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Production of unsaturated acids or esters thereof and catalysts therefor

This invention relates to the production of ethylenically unsaturated acids or esters thereof, particularly methacrylic acid or alkyl methacrylates, and in particular to novel catalysts therefor. Such acids or esters may be made by reacting an alkanoic acid (or ester) of the formula R' - CH_2 - COOR, where R and R' are each, independently, hydrogen or an alkyl group, especially a lower alkyl group containing for example 1-4 carbon atoms, with formaldehyde. Thus methacrylic acid or alkyl esters thereof, especially methyl methacrylate, may be made by the catalytic reaction of propionic acid, or the corresponding alkyl ester, e.g. methyl propionate, with formaldehyde in accordance with the reaction sequence:

CH_3 - CH_2 - COOR + HCHO -------> CH_3 - $CH(CH_2OH)$ - COOR

CH_3 - $CH(CH_2OH)$ - COOR ------> CH_3 - $C(:CH_2)$ - COOR + H_2O

The reaction is typically effected at an elevated temperature, usually in the range 250-400°C, using a basic catalyst. Where the desired product is an ester, the reaction is preferably effected in the presence of the relevant alcohol in order to minimise the formation of the corresponding acid through hydrolysis of the ester. Also for convenience it is often desirable to introduce the formaldehyde in the form of formalin. Hence for the production of methyl methacrylate, the reaction mixture fed to the catalyst will generally consist of methyl propionate, methanol, formaldehyde and water.

Suitable catalysts that have been used include alkali metal-doped, especially cesium-doped, silica catalysts. It has been found that certain cesium-doped silica catalysts, i.e. those based upon gel silicas, have an unacceptable service life as they lose their activity and selectivity in a relatively short time. This activity loss may be attributed to two factors.

Firstly the alkali metal compound employed may exhibit appreciable volatility under the reaction conditions employed and so there may be a loss of activity through loss of alkali metal. As described in US 4 990 662, this may be overcome by incorporating a suitable alkali metal compound into the process gas stream so that alkali metal compound is deposited on the catalyst during operation to compensate for any alkali metal compound lost through volatilisation.

Secondly, as may be inferred from US 4 942 258, it is believed that for the alkali metal to be active, the support should have a certain minimum surface area. The requisite area is dependent on the amount of alkali metal in the catalyst: thus it may be inferred that there is a minimum surface area required per unit of alkali metal. During operation, there is a tendency for the silica support to lose surface area. Thus under the reaction conditions there is a risk of hydrolysis of the silica, not only by the water produced by the reaction, but also from water present in the reaction mixture, for example resulting from introduction of the formaldehyde as formalin. We have found that the loss of

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Yoo discloses in "Applied Catalysis", **102**, (1993) pages 215-232 catalysts of cesium supported on silica doped with various modifiers. While bismuth appeared to be a satisfactory dopant, catalysts doped with lanthanum, lead or thallium gave short term improvements. However high levels of lanthanum gave products of low selectivity while low levels of lanthanum gave catalysts that sintered much faster than the bismuth doped catalysts. The effective additives were all highly toxic heavy metals with appreciable volatility: these considerations preclude their use as catalyst components.

The aforementioned US 3 933 888 indicated that it was important to use a pyrogenic silica and showed that other types of silicas were unsuitable. The pyrogenic silicas said to be suitable are those having a total surface area in the range 150-300 m^2/g, a total pore volume of 3-15 cm^3/g and a specified pore size distribution wherein at least 50% of the pore content is in the form of pores of diameter above 10000 Å (1000 nm) and less than 30% is in the form of pores of diameter below 1000 Å (100 nm). In contrast, in the present invention the silicas that may be employed are preferably porous high surface area silicas such as gel silicas, precipitated gel silicas and agglomerated pyrogenic silicas.

Accordingly the present invention provides a catalyst comprising a porous high surface area silica containing 1-10% by weight of an alkali metal (expressed as metal), wherein the catalyst contains a compound of at least one modifier element selected from boron, magnesium, aluminium, zirconium and hafnium in such amount that the catalyst contains a total of 0.25 to 2 gram atoms of said modifier element per 100 moles of silica, said modifier element compound being dispersed in the pores of said silica.

The silica employed in the invention preferably has a surface area of at least 50 m^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 5-150 nm. Preferably the bulk of the pore volume of the silica is provided by pores of diameter in the range 5-150 nm. By "the bulk" of its pore volume or surface area is provided by pores of diameter in the range 5-150 nm 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%.

Preferred alkali metals are potassium, rubidium, or especially cesium. The alkali metal content is preferably in the range 3-8%, by weight (expressed as metal).

Gel silicas are preferred although suitable pyrogenic silicas may also be used.

The preferred modifier elements are zirconium, aluminium or borium.

The invention also provides a process for the manufacture of ethylenically unsaturated acids or esters thereof, particularly methacrylic acid or alkyl methacrylates, by reaction of an alkanoic acid, or ester of an alkanoic acid, of the formula R' - CH_2 - COOR, where R and R' are each,

spheres with boron during gelation from tetraethyl orthosilicate (TEOS) is described by Jubb and Bowen in J Material Science, volume 22, (1987), pages 1963-1970. Methods of preparing porous silicas are described in Iler R K, The Chemistry of Silica, (Wiley, New York, 1979), and in Brinker C J & Scherer G W "Sol-Gel Science" published by Academic Press (1990). Thus methods of preparing suitable silicas are known in the art .

The catalysts are then preferably calcined, for example in air, at a temperature in the range 300 to 600°C, particularly at 400-500°C before use, although we have found that this may not always be necessary.

The catalysts will normally be used in the form of a fixed bed and so it is desirable that the composition is formed into shaped units, e.g. spheres, granules, pellets, aggregates, or extrudates, typically having maximum and minimum dimensions in the range 1 to 10 mm. Where an impregnation technique is employed, the silica may be so shaped prior to impregnation. Alternatively the composition may be so shaped at any suitable stage in the production of the catalyst. The catalysts are also effective in other forms, e.g. powders or small beads and may be used in this form.

The alkanoic acid or ester thereof and formaldehyde can be fed, independently or after prior mixing, to the reactor containing the catalyst at molar ratios of acid or ester to formaldehyde of 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. Water may be present up to 60% by weight of the reaction mixture, although this is preferably minimised due to its negative effect both on catalyst decay and hydrolysis of esters to acids. Formaldehyde can be added from any suitable source. These include but are not limited to aqueous formaldehyde solutions, anhydrous formaldehyde derived from a formaldehyde drying procedure, trioxane, diether of methylene glycol and paraformaldehyde. Where forms of formaldehyde which are not as free or weakly complexed formaldehyde are used, the formaldehyde will form in situ in the synthesis reactor or in a separate reactor prior to the synthesis reactor. Thus for example, trioxane may be decomposed over an inert material or in an empty tube at temperatures over 350°C or over an acid catalyst at over 100°C. As a second example, methylal may be decomposed by reaction with water to form formaldehyde and methanol or without water to form dimethyl ether and formaldehyde. This can be accomplished either within the reactor or in a separate reactor containing a catalyst such as an heterogeneous acid catalyst. In this case it is advantageous to feed the alkanoic acid or ester thereof ester separately to the synthesis reactor to prevent its decomposition over the acid catalyst.

When the desired product is an unsaturated ester made by reacting an ester of an alkanoic acid ester with formaldehyde, the alcohol corresponding to the ester may also be fed to the reactor either with or separately to the other components. The alcohol, amongst other effects, reduces the quantity of acids leaving the reactor. It is not necessary that the alcohol is added at the beginning

Example	Zr content (gram atoms per 100 moles of silica)	Surface area (m^2/g) after testing for (days)					
		0	2	5	9	12	18
1 (comparative)	none	307	134	122	102	100	88
2	0.5	316	189	155	-	110	104*
3	1.2	302	208	192	187	183	172
4 (comparative)	2.5	307	240	221	-	200	197*

* after 19 days testing

The catalytic performance of the catalyst samples was determined in an atmospheric pressure microreactor charged with approximately 3 g of catalyst comminuted to 1mm size particles. Before use, the catalyst was dried at 300°C in a 100 ml/min stream of nitrogen for a period of 30 minutes. The catalysts were started-up at 300°C and fed with a mixture of methyl propionate, methanol and formalin. The formalin had a formaldehyde : water : methanol weight ratio of 0.35:0.50:0.15 and the proportions of methyl propionate, methanol and formalin were such that the overall molar proportions of methyl propionate, methanol and formaldehyde were 1:1.45:0.187. The reactants were passed through the catalyst at such a rate that the contact time was initially approximately 5 seconds. After the feed had stabilised (approx. 30 mins), the catalyst temperature was increased to 350°C and left to stabilise overnight. After approximately 16 hours of operation, the catalysts were tested for activity and selectivity by varying the feed gas flow rate. The results are shown in the following table.

Example	Zr content *	Methyl methacrylate plus methacrylic acid - % yield (Y) or % selectivity (S) at residence time of T (sec)														
		T	Y	S	T	Y	S	T	Y	S	T	Y	S	T	Y	S
1(comp)	none	1.3	5	94	2.6	8	94	5.5	10	94	8.2	11	92	15.9	12	89
2	0.5	1.0	4	93	2.0	7	96	5.0	10	93	8.0	11	93	15.0	12	90
3	1.2	1.2	3	92	2.4	5	94	4.8	9	97	7.0	10	97	13.6	12	95
4 (comp)	2.5	1.1	3	93	2.2	5	92	4.6	8	90	6.5	10	92	15.6	11	88

* gram atoms per 100 moles of silica

It is seen that zirconium gave a significant improvement in the retardation of loss of surface area and a significant improvement in selectivity at the longer residence times, except when a relatively large amount of zirconium was employed. The effect on selectivity is also demonstrated by the following table which shows the yield of "heavy" components, i.e. unwanted by products.

Example 2 was repeated but using boron oxide dissolved in the cesium carbonate solution in place of zirconium nitrate to give a catalyst containing 0.8 gram atoms of boron per 100 moles of silica. The surface area was 172 m^2/g after 6 days testing and thereafter fell slowly, having a value of 157 m^2/g after 22 days testing. In the activity testing, at a contact time of 3.8 sec., the yield was 7% and the selectivity was 95%. At a contact time of 6.2 sec., the yield was 9% and the selectivity was 95%.

Example 9

Example 2 was repeated but using a mixture of aluminium nitrate and hafnium oxynitrate in place of zirconium nitrate to give a catalyst containing 0.2 gram atoms of aluminium and 0.3 gram atoms of hafnium per 100 moles of silica. In the activity testing, at a contact time of 3.0 sec., the yield was 7% and the selectivity was 94%. At a contact time of 6.7 sec., the yield was 10% and the selectivity was 94%.

Examples 10-13 (comparative)

Catalysts were made by the procedure of Example 1 using zirconia of 1 mm particle size in place of gel silica as the support. Catalysts were made with nominal cesium contents ranging from 2 to 8% by weight. The results and surface areas of the catalysts are shown in the following table.

Ex.	Cs (%)	Surface area (m^2/g)	Methyl methacrylate + methacrylic acid - % yield (Y) or % selectivity (S) at residence time of T sec					
			T	Y	S	T	Y	S
10	2	93	2.3	6	49	4.7	6	44
11	4	90	2.4	4	38	5.0	4	23
12	6	74	2.5	4	29	5.4	3	15
13	8	73	2.1	2	27	4.4	3	16

The very poor yields and selectivities demonstrate that cesium-doped zirconia is not a suitable catalyst.

Examples 14-16

A series of catalysts were made by the procedure of Example 2, but using a mixture of zirconium nitrate and aluminium nitrate. The results of accelerated hydrolysis and activity testing are shown in the following tables.

Example	Zr content *	Surface area (m^2/g) after testing for (days)						
		0	4	7	11	14	18	21
19	0.5	240	153	153	132	139	-	136
20	0.7	249	169	161	167	149	155	-
21	0.8	246	187	180	180	172	172	175
22	1.0	251	195	171	185	175	176	182

* g atoms per 100 moles of silica

Example	Zr content *	Methyl methacrylate plus methacrylic acid - % yield (Y) or % selectivity (S) at residence time of T sec													
		T	Y	S	T	Y	S	T	Y	S	T	Y	S	T	Y	S
19	0.5	1.0	3	89	2.1	5	90	4.4	8	93	7.1	10	92	15.4	11	89
20	0.7	1.0	3	88	1.9	5	88	4.2	9	91	7.3	11	91	14.8	13	89
21	0.8	1.1	2	80	2.3	5	81	4.9	9	82	8.6	11	83	20.3	12	80
22	1.0	1.0	2	64	2.0	4	65	4.2	5	67	7.3	7	68	13.7	7	65
23(comp)	none	1.2	4	94	2.3	6	93	4.3	8	95	7.0	10	92	13.3	11	90

* g atoms per 100 moles of silica

Examples 24-26

Example 20 was repeated to give catalysts containing 0.7 gram atoms of zirconium per 100 moles of silica but using different amounts of cesium. The activity of the catalysts was assessed as in Examples 1-4.

Example	Cs (wt%)	Methyl methacrylate plus methacrylic acid - % yield (Y) or % selectivity (S) at residence time of T sec											
		T	Y	S	T	Y	S	T	Y	S	T	Y	S
24	2	1.2	1	31	2.2	2	38	4.6	3	42	11.1	4	45
25	3	1.1	2	73	2.4	4	77	5.0	7	79	11.3	9	80
20	4	1.0	3	88	1.9	5	88	4.2	9	91	7.3	11	91
26	5	1.1	4	89	2.1	7	93	4.2	9	90	10.3	10	88

Examples 27 - 33

Example	Zr (g.atoms/100 g.moles silica)	Contact Time (s)	Yield of MMA + MAA	Selectivity to MMA + MAA
27 (comp)	0.00	1.83	10.30	94.06
28	0.13	1.54	10.03	93.36
29	0.26	2.63	12.86	93.81
30	0.39	1.64	7.45	93.79
31	0.49	3.02	10.00	94.14
32	0.66	2.16	10.78	89.84
33	1.31	38.82	3.20	75.84

Examples 34 - 38

Catalysts were prepared on crystalline zirconia powder (surface area 38 m^2g^{-1}) to which caesium nitrate was added by the method described in Example 28. Catalysts were tested for activity using the method of Example 27. The results are shown in the table below and show that zirconia alone is not a suitable support for MMA synthesis. The best result at 2 wt% caesium was not sustained and after 24 hours running fell to 60% selectivity. Levels of diethyl ketone (DEK), an unwanted by-product of the reaction, are also very high except for the most favourable loading of caesium. DEK is a particular problem at such levels because it has a boiling point which is very close to that of MMA and so it cannot be removed by distillation.

Example	Cs (wt%)	Contact Time (s)	Yield of MMA + MAA	Selectivity to MMA + MAA	DEK yield (% of MMA + MAA)
34	0	10.00	3.09	7.75	32.00
35	2	3.00	9.50	74.80	0.07
36	4	3.00	1.38	2.11	41.00
37	6	52.10	3.04	15.64	27.00
38	8	118.60	1.57	2.65	41.00

Examples 39 - 43 (comparative)

Catalysts were prepared by physically mixing the pure silica support used in Examples 1 - 4 ground to 0.6 - 1.0 mm mesh size with portions of the zirconia powder used in Examples 34 - 38 in various proportions. The mixed support was then impregnated with caesium nitrate using the method described in Examples 27 - 33 to give 4 wt% caesium based on weight of silica plus zirconia. The results of catalytic testing and for stability towards hydrothermal sintering using the methods of Examples 27 - 33 are shown in the table below:

Example	B (g.atom/100 g.atom SiO2)	contact Time (sec)	Yield of MMA + MAA (%)	Selectivity to MMA + MAA (%)	Surface area at start (m^2g^{-1})	Surface Area after 14 days (m^2g^{-1})	Fractional loss of surface area over test (%)
27 (comp)	0.00	1.83	10.30	94.06	273.20	13.10	95.20
44	0.39	1.66	9.50	93.59	311.30	99.60	68.80
45	0.78	5.33	9.97	93.88			
46	1.16	3.02	11.13	94.41			
47	2.00	3.88	11.61	92.05			
48	3.90	5.36	7.48	91.19			

Example 49

A catalyst was prepared by the method in Example 28 but using 0.39 gatom hafnium instead of 0.39 gatom zirconium, hafnium oxynitrate being used instead of zirconium nitrate. The catalyst was tested for stability towards hydrothermal sintering for catalytic activity by the method used in Example 27 - 33. The surface area fell from 309 m^2g^{-1} to 125 m^2g^{-1} over the test. At 1.9 second contact time the yield of methyl methacrylate plus methacrylic acid was 10.33% and selectivity was 92.5%.

Example 50

Catalysts containing caesium and zirconium were prepared on a high purity gel silica in the form of spheres of diameter in the range 2-4 mm having a purity of over 99%, a surface area of 127 m^2g^{-1} by the methods described in Example 28.

Example 51 - 54

Catalysts containing caesium and zirconium were prepared on high purity gel silicas in the form of powders with surface areas as indicated in the table below.

Example 55 - 58

Catalysts containing caesium and zirconium were prepared on a pyrogenic silica powder with compositions as indicated in the table below.

	Methyl methacrylate plus methacrylic acid - % yield (Y) or % selectivity (S) at residence time of T sec														
Example	T	Y	S	T	Y	S	T	Y	S	T	Y	S	T	Y	S
59	1.1	5.1	94.8	2.2	7.5	95.7	2.9	8.8	95.4	5.7	11.2	94.3	8.6	12.8	92.0
60	0.3	5.1	84.6	2.6	7.4	86.3	3.6	9.0	86.6	6.1	10.8	86.5	10.4	11.6	85.8
61	1.2	5.5	91.1	2.4	8.0	91.5	3.3	9.7	91.4	5.5	11.4	90.5	9.5	12.5	87.4
62	1.1	5.1	95.0	2.3	7.4	95.3	3.3	9.0	95.1	5.5	10.9	94.4	8.8	12.5	92.5

Example	Surface area after n days on line (m^2g^{-1})				
	Days on Line	0	7	14	28
59		309	165	112	99
60		296	167	169	158
61		296	142	119	103
62		309	159	132	128

Thus these catalysts display satisfactory catalytic performance and enhanced stability towards sintering of silica compared to Example 1.

10 A method of preparing a catalyst comprising mixing together particles of a porous high surface area silica with a solution of a compound of a modifier element selected from boron, magnesium, aluminium, zirconium and/or hafnium such that said compound is impregnated into said particles in such amount that the particles contain a total of 0.25 to 2 gram atoms of said modifier element per 100 moles of silica; impregnating said particles with a solution of a compound of an alkali metal such that the particles contain 1-10% by weight of said alkali metal (expressed as metal), said impregnation being carried out before during or after the impregnation with the modifier element compound; and subsequently drying said particles.

11 A method of preparing a catalyst as claimed in claim 1 comprising co-gelling or co-precipitating a compound of the modifier element with the silica, or hydrolysing a mixture of the modifier element halide with a silicon halide.

12 A process for the manufacture of ethylenically unsaturated acids or esters thereof by reaction of an alkanoic acid, or ester of an alkanoic acid, of the formula R' - CH_2 - COOR, where R and R' are each, independently, hydrogen or an alkyl group, with formaldehyde in the presence of a catalyst as claimed in any one of claims 1 to 8.

13 A process according to claim 12 wherein the ester of the alkanoic acid is methyl propionate and is reacted with formaldehyde in the presence of methanol.

14 A process according to claim 12 or claim 13 wherein the formaldehyde is supplied in the form of formalin.

15 A process for manufacturing methyl methacrylate comprising reacting methyl propionate with formaldehyde and methanol in the presence of a catalyst comprising a porous high surface area silica containing 1-10% by weight of cesium (expressed as metal), wherein the catalyst contains a zirconium compound in such amount that the catalyst contains a total of 0.25 to 2 gram atoms of zirconium per 100 moles of silica, said zirconium compound being dispersed in the pores of said silica.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/01029

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J23/04 B01J21/08 B01J35/10 C07C57/04 C07C51/353
C07C51/347 C07C51/09 C07C67/343 C07C69/54

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
—

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	US 4 845 070 A (MONTAG RUTH A) 4 July 1989 (1989-07-04) abstract column 9, line 12 - line 18 column 10, line 68 - column 11, line 2; claims 1,4,6; examples 1,2; table XI	1-8,11, 12,14
A	& US 4 990 662 A (HAGEN ET AL) 5 February 1991 (1991-02-05) cited in the application example 1	1-15

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 July 1999	27/07/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P B 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-2040, Tx 31 651 epo nl, Fax (+31-70) 340-3016	Veefkind, V

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 99/01029

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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Claims

1 A catalyst comprising a porous high surface area silica containing 1-10% by weight of an alkali metal (expressed as metal), wherein the catalyst contains a compound of at least one modifier element selected from magnesium, aluminium, zirconium and/or hafnium in such amount that the catalyst contains a total of 0.25 to 2 gram atoms of said modifier element per 100 moles of silica, said modifier element compound being dispersed in the pores of said silica.

2. A catalyst comprising a porous high surface area silica containing 1-10% by weight of an alkali metal (expressed as metal), wherein the catalyst contains a mixture of compounds of modifier elements selected from boron, magnesium, aluminium, zirconium and/or hafnium in such amount that the catalyst contains a total of 0.25 to 2 gram atoms of said modifier elements per 100 moles of silica, said modifier element compound being dispersed in the pores of said silica.

3 A catalyst as claimed in claim 1 or 2, wherein the surface area of the silica is at least $50m^2g^{-1}$.

4 A catalyst as claimed in claim 1 or 2, wherein at least 50% of the pore volume is provided by pores of diameter in the range 5-150nm.

5 A catalyst as claimed in claim 1 or 2, wherein at least 50% of the total surface area of the silica is present in pores of diameter in the range 5-150nm.

6 A catalyst according to claim 1 or 2, wherein the alkali metal is caesium.

7 A catalyst as claimed in any preceding claim, wherein the compound of at least one modifier element is present in the form of at least one oxide and/or hydroxide of said at least one modifier element.

8 A catalyst as claimed in any of the preceding claims as appendant to claim 1 wherein the modifier element comprises zirconium and/or aluminium.

9 A catalyst comprising a porous high surface area silica containing 1-10% by weight of an alkali metal (expressed as metal), wherein the catalyst contains a compound of at least one modifier element selected from boron, magnesium, aluminium, zirconium and hafnium in such amount that the catalyst contains a total of 0.25 to 2 gram atoms of said modifier element per 100 moles of silica, said modifier element compound being dispersed in the pores of said silica, wherein where the catalyst contains only boron as a modifier element it excludes boron up to a level of 0.29 gram atoms of said modifier element per 100 moles of silica.

10 A catalyst as claimed in claim 1 containing a total of 0.25 to 1.5 gram atoms of said modifier element per 100 moles of silica.

11. A catalyst comprising a porous high surface area silica containing 1-10% by weight of an alkali metal (expressed as metal), wherein the catalyst contains a compound of boron as a modifier element in such amount that the catalyst contains a total of 0.39 to 3.9 gram atoms of said modifier element per 100 moles of silica, said modifier element compound being dispersed in the pores of said silica.

12. A method of preparing a catalyst comprising mixing together particles of a porous high surface area silica with a solution of a mixture of compounds of modifier elements selected from boron, magnesium, aluminium, zirconium and/or hafnium such that said compounds are impregnated into said particles in such amount that the particles contain a total of 0.25 to 2 gram atoms of said modifier element per 100 moles of silica; impregnating said particles with a solution of a compound of an alkali metal such that the particles contain 1-10% by weight of said alkali metal (expressed as metal), said impregnation being carried out before during or after the impregnation with the modifier element compounds; and subsequently drying said particles.

13 A method of preparing a catalyst comprising mixing together particles of a porous high surface area silica with a solution of a compound of a modifier element selected from magnesium, aluminium, zirconium and/or hafnium such that said compound is impregnated into said particles in such amount that the particles contain a total of 0.25 to 2 gram atoms of said modifier element per 100 moles of silica; impregnating said particles with a solution of a compound of an alkali metal such that the particles contain 1-10% by weight of said alkali metal (expressed as metal), said impregnation being carried out before during or after the impregnation with the modifier element compound; and subsequently drying said particles.

14 A method of preparing a catalyst comprising mixing together particles of a porous high surface area silica with a solution of a compound of a modifier element boron such that said compound is impregnated into said particles in such amount that the particles contain a total of 0.39 to 3.9 gram atoms of said modifier element per 100 moles of silica; impregnating said particles with a solution of a compound of an alkali metal such that the particles contain 1-10% by weight of said alkali metal (expressed as metal), said impregnation being carried out before during or after the impregnation with the modifier element compound; and subsequently drying said particles.

Claims

1 A catalyst comprising a porous high surface area silica containing 1-10% by weight of an alkali metal (expressed as metal), wherein the catalyst contains a compound of at least one modifier element selected from magnesium, aluminium, zirconium and/or hafnium in such amount that the catalyst contains a total of 0.25 to 2 gram atoms of said modifier element per 100 moles of silica, said modifier element compound being dispersed in the pores of said silica.

2. A catalyst comprising a porous high surface area silica containing 1-10% by weight of an alkali metal (expressed as metal), wherein the catalyst contains a mixture of compounds of modifier elements selected from boron, magnesium, aluminium, zirconium and/or hafnium in such amount that the catalyst contains a total of 0.25 to 2 gram atoms of said modifier elements per 100 moles of silica, said modifier element compound being dispersed in the pores of said silica.

3 A catalyst as claimed in claim 1 or 2, wherein the surface area of the silica is at least $50m^2g^{-1}$.

4 A catalyst as claimed in claim 1 or 2, wherein at least 50% of the pore volume is provided by pores of diameter in the range 5-150nm.

5 A catalyst as claimed in claim 1 or 2, wherein at least 50% of the total surface area of the silica is present in pores of diameter in the range 5-150nm.

6 A catalyst according to claim 1 or 2, wherein the alkali metal is caesium.

7 A catalyst as claimed in any preceding claim, wherein the compound of at least one modifier element is present in the form of at least one oxide and/or hydroxide of said at least one modifier element.

8 A catalyst as claimed in any of the preceding claims as appendant to claim 1 wherein the modifier element comprises zirconium and/or aluminium.

9 A catalyst comprising a porous high surface area silica containing 1-10% by weight of an alkali metal (expressed as metal), wherein the catalyst contains a compound of at least one modifier element selected from boron, magnesium, aluminium, zirconium and hafnium in such amount that the catalyst contains a total of 0.25 to 2 gram atoms of said modifier element per 100 moles of silica, said modifier element compound being dispersed in the pores of said silica, wherein where the catalyst contains only boron as a modifier element it excludes boron up to a level of 0.29 gram atoms of said modifier element per 100 moles of silica.

10 A catalyst as claimed in claim 1 containing a total of 0.25 to 1.5 gram atoms of said modifier element per 100 moles of silica.

11. A catalyst comprising a porous high surface area silica containing 1-10% by weight of an alkali metal (expressed as metal), wherein the catalyst contains a compound of boron as a modifier element in such amount that the catalyst contains a total of 0.39 to 3.9 gram atoms of said modifier element per 100 moles of silica, said modifier element compound being dispersed in the pores of said silica.

12. A method of preparing a catalyst comprising mixing together particles of a porous high surface area silica with a solution of a mixture of compounds of modifier elements selected from boron, magnesium, aluminium, zirconium and/or hafnium such that said compounds are impregnated into said particles in such amount that the particles contain a total of 0.25 to 2 gram atoms of said modifier element per 100 moles of silica; impregnating said particles with a solution of a compound of an alkali metal such that the particles contain 1-10% by weight of said alkali metal (expressed as metal), said impregnation being carried out before during or after the impregnation with the modifier element compounds; and subsequently drying said particles.

13 A method of preparing a catalyst comprising mixing together particles of a porous high surface area silica with a solution of a compound of a modifier element selected from magnesium, aluminium, zirconium and/or hafnium such that said compound is impregnated into said particles in such amount that the particles contain a total of 0.25 to 2 gram atoms of said modifier element per 100 moles of silica; impregnating said particles with a solution of a compound of an alkali metal such that the particles contain 1-10% by weight of said alkali metal (expressed as metal), said impregnation being carried out before during or after the impregnation with the modifier element compound; and subsequently drying said particles.

14 A method of preparing a catalyst comprising mixing together particles of a porous high surface area silica with a solution of a compound of a modifier element boron such that said compound is impregnated into said particles in such amount that the particles contain a total of 0.39 to 3.9 gram atoms of said modifier element per 100 moles of silica; impregnating said particles with a solution of a compound of an alkali metal such that the particles contain 1-10% by weight of said alkali metal (expressed as metal), said impregnation being carried out before during or after the impregnation with the modifier element compound; and subsequently drying said particles.

15 A method of preparing a catalyst as claimed in claim 1 or 2 comprising co-gelling or co-precipitating a compound of the modifier element with the silica, or hydrolysing a mixture of the modifier element halide with a silicon halide.

16 A process for the manufacture of ethylenically unsaturated acids or esters thereof by reaction of an alkanoic acid, or ester of an alkanoic acid, of the formula R' - CH_2 - COOR, where R and R' are each, independently, hydrogen or an alkyl group, with formaldehyde in the presence of a catalyst as claimed in any one of claims 1 to 10.

17 A process according to claim 16 wherein the ester of the alkanoic acid is methyl propionate and is reacted with formaldehyde in the presence of methanol.

18 A process according to claim 17 or claim 18 wherein the formaldehyde is supplied in the form of formalin.

19 A process for manufacturing methyl methacrylate comprising reacting methyl propionate with formaldehyde and methanol in the presence of a catalyst comprising a porous high surface area silica containing 1-10% by weight of cesium (expressed as metal), wherein the catalyst contains a zirconium compound in such amount that the catalyst contains a total of 0.25 to 2 gram atoms of zirconium per 100 moles of silica, said zirconium compound being dispersed in the pores of said silica.

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Claims

1. A catalyst comprising a porous high surface area silica containing 1-10% by weight of an alkali metal (expressed as metal), wherein the catalyst contains a compound of at least one modifier element selected from magnesium, aluminium. zirconium and/or hafnium in such amount that the catalyst contains a total of 0.25 to 2 gram atoms of said modifier element per 100 moles of silica, said modifier element compound being dispersed in the pores of said silica.

2. A catalyst comprising a porous high surface area silica containing 1-10% by weight of an alkali metal (expressed as metal), wherein the catalyst contains a mixture of compounds of modifier elements selected from boron, magnesium, aluminium, zirconium and/or hafnium in such amount that the catalyst contains a total of 0.25 to 2 gram atoms of said modifier elements per 100 moles of silica, said modifier element compound being dispersed in the pores of said silica.

3. A catalyst as claimed in claim 1 or 2, wherein the surface area of the silica is at least $50m^2g^{-1}$.

4. A catalyst as claimed in claim 1 or 2, wherein at least 50% of the pore volume is provided by pores of diameter in the range 5-150nm.

5. A catalyst as claimed in claim 1 or 2, wherein at least 50% of the total surface area of the silica is present in pores of diameter in the range 5-150nm.

6. A catalyst according to claim 1 or 2, wherein the alkali metal is caesium.

7. A catalyst as claimed in any preceding claim, wherein the compound of at least one modifier element is present in the form of at least one oxide and/or hydroxide of said at least one modifier element.

8. A catalyst as claimed in any of the preceding claims as appendant to claim 1 wherein the modifier element comprises zirconium and/or aluminium.

9. A catalyst comprising a porous high surface area silica containing 1-10% by weight of an alkali metal (expressed as metal), wherein the catalyst contains a compound of at least one modifier element selected from boron, magnesium, aluminium, zirconium and/or hafnium in such amount that the catalyst contains a total of 0.25 to 2 gram atoms of said modifier element per 100 moles of silica, said modifier element compound being dispersed in the pores of said silica, wherein where the catalyst contains only boron as a modifier element it excludes boron up to a level of 0.26 gram atoms of said modifier element per 100 moles of silica.

10. A catalyst as claimed in claim 1 containing a total of 0.25 to 1.5 gram atoms of said modifier element per 100 moles of silica.

11. A catalyst comprising a porous high surface area silica containing 1-10% by weight of an alkali metal (expressed as metal), wherein the catalyst contains a compound of boron as a modifier element in such amount that the catalyst contains a total of 0.39 to 3.9 gram atoms of said

modifier element per 100 moles of silica, said modifier element compound being dispersed in the pores of said silica.

12. A method of preparing a catalyst comprising mixing together particles of a porous high surface area silica with a solution of a mixture of compounds of modifier elements selected from boron, magnesium, aluminium, zirconium and/or hafnium such that said compounds are impregnated into said particles in such amount that the particles contain a total of 0.25 to 2 gram atoms of said modifier element per 100 moles of silica ; impregnating said particles with a solution of a compound of an alkali metal such that the particles contain 1-10% by weight of said alkali metal (expressed as metal), said impregnation being carried out before during or after the impregnation with the modifier element compounds; and subsequently drying said particles.

13. A method of preparing a catalyst comprising mixing together particles of a porous high surface area silica with a solution of a compound of a modifier element selected from magnesium, aluminium, zirconium and/or hafnium such that said compound is impregnated into said particles in such amount that the particles contain a total of 0.25 to 2 gram atoms of said modifier element per 100 moles of silica; impregnating said particles with a solution of a compound of an alkali metal such that the particles contain 1-10% by weight of said alkali metal (expressed as metal), said impregnation being carried out before during or after the impregnation with the modifier element compound; and subsequently drying said particles.

14. A method of preparing a catalyst comprising mixing together particles of a porous high surface area silica with a solution of a compound of a modifier element boron, such that said compound is impregnated into said particles in such amount that the particles contain a total of 0.39 to 3.9 gram atoms of said modifier element per 100 moles of silica; impregnating said particles with a solution of a compound of an alkali metal such that the particles contain 1-10% by weight of said alkali metal (expressed as metal), said impregnation being carried out before during or after the impregnation with the modifier element compound; and subsequently drying said particles.

15. A method of preparing a catalyst as claimed in claim 1 or 2 comprising co-gelling or co-precipitating a compound of the modifier element with the silica, or hydrolysing a mixture of the modifier element halide with a silicon halide.

16. A process for the manufacture of ethylenically unsaturated acids or esters thereof by reaction of an alkanoic acid, or ester of an alkanoic acid, of the formula R'-CH_2-COOR, where R and R' are each, independently, hydrogen or an alkyl group, with formaldehyde in the presence of a catalyst as claimed in any one of claims 1 to 11.

17. A process for the manufacture of ethylenically unsaturated acids or esters thereof by reaction of an alkanoic acid, or ester of an alkanoic acid, of the formula R'-CH_2-COOR, where R and R' are each, independently, hydrogen or an alkyl group, with formaldehyde in the presence of a catalyst comprising a porous high surface area silica containing 1-10% by weight of an alkali metal (expressed as metal), wherein the catalyst contains a compound of at least one modifier element selected from boron, magnesium, aluminium, zirconium and/or hafnium in such amount that the catalyst contains a total of 0.25 to 2 gram atoms of said modifier element per 100 moles of silica, said modifier element compound being dispersed in the pores of said silica.

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18. A process according to claim 16 or 17, wherein the ester of the alkanoic acid is methyl propionate and is reacted with formaldehyde in the presence of methanol.

19. A process according to claim 16, 17 or 18, wherein the formaldehyde is supplied in the form of formalin.

20. A process for manufacturing methyl methacrylate comprising reacting methyl propionate with formaldehyde and methanol in the presence of a catalyst comprising a porous high surface area silica containing 1-10% by weight of cesium (expressed as metal), wherein the catalyst contains a zirconium compound in such amount that the catalyst contains a total of 0.25 to 2 gram atoms of zirconium per 100 moles of silica, said zirconium compound being dispersed in the pores of said silica.

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18. A process according to claim 16 or 17, wherein the ester of the alkanoic acid is methyl propionate and is reacted with formaldehyde in the presence of methanol.

19. A process according to claim 16, 17 or 18, wherein the formaldehyde is supplied in the form of formalin.

20. A process for manufacturing methyl methacrylate comprising reacting methyl propionate with formaldehyde and methanol in the presence of a catalyst comprising a porous high surface area silica containing 1-10% by weight of cesium (expressed as metal), wherein the catalyst contains a zirconium compound in such amount that the catalyst contains a total of 0.25 to 2 gram atoms of zirconium per 100 moles of silica, said zirconium compound being dispersed in the pores of said silica.

21. The use of boron as a stabilizer for a catalyst, the said catalyst comprising a porous high surface area silica containing 1 – 10% by weight of an alkali metal (expressed as metal) in such amount that the catalyst contains a total of 0.25 to 2 gram atoms of boron per 100 moles of silica, the boron being dispersed in the pores of the silica and stabilizing the catalyst.