

Claims

- 1 A catalyst comprising

a silica support, a modifier metal and a catalytic alkali metal, preferably caesium,

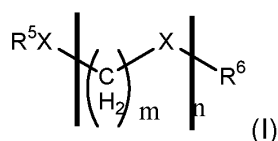
wherein the silica support has a multimodal pore size distribution comprising:-
 - a) a mesoporous pore size distribution having an average pore size in the range 2 to 50 nm and a pore volume of said mesopores of at least 0.1 cm³/g; and
 - b) a macroporous pore size distribution having an average pore size of more than 50 nm and a pore volume of said macropores of at least 0.1 cm³/g,
wherein the level of catalytic alkali metal on the silica support is at least 2 mol%,

and wherein the modifier metal is selected from Mg, B, Al, Ti, Zr and Hf, and is preferably selected from Ti, Zr and Hf.
- 2 A catalyst according to claim 1, wherein the level of catalytic alkali metal on the silica support is at least 3 mol%, more preferably at least 4 mol%, most preferably at least 5 mol%, especially, at least 6 mol% and/or up to 10 mol%, more preferably, up to 8 mol%, most preferably, up to 6 mol%.
- 3 A catalyst according to claims 1 or 2, wherein the amount of silica in the support is at least 50 wt%. more typically at least 80 wt%, even more typically at least 90 wt%, most typically at least 95 wt%, especially, about 96 or 97-100 wt%.
- 4 A catalyst according to any preceding claim, wherein the average mesopore volume of the catalyst particles is less than 1 cm³/g optionally in the range of 0.2-3 cm³/g, such as in the range 0.3-2.5 cm³/g, for example, 0.4-2 cm³/g, or for example, 0.5-1.5 cm³/g as measured by uptake of nitrogen.
- 5 A catalyst according to any preceding claim, wherein the average macropore volume of the catalyst particles is less than 1 cm³/g optionally in the range of 0.1-3 cm³/g, such as in the range 0.15-2.5 cm³/g, for example, 0.2-2 cm³/g, or for example, 0.5-1.5 cm³/g as measured by uptake of mercury.

- 6 A catalyst according to any preceding claim, wherein the macropore:mesopore volume ratio of the catalyst particles are in the range of 0.03-15, optionally in the range 0.4-4, more typically in the range 0.5-2.
- 7 A catalyst according to any preceding claim, wherein the catalyst is substantially free of tungsten and/or antimony and/or vanadium and/or bismuth and/or a metal of Group 3 and/or a metal of Group 10 and/or a metal of Group 13 and/or a metal of Group 14.
- 8 A catalyst according to any preceding claim, wherein the catalyst is substantially free of tungsten and/or antimony and/or vanadium and/or bismuth and/or lanthanum and/or cerium and/or platinum and/or tin.
- 9 A catalyst according to any of preceding claim, wherein the modifier metal is an adsorbate adsorbed on the silica support surface, preferably, chemisorbed thereon.
- 10 A catalyst according to any preceding claim, wherein the modifier metal is present as modifier metal oxide moieties.
- 11 A catalyst according to any preceding claim, wherein the silica support is in the form of a silica gel, more typically, a xerogel, aerogel or a hydrogel.
- 12 A catalyst according to any preceding claim, wherein the modifier metal is present in the support in the form of a co-gel.
- 13 A 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.
- 14 A 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.
- 15 A 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.

- 16 A catalyst according to any preceding claim, wherein the silica support is a calcined silica support.
- 17 A catalyst according to any preceding claim, wherein the catalytic alkali metal is one or more alkali metals selected from potassium, rubidium and caesium, suitably rubidium and caesium, for example caesium.
- 18 A catalyst according to any preceding claim, wherein catalytic alkali metal is present in the range 0.5-7.0 mol/mol modifier metal, such as 1.0-6.0 mol/mol, for example 1.5-5.0 mol/mol modifier metal.
- 19 A catalyst according to any preceding claim, wherein the catalytic alkali metal:modifier metal mole ratio is at least 1.4 or 1.5:1, preferably, it is in the range 1.4 to 5:1 such as 1.5 to 4.0:1, especially, 1.5 to 3.6:1.
- 20 A catalyst according to any preceding claim, wherein the average surface area is typically in the range 20-1000 m²/g, more typically 30-800 m²/g and most typically 35-500 m²/g.
- 21 A catalyst according to any preceding claim, wherein the total metal content of the catalyst is at least 80 wt% catalytic alkali metal and modifier metal as defined herein, typically, the total metal content of the catalyst is at least 85 wt% catalytic alkali metal and modifier metal as defined herein, more typically at least 90wt%, even more typically at least 95 wt%, most typically at least 99 wt%, especially at least 99.5 wt%, such as at least 99.9 wt%.
- 22 A method of producing a catalyst according to any of claims 1 to 21 comprising:-
- (a) preparing modified silica for a silica support with a modifier metal selected from Mg, B, Al, Ti, Zr and Hf
 - (b) treating the modified silica support with a catalytic alkali metal to provide a catalyst
 - (c) introducing macropores into the silica support either before step (a), before step (b) or after step (b).

- 23 A method of producing a catalyst according to claim 22, wherein the modified silica is a silica gel or pyrogenic silica which includes mesopores.
- 24 A method of producing a catalyst according to claims 21-23, wherein the macropores are introduced by hard templating, soft templating, binder techniques or other techniques.
- 25 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 to 21.
- 26 A process for preparing an ethylenically unsaturated acid or ester, typically α , β ethylenically unsaturated carboxylic acids or esters comprising contacting an alkanolic 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:



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 to 21, 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.

27 A process according to claim 25 or 26, wherein the α , β ethylenically unsaturated carboxylic acids or esters are acrylic acids or esters such as (alk)acrylic acids or alkyl (alk)acrylates, typically (meth)acrylic acids or alkyl (meth)acrylates for example, (meth)acrylic acids or alkyl methacrylates such as methacrylic acid (MAA) and methyl methacrylate (MMA).