CLAIMS

1. A catalyst comprising a modified silica support, the modified silica support comprising a modifier metal, and a catalytic metal on the modified silica support, wherein the modifier metal is selected from one or more of zirconium and/or hafnium, characterised in that at least a proportion, typically, at least 25%, of the said modifier metal is present in modifier metal oxide or hydroxide moieties having a total of up to 2 modifier metal atoms.

2. A catalyst comprising a modified silica support, the modified silica support comprising a modifier metal, and a catalytic metal on the modified silica support, wherein the modifier metal is selected from one or more of zirconium and/or hafnium, characterised in that at least a proportion, typically, at least 25%, of the said modifier metal is present in modifier metal oxide or hydroxide moieties derived from a monomeric and/or dimeric modifier metal cation source at the commencement of the modification.

3. A modified silica support for a catalyst comprising a silica support and a modifier metal wherein the modifier metal is selected from one or more of zirconium and/or hafnium, characterised in that at least a proportion, typically, at least 25%, of the said modifier metal is present in modifier metal oxide or hydroxide moieties having a total of up to 2 modifier metal atoms.

4. A modified silica support for a catalyst comprising a silica support and a modifier metal, wherein the modifier metal is selected from one or more of zirconium and/or hafnium characterised in that at least a proportion, typically, at least 25%, of the said modifier metal is present in modifier metal oxide or hydroxide moieties derived from a monomeric and/or dimeric modifier metal cation source at the commencement of the modification.

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

6. A modified silica support or catalyst according to any of claims 1, 2 or 5, wherein the modifier metal moieties are modifier metal oxide moieties.

7. 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.

8. A modified silica support or catalyst according to any of claims 1-4, 6 or 7, wherein the modifier metal is present in the support in the form of a co-gel.

9. A modified silica support or catalyst according to any preceding claim, wherein the modifier metal is present in the modified silica support in an effective amount to reduce sintering and improve selectivity of the catalyst.

10. 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 the modifier metal in the modified silica support is in moieties having a total of 1 and/or 2 metal atoms, especially in moieties having a total of 1 metal atom or is derived from a monomeric and/or dimeric modifier metal compound at the commencement of the modified silica formation at such levels of modifier metal as monomeric and/or dimeric compounds, especially, monomeric modifier metal compounds.

11. A modified silica support or catalyst according to any preceding claim, wherein the level of modifier metal 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.

12. A modified silica support or catalyst according to any preceding claim, wherein the level of modifier metal 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.

13. A modified silica support or catalyst according to any preceding claim, wherein the level of modifier metal 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.

14. A modified silica support according to any of claims 3-13, wherein the modified silica support is a calcined modified silica support.

15. A catalyst comprising a modified silica support according to any of claims 1, 2 or 5-14, 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.

16. A catalyst or modified silica support according to any preceding claim, wherein the monomeric and/or dimeric modifier metal cation at the commencement of the modification is in a compound with one or more non-labile ligands attached to the modifier 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 zirconium or hafnium 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.

17. A catalyst or modified silica support according to claim 16, wherein the non-labile ligands form complexes with the modifier element, for example tetrameric complexes, and are typically solubilised as non-labile ligand/alcohol complexes with the monomeric modifier element in solution.

18. A catalyst comprising a modified silica support according to any preceding claim, wherein catalytic metal is present in the range 0.5-7.0 mol/mol modifier metal, more preferably 1.0-6.0 mol/mol, most preferably 1.5-5.0 mol/mol modifier metal.

19. A method of producing a modified silica support according to any of claims 1-18 comprising the steps of:

providing a silica support having silanol groups;

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

20. A method according to claim 19 wherein the spacing apart of the modifier metal 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 modifier metal prior to treating the silica support.

21. 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 monomeric zirconium or hafnium modifier metal compound to effect adsorption of the said modifier metal 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. calcining the modified silica for a time and temperature sufficient to convert the monomeric zirconium or hafnium compound adsorbed on the surface to an oxide or hydroxide of zirconium or hafnium;

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.

22. 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 monomeric zirconium or hafnium modifier metal compound to effect adsorption of the said modifier metal onto the support, 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 monomeric zirconium or hafnium compound adsorbed on the surface to an oxide or hydroxide of zirconium or hafnium in preparation for catalyst impregnation.

23. A method as claimed in any of claims 19 to 22 wherein the silanol group concentration is decreased prior to treatment with the modifier metal compounds by calcination treatment, chemical dehydration or other suitable methods.

24. A method according to any of claims 19 to 24, wherein the modifier metal cation source is a solution of the said compounds so that the compounds are in solution when contacted with the support to effect adsorption onto the support.

25. A method according to claim 24, wherein the solvent for the said solution is other than water.

26. A method according to claim 23 or 24, wherein the solvent is an aliphatic alcohol, typically selected from C1-C6 alkanols such as methanol, ethanol, propanol, iso-propanol, butanols, pentanols and hexanols, more typically, methanol, ethanol or propanols.

27. A method as claimed in any of claims 19 to 26 wherein one or more non-labile ligands are attached to the modifier metal 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 zirconium or hafnium 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.

28. A method as claimed in claim 27, wherein the non-labile ligands form complexes with the monomeric modifier element, for example tetrameric complexes, and are typically solubilised as non-labile ligand/alcohol complexes with the monomeric modifier element in solution.

29. A method as claimed in any of claims 19 to 28, wherein the silanol concentration on the silica support when contacted with the modifier metal compound is 0.1-2.5 silanol groups per nm^2, more preferably 0.15-1.0 silanol groups per nm^2, most preferably 0.2-0.7 silanol groups per nm^2.

30. A method as claimed in any of claims 19 to 29, 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 modifier metal in the modifier metal compounds are in monomeric modifier metal compounds when the source thereof is contacted with the support to effect adsorption of the said compounds onto the support.

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

32. A method as claimed in any of claims 19 to 31, wherein the silica support is dried or calcined prior to treatment with the modifier metal compounds.

33. A method as claimed in any of claims 19, 20 or 22 to 32 wherein the modified silica formed by contact with the modifier metal compounds is dried or calcined prior to addition of the catalytic metal.

34. A method as claimed in any of claims 19 to 33 wherein the silica is in the form of a gel prior to treatment with the modifier metal compounds, the gel typically in the form of a hydrogel, a xerogel or an aerogel at the commencement of contact with the modifier metal compounds.

35. A method as claimed in any of claims 19 to 34 wherein the modifier metal is dispersed onto the internal and external surfaces of the silica support by adsorption, preferably chemisorption.

36. A method as claimed in any of claims 19 to 35 or a catalyst or silica support according to any of claims 16 or 17, wherein the modifier metal compound is in the form selected from organic metal complexes such as zirconium (pentane-2,4-dione)$_4$, zirconium(ethyl 3-oxobutanoate)4, zirconium(heptane-3,5-dione)$_4$, zirconium(2,2,6,6-tetramethylheptane-3,5-dione)$_4$, zirconium(propoxide)(pentane-2-3-dione)$_3$, zirconium(propoxide)$_3$(2,2,6,6-tetramethyl-3,5-heptanedione) (zirconium(Butyl)$_3$(t-butyl 3-oxobutanoate), zirconium(Ot-butyl)$_2$(t-butyl 3-oxobutanoate)$_2$ and metal salts such as zirconium perchlorate, zirconium oxynitrate and zirconium oxychloride, more typically, an organic metal complex.

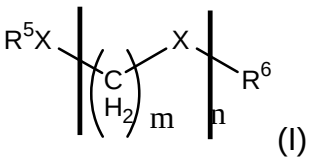
37. A method according to claim 36 or a catalyst or support according to claims 16- 18, wherein the modifier metal compound is in the form selected from zirconium(IV) acetylacetonate (zirconium, tetrakis(2,4-pentanedionato-O,O')) zirconium(heptane-3,5-dione)$_4$, zirconium(2,2,6,6-tetramethyl-3,5-heptanedione)$_4$, zirconium(IV) ethyl 3-oxobutanoate, zirconium(IV) t-butyl 3-oxobutanoate, or zirconium(IV) i-propyl 3-oxobutanoate in one of methanol, ethanol, isopropanol, propanol, butanol, isobutanol, or 2-butanol, optionally, with up to 20% water by volume.

38. A method according to any of claims 19 to 37, 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.

39. A method according to any of claims 19 to 38, wherein the catalyst formed is then calcined.

40. 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, 5-18 or 36-37~~, or produced by a method according to any of claims 19-39~~.

41. 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, 5-18 or 36-37, or produced by a method according to any of claims 19-~~40~~39, 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.

42. A method according to claim ~~39~~ 40 or ~~40~~41, 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.

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

providing a silica support having silanol groups;

treating the silica support with monomeric and/or dimeric modifier metal compounds so that modifier metal is adsorbed onto the surface of the silica support through reaction with silanol groups, wherein the modifier metal is selected from one or more of zirconium and/or hafnium, wherein the adsorbed modifier metal atoms are sufficiently spaced apart from each other to substantially prevent oligomerisation thereof with neighbouring modifier metal atoms, more preferably, sufficiently spaced apart from each other to substantially prevent trimerisation with neighbouring modifier metal atoms thereof.

44. A method according to claim 43 wherein the spacing apart of the modifier metal 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 modifier metal cation.

45. A method according to any of claims 43 or 44, including any one or more of the features of claims 19-20 ~~to~~or 22-42.

46. A method according to any of claims 19-45, wherein the support and/or catalyst is according to any of claims 1-18.

47. A modified silica support according to any of claims 3-14, 16 or 17, wherein the support comprises isolated silanol groups (-SiOH) at a level of <2.5 groups per nm^2.

48. A catalyst or modified silica support according to any of claims 1-18 or 47, wherein the support comprises the said zirconium or hafnium modifier metal moieties present and at a level of <2.5 moieties per nm^2.

49. A modified silica support according to any of claims 3-14, 16, 17, 47 or 48, 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.

50. A catalyst or modified silica support according to any of claims 1-18 or 47-49, wherein the support comprises the said zirconium or hafnium modifier metal moieties at a level of >0.025 and <2.5 groups per nm^2, more preferably, at a level of from 0.05 to 1.5, most preferably, at a level of from 0.1 to 1.0 moieties per nm^2.