphous.

28. The process as claimed in any one of the preceding claims wherein the
30 support comprises an ordered mesoporous material and/or a macroporous material.

29. The process as claimed in any one of the preceding claims wherein the support comprises a material designated as M41S.
- 5 30. The process as claimed in claim 29 wherein the support material is MCM-41.
31. The process as claimed in any one of the preceding claims wherein the support comprises alumina.
- 10 32. The process as claimed in any one of the preceding claims wherein the support comprises rutile titanium dioxide, anatase titanium dioxide or mixtures thereof.
33. The process as claimed in claim 32 wherein the support further comprises
15 zirconium dioxide.
34. The process as claimed in any one of the preceding claims wherein the salt or compound of one or more catalytically active metals is a salt or compound of one or more metals selected from the following groups:
- 20 Group 1 (Group IA) such as Li, Na or K; Group 2 (Group IIA) such as Mg, Ca and Sr; Group 3 (Group IIIA, IIIB) such as Sc, Y and La; Group 4 (Group IVA, IVB) such as Ti, Zr and Hf; Group 5 (Group VA, VB) such as V, Nb and Ta; Group 6 (Group VIA, VIB) such as Cr, Mo and W; Group 7 (VIIA, VIIB) such as Mn, Tc, and Re; Groups 8, 9 and 10 (Group
25 VIII, VIIIA) such as Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, and Pt; Group 11 (Group IB) such as Cu, Ag, and Au; Group 12 (Group IIB) such as Zn; Group 13 (Group IIIA, IIIB) such as Ga and In; and Group 14 (Group IVA, IVB) such as Ge and Sn.
- 30 35. The process as claimed in claim 34 wherein the salt or compound of one or more catalytically active metals is a salt or compound of one or more

of the following metals; copper, platinum, rhodium, palladium, cobalt, iron, nickel, rhenium, ruthenium or a mixture of two or more thereof as active metal.

36. The process according to any preceding claim wherein the compound or
5 salt of the catalytically active metal is a nitrate or nitrosyl nitrate.

37. A process for the production of C₅+ liquid hydrocarbons which comprises
manufacturing a catalyst by the process as claimed in any one of the preceding claims
and contacting a hydrogen and carbon monoxide synthesis gas at reaction conditions
10 with a said catalyst to produce said C₅+ liquid hydrocarbons.

38. A method for the removal of sulfur from a mixture comprising one or more
organic compounds and one or more sulfur containing compounds, which method
comprises manufacturing a catalyst, in the form of a material comprising active
15 metal dispersed on a support, by the process as claimed in any one of claims 1 to 36,
and contacting said mixture with said material comprising active metal dispersed on
an inorganic support under such conditions that sulphur is absorbed onto the material
comprising active metal dispersed on an inorganic support.