Claims

1. A process for producing a catalyst comprising the steps of:

   a) providing an uncalcined metal modified porous silica support wherein the modifier metal is selected from one or more of boron, magnesium, aluminium, zirconium, hafnium and titanium, and wherein the modifier metal is present in mono- or dinuclear modifier metal moieties;

   b) optionally removing any solvent or liquid carrier from the modified silica support;

   c) optionally drying the modified silica support;

   d) treating the uncalcined metal modified silica support with a catalytic metal to effect adsorption of the catalytic metal onto the metal modified silica support, wherein the catalytic metal is an alkali metal; and

   e) calcining the impregnated silica support of step d).

2. An uncalcined catalyst intermediate comprising an uncalcined porous silica support modified with a modifier metal wherein the modifier metal is selected from one or more of boron, magnesium, aluminium, zirconium, hafnium and titanium, wherein the said modifier metal is present in mono- or dinuclear modifier metal moieties and catalytic metal adsorbed on the said uncalcined modified silica support, wherein the catalytic metal is an alkali metal.

3. A method of producing a catalyst comprising the steps of:

   a) providing a porous silica support having isolated silanol groups;

   b) treating the said porous silica support with mono- or dinuclear modifier metal compound so that modifier metal is adsorbed onto the surface of the silica support through reaction with said isolated 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 prior to and preferably after calcination, more preferably, sufficiently spaced apart from each other to substantially prevent dimerisation or trimerisation thereof with neighbouring modifier metal atoms thereof wherein the modifier metal is selected from boron, magnesium, aluminium, zirconium, hafnium and titanium;

c) optionally removing any solvent or liquid carrier from the modified silica support;

d) optionally drying the modified silica support;

e) treating the uncalcined modified silica support with a catalytic metal to effect adsorption of the catalytic metal onto the modified silica support; and

f) calcining the impregnated silica support of step e).

4. A process according to claim 1:

wherein the porous silica support modified with a modifier metal is a modifier metal oxide-silica co-gel support.

5. An uncalcined catalyst intermediate according to claim 2, comprising a porous modifier metal oxide-silica co-gel support.

6. A catalyst comprising an intermediate according to any of claims 2 or 5, wherein the said uncalcined intermediate has been calcined.

7. A process or catalyst according to any of claim 1, 3, 4 or 6, wherein the calcination step is carried out at a temperature of at least 450˚C, more preferably, at least 475˚C, most preferably, at least 500˚C, especially, at least 600˚C, more especially, above 700˚C, and/or typically, the calcination temperature is in the range 400-1000˚C, more typically, 500-900˚C, most typically, 600-850˚C.

8. A process or catalyst intermediate or catalyst according to any of claims 1, 2, 6 or 7, wherein the modifier metal moieties are derived from mono- or dinuclear modifier metal compounds.

9. A process or catalyst intermediate or catalyst according to claim 8, wherein the modifier metal compound contacts the porous silica support as a mono- or dinuclear modifier metal compound in solution to effect adsorption of the said modifier metal onto the support.

10. A process or catalyst or catalyst intermediate according to any of claims 1-9, wherein the silica support is a hydrogel or xerogel, more preferably a xerogel.

11. A process or catalyst or catalyst intermediate according to any of claims 3 or 6-10, wherein the metal compound is a complex and the coordination sphere of the compound is generally sufficiently saturated to prevent oligomerisation of the modifier metal beyond dimerization prior to and/or after adsorption.

12. A process or catalyst or catalyst intermediate according to claim 11, wherein the compound is an organic complex.

13. A process or catalyst or catalyst intermediate according to any of claims 3 or 6-12, wherein the metal compound comprises one or more chelating ligands, preferably, 2, 3 or 4 chelating ligands, and/or wherein the chelating ligands are optionally bi, tri, tetra or polydentate.

14. A process or catalyst or catalyst intermediate according to any of claims 3 or 6-13, wherein the metal compound is tetracoordinate, pentacoordinate, hexacoordinate, heptacoordinate or octacoordinate.

15. A process or catalyst or catalyst intermediate according to any of claims 1-3 or 6-14, wherein the modifier metal is an adsorbate adsorbed on the silica support surface, typically, chemisorbed or physisorbed onto the silica support surface, more typically chemisorbed thereon.

16. A process or catalyst or catalyst intermediate according to any of claims 1-3 or 6-15, wherein one or more non-labile ligands are attached to the modifier metal(s) to at least partially form the said compound or moieties and are optionally selected from molecules with lone pair containing oxygen or nitrogen atoms able to form 5 or 6 membered rings with a modifier metal 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 process or catalyst or catalyst intermediate according to any preceding claim, wherein the modifier metal is selected from zirconium, hafnium or titanium, typically, titanium.

18. A process or catalyst or catalyst intermediate according to any preceding claim, wherein the catalytic metal is selected from caesium, potassium or rubidium, more typically, caesium.

19. A process or catalyst or catalyst intermediate according to any preceding claim, wherein the silica support comprises the said modifier metal at a level of <5 metal atoms per nm^2.

20. A process or catalyst or catalyst intermediate according to any preceding claim, wherein at least 25%, of the said modifier metal on the support either before or after catalytic metal calcination is present in the form of mono- or dinuclear modifier metal moieties.

21. A process or catalyst or catalyst intermediate according to any preceding claim, wherein the adsorbed or co-gelated modifier metal cations are sufficiently spaced

apart from each other to substantially prevent oligomerisation thereof during subsequent treatment steps such as the impregnation of catalytic metal and/or, calcination, more preferably di, tri or oligomerisation thereof with neighbouring modifier metal cations.

22. A process or catalyst or catalyst intermediate according to any preceding claim, wherein the silica support comprises isolated silanol groups (-SiOH) at a level of <2.5 groups per nm^2.

23. A process or catalyst or catalyst intermediate according to any of claims 9-22, wherein the solvent for the said solution is other than water.

24. A process or catalyst or catalyst intermediate according to any of claims 9-23, wherein the solvent is an organic solvent such as toluene or heptane, optionally, an aliphatic, aromatic or chlorinated solvent such as dichloromethane, more typically, the solvent is an aliphatic alcohol, typically selected from C1-C6 alkanols such as methanol, ethanol, propanol, isopropanol, butanols, pentanols and hexanols, most typically, methanol, ethanol or propanols.

25. A process or catalyst or catalyst intermediate according to any preceding claim, wherein the support comprises the said 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.

26. A process or catalyst or catalyst intermediate according to any of claims 3 or 8- 25 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 compound are mononuclear or dinuclear modifier metal compounds when the compound is contacted with the support to effect adsorption of the said compound onto the support.

27. A process or catalyst or catalyst intermediate according to any preceding claim, wherein the silica component of the modified silica support may typically form 80-

99.9 wt% of the modified support, more typically 85-99.8 wt%, most typically 90-99.7 wt% thereof.

28. A process or catalyst or catalyst intermediate according to any preceding claim, wherein the silica support has an average pore size of between 2 and 1000 nm, more preferably between 3 and 500 nm, most preferably between 5 and 250 nm.

29. A process or catalyst or catalyst intermediate according to any preceding claim, wherein the catalytic metal is an adsorbate adsorbed on the modified silica support surface of the catalyst, typically, the adsorbate may be chemisorbed or physisorbed onto the modified silica support surface, more typically, it is chemisorbed thereon.

30. A process or catalyst or catalyst intermediate according to any preceding claim, wherein the catalytic metals such as caesium may be present in the catalyst at a level of at least 1 mol/100 (silicon + modifier metal) mol more preferably, at least 1.5 mol/100 (silicon + modifier metal) mol, most preferably, at least 2 mol/100 (silicon + modifier metal) mol, and/or, the level of catalytic metal may be up to 10 mol/100 (silicon + modifier metal) mol in the catalyst, more preferably, up to 7.5 mol/100 (silicon + modifier metal) mol, most preferably, up to 5 mol/100 (silicon + modifier metal) mol in the catalyst.

31. A process or catalyst or catalyst intermediate according to any preceding claim, wherein, the catalytic metal:modifier metal mole ratio in the catalyst is at least 1.4 or 1.5:1, and/or preferably, it is in the range 1.4 to 5:1 such as 1.5 to 4 :1, especially, 1.5 to 3.6 :1, typically in this regard the catalytic metal is caesium.

32. A process or catalyst or catalyst intermediate according to any preceding claim, wherein, the 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.

33. A process or catalyst or catalyst intermediate according to any preceding claim, wherein the level of catalytic metal in the catalyst is in the range from 1-10 mol/100 (silicon + modifier metal) mol, more preferably, 2-8 mol/100 (silicon + modifier metal) mol, most preferably, 2.5-6 mol/100 (silicon + modifier metal) mol in the catalyst.

34. A process or catalyst or catalyst intermediate according to any preceding claim, wherein, the level of modifier metal present in the modified silica or catalyst may be up to 7.6 x 10^{-2} mol/mol of silica, more preferably up to 5.9 x 10^{-2} mol/mol of silica, most preferably up to 3.5 x 10^{-2} mol/mol of silica.

35. A process or catalyst or catalyst intermediate according to any preceding claim, wherein, the level of modifier metal is between 0.067 x 10^{-2} and 7.3 x 10^{-2} mol/mol of silica, more preferably, between 0.13 x 10^{-2} and 5.7 x 10^{-2} mol/mol of silica and most preferably between 0.2 x 10^{-2} and 3.5 x 10^{-2} mol/mol of silica.

36. A process or catalyst or catalyst intermediate according to any preceding claim, wherein, the level of modifier metal present is at least 0.1 x 10^{-2} mol/mol of silica, more preferably, at least 0.15 x 10^{-2} mol/mol of silica and most preferably at least 0.25 x 10^{-2} mol/mol of silica.

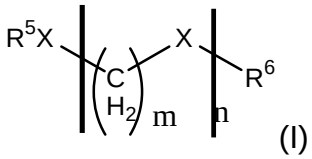
37. A process or catalyst or catalyst intermediate according to any preceding claim, wherein the average pore volume of the catalyst particles may be less than 0.1 cm^3/g but is generally in the range 0.1 – 5 cm^3/g as measured by uptake of a fluid such as water.

38. A process or catalyst or catalyst intermediate according to any preceding claim, wherein average pore volume of the catalyst is between 0.2-2.0 cm^3/g.

39. A catalyst obtainable by the process of any of claims 1 to 38.

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 6-40.

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 6-39, 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 40 or 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 process or catalyst or catalyst intermediate according to any preceding claim wherein the moieties or compounds are mononuclear.

44. A process or catalyst or catalyst intermediate according to any preceding claim wherein the moieties are uniformly distributed throughout the surface of the silica support.

45. A process or catalyst or catalyst intermediate according to any of claims 3 or 6-44, wherein the modifier metal compounds are uniformly distributed throughout the surface of the silica support.

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