catalyst is at least 0.5 mol%, and wherein the silica support is a ~~zero~~-xerogel comprising the step of:- contacting said silica supported depleted alkali metal catalyst with a solution of a salt of the alkali metal in a solvent system that has a polar organic solvent as the majority component.

The process of the invention is particularly suitable for regeneration of a used silica-supported catalyst. Such catalysts will typically have a reduced surface area. For instance, the depleted and subsequently regenerated catalyst may have a surface area of $<180m^2/g^{-1}$, more typically $<150m^2g^{-1}$. The surface area may be measured by well known methods, a preferred method being a standard BET nitrogen absorption method as is well known in the art. Preferably, the bulk of the surface area of the silica is present in pores of diameter in the range 5-150nm. Preferably, the bulk of the pore volume of the silica is provided by pores of diameter in the range 5-150nm. By the "bulk" of its pore volume or surface area is provided by pores of diameter in the range 5-150nm we mean that at least 50% of the pore volume or surface area is provided by pores of this diameter and more preferably at least 70%.

In addition, the depleted alkali metal catalyst may additionally include a second or further metal selected from the group consisting of zirconium, titanium, hafnium, aluminium, boron, and magnesium or mixtures thereof, preferably, zirconium, titanium, hafnium and aluminium or mixtures thereof, most preferably, hafnium and zirconium or mixtures thereof.

Suitable alkali metals may be selected form lithium, sodium, potassium, rubidium and caesium, preferably, potassium, rubidium and caesium. Caesium is preferred. The salt of the alkali metal may be selected from the group consisting of acetate, propionate, carbonate, hydrogen carbonate, nitrate and hydroxide.

Surprisingly, it has been found that strongly alkaline salts, for example alkali metal hydroxides such as caesium hydroxide may be used to re-impregnate the catalyst. This is surprising because it was understood from US6887822 that exposing the catalyst support to strongly alkaline salts would lead to hydrothermal ageing of the support with consequential damage to the catalyst and loss of surface area. In addition, exposing the catalyst to alkaline salts could lead to dissolution of the silica.

It has been found to be advantageous to use an impregnation solvent system that has a polar organic solvent as the majority component to act as carrier for the alkali metal salt in the impregnation. This solvent system advantageously reduces heat generation, which can cause catalyst bead cracking, and also reduces the risk of silica dissolution at high pH. Surprisingly, this is also contrary to the prior art teaching. US6887822 teaches that using an alcoholic solution of caesium for re-impregnation on a ~~zero~~-xerogel causes a high amount (76%) of bead

According to a second aspect of the present invention there is provided a re-impregnated catalyst prepared by the process of the first aspect of the invention optionally including any of the preferred or optional features thereof comprising a silica ~~zero~~-xerogel support and a catalytic metal selected from an alkali metal in the range 0.5-5 mol % on the catalyst, wherein the surface area of the silica support is <180m^2/g.

In one embodiment, the catalyst contains between 0.5 and 2.0wt% of the second metal. A particularly preferred second metal is zirconium. The second metal improves the catalyst crush resistance as described in US6887822.

In the case where it is desired to impregnate a silica-supported catalyst with caesium using methanol as the solvent, any methanol soluble caesium salt can be used, such as the carbonate, hydrogen carbonate, acetate, nitrate or propionate. The adsorption of caesium is found to proceed most efficiently at high pH ~13 and to reduce with falling pH necessitating the use of a greater concentration of caesium salt in solution. Accordingly, the adsorption of caesium proceeds most efficiently when a strongly basic caesium salt such as caesium hydroxide is used.

Surprisingly, the presence of water in the impregnation solution has no effect on the caesium uptake efficiency. In this regard, the presence of water has been tested up to 44 wt% and found to have no appreciable effect.

Water may typically be present in the impregnation solution at up to 40% by weight, more typically, up to 30% by weight in solution, most typically, up to 20% by weight.

In addition, significant levels of silica dissolution are avoided when low levels of alkali metal salt <2wt% in solution are used.

Surprisingly, a used catalyst that has a depleted surface area of <180m^2/g, more usually, <150 m^2/g, and that has been regenerated by adding more alkali metal as defined herein performs similarly in terms of %MMA & MAA yield and %MMA & MAA selectivity to a freshly prepared catalyst of high surface area (>250m^2/g) containing the same amount of alkali metal. This represents a considerable improvement in performance over that achieved before catalyst regeneration.

Typically, the level of alkali metal on the depleted catalyst prior to impregnation is at least 0.5mol%, more typically, at least 1.0 mol%. Upper levels for the alkali metal on the depleted catalyst prior to impregnation will depend on the reaction for which the catalyst has

temperatures are 0-100°C, more typically 5-60°C, most typically, 10-50°C. Suitable pressures for the reaction are 1-10bara.

Typically, the catalyst is in the form of a fixed bed during contact with the alkali metal solution which are thereby passed therethrough.

Suitable flow rates for the alkali metal solution in contact with the catalyst are 0.1 to 10 bed volumes/hr, more typically 0.2 to 2 bed volumes/hr, most typically 0.4 to 1 bed volumes/hr.

By bed volume is meant the amount equivalent to the bulk volume of the bed of catalyst to be treated.

By majority component of a solvent system is meant a component that makes up at least 50% by volume of the solvent system, more suitably, at least, 60%, most suitably, 70% or more. The majority component may make up 95% or more, for example, 99% or more, or approximately 100% of the solvent system by volume. If the majority component does not make up 100% by volume of the solvent system, the balance of the solvent system may be made up of one or more co-solvents.

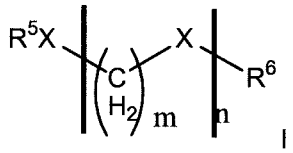
By solvent system herein is meant a single solvent or a solvent together with one or more co-solvents. By single solvent is meant more than 98% by volume, more typically, more than 99% by volume of the solvent system. Accordingly, by co-solvent is meant a solvent that makes up at least 1% by volume of the solvent system, more typically, at least 2% by volume.

By ~~zero-~~xerogel is meant a dried support typically, wherein >90% of the water has been removed from the hydrogel, more typically, >95%, most typically, >99%. A ~~zero~~xerogel may contain up to 6% water by weight, more usually, 3-5% by weight.

By mol% on the catalyst herein is meant mol% relative to moles of silica (SiO_2) in the catalyst. It is therefore assumed for the purpose of calculation that silica has a molecular weight equivalent to SiO_2 rather than that of a silica network. This more accurately reflects the nature of the catalyst. For example, 1 wt% caesium would equate to 0.45 mol% caesium in the catalyst, assuming molecular weights of 132.9 and 60.1 respectively.

Unless indicated to the contrary, amounts of alkali metal or alkali metal catalyst relate to the alkali metal ion and not the salt.

Levels of alkali metal on the catalyst whether mol% or wt% may be determined by appropriate sampling and taking an average of such samples. Typically, 5-10 samples of a



I

where R^5 is methyl and R^6 is H;

X is O;

n is 1;

and m is 1;

in the presence of a catalyst according to claim 20, and optionally in the presence of an alkanol; wherein R^1 is hydrogen or an alkyl group with 1 to 12 carbon atoms and R^3 is independently, hydrogen or an alkyl group with 1 to 12 carbon atoms.

22. A process according to claim 21, wherein the ethylenically unsaturated acid or ester is selected from methacrylic acid, acrylic acid, methyl methacrylate, ethyl acrylate or butyl acrylate.

23. A process according to claims 21 or 22, wherein the ester or acid of formula R^1-CH_2-$COOR^3$ is methyl propionate or propionic acid.

24. A process according to any one of claims 21 to 23, wherein the alcohol is methanol.

25. A process according to any one of claims 21 to 24, wherein the process is conducted at a molar ratio of acid or ester to formaldehyde from 20:1 to 1:20, and at a temperature of 250-400°C with a residence time of 1-100 seconds, and at a pressure of 1-10 bara.

26. The process according to any one of claims 21-25, wherein the re-impregnated catalyst is prepared by a process of contacting a silica supported depleted alkali metal catalyst with a solution of a salt of the alkali metal in a solvent system having a polar organic solvent as a majority component.