Mouldings based on silica

This invention relates to mouldings based on silica, to a process for their production, and their use as a catalyst for the acetoxylation of olefines.

Silicas, particularly pyrogenic silicas, are characterised by their extremely finely divided state and their correspondingly high specific surface, by their very high purity, by their spherical particles and by the absence of pores. Due to these properties, there is an increasing interest in pyrogenic silicas as supports for catalysts (D. Koth, H. Ferch, Chem. Ing. Techn. 52, 628 (1980)).

It is known from DE-B 21 00 778 that granular materials based on pyrogenic silicas can be used as catalyst supports for the production of vinyl acetate monomer.

It is known from DE-A 38 03 900 that cylindrical particles which have arched end faces and which are based on pyrogenic silicas can be used as catalyst supports for the production of vinyl acetate monomer.

A process for the production of pressed parts is known from DE-A 39 12 504 in which aluminium stearate, magnesium stearate and/or graphite are used as a lubricant, and in which urea as well as methyl cellulose are used as pore forming agents.

These known pressed parts which are produced with magnesium stearate are commercially available as Aerosil Tablets No. 350, as supplied by Degussa. They contain about 0.4 % by weight Mg.

Catalyst supports for catalysts for the synthesis of vinyl acetate monomer are known from EP 0 004 079 which consist of extruded sections with a star-shaped cross-section or which consist of ribbed lengths.

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Catalysts for the synthesis of vinyl acetate monomer, which comprise at least one passageway channel with an inside diameter of at least 1 mm, are known from EP-B 464 633.

DE-A 195 38 799 describes a catalyst support in the shape of a honeycomb which predominantly consists of SiO_2. According to Example 1 of said patent, this support has a diameter of 25 mm, a stay width of 1 mm, a stay spacing of 2 mm, and a length of 150 mm. After it has been coated with catalytically active elements, the resulting catalyst can be used for the production of unsaturated esters from olefines, acids and oxygen in the gas phase, for the purification of off-gas contaminated by organic substances, and for the alkylation of aromatic compounds.

WO 97/36679 also describes a catalyst support in the shape of a honeycomb, which is coated with SiO_2 and which after impregnation with palladium and gold and after activation with potassium acetate can be used for the production of unsaturated esters.

Honeycomb-shaped catalysts are characterised by a very low pressure drop. However, the use of honeycomb-shaped catalysts in industrial reactors, particularly in tube bundle reactors, results in problems which are not inconsiderable, particularly with regard to packing the reactor tubes. With tube reactors, it is sometimes necessary to pack several thousand tubes of an industrial installation with honeycomb catalysts. In the course of this procedure, it has to be ensured that the honeycomb bodies do not break down during filling. Considerable emphasis has to be placed on the avoidance of edge flow effects, since otherwise the catalysts are not capable of contributing their full effect. Moreover, honeycomb-shaped catalyst materials exhibit poor thermal condutivity in a radial direction. This is particularly disadvantageous in reactions in which there is considerable evolution of heat,

as in oxidation reactions for example. For the aforementioned reasons, there is currently no known industrial application in which a tube bundle reactor or thousands of tubes are operated with honeycomb-shaped catalyst materials. For this reason, reactors are packed with mouldings in the form of pellets, which likewise exhibit a low pressure drop.

It is known from EP-B 0 519 435 that SiO_2 can be pressed by means of binders to produce supports, followed by calcining the supports obtained and washing the calcined support particles with acid until cations from the binder are no longer released. In addition, a supported catalyst, a process for the production thereof, and the use thereof for the production of vinyl acetate are also described.

EP-A 0 807 615 describes pressed parts based on pyrogenic silica. These pressed parts can be used as a catalyst or catalyst support for the production of vinyl acetate monomer and for the hydration of ethylene. The pressed parts may be of different shapes, e.g. cylindrical, spherical or annular, with an outside diameter of 0.8 to 20 mm.

The present invention relates to mouldings based on silica, which are characterised in that that the supporting geometry consists of a hollow cylindrical configuration with internal reinforcing stays or spokes leading from the inner wall of the hollow cylinder to the centre the moulding, or is characterised by a multiplicity of passageway channels.

The mouldings according to the invention can have an outside diameter from 1 to 25 mm and a ratio of height to diameter of 0.2 to 5. Furthermore, they can have a total pore volume of 0.3 to 1,8 ml/g and a BET specific surface of 5 to 400 m^2/g.

The SiO_2 content of the mouldings according to the invention is preferably more than 99.0 % by weight. The proportion of other constituents can be less than 0.2 % by weight. The mouldings according to the invention can therefore be characterised as being free from binders. The fines can amount to less than 5 % by weight. The bulk density can range from 100 to 700 g/l.

The present invention further relates to a process for the production of mouldings based on silica, which is characterised in that silica is subjected to a kneading and working process, is extruded, the extrudate is optionally cut to the desired length by means of a cutting device, is dried at a temperature of 20 to 150°C, and is annealed for a period from 0.5 to 10 hours at a temperature from 400 to 1200°C.

In one particular embodiment of the invention, the silica can be a pyrogenic silica. Silica which can be used according to the invention, which thus includes pyrogenic silica, is described in Ullmanns Enzyklopädie der technischen Chemie, 4th Edition, Volume 21, pages 451 to 476 (1982).

One preferred embodiment of the invention is a process for the production of mouldings based on silica, which is characterised in that silica is homogenised with methyl hydroxyethyl cellulose, wax and/or polyethylene glycol with the addition of water and optionally with the addition of an aqueous alkaline ammonia solution, is subjected to a kneading and working process, is shaped and/or extruded, the mouldings are optionally cut to the desired length by means of a cutting device, are dried at a temperature from 10 to 150°C and are annealed for a period from 30 minutes to 10 hours at a temperature from 400 to 1200°C.

Kneaders, mixers or mills which enable good homogenisation and compaction of the mixed material to be effected, such as blade, fluidised bed, rotary or air jet mixers for example, can be used for carrying out the process according to the invention. In particular, mixers can be used which make it possible to effect additional compaction of the mixed material, such as plough mixers, kneaders, pan grinders or ball mills. Mixing and kneading can also be effected directly in the extruder, however. The production the mouldings can be effected in single- or twin-screw extruders, in extrusion presses or in tabletting machines also. The mouldings according to the invention are preferably producted by means of extruders.

In one particular embodiment of the invention, the mixture can have the following composition before it is shaped:

50 - 90 % by weight	silica, preferably 65-85 % by weight;
0.1 - 20 % by weight	methyl hydroxyethyl cellulose, preferably 5-15 % by weight;
0.1 - 15 %	wax, preferably 5-12 % by weight;
0.1 - 15 %	polyethylene glycol, preferably 5-10 % by weight.

The mouldings can be annealed at 400 - 1200 °C for 30 minutes to 10 hours. The fracture strength, total specific surface and the pore volume can be varied within certain limits by varying the amounts of substances used and by varying the pressing pressure.

The mouldings according to the invention can be used either directly as a catalyst or as a catalyst support.

For use as a catalyst support, the mouldings can be brought into contact with a catalytically active substance after

their production and can be activated, if necessary, by suitable further treatment.

In particular, mouldings made from pyrogenic silica can be used as a support for the catalyst for the production of vinyl acetate monomer from ethylene, acetic acid and oxygen.

The mouldings according to the invention comprise the following properties or enable such properties to be obtained:

- low pressure drops
- low bulk density
- relatively large external surface per unit volume of a reaction vessel
- improved mass and heat transfer
- comparatively simple packing and emptying of industrial tube bundle reactors, particularly by comparison with known honeycomb-shaped catalysts.

The low pressure drop across mouldings according to the invention results, amongst other causes, from their geometric dimensions, due to which there is an extremely high free surface area over the cross-section of the mouldings and/or a very high voids fraction in the catalyst packing.

Catalysts can be produced based on mouldings according to the invention which enable higher which enable higher space-time yields and selectivities to be achieved.

The invention is explained in greater detail below with reference to the drawings.

The drawings are as follows:

Figure 1 is a cross-section through a pressed part or supported catalyst in the form of a cart wheel;

Figure 2 is a perspective illustration of the cart wheel shape shown in Figure 2;

Figure 3 shows a pressed part or supported catalyst in the form of what is termed a minilith; and

Figure 4 is a perspective illustration of the minilith shown in Figure 3.

The Figures relate to embodiments of the invention. The maximum outside diameter d_1 of the cart wheels and of what are termed miniliths is preferably 25 mm, wherein the ratio of height h to outside diameter (h/d_1) can range from 0.2 to 5. The inside diameter of the mouldings is denoted by d_2. The wall thickness the mouldings ($(d_1 - d_2) \times 0.5$) can fall within the range from 0.05 to 0.3 times the outside diameter. The stay or spoke thickness of the mouldings is denoted by d_3 and can fall within the range from 0.05 to 0.3 times the outside diameter. The number of internal reinforcing stays or spokes or passageway channels can amount to at least 3.

The present invention also relates to a supported catalyst for the production of vinyl acetate monomer (VAM), which catalyst contains, as catalytically active components on a support (moulding), palladium and/or compounds thereof and alkali compounds, and which additionally contains gold and/or compounds thereof (Pd/alkali/Au system) or cadmium and/or compounds thereof (Pd/alkali/Cd system) or barium and/or compounds thereof (Pd/alkali/Ba system) or palladium, alkali compounds and mixtures of gold and/or cadmium and/or barium, and which is characterised in that the support is a moulding according to the invention.

Potassium compounds, such as potassium acetate for example, are preferably used as alkali compounds.

The catalytically active components can be present in the following systems:

Pd/Au/alkali compounds
Pd/Cd/alkali compounds
Pd/Ba/alkali compounds

The supported catalysts according to the invention can be used for the production of vinyl acetate monomer. For this purpose, ethene, acetic acid and molecular oxygen or air are reacted in the gas phase, optionally with the addition of inert gases, at temperatures between 100 and 250°C and at normal or elevated pressure in the presence of the supported catalysts according to the invention.

A production process of this type is known from the documents DE 16 68 088, US 4,048,096, EP-A 0 519 435, EP-A 0 634 208, EP-A 0 723 810. EP-A 0 634 209, EP-A 0 632 214, EP-A 0 654 301 and EP-A 0 0807 615.

The poresent invention also relates to a process for the production of the supported catalyst for the production of vinyl acetate monomer by depositing Pd, Au, Cd or Ba metal compounds by impregnation, spraying, evaporation, immersion or precipitation, optionally reducing the reducible metal compounds which are deposited on the support, optionally washing in order to remove chloride fractions which may be present, impregnating with alkali acetates or with alkali compounds which under the reaction conditions for the production of vinyl acetate monomer are completely or partially converted into alkali acetates, in a suitable sequence, which is characterised in that the support is a moulding according to the present invention.

The present invention further relates to a process for the production of the supported catalyst for the production of vinyl acetate monomer by impregnating the support with a basic solution and a solution which contains gold and palladium salts, wherein impregnation is effected simultaneously or in succession, with or without intermediate drying, optionally washing the support in order to remove chloride fractions which may be present and reducing the insoluble compounds which are precipitated on the support before or after washing, drying the catalyst precursor which is thus obtained, and impregnating with alkali acetates or with alkali compounds which under the reaction conditions for the production of vinyl acetate monomer are completely or partially converted into alkali acetates, which is characterised in that the support is a moulding according to claim 1.

The supported catalysts according to the invention can be used for the production of unsaturated esters from olefines, organic acids and oxygen in the gas phase.

The catalysts of the Pd/alkali/Au system according to the invention can be obtained by impregnating the support with a basic solution and with a solution which contains gold and palladium salts, wherein the impregnation steps can be carried out simultaneously or in succession, with or without intermediate drying. The support is subsequently washed in order to remove chloride fractions which may be present. The insoluble metal compounds which are precipitated on the support can be reduced before or after washing. The catalyst precursor which is thus obtained can be dried in order to activate the catalyst can be impregnated with alkali acetates or with alkali compounds which under the reactions conditions for the production of vinyl acetate monomer are completely or partially converted inton alkali acetates. In general, the noble metals of

Pd/Au catalysts can be present in the form of a shell on the support.

For Pd/alkali/Ba catalysts, the metal salts can be deposited by impregnationg, spraying, immersion or precipitation (EP 0 519 436). The same methods are known for Pd/alkali/Cd catalysts (US-PS 4,902,823, US-PS 3,393,199, US-PS 4,668,819).

Depending on the catalyst system, the the supported catalyst can be reduced.

Reduction of the catalyst can be effected in an aqueous phase or in the gas phase. Formaldehyde or hydrazine are suitable for reduction in an aqueous phase, for example. Reduction in the gas phase can be effected with hydrogen or forming gas (95 % by volume N_2 + 5 % by volume H_2), ethene or ethene diluted with nitrogen. Reduction with hydrogen can be conducted at temperatures between 40 and 260 °C, preferably between 70 and 200 °C. Reduction with forming gas (95 % by volume N_2 and 5 % by volume H_2) can be conducted at temperatures between 300 and 550 °C, preferably between 350 and 500 °C. The catalyst can also be reduced with ethene in the production reactor, after activation with alkali acetate.

The catalyst supports according to the invention advantageously retain their mechanical strength under the reaction conditions of the catalytic process, particularly under the effect of acetic acid.

The production of supported catalysts of the Pd/alkali/Au system on mouldings according to the invention is described in greater detail below.

The mouldings according to the invention are impregnated with a solution which contains palladium and gold. Simultaneously with the solution which contains noble

metals, or in any desired sequence in succession, the mouldings according to the invention are impregnated with a basic solution which may contain one or more basic compounds. The basic compound or compounds serve to convert palladium and gold into their hydroxides.

The compounds in the basic solution may consist of alkali hydroxides, alkali bicarbonates, alkali carbonates, alkali silicates or mixtures of these substances. Potassium hydroxide and/or sodium hydroxide are preferably used.

Palladium chloride, sodium or potassium palladium chloride or palladium nitrate, for example, can be used as palladium salts for the production of the solution which contains noble metals. Gold(III) chloride and tetrachloroauric(III) acid can be used as gold salts. Potassium palladium chloride, sodium palladium chloride and/or tetrachloroauric acid are preferably used.

Impregnation of the mouldings according to the invention with the basic solution has an effect on the deposition of the noble metals in the support material. The basic solution can be used either simultaneously with the solution of noble metal or can be used in any desired sequence with this solution. The mouldings according to the invention are brought into contact with the basic solution and with the solution of noble either simultaneously or in any desired sequence in succession. When the mouldings according to the invention are impregnated in succession with the two solutions, an intermediate drying step can be carried out after the first impregnation step.

The pressed parts according to the invention are preferably first impregnated with the basic compound. Subsequent impregnation with the solution which contains palladium and gold results in the precipitation of palladium and gold in a surface shell on the moulding. The reverse sequence of impregnation generally results in a

more or less homogeneous distribution of the noble metals over the cross-section of the moulding used. When the process is conducted appropriately, however, catalysts comprising a defined shell can also be obtained when employing the reverse sequence of impregnation (see US 4,048,096 for example). Catalysts which comprise a homogeneous or almost homogeneous distribution of noble metal generally exhibit reduced activity and selectivity.

Catalysts with shell thicknesses less than 1 mm are particularly suitable. The shell thickness is influenced by the amount of basic compound which is deposited on the moulding in relation to the desired amount of noble metal. The higher this ratio is, the lower is the thickness of the shell which is formed. The quantitative ratio of basic compound to noble metal compounds which is necessary for a desired shell thickness depends on the nature of the moulding and on the basic compound and noble metal compounds which are selected. The requisite quantitative ratio is advisedly determined by a few preliminary tests. The shell thickness which is present can easily be determined in such tests by cutting open the catalyst particles.

The minimum necessary amount of basic compound results from the stoichiometrically calculated amount of hydroxide ions which are necessary for the conversion of the palladium and gold in the hydroxide. As an approximate value, the basic compound should be used in a 1 to 10-fold stoichiometric excess for a shell thickness of 0.5 mm.

After the pore volume impregnation process, the mouldings according to the invention can be coated with the basic compounds and with noble metal salts. If intermediate drying is employed, the volume of both solutions is selected so that they each correspond to about 90 to 100 % of the absorption capacity of the moulding used. If

intermediate drying is omitted, the sum of the individual volumes of the two impregnation solutions has to correspond to the above condition, wherein the individual volumes can be in a ratio of 1 : 9 to 9 : 1 to each other. A volume ratio from 3 : 7 to 7 : 3 is preferably employed, particularly a ratio of 1 : 1. Water is preferably used as the solvent in both these cases. Suitable organic or aqueous-organic solvents can also be used, however.

The reaction of the noble metal salt solution with the basic solution to form insoluble noble metal compounds occurs slowly and is generally complete after 1 to 24 hours, depending on the method of preparation. Thereafter, the water-insoluble noble metal compounds are treated with reducing agents. Wet reduction can be effected, with aqueous hydrazine hydrate for example, or a gas phase reduction can be effected with hydrogen, ethene, forming gas or methanol vapour. Reduction can be effected at normal temperature or at an elevated temperature, and at normal pressure or under an elevated pressure, optionally with the addition of inert gases also.

Before and/or after the reduction ofthe noble metal compounds, any chloride which may be present on the moulding is removed by thoroughly washing the latter. After washing, the moulding should contain less than 500 ppm, preferably less than 200 ppm, of chloride.

The moulding which is obtained after reduction as a catalyst precursor is dried and is subsequently impregnated with alkali acetates or with alkali compounds which under the reaction conditions for the production of vinyl acetate monomer are completely or partially converted into alkali acetates. The moulding is preferably impregnated with potassium acetate. A pore volume impregnation method is preferably used again here. This means that the requisite amount of potassium acetate is dissolved in a solvent,

preferably water, the volume of which approximately corresponds to the absorption capacity of the moulding for the selected solvent. This volume is approximately equal to the total pore volume of the mouldings.

The finished, coated moulding is subsequently dried to a residual moisture content of less than 2 %. Drying can be effected in air, or can also optionally be effected under nitrogen as an inert gas.

The production of supported catalysts of the Pd/alkali/Cd or Pd/alkali/Ba systems on mouldings according to the invention is effected in a known manner according to the patent specifications cited above.

For the synthesis of vinyl acetate monomer it is advisable to coat the mouldings with 0.2 to 4, preferably 0.3 to 3 % by weight palladium, 0.1 to 2, preferably 0.15 to 1.5 % by weight gold and 1 to 10, preferably 1.5 to 9 % by weight potassium acetate, with respect to the weight of the moulding used in each case. These data are applicable to the Pd/alkali/Au system. In the case of mouldings with a bulk density of 500 g/l, these concentration data correspond to volume-based concentrations of 1.0 to 20 g/l palladium, 0.5 to 10 g/l gold and 5 to 50 g/l potassium acetate. In order to prepare the impregnation solution, the corresponding amounts of palladium and gold compounds are dissolved in a volume of water which approximately corresponds to 90 - 100 % of the water absorption capacity of the moulding in question. The same procedure is employed for the preparation of the basic solution.

The cadmium content of the Pd/alkali/Cd catalyst (finished, coated moulding) can generally range from 0.1 to 2.5 % by weight, preferably 0.4 to 2.0 % by weight.

The barium content of the Pd/alkali/Ba catalyst (finished, coated moulding) can generally range from 0.1 to 2.0 % by weight, preferably 0.4 to 1.8 % by weight.

The palladium content of the Pd/alkali/Cd or Pd/alkali/Ba catalyst (finished, coated moulding) can generally range from 0.2 to 4 % by weight, preferably 0.3 to 3 % by weight palladium.

The potassium acetate content of the Pd/alkali/Cd or Pd/alkali/Ba catalyst (finished, coated moulding) can generally range from 1 to 10 % by weight, preferably 1,5 to 9 % by weight.

Silicas which have the following physical and chemical properties, and which are also known by the name Aerosil® of the Degussa company, can be used as pyrogenic silicas:

		Aerosil OX 50	Aerosil 90	130	150	200	300	380
surface nach BET	m^2/g	50 ± 15	90 ± 15	130 ± 25	150 ± 15	200 ± 25	300 ± 30	380 ± 30
Average size of primary particles	nm	40	20	16	14	12	7	7
Tamped density [1] g/l		about 130	about 80	about 50	about 50	about 50	about 50	about 50
Loss on drying [2] (2 hours at 105 °C)	% wt.	< 1.5	< 1	< 1.5	< 0.5	< 1.5	< 1.5	< 1.5
Loss on ignition [2] [5] (2 hours at 1000 °C)	% wt.	< 1	< 1	< 1	< 1	< 1	< 2	< 2.5
pH [3] (in a 4 % aqueous dispersion)		3.8 - 4.8	3.6 - 4.5	3.6 - 4.3	3.6 - 4.3	3.6 - 4.3	3.6 - 4.3	3.6 - 4.3
SiO_2 [6]	% wt.	> 99.8	> 99.8	> 99.8	> 99.8	> 99.8	> 99.8	> 99.8
Al_2O_3 [6]	% wt.	< 0.08	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Fe_2O_3 [6]	% wt.	< 0.01	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003
TiO_2 [6]	% wt.	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
HCl [6] [7]	% wt.	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025	< 0.025
Residue on sieve [4] (Mocker, 45 µm)	% wt.	< 0.02	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05

[1] according to DIN 53 194
[2] according to DIN 55 921
[3] according to DIN 53 200
[4] according to DIN 53 580
[5] with respect to the substance dried for 2 hours at 105 °C
[6] with respect to the substance calcined for 2 hours at 1000°C
[7] The HCl content is a constituent of the loss on ignition

In order to produce AEROSIL®, a volatile silicon compound is injected through a nozzle into an oxyhydrogen gas flame formed from hydrogen and air. Silicon tetrachloride is used in most cases. This substance hydrolyses to form silica and hydrochloric acid under the effect of the water formed during the oxyhydrogen gas reaction. After leaving the flame, the silica enters what is termed a coagulation zone, in which the AEROSIL® primary particles and primary aggregates agglomerate. The product, which at this stage is present as a kind of aerosol, is separated from the accompanying gaseous substances in cyclones, and is subsequently post-treated with moist hot air. The residual content of hydrochoric acid can be reduced to less than 0.025 % by this procedure. Since at the end of this process the AEROSIL® only has a bulk density of about 15 g/l, is is subjected to a subsequent vacuum compaction step by means of which tamped densities of about 50 g/l or more can be achieved.

The particle size of products obtained in this manner can be varied by varying the reaction conditions, such as the flame temperature, the content of hydrogen or oxygen, the amount of silicon tetrachloride, the residence time in the flame or the length of the coagulation section, for example.

The BET specific surface is determined using nitrogen according to DIN 66 131. The pore volume is determined by calculation from the sum of the micro-, meso- and macropore volumes.

Determination of the micro- and mesopores is effected by plotting an N_2 isotherm and evaluating the latter by the BET, de Boer and Barret, Joyner or Halenda methods.

The macropores are determined by the Hg penetration method.

The invention is explained by the Examples given below.

Example 1

85 % by weight	Aerosil® 200
5 % by weight	methyl hydroxyethyl cellulose
5 % by weight	wax
5 % by weight	polyethylene glycol

were compacted in a kneader, with the addition of water which had been made slightly alkaline with an aqueous alkaline ammonia solution (15 ml of a 32% solution for a 2 kg batch). The kneaded material was shaped in a single-screw extruder to form hollow cylindrical extrudates in the form of so-called cart wheels comprising five internal reinforcing spokes or stays leading from the inner wall of the hollow cylinder to the centre of the moulding, and was cut to the desired length of 3.5 to 5.5 mm by a cutting device. The mouldings were dried on a belt drier at 90°C and were subsequently calcined for 6 hours at 900°C.

The mouldings obtained had the following physical and chemical properties:

Moulding dimensions:	
outside diameter (mm)	7.5 ± 0.5
height (mm)	4.5 ± 1
Wall thickness:	1.3 ± 0.05
Stay width:	1.3 ± 0.05
BET specific surface (m^2/g)	79
Pore volume (ml/g)	0.69
Bulk density (g/l)	398
SiO_2 content (% by weight)	99.9
Height/diameter ratio	0.6

Example 2

85 % by weight	Aerosil® 200
5 % by weight	methyl hydroxyethyl cellulose
5 % by weight	wax
5 % by weight	polyethylene glycol

were compacted in a kneader, with the addition of water which had been made slightly alkaline with an aqueous alkaline ammonia solution (15 ml of a 32% solution for a 2 kg batch). The kneaded material was shaped in a single-screw extruder to form hollow cylindrical extrudates in the form of so-called cart wheels comprising five internal reinforcing spokes or stays leading from the inner wall of the hollow cylinder to the centre of the moulding, and was cut to the desired length of 5.5 to 6.5 mm by a cutting device. The mouldings were dried on a belt drier at 90°C and were subsequently calcined for 6 hours at 850°C.

The mouldings obtained had the following physical and chemical properties:

Moulding dimensions:	
outside diameter (mm)	6.0 ± 0.2
height (mm)	6.0 ± 0.5
Wall thickness:	0.95 ± 0.05
Stay width:	0.95 ± 0.05
BET specific surface (m^2/g)	148
Pore volume (ml/g)	0.75
Bulk density (g/l)	390
SiO_2 content (% by weight)	99.9
Height/diameter ratio	1.0

Example 3

85 % by weight	Aerosil® 200
5 % by weight	methyl hydroxyethyl cellulose
5 % by weight	wax
5 % by weight	polyethylene glycol

were compacted in a kneader, with the addition of water which had been made slightly alkaline with an aqueous alkaline ammonia solution (15 ml of a 32% solution for a 2 kg batch). The kneaded material was shaped in a single-screw extruder to form hollow cylindrical extrudates in the form of so-called cart wheels comprising five internal reinforcing spokes or stays leading from the inner wall of the hollow cylinder to the centre of the moulding, and was cut to the desired length of 3.5 to 5.5 mm by a cutting device. The mouldings were dried on a belt drier at 90°C and were subsequently calcined for 6 hours at 800°C.

The mouldings obtained had the following physical and chemical properties:

Moulding dimensions:	
outside diameter (mm)	7.5 ± 0.5
height (mm)	4.5 ± 1
Wall thickness:	1.3 ± 0.05
Stay width:	1.3 ± 0.05
BET specific surface (m^2/g)	170
Pore volume (ml/g)	0.9
Bulk density (g/l)	360
SiO_2 content (% by weight)	99.9
Height /diameter ratio	0.6

Example 4

85 % by weight	Aerosil® 200
5 % by weight	methyl hydroxyethyl cellulose
5 % by weight	wax
5 % by weight	polyethylene glycol

were compacted in a kneader, with the addition of water which had been made slightly alkaline with an aqueous alkaline ammonia solution (15 ml of a 32% solution for a 2 kg batch). The kneaded material was shaped in a single-screw extruder to form hollow cylindrical extrudates in the form of so-called cart wheels comprising five internal reinforcing spokes or stays leading from the inner wall of the hollow cylinder to the centre of the moulding, and was cut to the desired length of 5.5 to 6.5 mm by a cutting device. The mouldings were dried on a belt drier at 90°C and were subsequently calcined for 6 hours at 800°C.

The mouldings obtained had the following physical and chemical properties:

Moulding dimensions:	
outside diameter (mm)	6.0 ± 0.2
height (mm)	6.0 ± 0.5
Wall thickness:	0.95 ± 0.05
Stay width:	0.95 ± 0.05
BET specific surface (m^2/g)	170
Pore volume (ml/g)	0.9
Bulk density (g/l)	350
SiO_2 content (% by weight)	99.9
Height/diameter ratio	1.0

Example 5

85 % by weight	Aerosil® 200
5 % by weight	methyl hydroxyethyl cellulose
5 % by weight	wax
5 % by weight	polyethylene glycol

were compacted in a kneader, with the addition of water which had been made slightly alkaline with an aqueous alkaline ammonia solution (15 ml of a 32% solution for a 2 kg batch). The kneaded material was shaped in a single-screw extruder to form hollow cylindrical extrudates in the form of what are termed miniliths as shown in Figure 3 and 4, comprising nine passageway channels, and was cut to the desired length of 4 to 5 mm by a cutting device. The mouldings were dried on a belt drier at 90°C and were subsequently calcined at 800°C.

The mouldings obtained had the following physical and chemical properties:

Moulding dimensions:	
outside diameter (mm)	5.8 ± 0.2
height (mm)	4.5 ± 0.5
Wall thickness:	0.8 ± 0.05
Stay width:	0.8 ± 0.05
BET specific surface (m^2/g)	170
Pore volume (ml/g)	0.9
Bulk density (g/l)	350
SiO_2 content (% by weight)	99.9
Height/diameter ratio	0.78

Comparative examle 1

A palladium-gold-potassium acetate catalyst was prepared according to Example 11 of EP 0 807 615 A1. The catalyst support which was used was a moulding according to Example 5 of EP 0 807 615 A1, but which had the dimensions 8 x 5 x 3 mm (outside diameter x height x inside diameter) and which had faceted edges.

The concentrations of the impregnation solutions were selected so that the finished catalyst contained a concentration of 0.55 % by weight palladium, 0.25 % by weight gold and 5.0 % by weight potassium acetate.

In a first step, the support was first of all impregnated with a basic solution of sodium hydroxide in water. The volume of the aqueous NaOH solution corresponded to 50 percent of the water absorption capacity of the dry support. After impregnation with sodium hydroxide, the support was immediately impregnated, without intermediate drying, with an aqueous solution of noble metals comprising sodium palladium chloride and tetrachloroauric acid, the volume of which likewise corresponded to 50 percent of the water absorption capacity of the dry support.

After a holding time of 1.5 hours, during which the noble metal compounds hydrolysed, the support particles were washed until they were free from chloride. The support particles were dried and were reduced at 450°C in the gas phase with forming gas (95 % by volume N_2, 5 % by volume H_2). Thereafter, the catalyst was impregnated with an aqueous solution of potassium acetate and was dried again. Drying was effected in the gas phase with nitrogen.

The sodium hydroxide concentration of the basic solution was calculated so that a shell which contained noble metals and which was formed on the support particles had a thickness < 1.0 mm.

Example 6

A palladium-gold-potassium acetate catalyst as described in comparative example 1 was produced on the moulding according to the invention according to Example 1.

Example 7

A palladium-gold-potassium acetate catalyst as described in comparative example 1 was produced on the moulding according to the invention according to Example 2.

Example of use 1

The activity and selektivity of the catalysts from comparative example 1 and from Examples 6 and 7 were measured during a test procedure which had a duration of up to 24 hours.

The catalysts were tested with the following gas composition: 75 % by volume ethene, 16.6 % by volume acetic acid, 8.3 % by volume oxygen, in an oil-heated tubular flow reactor (reactor length 710 mm, inside diameter 23.7 mm) at normal pressure and at a space velocity (GHSV) of 400 h^{-1}. The catalysts were investigated over the temperature range from 120 to 165°C, as measured in the catalyst bed.

The reaction products were analysed at the outlet of the reactor by means of on-line gas chromatography. The space-time yield of the catalyst in grams of vinyl acetate monomer per hour per kilogram of catalyst (g VAM/(h x $kg_{cat.}$) was determined as a measure of the catalyst activity.

The carbon dioxide which was formed by the combustion of ethene was also determined and was employed for assessing the selectivity of the catalyst.

The test results on catalysts from comparative example 1 and from Examples 6 and 7 are presented in Table 1. The catalyst activity and the catalyst selectivity of the catalyst according to comparative example 2 were taken as 100 percent.

Table 1:

Catalyst	Activity [g VAM/(h x $kg_{cat.}$] in [%] of comp.ex.1	Selectivity CO_2 in the off-gas in [% per unit area] in [%] of comp.ex.1	Catalyst temperature [°C]
Comp. ex. 1	100	100 (3.2)	146.4
B 6	84.5	56.3	131.8
	108.5	84.4	143.5
	123.5	87.5	149.9
B 7	104.1	65.6	132.2
	135.3	75.0	144.7
	153.7	103.1	152.0

The results show that the catalysts according to the invention, which are based on the mouldings according to the invention, exhibit a significantly higher actvity than that of the known comparative catalyst, whilst exhibiting a comparable selectivity or even an improved selectivity.

Claims

1. A moulding based on silica, characterised in that the supporting geometry consists of a hollow cylindrical configuration having internal reinforcing stays or spokes leading from the inner wall of the hollow cylinder to the centre of the moulding or is characterised by a multiplicity of passageway channels.

2. A moulding according to claim 1, characterised in that the moulding has a diameter from 1 to 25 mm and a ratio of height to diameter of 0.2 to 5.

3. A moulding according to claims 1 or 2, characterised in that the moulding has a wall thickness within the range from 0.05 to 0.3 times the diameter and a stay or spoke thickness within the range from 0.05 to 0.3 times the diameter.

4. A moulding according to claims 1 - 3, characterised in that the number of internal reinforcing stays or spokes or passageway channels is at least 3.

5. A moulding according to claims 1 to 4, characterised in that a pyrogenic silica is used as the silica.

6. A process for the production of mouldings based on silica according to claim 1, characterised in that silica is subjected to a kneading and working process, is extruded, the extrudate is optionally cut to the desired length by means of a cutting device, is dried at a temperature of 20 to 150°C, and is annealed for a period from 0.5 to 10 hours at a temperature from 400 to 1200°C.

7. A process for the production of mouldings based on silica according to claim 1, characterised in that silica is homogenised with methyl hydroxyethyl cellulose, wax and/or polyethylene glycol with the addition of water and optionally with the addition of an aqueous alkaline ammonia solution, is subjected to a kneading and working process and/or is extruded, the mouldings are optionally cut to the desired length by means of a cutting device, are dried at a temperature from 10 to 150°C and are annealed for a period from 30 minutes to 10 hours at a temperature from 400 to 1200°C.

8. A process for the production of mouldings based on silica according to claims 6 or 7, characterised in that a pyrogenic silica is used as the silica.

9. The use of the mouldings according to claim 1 as a catalyst or catalyst support.

10. A supported catalyst for the production of vinyl acetate monomer (VAM), which catalyst contains, as catalytically active components on a support (moulding), palladium and/or compounds thereof and alkali compounds, and which additionally contains gold and/or compounds thereof (Pd/alkali/Au system) or cadmium and/or compounds thereof (Pd/alkali/Cd system) or barium and/or compounds thereof (Pd/alkali/Ba system) or palladium, alkali compounds and mixtures of gold and/or cadmium and/or barium, characterised in that the support is a moulding according to claim 1.

11. A process for the production of the supported catalyst according to claim 10 for the production of vinyl acetate monomer by depositing Pd, Au, Cd or Ba metal compounds by impregnation, spraying, evaporation,

immersion or precipitation, optionally reducing the reducible metal compounds which are deposited on the support, optionally washing in order to remove chloride fractions which may be present, impregnating with alkali acetates or with alkali compounds which under the reaction conditions for the production of vinyl acetate monomer are completely or partially converted into alkali acetates, in a suitable sequence, characterised in that the support is a moulding according to claim 1.

12. A process for the production of the supported catalyst according to claim 10 for the production of vinyl acetate monomer by impregnating the support with a basic solution and with a solution which contains gold and palladium salts, wherein impregnation is effected simultaneously or in succession, with or without intermediate drying, optionally washing the support in order to remove chloride fractions which may be present and reducing the insoluble compounds which are precipitated on the support before or after washing, drying the catalyst precursor which is thus obtained, and impregnating with alkali acetates or with alkali compounds which under the reaction conditions for the production of vinyl acetate monomer are completely or partially converted into alkali acetates, characterised in that the support is a moulding according to claim 1.

13. The use of the supported catalyst according to claim 10 for the production of unsaturated esters from olefines, organic acids and oxygen in the gas phase.