CLAIMS

1 A catalyst comprising a modified silica support, the modified silica support comprising titanium modifier metal, and a catalytic metal on the modified silica support, characterised in that at least a proportion, typically, at least 25%, of the said modifier metal is present in the form of mononuclear titanium moieties, wherein the catalytic metal is one or more alkali metals.

2. A catalyst comprising a modified silica support, the modified silica support comprising titanium modifier metal, and a catalytic metal on the modified silica support, characterised in that at least a proportion, typically, at least 25%, of the said modifier metal is present in modifier metal moieties derived from a mononuclear titanium cation source at the commencement of the modification, wherein the catalytic metal is one or more alkali metals.

3. A modified silica support for a catalyst comprising a silica support and titanium modifier metal, characterised in that at least a proportion, typically, at least 25%, of the said modifier metal is present in the form of mononuclear titanium moieties.

4. A modified silica support for a catalyst comprising a silica support and a titanium modifier metal, characterised in that at least a proportion, typically, at least 25%, of the said modifier metal is present in modifier metal moieties derived from a mononuclear titanium cation source at the commencement of the modification.

5. A catalyst according to claim 1, wherein the mononuclear titanium moieties are derived from a mononuclear titanium cation source at the commencement of the modification.

6. A modified silica support according to claim 3, wherein the mononuclear titanium moieties are derived from a mononuclear titanium cation source at the commencement of the modification.

7. A modified silica support or catalyst according to any preceding claim, wherein the titanium is an adsorbate adsorbed on the silica support surface, preferably, chemisorbed thereon.

8. A modified silica support or catalyst according to any preceding claim, wherein the titanium moieties are titanium oxide moieties.

9. A modified silica support or catalyst according to any preceding claim, wherein the silica support is in the form of a silica gel, more typically, a xerogel or a hydrogel.

10. A modified silica support or catalyst according to any of claims 1-6, 8 or 9, wherein the mononuclear titanium moieties are present in the support as part of a co-gel.

11. A modified silica support or catalyst according to any preceding claim, wherein the mononuclear titanium moieties are present in the modified silica support in an effective amount to reduce sintering and improve selectivity of the catalyst.

12. A modified silica support or catalyst according to any preceding claim, wherein at least 30% , such as at least 35%, more preferably at least 40%, such as at least 45%, most suitably at least 50%, such as at least 55%, for example at least 60% or 65%, and most preferably at least 70% such as at least 75% or 80%, more typically, at least 85%, most typically, at least 90%, especially, at least 95% of titanium in the modified silica support is in mononuclear moieties or is derived from a titanium compound at the commencement of the modified silica formation with mononuclear titanium species at such levels.

13. A modified silica support or catalyst according to any preceding claim, wherein the level of titanium present is up to 7.6×10^{-2} mol/mol of silica, more preferably up to 5.9×10^{-2} mol/mol of silica, most preferably up to 3.5×10^{-2} mol/mol of silica.

14. A modified silica support or catalyst according to any preceding claim, wherein the level of titanium is between 0.067×10^{-2} and 7.3×10^{-2} mol/mol of silica, more preferably, between 0.13×10^{-2} and 5.7×10^{-2} mol/mol of silica and most preferably between 0.2×10^{-2} and 3.5×10^{-2} mol/mol of silica.

15. A modified silica support or catalyst according to any preceding claim, wherein the level of titanium present is at least 0.1×10^{-2} mol/mol of silica, more preferably, at least 0.15×10^{-2} mol/mol of silica and most preferably at least 0.25×10^{-2} mol/mol of silica.

16. A modified silica support or catalyst according to any of claims 3-15, wherein the modified silica support is a calcined modified silica support.

17. A catalyst according to any of claims 1, 2, 5 or 7-16, wherein the catalytic metal is ~~one or more alkali metals and is preferably~~ selected from potassium, rubidium and caesium, suitably rubidium and caesium, caesium being most preferred.

18. A catalyst or modified silica support according to any preceding claim, wherein the titanium metal cation at the commencement of the modification is in a compound with one or more non-labile ligands attached to the titanium metal cations which non-labile ligands are selected from molecules with lone pair containing oxygen or nitrogen atoms able to form 5 or 6

membered rings with a titanium atom, including diones, diimines, diamines, diols, dicarboxylic acids or derivatives thereof such as esters, or molecules having two different such functional groups and in either case with the respective N or O and N or O atom separated by 2 or 3 atoms to thereby form the 5 or 6 membered ring, for example, pentane-2,4-dione, esters of 3-oxobutanoic acid with aliphatic alcohols containing 1-4 carbon atoms such as ethyl 3-oxobutanoate, propyl 3-oxobutanoate, isopropyl 3-oxobutanoate, n-butyl 3-oxobutanoate, t-butyl 3-oxobutanoate, heptane-3,5-dione, 2,2,6,6,-tetramethyl-3,5-heptanedione, 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,2-butanediol, 1,2-diaminoethane, ethanolamine, 1,2-diamino-1,1,2,2-tetracarboxylate, 2,3-dihydroxy-1,4-butanedioate, 2,4-dihydroxy-1,5-pentanedioate, salts of 1,2-dihydroxylbenzene-3-5-disulphonate, diethylenetriaminepentaacetic acid, nitrolotriacetic acid, N-hydroxyethylethylenediaminetriacetic acid, N-hydroxyethyliminodiacetic acid, N,N-dihydroxyethylglycine, oxalic acid and its salts, more typically, the non-labile ligands are selected from one or more of pentane-2,4-dione, 2,2,6,6,-tetramethyl-3,5-heptanedione, ethyl 3-oxobutanoate, t-butyl 3-oxobutanoate and heptane-3,5-dione.

19. A catalyst or modified silica support according to claim 18, wherein the non-labile ligands form complexes with titanium, for example tetrameric complexes, and are typically solubilised as non-labile ligand/alcohol complexes with the titanium in solution.

20. A catalyst according to any of claims 1, 2, 5 or 7-19, wherein the catalytic metal is present in the range 0.5-7.0 mol/mol titanium, more preferably 1.0-6.0 mol/mol, most preferably 1.5-5.0 mol/mol titanium.

21. A catalyst according to any of claims 1, 2, 5 or 7-20, wherein the catalyst is calcined.

22. A method of producing a modified silica support according to any preceding claims comprising the steps of:

providing a silica support having silanol groups;

treating the silica support with mononuclear titanium compounds so that titanium is adsorbed onto the surface of the silica support through reaction with silanol groups, wherein the adsorbed titanium atoms are sufficiently spaced apart from each other to substantially prevent oligomerisation thereof with neighbouring titanium atoms, more preferably, sufficiently spaced apart from each other to substantially prevent dimerization or trimerisation thereof with neighbouring titanium atoms thereof.

23. A method according to claim 22, wherein the spacing apart of the titanium atoms is effected by

a) decreasing the concentration of silanol groups on the silica support and/or

b) attaching a non-labile ligand of sufficient size to the titanium prior to treating the silica support.

24. A method of producing a catalyst comprising the steps of:-

i. providing a silica support with isolated silanol groups and optionally treating the said support to provide isolated silanol groups (-SiOH) at a level of <2.5 groups per nm^2;

ii. contacting the optionally treated silica support with a mononuclear titanium modifier metal compound to effect adsorption of the said titanium onto the support, typically to at least 25% of the said isolated silanol groups;

iii. optionally, removing any solvent or liquid carrier for the titanium compounds;

iv. calcining the modified silica for a time and temperature sufficient to convert the mononuclear titanium compound adsorbed on the surface to an oxide or hydroxide of titanium;

v. treating the said calcined modified silica with a catalytic alkali metal to impregnate the modified silica with the catalytic metal to form the catalyst and optionally, calcining the catalyst.

25. A method of producing a modified silica support for a catalyst comprising the steps of:-

i. providing a silica support with isolated silanol groups and optionally treating the said support to provide isolated silanol groups (-SiOH) at a level of <2.5 groups per nm^2;

ii. contacting the optionally treated silica support with a mononuclear titanium compound to effect adsorption of the said titanium onto the support, typically to at least 25% of the said isolated silanol groups;

iii. optionally, removing any solvent or liquid carrier for the modifier metal compounds;

iv. optionally calcining the modified support for a time and temperature sufficient to convert the mononuclear titanium compound adsorbed on the surface to an oxide or hydroxide of titanium in preparation for catalyst impregnation.

26. A method as claimed in any of claims 22 to 25, wherein the silanol group concentration is decreased to the required level prior to treatment with the titanium compounds by calcination treatment, chemical dehydration or other suitable methods.

27. A method according to any of claims 22 to 26, wherein the mononuclear titanium cation source is a solution of the titanium compounds so that the compounds are in solution when contacted with the support to effect adsorption onto the support.

28. A method according to claim 27, wherein the solvent for the said solution is other than water.

29. A method according to claim 27 or 28, wherein the solvent is an organic solvent such as an aliphatic solvent, for example heptane, an aromatic solvent, for example toluene, or a chlorinated solvent, for example dichloromethane, typically the solvent is an aliphatic alcohol, more typically selected from C1-C6 alkanols such as methanol, ethanol, propanol, iso-propanol, butanols, pentanols and hexanols, most typically, methanol, ethanol or propanols.

30. A method as claimed in any of claims 22 to 29, wherein one or more non-labile ligands are attached to the titanium cations to at least partially form the said compounds and are selected from molecules with lone pair containing oxygen or nitrogen atoms able to form 5 or 6 membered rings with a titanium atom, including diones, diimines, diamines, diols, dicarboxylic acids or derivatives thereof such as esters, or molecules having two different such functional groups and in either case with the respective N or O and N or O atom separated by 2 or 3 atoms to thereby form the 5 or 6 membered ring, for example, pentane-2,4-dione, esters of 3-oxobutanoic acid with aliphatic alcohols containing 1-4 carbon atoms such as ethyl 3-oxobutanoate, propyl 3-oxobutanoate, isopropyl 3-oxobutanoate, n-butyl 3-oxobutanoate, t-butyl 3-oxobutanoate, heptane-3,5-dione, 2,2,6,6,-tetramethyl-3,5-heptanedione, 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,2-butanediol, 1,2-diaminoethane, ethanolamine, 1,2-diamino-1,1,2,2-tetracarboxylate, 2,3-dihydroxy-1,4-butanedioate, 2,4-dihydroxy-1,5-pentanedioate, salts of 1,2-dihydroxylbenzene-3-5-disulphonate, diethylenetriaminepentaacetic acid, nitrolotriacetic acid, N-hydroxyethylethylenediaminetriacetic acid, N-hydroxyethyliminodiacetic acid, N,N-dihydroxyethylglycine, oxalic acid and its salts, more typically, the non-labile ligands are selected from one or more of pentane-2,4-dione, 2,2,6,6,-tetramethyl-3,5-heptanedione, ethyl 3-oxobutanoate, t-butyl 3-oxobutanoate and heptane-3,5-dione.

31. A method as claimed in claim 30, wherein the non-labile ligands form complexes with titanium, for example tetrameric complexes, and are typically solubilised as non-labile ligand/alcohol complexes with the titanium in solution.

32. A method as claimed in any of claims 22 to 31, wherein the proximity of the adsorbed titanium modifier metal to neighbouring titanium modifier metal cations may be controlled by the concentration of the said titanium modifier metal in the contacting step and:-

a) the concentration of silanol groups on the silica support and/or

b) the size of any non-labile ligand attached to the titanium modifier metal cation.

33. A method as claimed in any of claims 22 to 32, wherein the silanol concentration on the silica support when contacted with the titanium modifier metal compound is 0.4-2.5 silanol groups per nm^2, more preferably 0.5-2.0 silanol groups per nm^2, most preferably 0.8-1.5 silanol groups per nm^2.

34. A method as claimed in any of claims 22 to 33, wherein at least 30% , such as at least 35%, more preferably at least 40%, such as at least 45%, most suitably at least 50%, such as at least 55%, for example at least 60% or 65%, and most preferably at least 70% such as at least 75% or 80%, more typically, at least 85%, most typically, at least 90%, especially, at least 95% of the titanium modifier metal in the modifier metal compounds are mononuclear modifier metal compounds when the source thereof is contacted with the support to effect adsorption of the said compounds onto the support.

35. A method of producing a catalyst according to any of claims 1, 2, 5 or 7-21, comprising the steps of: forming a modified silica according to any of claims 3, 4, 6-16 or 18-21 and contacting the modified silica support with a solution containing a catalytic metal to impregnate the modified silica with the catalytic metal.

36. A method as claimed in any of claims 22 to 35, wherein the silica support is dried or calcined prior to treatment with the titanium compounds.

37. A method as claimed in any of claims 22, 23 or 25 to 36, wherein the modified silica formed by contact with the titanium compounds is dried or calcined prior to addition of the catalytic metal.

38. A method as claimed in any of claims 22 to 37, wherein the silica is in the form of a gel prior to treatment with the titanium compounds, the gel typically in the form of a hydrogel, a xerogel or an aerogel at the commencement of contact with the titanium compounds.

39. A method as claimed in any of claims 22 to 38 wherein the titanium modifier metal is dispersed, typically, uniformly distributed, onto the surface of the silica support by adsorption, preferably chemisorption.

40. A method as claimed in any of claims 22 to 39 or a catalyst or modified silica support according to any of claims 1-21, wherein the titanium cation source is in the form selected from organic metal complexes such as titanium tetrakis(methoxide), titanium tetrakis(ethoxide), titanium tetrakis(n-propoxide), titanium tetrakis(i-propoxide), titanium tetrakis(n-butoxide) titanium tetrakis(t-butoxide), titanium tetrakis(2-ethylhexyloxide), titanium oxide bis(acetylacetonate), titanium oxide bis(2,2,6,6-tetramethyl-3,5-heptanedionate), titanium

(triethanolaminato)isopropoxide, titanium bis(triethanolamine)di-isopropoxide, titanium tetrakis(diethylamide), titanium tetrakis(ethylmethylamide), titanium tetrakis(dimethylamide), titanium tetrakis(neopentyl) titanium(IV) bis(ammonium lactate)dihydroxideand metal salts such as titanium(IV) oxysulphate, titanium(IV) oxynitrate and titanium(IV) oxychloride, more typically, an organic metal complex.

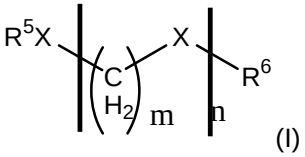
41. A method as claimed in any of claims 22 to 39 or a catalyst or modified silica support according to any of claims 1-21, wherein the titanium cation source is in the form selected titanium tetrakis(methoxide), titanium tetrakis(ethoxide), titanium tetrakis(n-propoxide), titanium tetrakis(i-propoxide), titanium tetrakis(n-butoxide) titanium tetrakis(t-butoxide), titanium tetrakis(2-ethylhexyloxide), titanium oxide bis(acetylacetonate), titanium oxide bis(2,2,6,6-tetramethyl-3,5-heptanedionate), titanium (triethanolaminato)isopropoxide, titanium bis(triethanolamine)di-isopropoxide, titanium tetrakis(diethylamide), titanium tetrakis(ethylmethylamide), titanium tetrakis(dimethylamide), titanium tetrakis(neopentyl) titanium(IV) bis(ammonium lactate)dihydroxidein one of methanol, ethanol, isopropanol, propanol, butanol, isobutanol, or 2-butanol, optionally, with up to 20% water by volume.

42. A method according to any of claims 22 to 41, wherein the catalytic metal is one or more alkali metals and is preferably selected from potassium, rubidium and caesium, suitably rubidium and caesium, caesium being most preferred.

43. A method according to any of claims 22 to 42, wherein the catalyst formed is then calcined.

44. A method of producing an ethylenically unsaturated carboxylic acid or ester, typically, an α, β ethylenically unsaturated carboxylic acid or ester, comprising the steps of contacting formaldehyde or a suitable source thereof with a carboxylic acid or ester in the presence of catalyst and optionally in the presence of an alcohol, wherein the catalyst is according to any of claims 1, 2, 5, 7-21, 40 or 41.

45. A process for preparing an ethylenically unsaturated acid or ester comprising contacting an alkanoic acid or ester of the formula R^1-CH_2-$COOR^3$, with formaldehyde or a suitable source of formaldehyde of formula (I) as defined below:



(I)

where R5 is methyl and R6 is H;

X is O;

m is 1;

and n is any value between 1 and 20 or any mixture of these;

in the presence of a catalyst according to any of claims 1, 2, 5, 7-21, 40 or 41, and optionally in the presence of an alkanol; wherein R1 is hydrogen or an alkyl group with 1 to 12, more suitably, 1 to 8, most suitably, 1 to 4 carbon atoms and R3 may also be independently, hydrogen or an alkyl group with 1 to 12, more suitably, 1 to 8, most suitably, 1 to 4 carbon atoms.

46. A method according to claim 44 or 45, wherein the carboxylic acid or ester or ester or acid of formula R^1-CH_2-$COOR^3$ respectively is methyl propionate or propionic acid and typically, the optional alkanol is methanol and the ethylenically unsaturated carboxylic acid or ester is methyl methacrylate or methacrylic acid.

47. A method of producing a modified silica support comprising the steps of:

providing a silica support having silanol groups;

treating the silica support with mononuclear titanium compounds so that titanium modifier metal is adsorbed onto the surface of the silica support through reaction with silanol groups, wherein the adsorbed titanium atoms are sufficiently spaced apart from each other to substantially prevent oligomerisation thereof with neighbouring titanium atoms, more preferably, sufficiently spaced apart from each other to substantially prevent dimerisation or trimerisation with neighbouring titanium atoms thereof.

48. A method according to claim 47 wherein the spacing apart of the titanium atoms is effected by

a) decreasing the concentration of silanol groups on the silica support and/or

b) attaching a non-labile ligand of sufficient size to the titanium cation.

49. A method according to any of claims 47 or 48, including any one or more of the features of claims 22 to 45.

50. A method according to any of claims 22-49, wherein the support and/or catalyst is according to any of claims 1-21.

51. A modified silica support according to any of claims 1-19, wherein the support comprises isolated silanol groups (-SiOH) at a level of <2.5 groups per nm^2.

52. A catalyst or modified silica support according to any of claims 1-21, 40, 41 or 51, wherein the support comprises the said titanium moieties present and at a level of <2.5 moieties per nm^2.

53. A modified silica support according to any of claims 3, 4, 6-19, 40, 41, 51 or 52, wherein the support comprises isolated silanol groups (-SiOH) at a level of >0.1 and <2.5 groups per nm^2, more preferably, at a level of from 0.2 to 2.2, most preferably, at a level of from 0.4 to 2.0 groups per nm^2.

54. A catalyst or modified silica support according to any of claims 1-21, 40, 41 or 51-53, wherein the support comprises the said titanium moieties at a level of >0.025 and <2.5 moieties per nm^2, more preferably, at a level of from 0.05 to 2.0 moieties per nm^2, most preferably, at a level of from 0.1 to 1.5 moieties per nm^2.